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LEA'S
CHEMISTRY
OF
CEMENT
AND
CONCRETE

FOURTH
EDITION

EDITED BY
PETER C. HEWLETT

Lea's Chemistry of Cement and Concrete

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Lea's Chemistry of Cement and Concrete

Fourth Edition

Edited by

Peter C. Hewlett

PhD, LLD, BSc, CChem, FRSC, FInstMat, FInstConcTech, FConcSoc

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Author Biographies

Peter C. Hewlett (Editor) is Director of the British Board of Agrément. He is President of the European Organisation for Technical Approvals (EOTA) and Past President of the European Union of Agrément (UEAtc). Before joining the BBA in March 1988, he was a Director of Cementation Research Limited, part of the then Trafalgar House group, working in construction and building research and development for almost 25 years. Professor Hewlett is a chartered chemist holding the degrees of BSc and PhD. In addition he was awarded a Doctor of Laws Honorary Degree (*honoris causa*) for his research into various materials aspects of concrete and in particular chemical modification and durability. He is a fellow of the Royal Society of Chemistry, Institute of Materials and the UK Concrete Society, of which he is President Designate, as well as an Honorary Fellow of the Institute of Concrete Technology. He holds a Visiting Industrial Professorship in the Department of Civil Engineering at the University of Dundee, Scotland, and has done so since 1986, working within the Concrete Technology Unit. He is currently Chairman of the Editorial Board of the *Magazine of Concrete Research* (published on behalf of the Institution of Civil Engineers) and has published and lectured widely around the world.

John Bensted read Chemistry for his BSc and PhD degrees at the University of London, before joining Blue Circle Cement at its research division in Greenhithe, Kent. Here he spent over 17 years in research, development, quality control and technical troubleshooting worldwide for the group's entire range of cement types. He rose to become a principal scientist, and was awarded the DSc degree of the University of London for his cement research work. In 1985 he joined British Petroleum at their Sunbury Research Centre, initially as a senior drilling engineer before becoming a research associate. He directed research programmes on oilwell cement and functioned as an internal consultant for all aspects of cement technology for the different BP businesses worldwide. Since 1992 John has become more involved with academic research in cement and concrete technology as a visiting professor at the Universities of Keele, Greenwich and London (Birkbeck College). He acts as a consultant in cement technology, operating internationally.

Robert G. Blezard spent 36 years in the cement industry as a materials technologist and developed a deep interest in the history of the cement industry. In 1950 he was appointed

Chief Analyst at the West Thurrock plant of Tunnel Cement Company, and in 1967 he became a section head in its newly formed Research and Development Department. Later in his career he moved to Blue Circle Cement where he specialised in the microscopy of cement materials. His work has appeared in many publications including *Chemistry and Industry*, *Analyst* and *Cement and Concrete Research*. He is a member of the American Concrete Institute's Committee on the History of Concrete.

Bev Brown is a Chartered Physicist who qualified with a Special Physics degree at the University of London in the early 1960s. He is now the Divisional Technical Executive of Readymix (UK) Limited and is responsible for technical services within the company, covering sand, gravel, mortar and ready mixed concrete activities. Bev is Chairman of the BSI Sub-Committee dealing with aggregates for concrete. Also active in Europe, he has represented the UK as lead delegate on the CEN Committee which is developing the European Standard for concrete aggregates. At the same time he has been Convenor of the task group considering geometrical requirements for all the end uses of aggregates. Bev has contributed to a number of conferences concerned with aggregates, concrete and quality assurance, and presented a range of papers on these topics. His published work includes the contribution on 'Marine Aggregates' in the book *Standards for Aggregates*. Well known in the industry, he also participates in various technical committees within the Concrete Society, Construction Industry Research and Information Association, European Ready Mixed Concrete Organisation, Quarry Products Association and the Quality Scheme for Ready Mixed Concrete.

Alain Capmas studied Physics at the Ecole Polytechnique Federale of Lausanne, Switzerland. After two years doing computational research in Compagnie Générale d'Electricité, he joined Lafarge in 1975 where he worked on refractory castables and Portland cement before progressing to run a factory producing calcium aluminate cement. In 1987 he transferred to the Central Research Laboratory where he led a research effort to understand the factors affecting the quality of calcium aluminate cements. During this time he developed a thermodynamic approach to understanding the hydration of calcium aluminate cements with the team of Professor Pierre Baret of the University of Dijon. He was then Director of Research and Development at Lafarge Fondu International (now Lafarge Aluminates) until 1995 when he became Research and Development Director of the Central Research Laboratory of Lafarge.

Rodney M. Edmeades graduated in Chemistry in 1953 and, following an intensive technical training course, worked in the cement industry (Blue Circle Group) for 11 years. Joining Cementation Research in 1964, he was appointed a Director in 1977 in charge of the Materials Technology Section. His work at the time encompassed the investigation of cement hydration mechanisms and the interaction of admixtures, together with the development of materials used in civil engineering, concrete repair, ground engineering and mining. He co-authored a number of papers and was elected a Member of the Institute of Concrete Technology in 1988. In that year as a result of a company reorganisation he became an Associate Director of Trafalgar House Technology, responsible for Construction Materials, and acted as Senior Consultant to various group units prior to retirement in May 1995.

Margi Eglinton is a graduate in science of the University of Adelaide, South Australia.

Although now retired, she was for more than 40 years a practical chemist. The later, and major part of her working life was spent as Chief Chemist to Wimpey Laboratories Limited. She developed a strong interest in the causes of damage to concrete, and an area of special interest to her has been microbiological causes of damage, particularly sulfate-reducing and sulfate-oxidising bacteria. She has served on several committees and working parties engaged in drawing up recommendations for the performance of concrete in difficult ground conditions, analytical test methods for the determination of harmful contaminants and the foundation of research programmes to investigate the behaviour of concrete in aggressive conditions. She has written several papers and a book on the subject.

Per Fidjestøl graduated from Norwegian Technical University in 1973 with a degree in Civil Engineering. He joined Det Norske Veritas working in the area of offshore and marine structures, including cold climate technology. His main role, however, concerned concrete technology. In 1986 he joined Elkem Materials and has since been engaged in a variety of capacities, mainly related to R&D, marketing and technical support in the area of microsilica for concrete. Per is a fellow of ACI and a member of several technical and board-appointed committees, including Chairman of the International Activities Committee. He has published about 50 technical papers mainly on corrosion and/or microsilica. He has also been a member of CEN groups related to microsilica, and is a member of ASTM C-9 on Concrete and D-18 on Geotechnics.

Fredrik P. Glasser is a Professor of Chemistry at the University of Aberdeen, Scotland. He is the author or co-author of more than 350 papers on material science, including many on cement. He is a Fellow of the Royal Society of Edinburgh and has received numerous distinctions, including Scientific Chairmanship of the 10th International Congress on the Chemistry of Cements and the Copeland Award of the American Ceramic Society. His current research includes the development of new and improved cementitious materials, with emphasis on low-energy clinkering. He leads a Commission of the European Programme which has as its objective establishing a scientific basis for the cement conditioning of nuclear wastes.

Peter J. Jackson entered the cement industry in 1952 at the Research Department of the Associated Portland Cement Manufacturers Limited after graduating in chemistry at the University and worked on the development and subsequent production of a range of special cements. After the award of an USC in 1962 he transferred into cement manufacture, and having attained Chartered status as Control Engineer was responsible for quality and process control at the eight works located in the Midlands. In 1972 he was appointed Chief Chemist of the Aberthaw and Bristol Channel Portland Cement Company Limited and in 1982 he became the Chief Chemist of the Rugby Portland Cement Company Limited. From 1989 he worked as an independent consultant dealing with matters associated with cement and its manufacture, while maintaining his membership of the European (CEN) Technical Committee on cement and the Convenorship of its Working Group on masonry cement.

Eric E. Lachowski is an electron microscopist in the Department of Chemistry, University of Aberdeen. He has over 15 years of experience in the application of electron microscopy to cement and related phases. Along with Professor H.F.W. Taylor he was a pioneer of the use of analytical electron microscopy for the study of cement hydration products. Current cement related research includes studies of novel, high-performance materials and also the application of cement and concrete to waste immobilisation. His other research activities lie mainly in the field of solid state and materials chemistry, much of it focusing on electroceramics. To date he has published over 60 papers.

C. David Lawrence was awarded a BSc in physical chemistry at Liverpool University in 1954. He has spent almost his entire working career at Wexham Springs, at the laboratories of the Cement and Concrete Association and its successor the British Cement Association. He investigated the physical structure of hardened cement paste by various sorption techniques under the direction of Mr F.G.R. Gimblett and Professor K.S.W. Sing at Brunel University, where he completed his PhD as an external student in 1981. More recently, the external sulfate attack on cement mortars and internal delayed ettringite expansion of heat cured specimens have been subjects of his laboratory researches. Since the closure of the BCA laboratories at Wexham Springs in 1993, he has been Senior BCA Research Fellow at the Centre for Cement and Concrete, The University of Sheffield, where he is continuing his laboratory studies on various durability problems in collaboration with Professor J.H. Sharp, Professor R.N. Swamy and Dr Cyril Lynsdale.

Robert Lewis is Technical Marketing Manager at Elkem Materials. He began his career in 1978 as a field technician for Tarmac Topmix and, having passed the two CGLI Concrete Practice and Concrete Technology Certificates, moved on to control the laboratory and field technicians for the UK Southern Region. By the time he left Tarmac Topmix he was Assistant to the two Area Managers for that Region. He moved to Elkem Materials in 1986, joining the technical services side of the concrete operation in the UK. Currently he provides technical support to Elkem Material's international market, covering the European, Middle Eastern, South East Asian and Far Eastern regions. Robert has written, co-authored and presented a number of papers on microsilica and its use, including work in the Concrete Society's Technical Report 41 on *Microsilica in Concrete in the UK*. He is a member of a number of British Standard Committees, as well as the UK representative to the CEN Committee on Silica Fume. He represents Elkem Materials on the Concrete Admixtures Association and on the Sprayed Concrete Association. He is an Associate Member of the Institute of Concrete Technology and a member of both the Concrete Society and the American Concrete Institute.

Donald E. Macphee is a lecturer in Chemistry at the University of Aberdeen. His interest in cement chemistry began in 1984 when he took up a research position with Professor F.P. Glasser at Aberdeen to investigate the scientific basis for radioactive waste immobilisation in cement-based matrices. His main focus in this study was on the development of models to predict phase composition and distribution in blended cement systems. Donald remained in Aberdeen until he was appointed by CSIRO Australia in 1989 as Research Scientist within the Division of Building, Construction and Engineering. Latterly, as Senior Research Scientist he was leader of the Cement and Concrete Technology Group until he returned to the UK in 1992 to his present appointment. His current research interests include the development of high-performance cements (pore reduced cements) based on Portland and aluminous cements, non-destructive testing of cements and concretes by electrical impedance spectroscopy, the development of toughened concretes (with and without fibre reinforcement) and waste immobilisation in cements and related materials. He has published around 35 papers on cement related research.

Franco Massazza was born in Cagliari, Italy, and received his degree in Chemistry in 1949. The same year he became Assistant Professor at Cagliari University where he taught chemistry, the chemistry of building materials and industrial chemistry for many years. He was Head of Italcementi's Research Laboratories from 1965 to 1992, and from 1975 to 1985 held the post of Professor of Technology of Materials and Applied Chemistry at Milan's Politecnico. Since 1965, he has lectured on ordinary and special concretes at the Politecnico. Professor Massazza is author or co-author of more than 150 publications, has appeared in a host of national and international technical magazines and on conference committees. Currently a member of the Editorial Board of *Cement and Concrete Research*, *Cement Composites* and *Advanced Cement Based Materials*, Professor Massazza was also on the Editorial Board of *Il Cemento* until it ceased publication in 1995.

Micheline Moranville-Regourd is Professor of Materials Science at the Ecole Normale Supèrieure de Cachan, the University of Paris, where she obtained her BSc, MSc and PhD in Physics. She is a Fellow of the American Ceramic Society and has worked in France and elsewhere as a consultant, acting as UNIDO Expert on a commission to Shanghai in 1984. She was awarded the National Order of Merit in 1981, the Mohan Malhotra Award from the Canadian Center for Mineral and Energy Technology in 1986 and the Elphège Baude Award for Industrial Basic Research in 1993. Author of over 150 papers and chapters in books, her fields of research are materials characterisation, cement hydration and the durability of concrete.

Ivan Odler is a native of Czechoslovakia. He earned a BSc degree in chemical engineering and a doctor degree in ceramic engineering from the Slovak Technical University. Ivan started his professional career as an Assistant Professor at the Komensky University in Bratislava and later worked for a Czechoslovak building materials research and testing institute, until his emigration to the United States in 1968. In the US he worked at Clarkson College of Technology (Potsdam NY) and for the Westvaco Research Center in Charleston SC and W.R. Grace Company in Cambridge MA. In 1976 he was appointed Professor of Materials Science at the Technical University of Clausthal (Germany) and became director of the Institute of Non-metallic Materials and head of the Materials Testing Laboratory, affiliated with the University. He held these positions until his retirement in 1995. Currently he lives in Boston, MA.

Karen L. Scrivener studied Materials Science at Cambridge University, followed by a year at the University of Pennsylvania in the USA. In 1980 she joined the research team of Professor Peter Pratt at the Department of Materials, Imperial College, London. Her PhD studies, entitled 'The development of microstructure during the hydration of Portland cement', concerned the use of electron microscopy to study cements and concrete and led, in particular, to the development of the use of backscattered electrons to study polished sections in the scanning electron microscope. This approach was developed in Karen's post-doctoral studies, examining and quantifying the microstructure of the interfacial transition zone between cement aggregate in concrete. In 1986 she was appointed Warren Research Fellow of the Royal Society to continue her studies on the microscopy of cement and concrete – especially its application durability – including an initial study on the durability of calcium aluminate cements. In 1991 she was appointed to a lectureship at Imperial College, where she took over responsibility for the cement and concrete group from Professor Pratt on his retirement. In 1995 she joined the Central Research Laboratory of Lafarge as head of the research group on calcium aluminate cements. She is the author of some 40 publications on cement and concrete, including keynote presentations at the two most recent International Congresses on the Chemistry of Cement.

Ian Sims read Geology at London University (Queen Mary College) and then obtained a doctorate in concrete technology, when his research involved studying a number of threats to the durability of concrete. Among other things, he found that UK flint aggregates were potentially alkali-reactive, formulated an explanation that has recently been confirmed and predicted that resultant damage to concrete could be expected in certain circumstances. After joining Sandberg in 1975, he established and developed its Geomaterials Department and later transferred to its Consultancy Group, rising to be a Senior Associate. Much of his work during this period concerned the assessment of aggregates for their suitability for use in concrete. These aggregates included materials from sources worldwide. Ian has been and remains actively involved in developing British Standards for testing and specifying aggregates. He was Secretary of the Geological Society working party on aggregates for construction and is currently Secretary of the international RILEM technical committee compiling accelerated tests for alkali-aggregate reactivity. Since 1996 Ian has been a main board Director of STATS Limited in St Albans, Hertfordshire, where he leads a team of construction materials specialists within the company's Consultancy Division. He himself provides advice on cementitious materials and their constituents such as aggregates and also natural stone. He frequently acts as an expert witness.

Foreword

Lea's Chemistry of Cement and Concrete has existed, literally, as a standard work for my life time, with the first edition jointly authored by Frederick Lea and Cecil Desch appearing in 1935. Much has changed since the third edition was published in 1970.

The cement industry itself has changed on the world stage, and there have been major improvements in the manufacturing process and quality control leading to a more uniform product. With the significant growth of the ready mixed and precast concrete industries over the past 40 years, customer demand has also changed (e.g. higher early strength for precasting). Finally in this list of changes in a changing world, the attitude of the ultimate customers for cement and concrete – the owners of structures – has been conditioned by the growing concern about durability. The somewhat disappointing durability performance of a proportion of the vast numbers of concrete structures built since the 1960s – interspersed by major concerns such as alkali–silica reaction (ASR) and the still persistent corrosion issue (due mainly to chlorides, in their various forms) – has provoked a much greater interest in the properties of cement and concrete on the part of a wider cross-section of the construction industry, and, indeed, by the public at large. This continuing saga, no doubt fuelled by fresh concerns over environmental and sustainability issues, will maintain that interest in the future, and will demonstrate the need for a further edition of this book in the years to come!

Another significant development influencing the content of this book is that construction (and with it cement and concrete) has gone truly international. The supporting generation of information and the ability to share that knowledge and experience has led to an information explosion, which is often difficult for the user to absorb, comprehend and apply. There is a genuine need among all professionals in the construction industry for a series of safe-havens, where all existing knowledge can be brought together on a particular topic and distilled by experts for easy reference and use. Such is the case for any authoritative reference and it is the case for the continued existence of *Lea's Chemistry of Cement and Concrete* – an acknowledged and respected standard work. The obvious next question is, has this quality and need been met by the team charged with replacing Lea himself and producing this fourth edition?

To answer that question, it is first necessary to reflect on how the book will be used, and by whom. This has always been an authoritative reference work, painstakingly compiled with an eye for detail. As such, it has been referred to by specialists such as cement chemists, and dipped into by other professionals in the construction industry in quest of detailed information on specific topics. Both uses will continue. However, the non-specialist use is likely to increase, for the reasons mentioned earlier, and there is a need for this edition to reflect that by taking account of the concerns and trends over the intervening 27 years.

The international flavour of construction (and the scale of the problem) is confirmed by the fact that the editor has brought together 17 other recognised and respected international experts to produce this volume. Under these circumstances, the job of editor is no sinecure. In maintaining the currency, calibre, continuity and content of the work (while ensuring a proper update, and looking ahead) there is the monumental task of integrating the output of so many individuals into a coherent and comprehensive whole. Peter Hewlett has achieved that successfully, while contributing himself as a co-author of Chapter 15. I have little doubt that Frederick Lea himself would have approved.

So, what about the book itself? How has it changed to face the modern world? The first clear impression is that it is bigger – around 1050 pages compared with the 740 of the third edition. A casual overview also tells us that there are fewer chapters – 16 compared with 21. In part, this perhaps reflects the expertise and interests of the individual contributors. More significantly, it represents restructuring into a more logical layout for current needs. Nothing is lost in doing this (the scope is largely unaffected) and, indeed, certain aspects have been strengthened. Moreover, some subjects have blossomed and are deserving of a chapter on their own; admixtures are one example and production of low-energy cement is another.

A further clear impression from a general overview is the comprehensive list of references that appear a the end of each chapter (several over 200 in number and, in one case, over 500). This reflects the information explosion mentioned earlier, has the merit of bringing all relevant information together, and is helpful to the reader should he or she wish to pursue interests in even greater depth. While the scope of Lea's book has always been more than just the chemistry of cement, there will inevitably be topics where further exploration is necessary for the in-depth study of related or interlocking subjects, and this new style makes that easier and represents a significant enhancement in this edition.

An awareness of the changes introduced by the new team comes first with Chapter 2 on the classification of cements. While, to a large extent, Lea's book transcends changes in standards, cement has become an international commodity and recognition of the requirements of standards is now more important. In particular, the development of a European Standard for cement is significant. For that reason, this chapter has been substantially rewritten, updated and expanded, with the emphasis on European and American standards. A classification is given both in terms of composition and of performance-related properties; this latter development is especially important in response to the greater interest in the characteristics of the wide range of cements now available with regard to durability. This same chapter comprehensively covers the manufacturing process (a separate chapter in earlier editions), where again there has been significant change.

The above brief description of Chapter 2 typifies those that follow – rewritten, updated and expanded are all key words, with a stronger emphasis on performance and on a wider range of engineering properties. Some chapters have substantially the same title, but with recast and updated content. Chapter 13 on calcium aluminate cements is a case in point; the original coverage is still there, in updated form, but with the addition of a broad and realistic perspective on usage following the failures in the UK in the early 1970s. Chapter

16 on aggregates is a mini-reference book in its own right, containing, among other things, an up-to-date review of alkali–aggregate reaction.

In my opinion, there has always been a need for this book – the safe-haven referred to earlier. That need has not fundamentally changed, and therefore it was essential to retain the character, coherence and calibre of Lea's original work, but to put it in a modern setting. In doing so, the attitudes of a modern readership had to be recognised; interest in the subject is wider, and, without doubt, the new style and approach permits easier understanding and access to the intelligent non-expert. That is as it should be for the next millennium.

The production of this fourth edition could not have been an easy task – modernising a standard respected work while avoiding sacrificing the principles and approach of the original author. Without doubt, the new team has been successful in meeting its brief of providing an authoritative reference, in the tradition begun by Frederick Lea more than 60 years ago.

Professor George Somerville November 1997
Director of Engineering
British Cement Association

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Preface

The fourth edition of F.M. Lea's book is intended to follow the tradition of the previous three. The other editions were noted reference works that maintained a relevance for some 60 years or more, being first published in 1935. While each of those editions was revised and extended, the present edition represents a radical restructuring in content and style, but hopefully is no less substantive.

The core purpose of the book remains unchanged, dealing with the physical and chemical properties of cements and concretes based on them, but linking back to their manufacture and use. As such it is a blend of the academic and pragmatic and should capture the interest of scientists, engineers and those that research, design, manufacture, educate and use this unique, cold, mouldable, inorganic plastic that we refer to as concrete.

Lea's previous editions represented a life's dedicated work and in that regard cannot be emulated. The technical sweep of those editions was both wide and deep and in manner of presentation that of Lea himself.

As Editor and contributor to this fourth edition it became readily and quickly apparent that this task required assistance from a range of individuals respected and acknowledged in their own right. In this regard the new edition consists of 16 chapters against the third edition's 21, although this edition has expanded the text by over 50 per cent. This has been achieved by consolidating several of the original chapters and also creating new ones. For instance, Chapters 2 and 3, 6 and 11, 9 and 10, 12, 19 and 20, have been melded together offering a fresh look at the inter-related aspects.

Three new chapters have been included, namely 'The production of low-energy cements', 'Microsilica as an addition' and 'Cement admixtures'. The latter perhaps presents my particular bias. The original Chapter 21 that dealt with concrete failures has been omitted because aspects of this topic have been dealt with in Chapters 5 and 7. In addition, the subject could not adequately be dealt with in a single chapter.

Notwithstanding these changes, the plan of this edition resembles closely that of the third edition, opening with the history of calcareous cement dealt with in perhaps greater detail than before.

Chapter 2 brings together the previous Chapters 2 and 3 and is updated to represent modern practices. There can be few mass produced commodities, such as Portland cement, that have been subject to such radical changes in production methodology driven by energy conservation and efficiency and resulting in a consistent high-quality volume material.

Chapter 3 covering cement components and their phase reactions, endeavours, and I judge succeeds, in presenting a difficult subject in a clear and concise way.

Chapter 4 is a melding together of previous Chapters 6 and 11 because constitution, structure and specification are closely related. The burning of Portland cement remains as a separate topic, as in the third edition, and like in the previous edition is dealt with exhaustively, updating and reorientating Lea's original.

Chapter 6 collects together three previous chapters covering cementing qualities, hydration and composition into a comprehensive statement while avoiding some of the previous overlaps. I trust nothing has been lost by reorganising the material in this way.

The attempts to bring topics and data together rather than keeping them apart continues into Chapter 7 dealing with natural destructive agencies such as acid groundwater, sulfate attack and inorganic compounds. This consolidates Chapters 12, 19 and 20 from the third edition, but, even so, such consolidation has resulted in more extensive text.

The physiochemical and mechanical properties of Portland cement are dealt with together, followed by a new chapter on the production of low-energy cements. This is a topic not considered in the last revision of Lea's book but has considerable relevance now.

The subject of pozzolanas and pozzolanic cements together with blastfurnace slag have been integrated into durable concrete technology and best practice and are deserving of comprehensive presentation. I trust this has been achieved.

The subject of silica fume postdates the third edition and has progressed rapidly for high and ultra high strength concretes and their associated durability. Concrete suffers from a populist pedestrian image and relatively few are privileged to experience the opportunity this material offers. The use of silica fume, coupled with chemical admixture advances, has opened up a new era for concrete in both the materials and design senses. The chapter on silicates is a foretaste of new ideas and thinking that leaves us with the prospect of concretes exceeding strengths of 250 MPa and a durability prognosis that is unlimited. Time will tell.

High alumina cement is given some prominence as it was in the third edition. The particular merits and limitations are categorised and the characteristics of conversion dealt with. As with all materials, engineering compromise is better achieved when supported by good science. This chapter now brings the matter up to date.

Concrete is still the subject of active innovation and this is demonstrated no better than in the field of oilwell cements and related materials. Interfacing new materials technology with large-scale problem solving has always underwritten concrete development. The connection between the two can no longer be naive pragmatism but rather understanding that in turn requires good science. I hope that bias is self evident in the new edition.

The final two chapters cover cement admixtures (a new chapter) and concrete aggregates. The former topic has developed substantially and globally over the past 20 years and is now integrated into best practice. Indeed the advantages offered by cement supplements such as silica fume could not be realised without dispersing type admixtures. A separate chapter seemed justified because there have been several excellent books on the subject in recent times and the technology has its own clear identity. The book concludes with concrete aggregates – a substantial topic dealt with substantively.

With hindsight and having taken several years to update Lea's book, it is inevitable other items come to mind that are worthy of inclusion. For instance, the fundamental matter of the role of water, sustainable technologies, design impact of ultra high strength concretes, durability and the use of waste and recycled materials. Rather than consider these items as omissions they should act as a spur to a fifth edition since that is at the root of Lea's first and follow-on editions. As concrete evolves so will Lea's book. It will be with us well into the third millennium. A legacy that Lea, I hope, would be proud of.

A book such as this has received support and input from many people, local and geographically dispersed. I am indebted to all of these and in particular to Keith Whittles from whom the original invitation came to attempt the rewrite of the third edition. Naturally I express my gratitude and thanks to the authors of chapters, to critics, to those that have read drafts and re-drafts, the endless conversations that have always ended in good advice. These people will know who they are and I thank them sincerely.

Finally, I am indebted to my family and in particular my wife Anne, who has tolerated the reams of paper and various preoccupations with encouragement and humour.

Professor Peter C. Hewlett November 1997

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In Chapter 1, Figures 1.2, 1.3 and 1.7 have been provided by the British Cement Association; Figure 1.4 was provided by Blue Circle Industries PLC; and Figures 1.1 and 1.5 were provided by Robert G. Blezard. The author of the chapter would also like to thank Mr A.E. Beety (Blue Circle Information and Patent Services) for assistance in locating references.

In Chapter 12, Figure 12.1 was provided courtesy of Elkem Materials, while in Chapter 16 picture credits are due as follows: to Mid-Essex Aggregates Limited (Figure 16.6); Mr E.V. Walters of ECC Limited, retired (Figure 16.9); Transport Research Laboratory, Crowthorne, UK (Figure 16.23); Mr D. Palmer of the British Cement Association, retired (Figure 16.26); Mr D. Stark, Construction Technology Laboratories Inc., Skokie, IL, USA (Figure 16.27); and the Building Research Establishment, Crown Copyright (Figure 16.32).

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International Cement Congresses

1918	*First International Symposium on the Chemistry of Cement*, London, January 1918. Published in: The setting of cements and plasters – a general discussion. *Transactions of the Faraday Society* (London, 1918): **14**: 1–69.
1938	*Second International Symposium on the Chemistry of Cement*, Stockholm, 1938. Published by Ingeniörsvetenskapsakademien, Stockholm, 1938.
1952	*Third International Symposium on the Chemistry of Cement*, London, 1952. Published by the Cement and Concrete Association, London, 1954.
1960	*Fourth International Symposium on the Chemistry of Cement*, Washington, 1960. Published by the National Bureau of Standards, Monograph 43, US Government Printing Office, Washington DC, 1962.
1968	*Fifth International Symposium on the Chemistry of Cement*, Tokyo, 1968. Published by the Cement Association of Japan, Tokyo, 1969.
1974	*Sixth International Congress on the Chemistry of Cement*, Moscow, 1974. Published by Stroyizdat, Moscow, 1976.
1980	*Seventh International Congress on the Chemistry of Cement*, Paris, 1980. Published by Editions Septima, Paris, 1980.
1986	*Eighth International Congress on the Chemistry of Cement*, Rio de Janeiro, 1986. Published by FINEP, Rio de Janeiro, 1986.
1992	*Ninth International Congress on the Chemistry of Cement*, New Delhi, 1992. Published by the National Council for Cement and Building Materials, New Delhi, 1992.
1997	*Tenth International Congress on the Chemistry of Cement*, Gothenburg, 1997. Published by Amarkai AB and Congrex Göteborg AB, Göteborg, 1977.

Abbreviated Formulae

The following abbreviated formulae are used in the text:

$C = \mathrm{CaO}$, $A = \mathrm{Al_2O3}$, $S = \mathrm{SiO_2}$, $F = \mathrm{Fe_2O_3}$, $T = \mathrm{TiO_2}$
$M = \mathrm{MgO}$, $K = K_2\mathrm{O}$, $N = \mathrm{Na_2O}$, $H = \mathrm{H_2O}$

Thus, for example:

$C_3S = \mathrm{3CaO\,.\,SiO_2}$
$C_2S = \mathrm{2CaO\,.\,SiO_2}$
$C_3A = \mathrm{3CaO\,.\,Al_2O_3}$
$CA = \mathrm{CaO\,.\,Al_2O_3}$
$C_2AS = \mathrm{2CaO\,.\,Al_2O_3\,.\,SiO_2}$

$C_2F = \mathrm{2CaO\,.\,Fe_2O_3}$
$C_4AF = \mathrm{4CaO\,.\,Al_2O_3\,.\,Fe_2O_3}$
$C_3MS_2 = \mathrm{3CaO\,.\,MgO\,.\,2SiO_2}$
$KC_{23}S_{12} = \mathrm{K_2O\,.\,23CaO\,.\,12SiO_2}$
$NC_8A_3 = \mathrm{Na_2O\,.\,8CaO\,.\,3Al_2O_3}$

1

The History of Calcareous Cements

Robert G. Blezard

Cements may be defined as adhesive substances capable of uniting fragments or masses of solid matter to a compact whole. Such a definition embraces a large number of very different substances having little in common with one another but their adhesiveness, and the very unequal technical and scientific importance of different members of the class has tended to bring about a restriction of the designation to one group of adhesive substances, namely, to the plastic materials employed to produce adhesion between stones, bricks, etc. in the construction of buildings and engineering works. Cements of this kind also bear a chemical relationship to each other, consisting as they do of mixtures which contain compounds of lime as their principal constituents. The term 'cements' in this restricted sense then becomes equivalent to 'calcareous cements', but it may be allowed to include certain allied compounds of magnesium.

The use of cements in building is not met with below a relatively advanced stage of civilisation. The earlier structures are composed of earth, sometimes raised in the form of walls or domes by ramming successive layers, or of stone blocks, set one above another without the aid of any cementing material, as in prehistoric megalithic structures, and in the Cyclopean masonry of Greece. The stability of walls of the latter kind is derived entirely from the regular placing of heavy masses of stone without any assistance from adhesion. Although remarkable works have been accomplished by such a method of construction, notably in the domed chambers of Mycenæ, where small stone wedges are driven between the large blocks in order to tighten the joints, yet Cyclopean work has always given place in later times to masonry or brickwork, erected with the aid of some plastic material.[1]

The simplest plan is that found in the brick walls of ancient Egyptian buildings. The bricks are dried in the sun without baking, and each course is covered with a moist layer of the loam (Nile mud) used for making the bricks, with or without the addition of chopped straw. The drying of this layer makes the wall a solid mass of dry clay. Such a mode of construction is only possible in a rainless climate, as the unburnt material possesses little power of resistance to water. It has nevertheless persisted throughout the ages, and towns such as Kuwait on the Persian Gulf have been entirely built of mud until recent years. Burnt bricks and alabaster slabs were employed by the Babylonians and Assyrians, and were cemented together with bitumen. This method is very efficacious, but being necessarily confined to those regions in which natural deposits of the material occur, it was not copied elsewhere.

In the massive masonry constructions of the Egyptians we meet with our present-day system of uniting blocks and slabs of stone with a mortar, consisting of a mixture of sand with a cementitious material. Whilst the typical Egyptian mortar has been generally described by writers on Egypt as burnt lime, even where found in buildings as old as the Great Pyramid, chemical examination shows[2] that the Egyptians never used lime until the Roman period and that the cementing material was always obtained by burning gypsum. As the gypsum was quarried in a very impure state, it usually contained calcium carbonate, which might be partly decomposed in the process of burning, or even if found in an undecomposed state in the mortar would produce the impression that lime had been used. The gypsum was very roughly burnt, so that a mixture of the unchanged mineral with 'dead-burnt' plaster was generally obtained. Such a mortar must have been irregular in setting, and troublesome to make use of successfully.

According to the valuable work of A. Lucas,[3] the reason for using gypsum instead of lime, although limestone was more abundant and more accessible than gypsum, was the scarcity of fuel, lime requiring a much higher temperature, and consequently more fuel for its calcination.

Although the early Egyptians were not acquainted with the use of lime, it was used at a very early period by the Greeks and earlier still in Crete, and the Romans must have borrowed it from Greece. The mortar was prepared in the modern fashion, by slaking the lime and mixing with sand, and the examples of Roman brickwork which still exist are sufficient evidence of the perfection which the art attained in ancient times. The remarkable hardness of the mortar in walls of Roman workmanship puzzled many engineers and has sometimes led to the assumption that some secret was possessed by the workmen which is now lost, but a comparison of the anaylses of the mortar with the descriptions of the method by ancient authors gives no ground for such a supposition.

The subject attracted special attention at the time of the construction of the great water works at Versailles. The ancient writers insisted on storing lime in the slaked condition for a long time, preferably several years, before use, but in 1765 Loriot, a French engineer engaged on this work, maintained that the passages in question had been misunderstood, and proposed the addition of quicklime to the mortar at the time of mixing, in order to obtain increased strength and impermeability.[4] De la Faye[5] contested this, and recommended that egg-sized lumps of lime should be immersed in water, transferred after a time to a cask, and there allowed to slake, evolving steam. This practice is borrowed from St Augustine. Faujus de Saint-Fond,[6] in the course of a very careful study of pozzolanic materials, favoured this latter plan of slaking, and also called attention to an Indian process, employed on the Malabar Coast, of mixing molasses with lime concrete in order to increase the hardness. Finally, Rondelet,[7] after a careful examination of Roman buildings and after making many experiments with the methods proposed by Loriot and others, came to the conclusion that the excellence of Roman mortars depended, not on any secret in the slaking or composition of the lime, but on the thoroughness of mixing and ramming.

The subsequent history of building abounds in examples of differences in the permanence of brickwork and masonry due to differences in the attention paid to this all-important point.

Rondelet's explanation is without doubt correct. Analyses show nothing abnormal in Roman mortars, but the texture is very close, and the interior is often found to contain lime which has not become carbonated, showing the impermeability of the mortar to gases. The practice of long-continued ramming is confirmed by Indian experience. In Bengal, where finely ground brick replaced the whole or part of the sand, fat lime and ground brick (*surki*) were mixed wet in an edge-runner until a sticky mass was formed, and this was then added to the aggregate, the whole being mixed thoroughly and rammed into place. After this, tamping was kept up for several hours until, on scooping a hole and filling it with water this was not absorbed.

Both the Greeks and the Romans were aware that certain volcanic deposits, if finely ground and mixed with lime and sand, yielded a mortar which not only possesses superior strength, but was also capable of resisting the action of water, whether fresh or salt. The Greeks employed for this purpose the volcanic tuff from the island of Thera (now called Santorin) and this material, known as Santorin earth, still enjoys a high reputation on the Mediterranean. The mortar used by the peasants of Santorin – an island destitute of wood for building – long remained identical in its composition and preparation with that of ancient times.[8]

The corresponding material of the Roman builders was the red or purple volcanic tuff found at different points on and near the Bay of Naples. As the best variety of this earth was obtained from the neighbourhood of Pozzoli or Pozzuoli (in Latin *Puteoli*), the material acquired the name of Pozzolana[9] and this designation has been extended to the whole class of mineral matters of which it is a type. Vitruvius says of it: 'There is a species of sand which, naturally, possesses extraordinary qualities. It is found under Baiæ and the territory in the neighbourhood of Mount Vesuvius; if mixed with lime and rubble, it hardens as well under water as in ordinary buildings.'[10]

If volcanic earth did not happen to be available, the Romans made use of powdered tiles or pottery, which produced a similar effect. To quote Vitruvius again, 'If to river or sea sand, potsherds ground and passed through a sieve, in the proportion of one-third part, be added, the mortar will be the better for use.'[11] It is remarkable that the word 'cement' in its Late Latin and Old French forms was first employed to designate such materials, now classed as artificial pozzolanas; its meaning then changed to denote the mortar prepared by mixing the three ingredients, and it is only in recent times that it assumed its modern meaning. There is evidence that crushed potsherds were added to lime mortar to give it hydraulicity in the Minoan civilisation of Crete and it seems that the Romans may have used crushed tile additions before they discovered the natural pozzolanas that occur near Rome.

The Romans carried their knowledge of the preparation of mortar with them to the remoter parts of their empire, and the Roman brickwork found in England, for example, is equal to the best of that in Italy. Ground tiles were the most commonly used ingredient, but in a few districts deposits bearing some resemblance to the natural pozzolanas of the Bay of Naples were found. The use of Rhenish volcanic tuffs known as Trass[12] was probably introduced at this time, and this material, like pozzolana, is still employed at the present day.

A gradual decline in the quality of the mortar used in buildings set in after Roman times, and continued throughout the Middle Ages. Saxon and Norman buildings, for instance, show evidence of badly mixed mortars, often prepared from imperfectly burnt lime. The conclusion appears certain, from the examination of French buildings,[13] that during the ninth, tenth and eleventh centuries the art of burning lime was almost completely lost, the lime being used in badly burnt lumps, without the addition of ground tiles. From the twelfth century onwards the quality improved, the lime being well burnt and well sifted. After the fourteenth century excellent mortar is found, and the precaution was evidently taken of washing the sand free from adhering dirt or clay. References to 'tarrice' or 'tarras' in documents of the seventeenth century[14] indicate that the use of pozzolanas in mortar must by then have been established again in England.

The term 'cement' was commonly applied in the Middle Ages to the mortar, for instance in the work, so much used as an authority in medieval and later times, the *De Proprietatibus Rerun* of Bartholomew Anglicus, in which we read: 'Lyme... is a stone brent; by medlynge thereof with sonde and water sement is made.'[15] The word 'mortar' was, however, also employed as early as 1290.[16]

The Roman mixture of lime and natural or artificial pozzolana long retained its position as the only suitable material for work under or exposed to water. Thus Belidor, for a long time the principle authority on hydraulic construction, recommends an intimate mixture of tiles, stone chips, and scales from a blacksmith's forge, carefully grounded, washed free from coal and dirt, dried and sifted, and then mixed with freshly slaked lime.[17] The same author mentions the use of pozzolana or trass where such materials are available. A very thorough and illuminating survey of the subject which will be referred to later is that in Rondelet's great work on building.[18] It is remarkable that even at this late date most of the authorities quoted are ancient, including Pliny, Vitruvius, and St Augustine.[19]

When we come to more recent times, the most important advance in the knowledge of cements, the forerunner of all modern inventions and discoveries in this connection, is undoubtedly the investigation carried out by John Smeaton. On being called upon in 1756 to erect a new lighthouse on the Eddystone Rock after the destruction of the previously existing building by fire, he proceeded to make inquiries as to the best building materials for work under such severe conditions.[20] He found that the usual mortar for work under water was composed of 'two measures of quenched or slaked lime, in the dry powder, mixed with one measure of *Dutch Tarras*,[21] and both very well beat together to the consistence of paste, using as little water as possible.' Since the results with this mixture were not always satisfactory, he attempted to discover the effect of using limes of different origin, comparing the mixtures by a cold-water test (immersing a stiffly worked ball of mortar in water immediately after setting). Finding that lime from the Aberthaw Limestone, in Glamorgan, gave better results than ordinary lime, he compared the chemical behaviour of different limestones, and discovered that those which gave the best results as mortars agreed in containing a considerable proportion of clayey matter. This was the first occassion on which the properties of hydraulic lime were recognised. He also compared several varieties of natural and artificial pozzolana as substitutes for trass, including burnt ironstone and forge scales. Ultimately, mortar prepared with blue Lias hydraulic lime, and pozzolana from Civita Vecchia, in equal quantities very thoroughly mixed, was used for the work. Smeaton's lighthouse tower was erected on the Eddystone rocks in 1759. It had a height of 72 feet and had 93 steps. When this lighthouse was replaced by a newer, larger lighthouse in 1882, Smeaton's tower was removed stone by stone to its present site (1882) on Plymouth Hoe, where it has been Plymouth's most famous landmark ever since (Figure 1.1).

In spite of the success of Smeaton's experiments, the use of hydraulic lime made little progress, and the old mixture of lime and pozzolana retained its supremacy for a long period.[22] The discovery that a hydraulic cement could be made by calcining nodules of argillaceous limestone, known as septaria, found in certain Tertiary strata, was patented in 1796.[23] The product thus obtained was given the inappropriate and misleading name of Roman cement, from its hydraulic properties, although it no way resembled the Roman mortar. The term 'Roman' applied to the cement was given by James Parker for the first time in a pamphlet (1798) entitled *Roman cement, artificial terras and stucco* containing a copy of a letter from Thomas Telford to John MacKenzie, Secretary to the British Society for the Fisheries, etc., dated 12 April 1796, in which Telford details experiments that he had carried out with the cement on 23 and 26 March and on 4 April by direction of the Directors of the Society. Telford concluded that he is 'fully justified in recommending to the Directors to use Mr. Parker's Composition, in place of Dutch Tarras, in constructing of the Pier at Lochbay in Skye'.

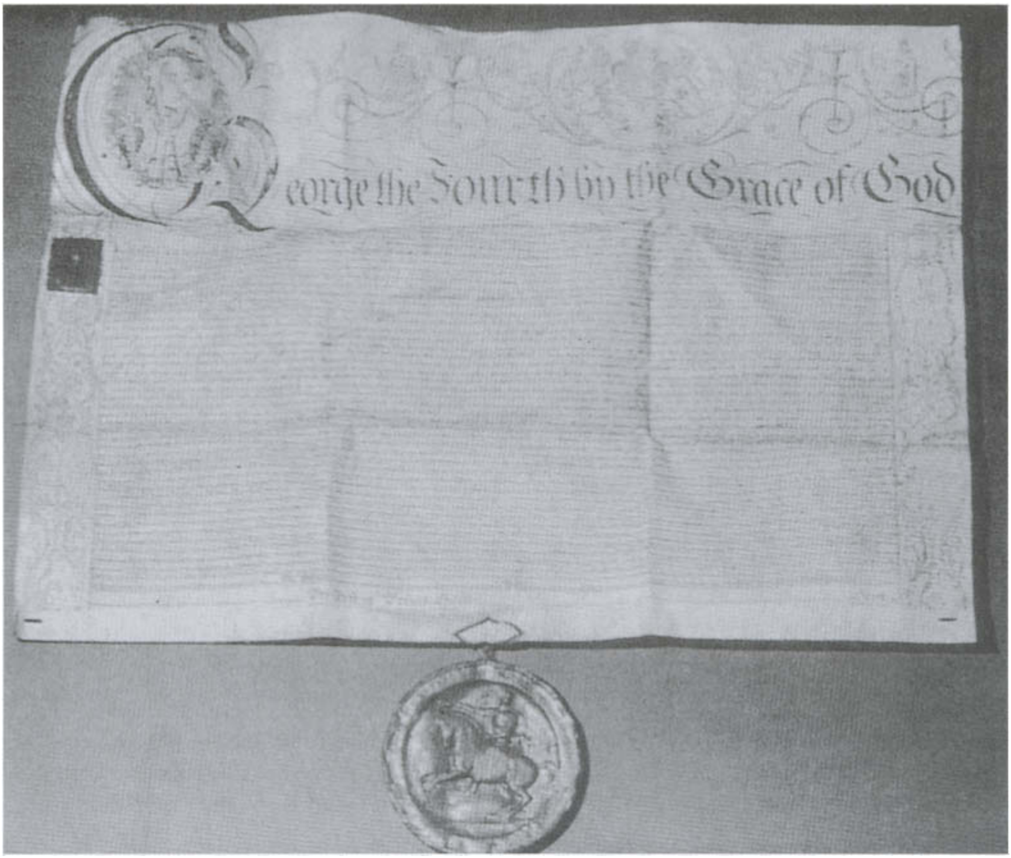
Roman cement was a quick-setting cement and was found useful in work in contact with water and steadily grew in favour.[24-26] Its heyday for civil engineering work lasted until

Fig. 1.1 Smeaton's Eddystone lighthouse tower.

about 1850, after which it was gradually 'driven-out' by Portland cement. The development of hydraulic cements proceeded as a gradual evolution not only in Britain but also in other countries. About the same time as Roman cement was introduced, a similar natural cement was prepared in France from similar concretions found near Boulogne, and deposits of 'cement rock', capable of yielding a hydraulic cement on calcination, were found at Rosendale and at Louisville, in the USA. It was not long before the American natural cement industry attained great importance, particularly in the building of canals.

The investigations of L.J. Vicat[27] on hydraulic lime led him to prepare an artificial hydraulic lime by calcining an intimate mixture of limestone (chalk) and clay, ground together in a wet mill. This process may be regarded as the principal forerunner of the manufacture of Portland cement.[28] Edgar Dobbs of Southwark patented[29] a cement of this kind in 1811. In 1825 James Frost established a manufacturing plant at Swanscombe (Kent) – this was the first calcareous cement works in the London district. He only lightly calcined his raw mixture, and the product was evidently inferior to Roman cement, as it was sold at a lower price.

Among the numerous patents for hydraulic cements which appeared in the early nineteenth century one stands out in historic importance to the others; this was the famous patent,[30] no. 5022 (Figure 1.2), dated 21 October 1824 by Joseph Aspdin. Aspdin was a Leeds builder or bricklayer who was conversant with building stones, and in his patent he described his material as 'Portland Cement'. This choice of name was applied because at that time Portland stone had a high reputation for quality and durability and Aspdin wanted to direct people's attention to the resemblance of the colour and quality of his cement to Portland stone – a limestone quarried in Dorset, much favoured by Wren in the late seventeenth century.



George the Fourth by the Grace of God

Fig. 1.2 British Patent 5022 (21 October 1824) granted to Joseph Aspdin in the pre-Victorian era of cement investigation.

Aspdin used a hard limestone as used for the repairing of roads, crushed and calcined it,[31] and mixed the lime with clay, grinding it to a fine slurry with water. 'Then I break the said mixture into suitable lumps and calcine them in a furnace similar to a lime kiln till the carbonic acid is expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone.' Like Frost, he probably used a low temperature, and the product must have been of poor quality. He appears to have been guided by the idea that artificial heat applied to clay must produce a material similar in properties to the natural volcanic earths. His first works were at Wakefield (Figure 1.3).

Aspdin's early cement was nothing more than a hydraulic lime, but his 1824 patent gave him the priority for the use of the term Portland cement even though his product was not the Portland cement that we know today. Its mineralogy was completely different, as was its hydraulic activity. Nevertheless, Aspdin's patent cement was an essential link in the development that led, through technological advancement, to the calcium silicates of today which we call Portland cement.

Going back in time, Bryan Higgins[22] (1780) described the quality of one of his experimental mortars as '...in three months was almost as hard as Portland Stone at the surface.' Higgins changed his method of preparation and he then stated '...in the course of a month, I found this piece of stucco harder and closer than the former and at the surface as much superior in these particulars to Portland Stone as the other was inferior to it.' Later, John Smeaton[20] (1791) had described how he had aimed '...to make a cement that would equal the best merchantable Portland Stone in solidity and durability.'

Fig. 1.3 Joseph Aspdin's first cement works at Kirkgate, Wakefield (*ca* 1828); proto-Portland cement was manufactured at this plant.

The patent cement manufactured by Joseph Aspdin's process was a precursor to modern Portland cement. The younger son of Joseph Aspdin, William, spent nearly 12 years at his father's firm gaining a thorough knowledge of the business. However, in July 1841 he unexpectedly left the firm, probably as a result of a family quarrel, and started a cement plant at Rotherhithe on the south bank of the River Thames in London during the summer of 1843. The plant was owned by J.M. Maude, Son & Co., and operated to manufacture an improved cement. William Aspdin had discovered that clinkered or 'overburnt' material substantially increased the strength of his cement. As William had only a limited knowledge of chemistry, the discovery must almost certainly have been accidental. In early 1846 a new works was set up at Northfleet, but its operating was dogged by financial problems and associated ownership. William Aspdin continued cement manufacure both on the Thames and at Gateshead-on-Tyne. A preserved Aspdin beehive kiln at Northfleet is illustrated in Figure 1.4 – this kiln was in operation during the period 1847–50. Skempton[32] has indicated that in 1848 Aspdin's cement was 2.4 times stronger than the best Roman cement of that time and 20% stronger than the Portland-type cement made by Messrs J.B. White (the manager was I.C. Johnson). A retrospective microscopical examination of 'preserved' Portland-type cement[33] made by Aspdin's plant at Northfleet indicated that he attained vitrification in his kiln and produced alite crystals (Figure 1.5).

I.C. Johnson had also observed that 'overburnt' lumps found in kilns, although slower setting when ground, made better cement than the usual product. Johnson had some difficulty in finding the correct proportions of clay and chalk, but this appeared to have been resolved as Johnson decided to leave his employer and build his own plant at Rochester, which started production on 1 May, 1851. He later took over William Aspdin's abandoned works at Gateshead.

A higher temperature of firing must have been introduced in Aspdin's works before this, as on the resumption of the construction of the Thames Tunnel in 1838, Brunel employed Portland cement in spite of the fact that its price was double that of Roman cement, and in the face of strong opposition.[34]

Cement was being manufactured in a highly competitive environment. Aspdin did not protect his improved technique but resorted to subterfuge. Aspdin long kept his process secret, and according to Johnson, who claimed to have suggested the firing at a temperature high enough to produce vitrification, he used to carry trays of copper sulphate into the kilns when charging, in order to convey an impression that the process depended on the addition of salts. Aspdin (1848) stated[35] that his father's 1824 patent was the only patent for the manufacture of Portland cement.

The story of the invention of Portland cement has not been easy to disentangle.[36,37] As has happened so often in chemical history, the real innovator of an industry was not the initial discoverer of a reaction. Joseph Aspdin's contribution was the name 'Portland' cement (from his dubious 1824 patent) and, although his product was a detectable improvement on previous material, this was only a proto-Portland cement. It was not until the mid-1840s that William Aspdin accidentally synthesised the calcium silicates which were the basis of meso-Portland cement. It was Johnson who developed meso-Portland cement after Aspdin's initial work at Northfleet. Johnson had some chemical training and he nurtured the process and watched the industry grow to maturity in the Twentieth century before he died in 1911 at the age of 100.

William Aspdin was nefarious[38] in his business transactions and as a consequence his business partnerships continually failed. In the late 1850s he was involved in several cement ventures in Germany, but the factories were short-lived in operation and he died at Itzehoe as a result of a fall in 1864 at the age of 49.

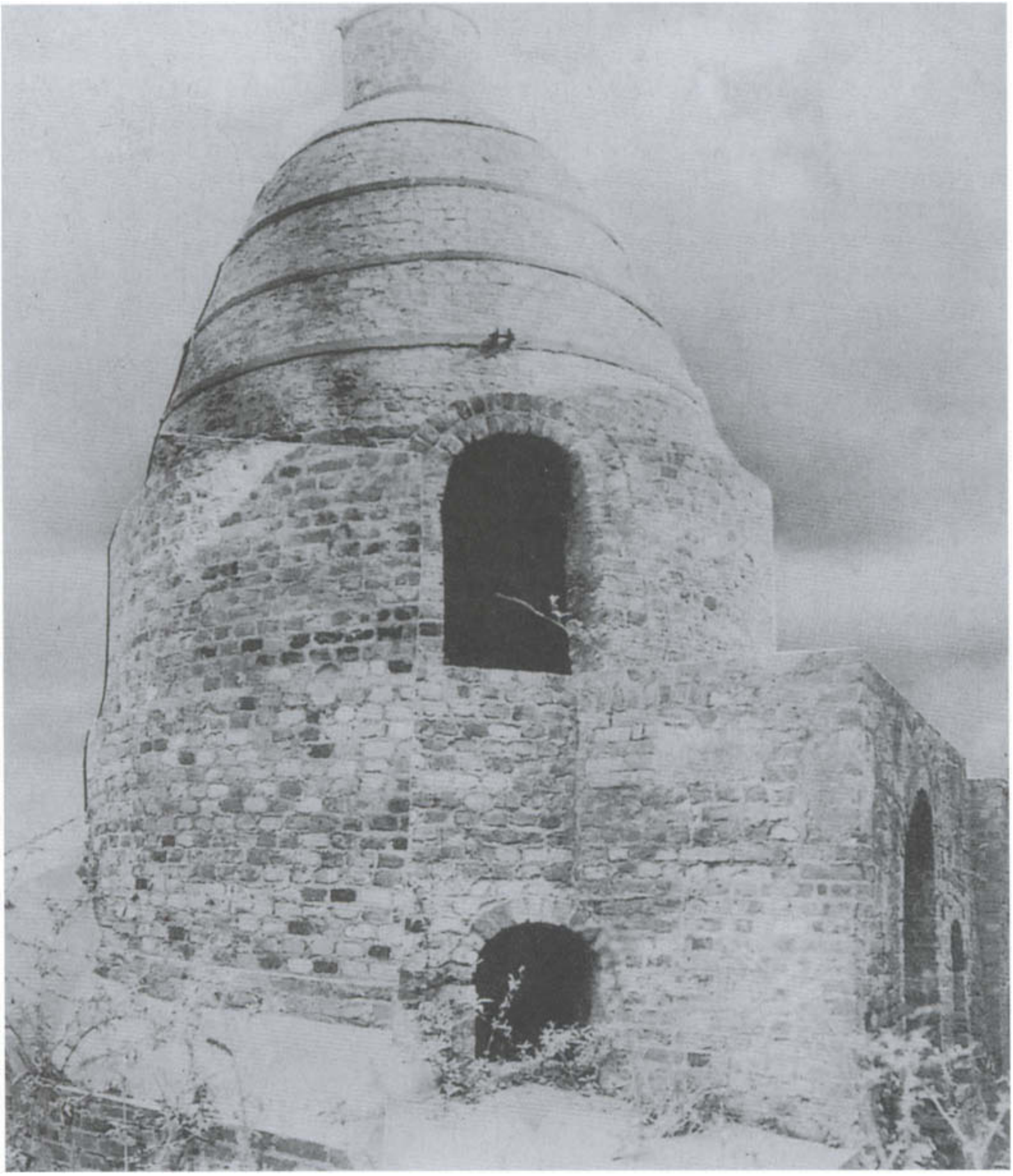


Fig. 1.4 William Aspdin's preserved beehive kiln at Northfleet, Kent, which operated from 1847 to 1850. This is the oldest surviving Portland cement kiln in the world. Meso-Portland cement was manufactured in this kiln.

In the history of Portland cement the most important event, from the point of view of production technique and quality control, was the introduction and technical development of the rotary kiln, which replaced the shaft kiln. Cement manufacture was changed from a batch process to a continuous production process. This change took place, slowly, at the

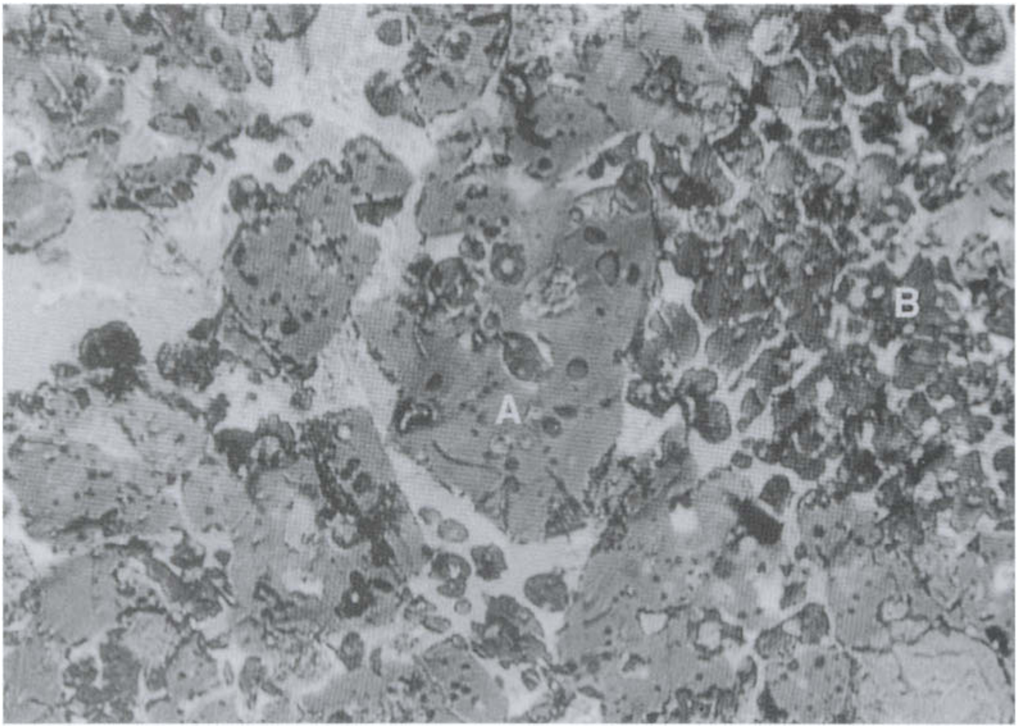


Fig. 1.5 Photomicrograph of a polished section of meso-Portland cement clinker from Aspdin's preserved kiln (magnification ×300). Note the alite and belite crystals cooled slowly in a well-differentiated flux. A indicates a large alite crystal; B indicates small belite crystals. The view portrays a very slow cooling regime.

beginning of the twentieth century, and some 70 years after this, quality control was further improved with the implementation of computer monitoring.

Looking back in retrospect it is possible to differentiate stages in the development of historic Portland cement through a study of the mineralogical assemblage comprising 'Portland' cements manufactured at different periods.[39] This approach facilitates a classification with the following terminology:

- proto-Portland cement;
- meso-Portland cement;
- normal Portland cement.

By studying the unhydrated mineral assemblage in mortar by reflected light microscopy, the nature of the original cement may be ascertained.

Proto-Portland cement is essentially a calcined mixture of limestone and clay with little evidence of $CaO-SiO_2$ interaction, because the burning temperature is too low for compound synthesis. Joseph Aspdin's original patent cement made at Wakefield may be termed proto-Portland cement.

Meso-Portland cement is an extremely heterogeneous material but with definite evidence of $CaO-SiO_2$ interaction (producing β-$2CaO{\cdot}SiO_2$ and a small content of $3CaO{\cdot}SiO_2$)

and poorly defined flux phases. Meso-Portland cement displays clear evidence of slow cooling, the presence of low temperature ternary solid solution occasionally with unreacted grains of silica (grinding the raw material with grinding stones) and flakes of iron (from bars in the vertical kiln). Figure 1.5 shows a photomicrograph of meso-Portland cement.

Normal Portland cement, as we know it today, is a quality calcareous cement manufactured in a rotary kiln and a definition of this product can be made. Normal Portland cement is a synthetic mixture of calcium silicates formed in a molten matrix from a suitably proportioned and homogeneously prepared mixture of calcareous and argillaceous components. The calcination period, the reaction temperature and the residence time in the burning zone of the rotary kiln should be such as to minimise the uncombined lime and maximise the calcium silicates in the product which, through its basic proportioning, will yield a suitable ratio of $3CaO \cdot SiO_2$ to $2CaO \cdot SiO_2$. The product, when ground to an optimum particle size distribution can then hydrate under certain conditions to agree with commercial requirements within the relevant national standard specifications (e.g. BS 12: 1991). Normal Portland cement (unlike earlier proto- or meso-Portland cement) will contain a controlled amount of interground calcium sulfate as a setting retarder.

Table 1.1 shows a comparison of meso- and normal Portland cement by looking at the crystal characteristics using Ono's micro-mensuration techniques.

The development of cement technology may be studied as a function of strength improvement[40] of the hydrated mix of a mortar with respect to the chronological period studied, as indicated in Figure 1.6. Period 1 on this graph plots the era of meso-Portland cement whilst period 2 is the transitional stage with the beginning of quality control procedures leading to period 3 which represents normal Portland cement. Period 1 was dominated by British technology whilst period 2 was dominated by German technology. Normal Portland cement, after World War II, was made in two grades: ordinary and rapid

Table 1.1 A comparison of meso- and normal Portland cement based on the crystal characteristics of the essential silicates (after Blezard, Ref. 70, p. 632)

Relative operating factor (measurement parameter)	Meso-Portland cement Aspdin clinker (1848)	Normal Portland cement 'present-day' rotary kiln clinker
Relative burning rate	Slow (poor)	Quick (excellent–average)
Alite size	60 μm	10–40 μm
Relative maximum temperature	Low (poor)	High (good)
Alite birefringence	0.002	0.007
Relative burning time	Long (poor)	Quick (good–excellent)
Belite size	5–10 μm	20–60 μm
Relative cooling rate	Slow (poor)	Quick (average–good)
Colour of belite	Amber	Faint yellow–yellow
α-$2CaO \cdot SiO_2$	Nil	10–20%
Scale of process	Batch	Continuous
Kiln	Static beehive vertical kiln	Long rotating tube kiln with cooling system

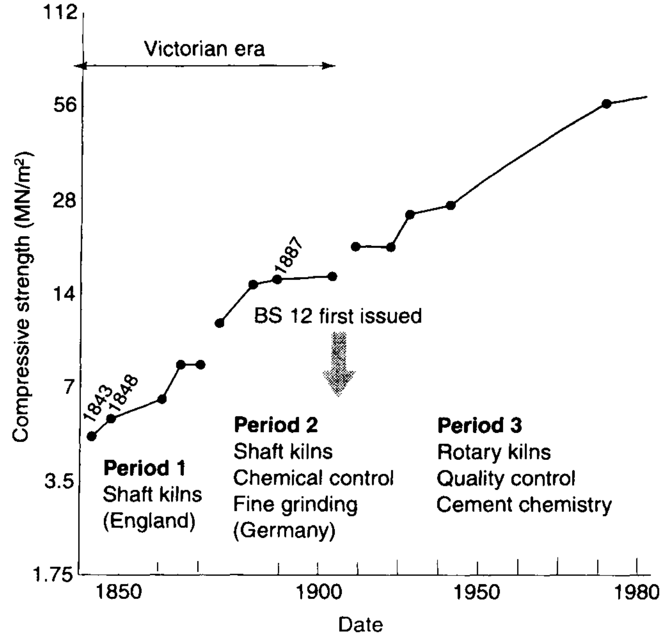


Fig. 1.6 Stages of technological improvement; compressive strength of Portland cement mortar (1:3 by weight at 28 days stored in water). Note the compressive strength scale units are not linear. (After Ref. 41.)

hardening (finer grinding and enhanced $3CaO{\cdot}SiO_2$). BS 12: 1991 specifies four strength classes in accordance with EN 196 Part 1, bringing it into line with ASTM and continental specifications. Portland cement shall be identified by at least the name and the subclass of early strength.

Since the development of meso-Portland cement (by William Aspdin and I.C. Johnson), the prime property looked for in calcareous cement was the ability of the hydrated product to develop strength, and over the years this aspect has been the major area of competition. The use of higher burning temperatures allowed the production of silicates with a greater lime content, which are essential for the more rapid development of strength in concrete. The heterogeneous character of the meso-Portland cement created a slow-setting cement and it was not necessary to intergrind the clinker with a retarding agent to control the setting of the gel. The strength-giving properties of Portland cement have steadily increased over the years as the thermal processing of the feedstock has been intermittently redesigned with the development of technology. Improvements at the end of the nineteenth century were the introduction of the ball mill for cement grinding and the gradual replacement of the batch-process shaft kilns by the continuous-process rotary kiln.

The converted lime-burning bottle kilns of the 1860s were replaced by horizontal arched chamber kilns (1872, I.C. Johnson) and by 1898 there were about 1000 kilns of various designs on the Thames and Medway rivers.

In 1877 Thomas Crampton, a locomotive engineer, patented a kiln with a revolving cylinder lined with firebricks. In 1885 an American, Frederick Ransome, produced a 6.5 m long cylindrical kiln but he had operational problems. The Americans continued their experimentation and in 1898 Hurry and Seaman perfected the first fully operational rotary kiln fired with powdered coal. The first rotary kilns to be erected in the UK were a battery of six small kilns at Thurrock in Essex (1900) to provide a source of cement for the construction of Dover harbour. The development of the rotary kiln towards the end of the Victorian era not only modified the scale of production but also assisted in creating a more homogeneous product where the nature of the mineral assemblage and the degree of comminution required a gel-setting retarder. To control the hydration of the $3CaO \cdot Al_2O_3$ component, gypsum was added at the grinding stage.

In the ensuing 90 years following the erection of the first rotary kilns in the UK, the kiln reaction stages have undergone many changes directed by aspects of quality and economy. The changes have involved a reduction in feedstock water content, the nature of the firing flame, fuel economy and later by computerised operation. The semi-dry and semi-wet processes were introduced[42] in the 1950s and by 1960 over 5 per cent of the UK cement clinker production was manufactured in this way. Between 1960 and 1980 major changes were introduced in the size of units installed and the material throughput increased some fourfold in the later designs. By 1980 over 50 per cent of UK Portland cement clinker was being made using the more thermally efficient processes. Over the period 1955–85 experimentation was made with fuel sources. Using pulverised coal the ash content is an integral part of the feedstock and has to be considered in raw feed calculations. The high cost of fuel has necessitated economies. The wet process used in the southeast of England was not thermally efficient because only a third of the total heat was used for the clinkering reactions after the water had been driven off and the feedstock decarbonated. As an alternative to pulverised coal, heavy fuel oil was tried and in the early 1970s some very attractive prices were available for natural gas. However, with the increase in gas prices in the late 1970s, cement manufacturers reverted back to coal firing with some plants augmenting their fuel input with the use of domestic refuse and even rubber tyres. Greater control of the firing conditions has assisted the clinkering reactions, lowered the amount of uncombined lime and has had a significant effect on the strength-giving properties.

The essential difference between the meso-Portland cement of the Aspdin era and modern Portland cement is in the combinability efficiency and mineral homogeneity (compound assemblage and crystal characteristics). The differences result from the level of the applied technology of the different ages. It is obvious that there have been changes in the properties of ordinary Portland cement during the twentieth century. The most significant change has been with the ratio of tricalcium silicate to dicalcium silicate, though the total proportion of calcium silicate in cement has remained approximately constant. Concern was expressed[43] in the 1980s about the implication of the gradual increase of strength of Portland cement with the possible effect on the durability of concrete.

If concrete mix design is based on a strength-only specification, the required strength could be achieved with a considerably lower cement content and a higher water–cement ratio than hitherto used. This clearly has serious implications for the durability of concrete. It is therefore essential to specify concrete properly to ensure durability in the environment to which it will be exposed. This means specifying minimum cement contents, maximum water–cement ratios and concrete strengths that are compatible with the former two characteristics.

Similar property changes were recorded in the USA and numerous investigations were undertaken to study the changes in cement characteristics. The best-known study was that by Gonnerman and Lerch (1952)[44] who undertook a detailed survey of American cements over the period 1904–50. Direct comparison of American and British data was not possible because of differences in test methods, but the slope of strength characteristics over the years was similar, giving confidence that American data could be correlated to British

Standard 28-day cement strengths. During the twentieth century there has been a four- or five-fold increase in cement strength at 28 days and a corresponding capacity for design concrete strengths to be increased. It is clear that structures built today in concrete would have been impossible with the low-strength cement that was available earlier in the century.

The use of concrete, an artificial conglomerate of gravel or broken stone with sand and lime or cement, is also of great antiquity. The term 'concretum' was applied by the Romans only to the finished mass. Pliny[45] thus refers to the construction of cisterns: 'Cisterns should be made of five parts of pure gravelly sand, two of the very strongest quicklime, and fragments of silex[46] not exceeding a pound each in weight; when thus incorporated, the bottom and sides should be well beaten with iron rammers.' A form of concrete made with broken tiles was much employed for pavements, and cement mixed with oil or other organic matter was often applied as a surface coat for waterproofing purposes. Much of the best concrete was made from broken brick, lime and pozzolana, whilst in large works volcanic tuff generally took the place of brick. The great vaults of the Thermæ and of the Basilica of Constantine are cast in concrete.[47,48]

The most famous of Roman buildings erected in concrete is the Pantheon, the walls of which, 6 m thick, are of tuff and pozzolana concrete thinly faced with brick, whilst the dome, 43.5 m in span, is cast solid in concrete containing pumice and pozzolana. Wooden boards were used as moulds, and the concrete was filled in in a semi-fluid condition. The Pantheon[49,50] was one of the few buildings in Rome to survive intact after the decline of the Roman Empire. Lightweight concrete involving volcanic tuff and pozzolana was developed by Roman builders and used in some of the arches of the Colosseum and the dome of the Pantheon (Figure 1.7). The light streaming down from the 8 m opening in the crown of the rotunda of the Pantheon falls from a height which is exactly the same as the diameter of the building – as required by the Roman theory of architectural proportions. The unique dome of the Pantheon and its durability inspired Sir Christopher Wren in his design of the dome for St Paul's Cathedral in London. The present condition of many Roman buildings of this class is a sufficient testimony to the excellence of the material. That the process was well understood is further shown by the existence of great masses of Roman concrete on the coast between Naples and Gaeta, polished by the sea but uninjured.

Concrete was also employed in building walls throughout the Middle Ages, but less systematically, and with less knowledge of the material, than under the Romans. The early Christian churches of Rome have concrete walls, whilst examples of the same mode of construction in England are Kendal Castle[51] and Corfe Castle, a Saxon structure, from which Smeaton derived the idea of using concrete in engineering works. Much of the concrete in medieval buildings is of very inferior quality. It is not until quite modern times that it again assumes importance, the first instance being the construction of the West India Docks in 1800. A great impetus was given to its use by the introduction of Portland cement, and since that time the use of concrete has grown until it has become the most versatile constructional material. The invention of reinfored concrete, a material in which the resistance to compression of well-mixed and hardened concrete is combined with the tensile strength of steel, increased the use of concrete and had a far-reaching effect in bringing about a steady improvement in the quality of cement. Whilst the first patent for a system of reinforced concrete construction[52] was taken out by W.B. Wilkinson in 1854, it has been observed that the decorative Fleurs-de-Lys at William Aspdin's Portland Hall (Gravesend, Kent), built in 1850, were made of reinforced concrete.

As the demand for Portland cement, especially as an ingredient of concrete, increased, and the requirements of engineers called for a more perfect material, it became increasingly

Fig. 1.7 The Pantheon, Rome.

desirable that standards of quality should be set up, by which any consignment could be judged after the performance of certain agreed tests. In this way standard specifications have arisen in most countries, either under official auspices, or as the work of voluntary organisations of engineers and consumers, or of associations of cement manufacturers. Such an association was founded in Germany[53] so far back as 1877, and shortly afterwards established rules for controlling the quality of the product. The first German Standard Specification was drawn up by this body. The formation of the VDZ (German Cement Works Association) was significant insomuch that Germany took over the mantle from Britain as the main region of development of cement technology, and this was mainly as a result of adherence to quality. During the rapid economic expansion in the USA following the Civil War, European-produced Portland cement, particularly German, was used. Some 8000 barrels of Dyckerhoff cement was imported in 1884, from Germany to build the concrete foundation of the Statue of Liberty in New York. This is one example – other buildings in New York which used German cement were the Waldorf-Astoria Hotel and the Metropolitan Opera House.

The first British Standard Specification (BS 12) was drawn up in 1904 by the Engineering Standards Committee (now the British Standards Institution) and its 14th revision appeared in 1996. A specification for Portland blastfurnace cement (BS 146) was issued in 1923 and its eighth revision appeared in 1991. To counteract the failure of ordinary Portland cement concrete in an aggressive sulfate environment, a sulfate-resisting cement was introduced and the first British Standard Specification (BS 4027) was drawn up in 1966, and its fourth revision appeared in 1991. The first ASTM specification was issued in 1904. All such specifications are liable to revision from time to time, the alterations made being almost invariably in the direction of increasing the stringency of the requirements. At the same time, most commercial cements commonly more than fulfil the conditions of the official specifications.

With the deliberate variation of the mineral character of a Portland cement, specialised application cements may be prepared and the term 'Portland cement' now achieves the status of a generic term.[54]

With the closer economic ties with the European community through the treaties of Rome and Maastricht, the European Committee for Standardisation (CEN) is preparing a European Prestandard for cements. As an intrinsic part of this activity, CEN has published EN 196, a series of methods for testing cement. BS 12: 1991 specifies requirements in terms of the EN 196 test procedures.

The scientific study of cements is of relatively recent date. Even the earliest authors dealt with the theory of setting, but their explanations were naturally of an extremely hypothetical character. Thus Vitruvius, who probably only recorded the current opinion of his time, and did not make any original contribution to the subject, is only able to suggest, in explanation of the properties of mortar, that

> stones...having passed through the kiln, and having lost the property of their former tenacity by the action of intense heat, their adhesiveness being exhausted, the pores are left open and inactive. The moisture and air which were in the body of the stone having, therefore, been extracted and exhausted, the heat being partially retained, when the substance is immersed in water before the heat can be dissipated, it acquires strength by the water rushing into all its pores, effervesces, and at last all the heat is excluded. ...The pores of limestone, being thus opened, it more easily takes up the sand mixed with it, and adheres thereto, and thence, in drying, binds the stones together, by which sound work is obtained.[10]

An ancient belief that the quality of a lime depended on the texture of the limestone from which it was made, a harder limestone giving a more durable mortar, persisted until long after the introduction of Portland cement.

Smeaton's remarkable experiments, in which he showed that the hydraulic limes owed their special properties to the clayey constituents of the limestone, were of fundamental importance for the understanding of the nature of cements, but they received little attention from chemists. The hypothesis of Bergman,[55] assigning the hydraulic properties of cements to the presence of manganese salts, although based on the accidental finding of some manganese in a hydraulic lime, was generally accepted, and was only overthrown by the work of Collet-Descotils,[56] who proved that the burning converted the silica into a soluble form, and especially by the very thorough theoretical and practical investigations of Vicat.[27]

The great range of materials studied by this author rendered his work particularly valuable. His principal theoretical conclusion was that the silica of the clay was the essential agent in the hardening process. On the other hand, Frémy,[57] who failed to prepare a calcium silicate with hydraulic properties, but succeeded in obtaining artificially a hydraulic calcium aluminate, assigned the principal share to the alumina. Frémy's work also contains an interesting anticipation of the thesis maintained later by Michaëlis, that the hardening of Portland cement and the reaction between lime and pozzolana are processes of the same chemical nature. The proof by J.N. Fuchs[58] that quartz and other forms of crystalline silica are inactive, whilst the amorphous and hydrated forms behave as pozzolanas, marked a further step in advance. The view that basic silicates are formed in burning, and are then hydrolysed by water, yielding lime and hydrated lower silicates, was propounded by A. Winkler[59] and has since fully established itself.

The scientific study of Portland cement began to gain momentum towards the end of the nineteenth century. Theories on the setting and the hardening of Portland cement were proposed by Le Chatelier[60] (1883; crystalline theory), W. Michaëlis[61] (1893; colloidal–gelatinous theory) and later by Baikov[62] (1926; three periods in the setting process) and then Rebinder[63] (1954, condensation–crystallisation three-dimensional model).

The most rewarding examination technique has been microscopy. Le Chatelier[64] used the petrological approach, and by microscopy he considered the essential component in Portland cement to be $3CaO{\cdot}SiO_2$ as one of four kinds of crystal. An independent study by Törnebohm[65] (1897) reported four types of crystal to which he gave the names alite, belite, celite and felite. Assarson and Sundius[66] re-examined (1929) Törnebohm's specimens and their crystallographic work showed that alite was essentially $3CaO{\cdot}SiO_2$, belite and felite were β-$2CaO{\cdot}SiO_2$ and celite was a solid solution.

Systematic work on the constitution of Portland cement was begun in the USA in the Geophysical Laboratory of the Carnegie Institution in Washington, as a development of the investigations of igneous rocks which have formed a principal part of the work of that institution. A brilliant application of thermal and petrological methods to the problem from 1906 onwards set the knowledge of cements on an entirely new basis. An important result of this work was the publication of the fundamental study on the ternary system CaO–Al_2O_3–SiO_2 by Rankin and Wright (1915).[67]

An interesting retrospective examination of concrete based on Aspdin's meso-Portland cement paste was made in the mid-1980s by various investigators[68–75] working independently on material from the same source. The material was the decorative concrete from William Aspdin's Portland Hall (Gravesend, Kent) which was built in the 1850 period. A range of techniques was applied including optical microscopy and electron microprobe analysis. The work clearly showed that it was meso-Portland cement and that Aspdin did reach a high enough temperature to produce alite and belite. Rayment[75] produced electron microprobe data around the inner and outer 'C-S-H' around alite groups, and he proved that hydrates were identical to the compositions of inner and outer hydrates of modern ordinary Portland cement.

Portland cement is composed of a number of hydraulic compounds and each reacts with water specifically, and the summation of the reactions leads to the setting and hardening of the cement. The study of cement hydration, and cement technology in general, was undertaken in many countries. For instance, the study of setting was undertaken in the laboratories of the US Bureau of Standards during World War I, and since 1926 much work on Portland cement has also been conducted by the Portland Cement Association. In Germany scientific work on cements continued to be conducted in an increasing number of laboratories, whilst fundamental contributions to the chemistry of cements began to grow from France, Italy, Sweden and other European countries and later from Canada, the USSR, and elsewhere. Contributions from the UK in the early years of the twentieth century were not proportional to the magnitude of the industry, nor to its pioneer work in the development of Portland cement in the preceding century, but with the establishment by the Department of Scientific and Industrial Research of the Building Research Station in 1921, systematic research on cements commenced as part of its programme and many major contributions have since come from it. Following World War II a research laboratory was established by the Cement and Concrete Association. whilst schools of research, interested in the nature of the cement compounds and products, grew in some of the universities, particularly Birkbeck College (University of London) and later the University of Aberdeen.

Periodic symposia on the chemistry of cement acts as a series of watersheds for the dissemination of research data and ideas. A list of the locations of the symposia is given on the page preceding this chapter.

The literature of cement has now become so large that, without the aid of specialised journals of abstracts and computerised data retrieval systems, it is difficult to keep in touch with it. *Building Science Abstracts* were published monthly by the Building Research Station commencing in 1928, but it was suspended in December 1976. However, the computerised database of which *Building Science Abstracts* has formed a part since 1973 was maintained. The Building Research Station was redesignated the Building Research Establishment in the Autumn of 1972 and is still located at Garston (Watford, Hertfordshire, UK). Another key to the literature is to be found in the *Documentation Bibliographique*, which was issued quarterly by CERILH (the Centre d'etudes et de Recherches de L'Industrie des Liants Hydrauliques) in France since 1948. As a result of a reorganisation, CERILH was redesignated ATILH (Association Technique de l'Industrie des Liants Hydrauliques). The quarterly journal ceased in 1967 but ATILH provides an on-line database (version of the abstracts bulletin) a monthly *Bulletin Analytique* was published by *CERILH* but the name of this publication, under ATILH is now known as *Bulletin de Documentation*. Wecke's *Handbuch der Zement Literatur*, which is a compilation of abstracts of papers up to 1925, facilitates reference to the older literature. In 1987 the Cement and Concrete Association amalgamated with the Cement Makers' Federation and the new organisation was designated the British Cement Association.

The history of calcareous cement has reflected different moods of economic buoyancy. There have been periods of growth – and periods of recession. In modern times no other material has had so great an influence upon the construction world. In fact, no other building material has made so lasting an impression on the general public as cement-based structures.

The first cement kilns were dome-like (beehive) static vertical kilns – their shape and operation was much like a brick or lime kiln. The operation was batchwise, the kiln capacity was limited and the quality of the output was uncertain. It is still possible to see one of these early kilns in a preserved state (Figure 1.4) at Northfleet, Kent, UK. The development of the rotary kiln started at the turn of the twentieth century and the design has, through technical advancement and sophistication, progressed to the current large throughput, controlled quality (thermal gradient, optimised burning zone and cooling regimes) and computer-involved kilns.

The modern cement plant is highly capital intensive but economy restraints, environmental requirements and market demand have affected the scale of operations. The calcareous cement industry in the UK reached a maximum size in the 1960s, and then began to decline. The growth of cement plants in the African continent reduced the need to export cement. In the two decades, 1970–90, the cement industry in the UK was reduced in size and the Thames-side cement industry – the cradle of the Portland cement industry – was decimated. In 1973 the UK industry produced nearly 20 Mt of cement, but by 1981 production had deteriorated to 12 Mt. Exports became nonexistent in 1985 and the importation of cement had started in 1983. All the UK cement manufacturers are independently quality assured and the industry now looks forward to the changes and challenges resulting from the harmonisation of specifications with mainland Europe from 1992.

This first chapter has, to a degree, reviewed the history of calcareous cement as yesterday's technology. The development of Portland and other cements with their application in concrete has resulted in the technology described in the following chapters of this book. Today's technology will be tomorrow's technical history. Looking to the future, current research and planning directs the trends of tomorrow's technology into the twenty-first century. Amongst current planners, Uchikawa[76] has explored key areas to be addressed in planning a strategy for future cement technology. The strategy may be planned in such a way as to meet the challenges of a more discerning and sophisticated market and address environmental constraints by controlling quarried raw material consumption, reducing energy consumption and process waste emission. The trend for calcareous cements may be the creation of high-performance multifunctional cements (giving enhanced specific properties) with associated optimum hydration conditions and durability being an essential index.

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2

Portland Cement: Classification and Manufacture

Peter J. Jackson

Two approaches are normally used to classify cements – the first is in respect of their composition, and the second is in terms of their performance-related properties.

2.1 Composition

When dealing with the composition it is appropriate to consider the general characteristics of the components against the overall concept of binders. British Standard BS 6100 Section 6.1[1] and the American Society for Testing and Materials C 219-94[2] and C 59-91[3] set this out in the terms given in Table 2.1 and for limes in Table 2.2.

A large number of European countries, Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom, have been involved in the development of a European Prestandard for Common Cements (ENV 197-1:1992[4]), a Prestandard for masonry cements (ENV 413-1:1994[5]), a draft proposal for hydraulic binders for roads[6], and a Prestandard for building limes (ENV 459-1:1994[7]). These incorporate many of the general definitions given in Tables 2.1 and 2.2 and in a number of cases extend them in quantitative terms. They also include a wide range of different compositions, full details of which are given in Tables 2.3 and 2.4, and cover virtually all the compositions marketed in the countries listed.

The other major international contribution to the classification of cements has been made in the USA through the Amerian Society for Testing and Materials (ASTM). Their work is covered in Standards C 150-95[8] (Standard Specification for Portland Cement, C 219-94[2] (*Standard terminology relating to hydraulic cement*) and C 595M-95[9] (*Standard specification for blended hydraulic cements*) and is summarised in Table 2.5. Detailed information on the compositions of cements made and marketed in other countries is to be found in the Cembureau publication *Cement standards of the world* 1991[10] and also in Refs 11 and 12. Cements for specialised applications are dealt with in chapter 14 of this book.

2.1.1 COMMON CEMENTS

The European Prestandard ENV 197-1[4] and the ASTM Standards C 150-95[8], C 219-94[2] and C 595M-95[9] define in more detail cement and the nature of the component materials in the following ways.

Table 2.1 Classification of binders

Term	BS 6100 Section 6.1	ASTM C 219
Binder	Material used for the purpose of holding solid particles together in a coherent mass	
Hydraulic binder	Binder that sets and hardens by chemical interaction with water and is capable of doing so under water	
Active hydraulic binder	Hydraulic binder that acts without the addition of an activator such as lime	
Latent hydraulic binder	Hydraulic binder that acts by the addition of an activator, usually lime and water	
Blended hydraulic binder	Mixture of active hydraulic binder and latent hydraulic binder	
Clinker	Solid material formed in high temperature processes by total or partial fusion	
Hydraulic cement	Active hydraulic binder formed by grinding clinker	A cement that sets and hardens by chemical interaction with water and that is capable of doing so under water
Portland cement clinker	Clinker formed from a predetermined homogeneous mixture of materials comprising lime, silica, a small proportion of alumina and generally iron oxide	A partially fused clinker consisting primarily of hydraulic calcium silicates
Portland cement	Active hydraulic binder based on ground Portland cement clinker	A hydraulic cement produced by pulverising Portland-cement clinker, and usually containing calcium sulfate

ENV 197-1 states that:

> Cement is a hydraulic binder, i.e. a finely ground inorganic material which, when mixed with water, forms a paste which sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water.
>
> Cement conforming to this European Prestandard, termed CEM cement, shall, when appropriately batched and mixed with aggregate and water, be capable of producing concrete or mortar which retains its workability for a sufficient time and shall after defined periods attain specified strength levels and also long-term volume stability.

Table 2.2 Classification of limes

Term	ENV 459-1	BS 6100 Section 6.1	ASTM C 59-91
Air limes	Limes mainly consisting of calcium oxide or hydroxide which slowly harden in air by reacting with atmospheric carbon dioxide. Generally, they do not harden under water as they have no hydraulic properties		
Quicklime	Air limes mainly consisting of calcium oxide and magnesium oxide produced by calcination of limestone and/or dolomite rock. Quicklimes have an exothermic reaction when in contact with water. Quicklimes are offered in varying sizes ranging from lumps to finely ground materials	A product obtained when calcareous material is heated at a temperature high enough to drive off carbon dioxide	A calcined limestone, a major part of which is calcium oxide or calcium oxide in association with magnesium oxide, capable of slaking with water
Dolomitic lime	Quicklimes mainly consisting of calcium oxide and magnesium oxide	Quicklime of high magnesium content	(Dolomitic) – indicates the presence of 35–46% *magnesium* carbonate ($MgCO_3$) in the limestone from which the material was formed
Grey lime		Quicklime made from grey chalk – usually having semi-hydraulic properties	
Magnesian lime		Quicklime containing more than 5% of magnesium oxide	(Magnesian) – indicates the presence of 5–35% magnesium carbonate ($MgCO_3$) in the limestone from which the material was formed

Table 2.2 *Continued*

Term	ENV 459-1	BS 6100 Section 6.1	ASTM C 59-91
Hydraulic lime	Limes mainly consisting of calcium silicates, calcium aluminates and calcium hydroxide produced either by burning of argillaceous limestones and subsequent slaking and grinding and/or mixing of suitable materials with calcium hydroxide	Quicklime containing sufficient soluble silica, aluminates, etc. to enable it to hydrate and set in the presence of water	(Hydraulic hydrated lime) the hydrated dry cementitious product obtained by calcining a limestone containing silica and alumina to a temperature short of incipient fusion so as to form sufficient free lime (CaO) to permit hydration, and at the same time, leaving unhydrated sufficient calcium silicates to give a dry powder meeting hydraulic property requirements
Semi-hydraulic lime		Similar to hydraulic lime but containing less soluble silica, aluminates, etc. (minimum soluble silica usually 6%)	
Hydrated lime	Slaked limes mainly consisting of calcium hydroxide	Fine white dry powder, produced by mixing together quicklime and water in controlled quantities, removing gritty material from the resulting product and drying it. The main constituent is calcium hydroxide	A dry powder obtained by treating quicklime with water enough to satisfy its chemical affinity for water under the conditions of its hydration. It consists essentially of calcium hydroxide or a mixture of calcium hydroxide and magnesium hydroxide or both

Table 2.3 ENV 197-1[4] common cement types and composition: proportion by mass[a]

Cement type	Designation	Notation	Clinker K	Granulated blastfurnace slag S	Silica fume D[c]	Pozzolana		Fly ashes		Burnt shale T	Limestone L	Minor additonal constituents[b]
						Natural P	Industrial Q[d]	Siliceous V	Calcareous W			
I	Portland cement	I	95–100	–	–	–	–	–	–	–	–	0–5
II	Portland slag cement	II/A-S	80–94	6–20	–	–	–	–	–	–	–	0–5
		II/B-S	65–79	21–35	–	–	–	–	–	–	–	0–5
	Portland silica fume cement	II/A-D	90–94	–	6–10	–	–	–	–	–	–	0–5
	Portland pozzolana cement	II/A-P	80–94	–	–	6–20	–	–	–	–	–	0–5
		II/B-P	65–79	–	–	21–35	–	–	–	–	–	0–5
		II/A-Q	80–94	–	–	–	6–20	–	–	–	–	0–5
		II/B-Q	65–79	–	–	–	21–35	–	–	–	–	0–5
	Portland fly ash cement	II/A-V	80–94	–	–	–	–	6–20	–	–	–	0–5
		II/B-V	65–79	–	–	–	–	21–35	–	–	–	0–5
		II/A-W	80–94	–	–	–	–	–	6–20	–	–	0–5
		II/B-W	65–79	–	–	–	–	–	21–35	–	–	0–5
	Portland burnt shale cement	II/A-T	80–94	–	–	–	–	–	–	6–20	–	0–5
		II/B-T	65–79	–	–	–	–	–	–	21–35	–	0–5
	Portland limestone cement	II/A-L	80–94	–	–	–	–	–	–		6–20	0–5
		II/B-L	65–79	–	–	–	–	–	–	–	21–35	0–5
	Portland composite cement	II/A-M	80–94	← 6–20[e] →								
		II/B-M	65–79	← 21–35[e] →								
III	Blastfurnace cement	III/A	35–64	36–65	–	–	–	–	–	–	–	0–5
		III/B	20–34	66–80	–	–	–	–	–	–	–	0–5
		III/C	5–19	81–95	–	–	–	–	–	–	–	0–5
IV	Pozzolanic cement	IV/A	65–89	–	← 11–35 →				–	–	–	0–5
		IV/B	45–64	–	← 36–55 →				–	–	–	0–5
V	Composite cement	V/A	40–64	18–30	–	← 18–30 →			–	–	–	0–5
		V/B	20–39	31–50	–	← 31–50 →			–	–	–	0–5

[a] The values in the table refer to the cement nucleus, excluding calcium sulfate and any additives.

[b] Minor additional constituents may be filler or may be one or more of the main constituents unless these are included as main constituents in the cement.

[c] The proportion of silica fume is limited to 10%.

[d] The proportion of non-ferrous slag is limited to 15%.

[e] The proportion of filler is limited to 5%.

Table 2.4 Building limes

Lime type	ENV 459-1[7] CaO + MgO min[a] (%)	ENV 459-1[7] MgO[a] (%)	ASTM C 5-79[14], C 141-85[15], C 206-84[16], C 207-91[17] CaO + MgO min[a] (%)	ASTM C 5-79[14], C 141-85[15], C 206-84[16], C 207-91[17] MgO[a] (%)
Calcium CL 90	⩾90	⩽5	⩾95	⩽20
Calcium CL 80	⩾80	⩽5		
Calcium CL 70	⩾70	⩽5		
Magnesium			⩾95	⩾20
Dolomitic DL 85	⩾85	⩾30		
Dolomitic DL 80	⩾80	>5		
Hydraulic			⩾65	⩽5[b]

[a] Expressed in terms of quicklime.
[b] Magnesium hydraulic lime >5%.

Table 2.5 American (ASTM) Standards[8,9]

Cement type	Clinker and calcium sulfate (%)	Slag (%)	Pozzolan (%)	Processing additions
Portland I, IA, II, IIA, III, IIIA, IV, V	100	0	0	Permitted
Slag-modified Portland I (SM)	>75	<25	0	Permitted
Pozzolan-modified Portland I (PM)	>85	0	<15	Permitted
Portland blastfurnace slag IS	30–75	25–70	0	Permitted
Portland-Pozzolan IP, P	60–85	0	15–40	Permitted
Slag S	Permitted[a]	⩾70	0	Permitted

[a] May also contain hydrated lime.

Hydraulic hardening of CEM cement is primarily due to the hydration of calcium silicates but other chemical compounds may participate in the hardening process, e.g. aluminates. The sum of the proportions of reactive calcium oxide (CaO) and reactive silicon dioxide (SiO_2) in CEM cement shall be at least 50% by mass.

CEM cements consist of individual small grains of different materials but they shall be statistically homogeneous in composition. A high degree of uniformity in all cement properties shall be obtained through continuous mass production processes, in particular, adequate grinding and homogenization processes. Qualified and skilled personnel and the facilities to test, evaluate and adjust product quality are essential for producing cements included in this European Prestandard.

> The cement manufacturing process and its control shall ensure that the composition of CEM cements is kept within the limits fixed in this European Prestandard.

ASTM Standard C 219-94[2] defines Portland cement as 'a hydraulic cement produced by pulverizing portland-cement clinker, and usually containing calcium sulfate' and blended hydraulic cement as 'a hydraulic cement consisting of two or more inorganic constituents (at least one of which is not portland cement or portland-cement clinker) which separately or in combination contribute to the strength-gaining properties of the cement, (made with or without other constituents, processing additions and functional additions, by intergrinding or other blending).' However, in ASTM terminology the word Portland may appear in the names of cements containing as little as 30 per cent Portland cement clinker and gypsum, whereas in CEN terminology cement names which incorporate Portland are those required to contain a minimum of 65 per cent Portland cement clinker.

In addition to having requirements in respect of the secondary components which are permitted to be incorporated into the cement, there are also chemical constraints on the cements themselves. ENV 197-1[4] limits the amount of magnesia (MgO) in the Portland cement clinker to 5.0 per cent, whilst ASTM C 150,[8] which deals only with cements comprising 100 per cent Portland cement clinker and gypsum rock (apart, that is, from small amounts of processing additions and air-entraining agents, etc.), limits the amount to 6.0 per cent (with an autoclave soundness test in addition), as does ASTM C 595M[9] for the pozzolan-containing cements and just the autoclave test for the slag containing blended cements. The reason for this restriction is the danger of having an excessive amount of magnesia in the form of periclase, the presence of which may lead to long-term expansions. ENV 197-1[4] also places a restriction on the amount of chloride present since this can have an adverse effect upon the corrosion of steel reinforcement. Limits are also included on the amount of sulfate (expressed in cement terminology as SO_3) incorporated. This is to prevent long-term expansion characteristics and restricts the amount of gypsum rock which may be added. These requirements are there to provide long-term safeguards in the absence of generally acceptable short term performance tests. The other compositional requirements are associated with deterioration on storage or the use of Portland cement clinker which has been excessively weathered through long-term outside storage. Cements with excessively high loss on ignition values normally have low strengths. ASTM C 150[8] sets a maximum at 2.5–3.0 per cent depending upon the type of cement, whereas the equivalent cement in ENV 197-1[4] sets a maximum of 5.0 per cent because this Prestandard permits the incorporation of up to 5 per cent of a secondary material which could be limestone. A not dissimilar situation occurs with regard to the other chemical constraint – the insoluble residue. This is essentially to prevent manufacturers from using poor quality gypsum rock. The ASTM C 150[8] maximum for cements comprising 100 per cent Portland cement clinker and gypsum is 0.75 per cent, but the ENV 197-1[4] figure is higher at 5.0 per cent because the equivalent grade of cement may contain up to 5 per cent of fly ash as a 'minor additional constituent'.

ASTM C 150[8] incorporates optional maxima for tricalcium silicate (35 per cent) and tricalcium aluminate (7 per cent) and a minimum for dicalcium silicate (40 per cent) where a heat release test is not carried out and where the cement is for use in applications demanding low heat release (Type IV). The amounts of these compounds present are calculated from the oxide analysis using the Bogue equations. The Type V sulfate-resisting cement has a requirement for no more than 5 per cent tricalcium aluminate unless the performance test for sulfate resistance is carried out and its requirements are met. It also has a restriction for this cement on the maximum amount (25 per cent) of tetracalcium aluminoferrite plus twice the tricalcium aluminate present – again, if the performance test is not carried out and its requirements met. Other constraints include a maximum of 15 per cent tricalcium aluminate in the Type III high early strength cement and of 8 per cent for the moderately sulfate-resisting/moderately low heat Type II cement. Among other optional requirements in C 150 are a maximum of 0.60 per cent for sodium and potassium alkalis, expressed as sodium oxide equivalent $(Na_2O)_e$. C 595M for blended hydraulic cements incorporates a performance test for alkali–silica reaction. Some typical chemical analyses of Portland (ENV 197-1–CEM I) common cements manufactured in the UK are given in Table 2.6.

2.1.1.1 Portland cement clinker (K)

The definition given in ENV 197-1[4] is as follows:

> Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates ($(CaO)_3 \cdot SiO_2$ and $(CaO)_2 \cdot SiO_2$), the remainder containing aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) and other oxides. The ratio by mass (CaO/SiO_2) shall be not less than 2.0. The content of magnesium oxide (MgO) shall not exceed 5.0 per cent by mass.

Table 2.6 Typical chemical analyses of CEM I common (Portland) cements available in the UK in 1987

Reference	DO	DOX	EO	FO	GO	HO
SiO_2 (%)	22.2	21.8	20.9	20.1	19.5	20.2
Al_2O_3 (%)	4.2	4.1	4.6	5.0	6.2	5.3
Fe_2O_3 (%)	2.4	3.3	2.1	2.8	2.0	2.2
Mn_2O_3 (%)	0.08	0.07	0.06	0.16	0.03	0.04
P_2O_5 (%)	0.15	0.10	0.23	0.10	0.17	0.07
TiO_2 (%)	0.27	0.23	0.20	0.20	0.31	0.23
CaO (%)	63.9	64.2	66.3	63.2	64.7	66.4
MgO (%)	1.0	1.4	0.8	2.2	1.2	0.9
SO_3 (%)	2.7	2.5	2.8	3.0	3.0	2.5
CO_2 (%)	0.79	0.3	0.48	–	–	–
K_2O (%)	0.74	0.61	0.80	0.78	0.43	0.56
Na_2O (%)	0.14	0.15	0.16	0.13	0.24	0.23
Free lime (%)	1.5	1.4	1.4	2.1	0.9	1.2
Loss on ignition (%)	1.7	1.5	0.75	1.0	1.1	0.7
Insoluble residue (%)	1.7	0.8	1.1	0.84	0.85	0.5
Na_2O equivalent (%)	0.63	0.55	0.69	0.64	0.52	0.60
C_3S[a] (%)	46	51	63	50	58	66
C_2S[b] (%)	29	24	12	20	12	8
C_3A[c] (%)	7.1	5.3	8.6	8.5	13	10.3
C_4AF[d] (%)	7.3	10.0	6.4	8.5	6.1	6.7
Density (kg/m^3)	3130	3130	3120	3150	3110	3140
Surface area (m^2/kg)	383	380	343	443	394	344
Coarser than 45 μm (%)	13.4	12.5	16.7	9.0	12.3	17.4

Calculated from the oxide analysis using Bogue formulae: [a] tricalcium silicate; [b] dicalcium silicate; [c] tricalcium aluminate; [d] tetracalcium aluminoferrite.

Portland cement clinker is made by burning, at least to sintering, a precisely specified mixture of raw materials (raw meal, paste or slurry) containing CaO, SiO_2, Al_2O_3 and small quantities of other materials. The raw meal, paste or slurry shall be finely divided, intimately mixed and therefore homogeneous.

In the USA, ASTM C 219-94[2] gives the following definition: 'a partially fused clinker consisting primarily of hydraulic calcium silicates'.

2.1.1.2 Granulated blastfurnace slag (S)

ENV 197-1[4] states that:

> Granulated blastfurnace slag is a latent hydraulic material, i.e. it possesses hydraulic properties when suitably activated. It shall contain at least two-thirds by mass of glassy slag. The granulated blastfurnace slag shall consist of at least two-thirds by mass of the sum of CaO, MgO and SiO_2. The remainder contains Al_2O_3 together with small amounts of other oxides. The ratio by mass (CaO + MgO)/(SiO_2) shall exceed 1.0.
>
> Granulated blastfurnace slag is made by rapid cooling of a slag melt of suitable composition, as obtained by smelting iron ore in a blastfurnace.

ASTM C 219-94[2] gives the definition as:

> 'the glassy granular material formed when molten blast-furnace slag is rapidly chilled, as by immersion in water – with the following items under the heading of Discussion:
>
> Granulation may be achieved by quenching blastfurnace slag from its original molten state or by quenching air-cooled blastfurnace slag after remelting. Also small percentages of silica and alumina may be added whilst the slag is molten to enhance desired characteristics.'

Typical chemical analyses of slags are given in Table 2.7.

The alumina content of slags has been reported to have a significant effect upon the strength obtained when used in conjunction with Portland cements;[19] 2-day strengths are improved with increasing alumina contents up to 15 per cent and 28-day strengths improved with up to 13 per cent. However, 91-day strengths showed an optimum strength at 13 per cent, decreasing at higher percentages.

2.1.1.3 Pozzolanic material (P, Q)

ENV 197-1[4] states that:

Pozzolanic materials are natural substances or industrial pozzolanas, siliceous or

Table 2.7 Typical chemical analyses of blastfurnace slags (per cent)

	Range[18]	Typical in UK, 1994
Silica	30–40	34
Alumina	5–17	12
Ferric + ferrous oxides	0.2–1.0	0.3
Lime	35–48	42
Magnesia	2–15	7
Manganous oxide	0.3–1.0	–
Sulfur	0.6–2.0	–

silico-aluminous, or a combination thereof. Although fly ash and silica fume have pozzolanic properties, they are specified in separate clauses.

Pozzolanic materials do not harden in themselves when mixed with water but, when finely ground and in the presence of water, they react at normal ambient temperature with dissolved hydroxide ($Ca(OH)_2$) to form strength-developing calcium silicate and calcium aluminate compounds. These compounds are similar to those which are formed in the hardening of hydraulic cements. Pozzolanas shall consist essentially of reactive SiO_2 and Al_2O_3. The remainder contains Fe_2O_3 and other oxides. The proportion of reactive CaO is negligible. The reactive SiO_2 content shall be not less than 25 per cent by mass. Pozzolanic materials shall be correctly prepared, i.e. selected homogenised, dried and comminuted, depending on their state of production or delivery.

2.1.1.4 *Natural pozzolana (P)*

ENV 197-1[4] states that 'natural pozzolanas are usually substances of volcanic origin or sedimentary rocks with suitable chemical and mineralogical composition.'

Natural pozzolanas[20] of volcanic origin occur in the vicinity of Naples and of Rome and also as the Santorin Earth from the Grecian island of Santorin. There are also vitreous rhyolites from the Rocky mountains in the USA and from the Bombay area of India. Another source of these materials are the German trasses. The pozzolanic activity is dependent upon their physical form and the amounts of glass and zeolites present. If they contain significant amounts of relatively unreactive clay minerals, this can appreciably lower their activity.[21] Chemical analyses of these types of materials are given in Table 2.8.

In addition to the above materials of volcanic origin, there are diatomaceous earths, which are derived from waterborne deposits. These materials have a high water demand which does not make them attractive for use with cements. It has been shown to be possible to lower this with the use of a super-plasticiser.[23]

2.1.1.5 *Industrial pozzolana (Q)*

ENV 197-1[4] states that:

> Industrial pozzolanas are thermally treated and activated clays and shales, air cooled slags from lead, copper, zinc and other products from the ferroalloys industry. Industrial pozzolanas shall not increase the water demand of the cement appreciably, impair the resistance of the concrete or mortar to deterioration in any way or reduce the corrosion protection of the reinforcement.

Table 2.8 Typical chemical analyses of natural pozzolanas (per cent)

	Range	Chilean Pudahuel[22]
Silica	50–75	68.9
Alumina	10–20	13.4
Ferric oxide	3–9	1.9
Lime	2–9	2.0
Magnesia	1–6	0.6
Sodium oxide (Na_2O)	1–3	3.4
Potassium oxide (K_2O)	2–7	3.7

These include a wide range of materials from heat-treated clays and shales to ashes derived from burning rice husks as well as slags from various non-ferrous metal-processing industries. In common with natural pozzolanas, it is desirable that they should contain reactive silica and some glass. Some such as rice husks significantly increase the water demand. The non-ferrous slags are derived from copper,[24] nickel,[25] lead[26] and zinc processing and, unlike the slags from iron manufacture, have very much lower lime contents. Silica is normally present in the range 20–40 per cent. However, the significance of the residual metal contents (up to 1.3 per cent CuO and 3.9 per cent ZnO in copper slags,[24] up to 1.2 per cent nickel in nickel slags[27] and as high as 4.8 per cent lead[26] with 10–18 per cent zinc in lead slags[28] needs careful consideration, both from the possible effect on cement hydration and also in connection with possible leaching from any products made from the cement in question – particularly when it has carbonated and the pH is lowered.

2.1.1.6 Fly ashes (V, W)

ENV 197-1[4] states that:

> Fly ash may be silico-aluminous or silico-calcareous in nature. The former has pozzolanic properties; the latter may have, in addition, hydraulic properties. The loss on ignition of fly ash shall not exceed 5.0 per cent by mass.
>
> Fly ash is obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases from furnaces fired with pulverised coal. Ash obtained by other methods shall not be used in cement that conforms to this European Prestandard.

Some typical fly ash analyses are given below in Table 2.9.

ASTM Standard C 618-85[30] specifies a Class F fly ash as one normally produced from burning anthracite or bituminous coal and has a minimum of 70 per cent for the sum of the silica, alumina and ferric oxide present. It also requires that the SO_3 content should be less than 5.0 per cent, the moisture content less than 3.0 per cent and the loss on ignition less than 6.0 per cent. It also specifies a Class C fly ash as one normally produced from lignite or sub-bituminous coal. In this case the minimum for the sum of the oxides is 50 per cent with the other requirements as for the Class F fly ash.

Table 2.9 Typical fly ash analyses (per cent)[29]

Fuel burnt	Coal (siliceous fly ashes)	Lignite (calcareous fly ashes)
Silica	47–54	18–25
Alumina	28–35	12–15
Ferric oxide	4–12	6–8
Lime	1–4	43–49
Magnesia	1–2.5	2–3
Sulfate (as SO_3)	0–1	5–9
K_2O	1–6	5
Na_2O	0.2–2	
Loss on ignition	2.5–14[a]	2–4[b]

[a] Includes carbon 0.5–12%.

[b] Includes carbon 1–3%.

The specific surface area (Blaine) of fly ashes can range between 250 and 510 m^2/kg with between 62 and 92 per cent finer than 45 μm.[31]

The maximum loss on ignition requirement given in the European Prestandard for Common Cements[4] is lower than that required by some other standards.[32,33] This is because of concerns that the unburnt coal particles which form the greater part of the loss on ignition can aggravate surface scaling of concrete under conditions of frost attack and de-icer usage,[34] the adverse effect that they can have upon air entrainment, and the stability of the entrained air – in some cases requiring up to six times the amount of air-entraining agent to achieve a given air content,[31,34] and the darker colour which can result if such fly ashes are interground with Portland cement clinker. These matters are more important with factory-made cements where the end use may vary widely.

The ASTM Standard for Blended Cement C 595M-95[9] defines fly ashes under the same grouping as other pozzolanic materials as pozzolan: 'Pozzolan shall be a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties'. These materials are required to meet fineness, expansion and pozzolan activity index requirements. The latter being the 28-day strength attained by replacing 35 per cent of the Portland cement by the pozzolan, curing at 38°C and expressing this value as a percentage of the strength obtained by the same Portland cement when tested under similar conditions and at the same mortar consistence.[35]

2.1.1.6.1 Siliceous fly ash (V)

ENV 197-1 states that: 'siliceous fly ash is a fine powder of mainly spherical particles having pozzolanic properties. It shall consist essentially of reactive SiO_2 and Al_2O_3. The remainder contains Fe_2O_3 and other oxides. The proportion of reactive CaO shall be less than 5 per cent by mass. The reactive SiO_2 content of siliceous fly ash conforming to this European Prestandard shall be not less than 25 per cent by mass.' Modal compositions for UK siliceous fly ashes have been reported[36] as presented in Table 2.10.

The suitability of a fly ash for incorporation in a Portland fly ash cement may be judged by its 'cementing efficiency index'[37]. This is defined by K where

$$\frac{(W)}{(C)_s} = \frac{W}{C + FK}$$

where W, C and F are the weights of water, cement and fly ash in the mix and $(W)/(C)_s$ is the equivalent water/cement ratio, i.e. that for a mix of the same strength, but without fly ash.

Table 2.10 Typical compositions of UK siliceous fly ashes (per cent)[36]

Mullite	9–43
Quartz	1–9
Magnetite	2–9
Hematite	3–11
Coal	1–12
Amorphous aluminosilicate	29–74

The values of K vary between 0.15 and 0.38 for concrete at 20°C and between 0.61 and 1.22 for concrete at 50°C, thus illustrating the significant advantages of cements containing fly ashes for applications which involve humid high-temperature curing, and conversely the problems which can be expected at lower than ambient temperatures.[38]

Low-alkali fly ashes may assist in minimising expansions due to the alkali-silica reaction; however, it has been shown[39] that in the presence of Portland cements alkalis are released from the fly ashes.

2.1.1.6.2 Calcareous fly ash (W)

ENV 197-1[4] states that:

> Calcareous fly ash is a fine powder, having hydraulic and/or pozzolanic properties. It shall consist essentially of reactive calcium oxide CaO, reactive silica SiO_2 and alumina Al_2O_3. The remainder contains iron oxide Fe_2O_3 and other oxides. The proportion of reactive calcium oxide CaO shall not be less than 5 per cent by mass. Calcareous fly ash containing between 5 per cent and 15 per cent of reactive calcium oxide CaO shall contain not less than 25 per cent by mass of reactive silica SiO_2.
>
> Finely ground calcareous fly ash containing more than 15 per cent of reactive calcium oxide CaO, shall have a compressive strength of at least 10 N/mm^2 at 28 days when tested in accordance with EN 196-1.[40]

(Subject to certain provisions regarding the fineness to which it is ground before testing, demoulding the specimens at 48 h, and curing at >90 per cent RH after demoulding.) 'The expansion of calcareous fly ash shall be less than 10 mm when tested in accordance with EN 196-3[41] using a mixture of 30 per cent by mass of ground fly ash and 70 per cent by mass of reference cement' (CEM Type 1).[4]

Concern has been expressed[42] that calcareous fly ashes can potentially contain hard-burnt calcium oxide which may hydrate after some years and give rise to delayed expansions. This is reflected in the special requirements for soundness in the CEN Prestandard for common cements. Calcareous fly ashes have been reported[34] to have less effect upon air entrainment, although this may be associated with the fact that they generally contain less unburnt carbon.

2.1.1.7 Burnt shale (T)

ENV 197-1[4] states that:

> Burnt shale, specifically burnt oil shale, is produced in a special kiln at temperatures of approximately 800°C. Owing to the composition of the natural material and the production process, burnt shale contains clinker phases, mainly dicalcium silicate and monocalcium aluminate. It also contains, besides small amounts of free CaO and calcium sulfate, larger proportions of pozzolanically reacting oxides, especially SiO_2. Accordingly, in a finely ground state burnt shale shows pronounced hydraulic properties like Portland cement and in addition pozzolanic properties.
>
> Finely ground burnt shale shall have a compressive strength of at least 25.0 N/mm^2 at 28 days when tested in accordance with EN 196-1.[40]

(Provision is made for demoulding at 48 h and curing at >90 per cent RH after demoulding.) 'The expansion of burnt shale shall be less than 10 mm when tested in accordance with EN 196-3[41] using a mixture of 30 per cent by mass ground burnt shale and 70 per cent by mass of reference cement' (CEM Type 1)[4].

These materials are obtained as by-products after the removal, at temperatures of the order of 750°C, of oil from oil-bearing shales. They can have a wide range of compositions. Calcium oxide contents vary from 16 to 60 per cent and silica contents from 12 to 25 per cent. This means that when finely ground, some will react as pozzolanas; others (those permitted in ENV 197-1[4]) have strength development properties in their own right and some can act as both cements and as pozzolanas. The cementing properties are due to the presence of dicalcium silicate and also monocalcium aluminate; the pozzolanic properties are a consequence of reactive silica[43]. Some burnt shales may increase the water demand of the cement in which they are incorporated and high sulfate levels (9–10 per cent) can create difficulties in complying with the maxima required in cement standards. Their composition and reactivity are very dependent upon the deposit from which they are derived and the temperature to which they are heated in order to remove the oil.

2.1.1.8 Limestone (L)

ENV 197-1[4] states that:

> In addition to the requirements appropriate when used as a filler (see 2.1.1.10) in proportions exceeding 5 per cent by mass (i.e. a main constituent), limestone shall meet the following requirements: Limestone content $CaCO_3 \geqslant 75$ per cent by mass, clay content; methylene blue adsorption $\leqslant 1.20$ g/100 g. Organic material content (TOC) $\leqslant 0.20$ per cent by mass. Limestone with an organic material content (TOC) between 0.20 per cent and 0.50 per cent by mass may also be suitable for producing a satisfactory cement with acceptable performance. Until adequate performance tests are developed by WG 12, cements containing these limestones are permitted to be specified in national standards and other regulations valid in the place where the cement is used.[52]

(Note that WG 12 is a Working Group responsible to the European (CEN) Technical Committee (TC 51) dealing with Standards for Cements and Building Limes, for the development of performance tests for cement.)

The requirements in ENV 197-1[4] have been derived from performance tests.[44] Limestones, when ground sufficiently fine (specific surface areas $>500\,m^2/kg$ Blaine) and suitably incorporated into cements can be used to lower the water demand by improving the overall particle grading.[45] [48] In the case of 28-day strength, their presence is essentially that of a diluent, but early strengths may improve relative to those achieved with pozzolanas. This effect has not, as yet, been completely explained, with some workers[48] supporting the concept that it results from a more favourable packing of particles, whilst others[49] consider it to be associated with an acceleration of the hydration of the tricalcium silicate in the presence of calcium carbonate. Calcium carbonate has also been reported[50] to react with the tricalcium aluminate to form high and low forms of the carboaluminate, $C_3A \cdot 3CaCO_3 \cdot 32\,H_2O$ and $C_3A \cdot CaCO_3 \cdot 12H_2O$ respectively, supporting other evidence that small amounts of limestone can act as partial substitutes for gypsum.[51]

2.1.1.9 Silica fume (D)

ENV 197-1[4] states that:

> Silica fume consists of very fine spherical particles with a high content of amorphous silica. If the proportion of silica fume in the cement exceeds 5 per cent by mass (i.e.

> a main constituent) then only silica fume which meets the following requirements shall be used: Amorphous silica (SiO_2) ≥ 85 per cent by mass, loss on ignition ≤ 4 per cent by mass, specific surface area (BET) (untreated) $\geq 15\,m^2/g$. For intergrinding with clinker and gypsum the silica fume may be in its original state or compacted or pelletised (with water). Silica fume originates from the reduction of high purity quartz with coal in electric arc furnaces in the production of silicon and ferrosilicon alloys.

More correctly described as 'condensed silica fume', this material comprises 0.1–0.2 μm particles of what is essentially, but not completely, amorphous silica. Unless used with a water-reducing additive, it can be expected to increase the water demand of a cement. Also, on account of its fineness (15 000–20 000 m^2/kg using the BET method), it has a tendency to agglomerate and as a result special care needs to be taken to disperse it when incorporated into a cement. In view of concerns regarding the presence of crystalline silica, the Norwegian authorities have established a threshold limit value (TLV) of 2.0 mg/m^3 for respirable silica fume.[53]

2.1.1.10 Fillers (F)

ENV 197-1[4] states that:

> Fillers are specially selected, natural or artificial inorganic mineral materials which after appropriate preparation, on account of their particle size distribution, improve the physical properties of the cement (such as workability or water retention). They can be inert or have slightly hydraulic, latent hydraulic or pozzolanic properties. However, no requirements are set for them in this respect. Fillers shall be correctly prepared, i.e. selected, homogenized, dried and comminuted depending on their state of production or delivery. They shall not increase the water demand of the cement appreciably, impair the resistance of the concrete or mortar to deterioration in any way or reduce the corrosion protection of reinforcement.

Fillers are normally either limestone or the raw meal which constitutes the feedstock to the cement kiln system. In some cases, if the chemistry is suitable (low alkali and chloride levels), the dust collected in the electrostatic precipitators has been used.

2.1.1.11 Calcium sulfate

ENV 197-1[4] states that:

> Calcium sulfate shall be added in small quantities to the other constituents of cement during its manufacture to control setting. Calcium sulfate can be gypsum (calcium sulfate dihydrate, $CaSO_4 \cdot 2\,H_2O$), hemihydrate ($CaSO_4 \cdot \frac{1}{2} H_2O$), or anhydrite (anhydrous calcium sulfate $CaSO_4$) or any mixture of them. Gypsum and anhydrite are found naturally. Calcium sulfate is also available as a by-product of certain industrial processes.

ASTM C 219-94[2] defines calcium sulfate as applied to cement manufacture as 'a product composed essentially of calcium sulfate in any hydration state or states: anhydrite ($CaSO_4$), gypsum ($CaSO_4 \cdot 2H_2O$) and hemihydrate ($CaSO_4 \cdot \frac{1}{2} H_2O$).

There are many forms of calcium sulfate now available – both natural and synthetic. Typical analyses of natural gypsum rocks are given in Table 2.11.[54] From this work it was concluded that the gypsum quality can often be as important as that of the clinker when

Table 2.11 Typical chemical analyses of natural gypsum rocks (per cent)

	A	B	C	D	E	F	G
SiO_2	1.4	2.0	4.0	1.9	0.1	2.4	6.0
Insoluble residue	3.6	8.0	9.4	2.1	0.6	15.1	8.1
Al_2O_3	0.3	0.7	1.6	0.3	<0.05	0.9	1.5
Fe_2O_3	0.6	0.7	1.2	0.3	0.1	0.7	2.3
Loss at 50°C	0.1	0.1	0.6	0.4	0.03	0.2	0.6
Loss 50–250°C	17.1	17.3	14.8	9.9	20.1	14.4	8.6
Loss 250–950°C	0.7	1.1	2.0	0.9	0.7	2.1	2.3
CaO	30.3	28.1	24.7	37.7	32.4	25.8	26.9
MgO	1.9	1.0	4.3	0.6	0.1	1.7	4.3
SO_3	40.1	39.5	34.0	35.3	45.5	32.9	35.7
CO_2	3.8	1.1	3.7	10.5	0.25	3.6	3.3
K_2O	0.05	0.07	0.13	0.06	<0.05	0.11	0.12
Na_2O	0.06	0.05	0.18	0.05	<0.05	0.10	0.84
$CaSO_4 \cdot 2H_2O$	81.7	82.7	70.7	47.3	96.0	68.8	41.1
$CaSO_4$	3.7	1.9	1.9	22.6	1.4	1.5	28.2
$CaCO_3$	3.9	0.7	3.7	23.2	0.6	5.0	3.4
$MgCO_3$	4.0	1.5	5.7	0.6	0.0	2.7	3.4
Moisture	0.1	0.1	0.6	0.4	0.0	0.2	0.6
Clay, etc.	6.6	13.1	17.4	5.9	2.0	21.8	23.3

considering overall Portland cement quality, particularly in the early stages of hydration. The presence of montmorillonites can cause high water demands, flash set at lower grinding temperatures and false set at higher ones. Illite behaves in a similar manner, but is less severe. This was considered to be due to the sorption of water by these clay minerals in competition with the cement minerals. The presence of natural anhydrite ($CaSO_4$) beneficially minimises or prevents early stiffening by diluting the effects of calcium ions and sulfate ions from hemihydrate and/or soluble anhydrite (supersaturated with respect to gypsum) when they rehydrate back to gypsum, and ensuring smooth rehydration. Too much natural anhydrite may cause flash set, owing to the sluggish rate of solution of its calcium and sulfate ions, which might be insufficient to react with the clinker tricalcium aluminate (and, to a lesser degree, tetracalcium alumino ferrite) to form enough ettringite to permit smooth regulation.

There are a number of by-product gypsums now being produced, notably from the desulfurisation of the gases from stations, from the production of phosphoric acid from boric acid and from citric acid. Work on gypsum derived from the manufacture of phosphoric acid[55] revealed that considerable increases in setting time could occur and that this was associated with the presence of very small quantities of water-soluble fluorine, water-soluble phosphates and phosphates in the crystal lattice of the gypsum. The amounts involved could be as little as 0.05 per cent water-soluble P_2O_5 and 0.05 per cent water-soluble F. Using synthetic gypsums with water-soluble P_2O_5 in the range 0.08–0.18 per cent and fluorine contents of 1.3 per cent, the present author has found initial setting times to be increased from 3 to 10 h with the concrete still soft at 24 h. Compressive strengths at 3 days were only 75 per cent of that obtained with natural gypsum and 28-day strengths 90 per cent. If the phosphogypsum can be effectively neutralised with lime and the content of water-soluble P_2O_5 and F reduced below 0.02 per cent, then the considerable retarding action which the material has on some clinkers can be virtually eliminated.

The relationship between the form of the natural calcium sulfate added to control the setting of cement can also have a considerable effect upon the water demand of the cement. With very reactive tricalcium aluminates present, it is necessary to produce a high sulfate ion concentration within a few seconds of the cement coming into contact with water. Conversely, if this is done with a low-reactivity tricalcium aluminate, then the calcium sulfate will precipitate as gypsum and give stiffening or false setting. The use of blends of gypsum (which is normally dehydrated to the more rapidly soluble hemihydrate in the cement mill) and natural anhydrite are helpful in controlling these problems.

The effect that the amount of calcium sulfates present in cements can have upon strengths has been ascribed to differences in pore size in the tested specimen.[56] Cements which are moderately high or high in C_3A and have low SO_3 levels tend to give larger pores which decrease in size with higher SO_3 contents. The pore size in low-C_3A cements is reported as independent of the amount of SO_3 present.

2.1.1.12 Additives

ENV 197-1[4] states that:

> Additives for the purpose of this European Prestandard are constituents not covered [by the other component definitions given in Ref. 4] which are added to improve the manufacture or the properties of the cement, e.g. grinding aids. The total quantity of additives should not exceed 1 per cent by mass of the cement. If it does, the quantity shall be stated on the packaging and/or on the delivery note. These additives shall not promote corrosion of the reinforcement or impair the properties of the cement or of the concrete or mortar made from the cement.

ASTM C 219-94[2] refers to these materials as 'additions' and defines them as 'a material that is interground or blended in limited amounts into a hydraulic cement during manufacture either as a "processing addition" to aid in manufacturing and handling the cement or as a "functional addition" to modify the use properties of the finished product.' Processing additions are required[8,9] to comply with the requirements of C 465[57]and, in the case of Ref. 9, functional additions with C 688[58].

The European Prestandard[4] makes no such distinction and the additive can be a processing addition such as a grinding aid or an air-entraining agent. The types of materials used as grinding aids are triethanolamine acetates, triethanolamine, and propylene glycol; these function by minimising the agglomeration of the cement particles and may have the effect of increasing the output of a given cement grinding mill by as much as 10 per cent. They also usually improve the flow properties of the cement. The amounts usually incorporated are normally less than 0.1 per cent. The air-entraining agents can be of the natural 'Vinsol Resin' type or synthetic compounds of the alkyl aryl sulfonate type. There are also water-reducing additives, such as lignosulfonates which may be added on their own or in combination with the other processing additions.

As the European Prestandard ENV 197-1[4] does not distinguish between the types of additives, it is possible that common cements complying with this Prestandard can be air entraining without any indication being given in the type classification. In the ASTM classification air-entraining cements carry an 'A' suffix after the type number.

It is also understood[59] that additives such as ferrous sulfate may be incorporated into the cement with the object of reducing the amount of water-soluble hexavalent chromium present.

To clear up any confusion it should be mentioned that it is normal in the European Concrete Standards to refer to materials added in much larger amounts, i.e. fly ashes, as 'additions' and such materials as air-entraining agents and water reducers as 'admixtures'.

2.1.2 FORMULATED COMMON CEMENTS

Tables 2.3 and 2.5 give details of the proportions of each of the components described above which are permitted in the various cements, and in order to establish the commercial significance of these various types an indication of the situation in 1990 in the European countries[60] is given in Table 2.12.

These data indicate that as far as Europe as a whole was concerned in 1990, the most used type cement was that based on Portland cement clinker, calcium sulfate and up to 5 per cent of a minor additional constituent, this situation also prevailed in Denmark, UK, Finland, France, Germany, Republic of Ireland, Italy, Norway, Spain, Sweden and Switzerland. However, in Austria the Portland slag cement was most favoured, in Belgium, Luxembourg and the Netherlands the blastfurnace cement, and in Greece and Portugal the composite cement. Overall, the II-M composite cement was the second most used cement in the European countries listed above, reflecting the high degree of popularity in France, Greece, Portugal and Spain.The Type IV pozzolanic cement owed its popularity to a high demand in Italy, which in terms of the annual tonnage in 1990 was more than the total amount of cement made in the UK that year.

Regarding acceptability for use, Type I is generally permitted and used in plain, reinforced and post-tensioned concretes. Type II-S is acceptable and used for these applications in something like 40 per cent of the European countries listed in Table 2.12. Type II-P having a maximum of 20 per cent natural pozzolana in 30 per cent, Type II-V in 40 per cent of the European countries, Type II-W in 15 per cent, Type II-L with a maximum of 20 per cent limestone in 20 per cent, Types II-T, II-D and IV 15%, Type II-M 20%, and Types III-A and III-B approximately 60 per cent of the European countries.

Overall, in Europe, the Portland cement which does not contain significant proportions of secondary materials is the favoured material, but on account of economic and environmental matters there is a distinct tendency towards the greater usage of cements containing granulated blastfurnace slags, fly ashes and natural pozzolanas. This applies particularly where a manufacturer can, through his processing skills, produce performance characteristics which equal or, in some directions, surpass those of the Type I cements.

All international standards for cements consider them to be dry powdered products which can be sampled as such and their properties verified. In the UK there is a practice which permits concrete makers to add separately to their mixer a Portland cement and certain specified secondary materials, such as ground granulated slags and also fly ashes,[61] and for these combinations to be accepted as equivalent to cements made to appropriate standards. In this case, it is not possible to sample and test the combination of these materials in the absence of the other components of the concrete. Such practices are considered to be more appropriate to concrete manufacture and are not discussed further in this chapter.

Table 2.12 Production of the various types of cement in Europe in 1990 (mega tonnes)

Type	I	II-S	II-P/Q	II-V/W	II-L	II-T	II-D	II-M	III	IV	V	Total
Secondary material		GBF slag	Pozzolana	Fly ashes	Limestone	Burnt shale	Silica fume	Composite	GBF slag	Pozzolanic	Composite	
Secondary material (%)	0–5	6–35	6–35	6–35	6–35	6–35	6–10	6–35	36–95	11–55	18–50	
Austria	0.3	3.7		0.8					0.1			4.9
Belgium	1.8			1.2					2.0			5.0
Denmark	0.9			0.3	0.1							1.3
UK	13.3			0.4					0.1			13.8
Finland	1.2							0.4				1.6
France	9.0	1.4	0.1	0.6	6.5			5.2	1.2		0.3	24.3
Germany	18.4	1.2		0.1	0.9	0.5		0.4	3.8	0.1		25.4
Greece	1.8							5.8				7.6
Republic of Ireland	1.3											1.3
Italy	22.9								2.3	14.8		40.0
Luxembourg	0.04	0.2							0.2			0.4
Netherlands	0.8			0.3					2.0			3.1
Norway	0.7			0.4								1.1
Portugal	1.7							5.3	0.1			7.1
Spain	7.1	1.1	5.3	4.8	3.0			3.2	0.2	2.0	0.9	27.6
Sweden	2.2											2.2
Switzerland	5.2											5.2
Total	88.6	7.6	5.4	8.9	10.5	0.5		20.3	12.0	16.9	1.2	171.9
Percentage	51.5	4.4	3.1	5.1	6.1	0.3	0	11.8	7.0	9.9	0.7	100

2.1.3 MASONRY CEMENTS

The European Prestandard for masonry cement (ENV 413-1)[5] defines four types: MC 5 which is required to contain a minimum of 25 per cent Portland cement clinker together with an air-entraining agent, Type MC 12.5 with a minimum of 40 per cent Portland cement clinker and an air-entraining agent, and types MC 12.5X and MC 22.5X which also have to have a minimum of 40 per cent clinker but no air-entraining agent. The ASTM Masonry Standard C 91-95[13] has no compositional requirements.

2.1.4 BUILDING LIMES

The European Prestandard for Building Limes (ENV 459-1)[7] uses the term 'air lime' to describe a lime 'mainly consisting of calcium oxide or hydroxide which slowly hardens in air by reacting with atmospheric carbon dioxide. Generally they do not harden under water as they have no hydraulic properties'.

It also covers two types of hydraulic limes. There is the 'natural hydraulic lime (NHL) which has been produced by burning (below 1250°C) of more or less argillaceous limestones with reduction to powder by slaking with or without grinding' and the NHL-P material which may contain up to 20 per cent of a suitable pozzolanic or hydraulic material. Organic additives such as air-entraining agents may be added to limes made to this European Prestandard.

Thus for masonry work there is, as far as European Prestandards are concerned, a full range of products from the very weak hydraulic limes through the (cement) fortified hydraulic limes to the three different types of masonry cements. In some countries the masonry cements (usually the MC 5 types) are made and tested as masonry cements but marketed as 'chaux hydrauliques artificielles' or 'calce eminentamente idraulica artificale'.

2.1.5 HYDRAULIC ROAD BINDERS

The European draft proposals for road binders[6] restrict the component materials to those permitted in ENV 197-1. No absolute minimum content of Portland cement clinker is required except in the higher strength classes where the minimum is 20 per cent. Manufacturers are however required to maintain a specified tolerance upon their declared compositions.

2.2 Performance-orientated properties

2.2.1 STRENGTH-GIVING PROPERTIES

The classification of cements in terms of their strength-giving properties has been practised for many years. It is impractical for cement producers to test the cements they make with all the many different sands and aggregates and in the wide range of mix proportions they are likely to meet in practice. Standard test procedures have therefore been developed to enable manufacturers to control their production. In the early days, the strength of the cement was determined by inducing a tensile break in briquettes formed from either cement and water or from cement, a standard sand and water. This test failed to provide the level of reliability required and was replaced by tests which involved the breaking of moulded specimens in compression. In order to move closer towards practice, in the late 1930s the UK cement industry introduced a test which involved measuring the strength of the cement when made under standard conditions into a concrete. This was the subject of continuous development and served the industry well for more than 50 years.[62] However, pressure for European and international harmonisation dictated that it should be replaced by a mortar test in common use in many other countries.[40]

The strength-giving characteristics of cements can take the form of assessments at early (2–3 days) or late (28 days) ages or both. The European Prestandard ENV 197-1[4] places primary emphasis upon the 28-day strength and for this purpose introduces three classes, 32.5, 42.5 and 52.5; these numbers represent the minimum characteristic strength, in N/mm^2, which the cement is required to achieve at 28 days from tests made in accordance with the test method described in European Standard EN 196-1[40]. The use of characteristic requirements, together with a defined minimum testing frequency, means that 5 per cent of the results are permitted to be below the minimum value with an associated consumer risk of 5 per cent. However, as a safeguard, there are also 'absolute' minima (the points at which the 100 per cent pass and the 100 per cent fail situations meet) of 30, 40 and 50 N/mm^2, below which no results are permitted to fall if the cement is to meet the specification requirement for the particular class. The European Prestandard also incorporates maximum characteristic strength limits for the 28-day strength of the 32.5 and 42.5 classes. These are 52.5 and 62.5 N/mm^2 respectively.

Subclasses, designated by a suffix R, are introduced in order to provide a measure of classification in respect of early strength and the overall situation is given in Table 2.13. The strength range permitted may upon first impressions appear to be excessively large; however, it should be borne in mind that the conformity procedure introduced into the Prestandard requires that the standard deviation is incorporated into the assessment. In simple terms, if the standard deviation of manufacture and testing is, say, 2.0 N/mm^2 at 28 days then the lowest target for manufacturing purposes for a class 42.5 has to be of the order of $42.5 + (2^* \times 2.0) = 46.5$ N/mm^2, and if the standard deviation is 4.0 then the figure becomes 50.5 N/mm^2 [*this value varies from 1.84 to 2.13 depending upon the number of test results involved].

The ASTM adopts a somewhat different approach. In their case the requirements are expressed only as minima and they are of the 100 per cent pass or 100 per cent fail variety (i.e. not characteristic). When expressed in terms of the EN 196-1 test, the minimum requirement (optional) in the C 150-95 Standard[8] for the non-air-entraining Portland

Table 2.13 European Prestandard ENV 197-1 – classification of common cement types by strength classes

Cement class	Characteristic compressive strength (N/mm^2) 2 days	7 days	Absolute minima (N/mm^2) 2/7 days	Characteristic 28-day compressive strength (N/mm^2) Minimum	Maximum	Absolute minima (N/mm^2) 28 days
32.5	–	⩾16	⩾14	32.5	52.5	⩾30.0
32.5R	⩾10	–	⩾8	32.5	52.5	⩾30.0
42.5	⩾10	–	⩾8	42.5	62.5	⩾40.0
42.5R	⩾20	–	⩾18	42.5	62.5	⩾40.0
52.5	⩾20	–	⩾18	52.5	–	⩾50.0
52.5R	⩾30	–	⩾28	52.5	–	⩾50.0

cement approximates to 40 N/mm^2, which is virtually the same as the 100 per cent pass/100 per cent fail limit in the European Prestandard ENV 197-1.[4] The minimum value for air-entrained Portland cements in the same ASTM Standard approximates, when assessed in a similar manner, to the minimum value for the 32.5 class in the European Prestandard. The equivalent minimum requirements in the ASTM Standard C 595M-95[9] for blended hydraulic cements are approximately 10 per cent higher than those for the European Prestandard's 32.5 class. Thus, within the realms of usage of two major international standardising agencies the minimum 28-day strength requirements are broadly similar. In practice, however, on account of competitive pressures the strength giving properties of the European cements are often closer to the upper limit, than to the lower limit. Table 2.14 gives the compressive strength results obtained from EN 196-1 tests on the cements the chemical analyses of which are given in Table 2.6.

In both the European Prestandard and in American Standards, the 28-day strength requirements are generally similar irrespective of the composition. However, although permitted in the European Prestandard it is unlikely on technical grounds that it is possible to produce a 52.5R strength class with cement Types III, IV and V, since these are required to contain relatively high contents of secondary materials such as granulated blastfurnace slag or fly ash. These secondary materials are not sufficiently active at the test temperature of 20°C to contribute significantly to the strength at 2 days.

It has not been possible to establish with a significant level of certainty the relative commercial significance of the different strength classes adopted in Europe, but an estimate based upon 80 per cent of the production tonnages for the mid-1980s is given in Table 2.15. This suggests that most of the Type I cements fall into the 42.5 classes and most of the others into the 32.5 classes.

2.2.2 COSTS

With the increased use of 'designed' concrete mixes, i.e. those where a specifier defines a certain minimum strength requirement in the concrete (usually at 28 days) rather than a certain cement content, the strength-giving characteristics of a cement are open to be assessed on the grounds of cost to the concrete maker. Thus, provided that the cement content of the concrete is above the specification minimum, concrete makers may wish to enhance the profitability of their operations by minimising the amount of cement required

Table 2.14 EN 196-1 strength test results on cements detailed in Table 2.6[63]

Compressive strength (N/mm^2)	DO	DOX	EO	FO	GO	HO
24 h	16.0	15.2	18.8	17.0	28.4	17.3
2 days (estimated)	28	27	29	28	35	29
3 days	30.6	33.9	35	34.6	38.9	36.1
7 days	38.7	42.2	42.3	42.1	52.3	47.2
28 days	53.7	54.9	55.1	57.0	56.8	58.9
ENV 197-1 class characteristic requirements	42.5R	42.5R	42.5R	42.5R	42.5R	52.5
Min. at 2 days	⩾20	⩾20	⩾20	⩾20	⩾20	⩾20
Min. at 28 days	⩾42.5	⩾42.5	⩾42.5	⩾42.5	⩾42.5	⩾52.5
Max. at 28 days	⩽62.5	⩽62.5	⩽62.5	⩽62.5	⩽62.5	–

Table 2.15 Distribution of cement types and classes produced in Europe in the mid-1980s

Type	%	% as 32.5 class	% as 42.5 class
I	43	39	61
II-S Slag	2	80	20
II-M Composite	16	75	25
II-V Siliceous fly ash	1	50	50
II-W Calcareous fly ash	6	100	0
III-B Blastfurnace slag	3	50	50
IV Pozzolanic	9	100	0
Total	80	–	–

to achieve the required strength. A simple calculation illustrates this approach. The EN 196-1 test method gives strengths which are approximately 25 per cent higher than those achieved when using the BS 4550 'standard' concrete test and a change of something like 6 kg of an ENV 197-1 Type I class 42.5 cement is required to change the 28-day strength of the 'standard' concrete by 1.0 N/mm^2. If the concrete contains 320 kg of this cement in 1 m^3 of concrete and the cement strength as assessed on the EN 196-1 method drops by 1.0 N/mm^2 (equivalent to 0.8 N/mm^2 in the concrete), then approximately 5 kg extra cement must be added to maintain the strength level. This additional 5 kg represents an effective 1.6 per cent increase in the cost of cement to the user. Applying this approach to the 32.5 and 42.5 class cements and, assuming a 10 N/mm^2 EN 196-1 28-day strength difference between the two classes, the effect on cost in this particular type of application as a first approximation amounts to 16 per cent on the price of the cement.

2.2.3 SULFATE-RESISTING PROPERTIES

Cements having improved sulfate resistance properties have traditionally been produced in two ways, notably by reducing the amount of the tricalcium aluminate (C_3A) in ENV 197-1 Type I Portland cements as this is the compound which is specifically attacked by the sulfates, and also by replacing a high proportion of the Type I Portland cement (without, necessarily, a reduced C_3A) by a suitable granulated blastfurnace slag, i.e. making an ENV 197-1 Type III cement.

The composition adopted is dependent upon the level of sulfate resistance required and the cement content of the concrete to be used. BRE Digest 363[64] sets out the options and these are summarised as far as cement types are concerned in Table 2.16, which has been adapted to relate to ENV 197-1 cements.

In the USA and in some other countries, Portland cements (without secondary materials) having moderate sulfate-resisting properties are available. These are for use in situations where SO_4 content of the water is within the range 150–1500 ppm[11] and involve a restriction on the amount of C_3A to a maximum of 8 per cent. In some cases this is also accompanied by a maximum limit to the amount of $C_3S + C_3A$ of 58 per cent and/or a constraint that the percentage of SiO_2 should be $\geqslant$20–21 per cent. Elsewhere various combinations of C_3A levels in the Portland cement component and types and proportions of secondary materials are considered to be satisfactory for moderate and also for high sulfate resistance.[11] ASTM Standards also permit the assessment of the sulfate resistance to be made using a

Table 2.16 Classification of cement types and amount required to be present in concrete in respect of their sulfate-resisting characteristics[64]

	Concentration of sulfate and magnesium							
	In soil or fill			In ground-water (g/L)				
	By acid extraction	By 2:1 water/soil extract (g/L)				Minimum cement content (kg/m^3)	Maximum water/cement ratio	Cement Type ENV 197-1 classification
Class	% SO_4	SO_4	Mg	SO_4	Mg			
1	<0.24	<1.2		<0.4		275[d] 300[c]	0.65	I, II-S, III-A/B, II-V, IV[b]
2	[e]	1.2/2.3	–	0.4/1.4	–	330	0.50	I, II-S, III-A/B, II-V, IV[b]
						280	0.55	I[a]
						300	0.55	III-B/C[f] II-V[g], IV-V[h]
3	[e]	2.3/3.7	–	1.4/3.0	–	320	0.50	I[a]
						340	0.50	III-B/C[f] II-V[g], IV-V[h]
4	[e]	3.7/6.7	<1.2	3.0/6.0	<1.0	360	0.45	I[a]
						380	0.45	III-B/C[f] II-V[g], IV-V[h]
		3.7/6.7	>1.2	3.0/6.0	>1.0	360	0.45	I[a]
5	[e]	>6.7	<1.2	>6.0	<1.0	[i]	[i]	[i]
		>6.7	>1.2	>6.0	>1.0			

[a] Maximum C_3A of 3.5%, maximum SO_3 2.5%. No added minor additional constituent. To comply with BS 4027.
[b] With siliceous fly ash only.
[c] Reinforced concrete.
[d] Unreinforced concrete.
[e] If in excess of 0.24 classify on the basis of the 2:1 extract.
[f] Slag content 74–90%.
[g] Not less than 25% fly ash.
[h] Not more than 40% of siliceous fly ash.
[i] As for class 4 plus surface protection.

14-day expansion test, and work is in hand in Europe in order to achieve a similar objective.[65]

Normally the high sulfate-resisting cements (those with less than 3.5 or 5 per cent C_3A) give lower early strengths than the equivalent Portland cements, although some manufacturers grind their products somewhat finer in order to minimise this effect. Generally speaking, the Portland-type sulfate-resisting cements find their most important use in the precast concrete products industry where early strength is important in respect of mould turnover, whilst those containing large amounts of slag are used to advantage in large concrete structures where curing is good, low temperatures are avoided and their low heat release is also helpful.

2.2.4 LOW HEATS OF HYDRATION

The European Prestandards have not, to date, addressed this matter sufficiently to have produced a definitive position. However, from the various national standards in Europe the favoured approach is to use cements which have a low early strength where heat release in mass concrete applications is considered to be a problem. ENV 197-1 Type I cements have been produced with low heat release characteristics by reducing their content of C_3A and also of C_3S. A typical chemical analysis (per cent) would be:

SiO_2	22.39	Free lime	0.7
Al_2O_3	4.72	Insoluble residue	0.38
Fe_2O_3	6.17	C_3S	34
CaO	62.08	C_2S	39
MgO	0.70	C_3A	2.1
SO_3	1.94	C_4AF	18.8
LOI	0.76		
K_2O	0.61		
Na_2O	0.25		

However, the approach which is now more commonplace is to incorporate the appropriate amount of a secondary material such as a slag or a pozzolan into the cement formulation. The two main methods required in standards to measure the amount of heat released are the heat of solution method and the semi-adiabatic calorimetry method. The former suffers from the disadvantage[66] that it provides little significant information upon the heat released over the critical first 48 h, or the rate at which the heat is released. The latter method[67] is able to do this and also makes it easier to establish the amount of heat released and the temperature rise achieved with elevated temperature curing. This is an important facility since the heat released from latent hydraulic binders such as slag and pozzolans in the presence of Portland cement increases considerably as the temperature of the concrete or mortar is increased and tests at ambient temperatures may be misleading.

At 60°C a cement containing 50 per cent slag has been shown after 15 h to release more heat than the Portland cement on its own, even though at 27°C it only released about half as much heat as the Portland cement.[68] Isothermal conduction calorimetry[69] is also very useful as a research tool to provide a means of assessing when heat is released and also the rate at which it is released.

Using the heat of solution method at 7 days and/or the semi-adiabatic method at 42 hours, the draft CEN standard for moderate release characteristics sets a maximum characteristic value of 320 kJ/kg. For cement with low heat release the maximum is 270 kJ/kg; for cements with very low heat release the maximum is 220 kJ/kg. Type I Portland cements have heats of hydration of 280–360 kJ/kg when assessed using this method.

2.2.5 CONTROLLED-FINENESS CEMENTS

Special provision was made in earlier British Standards for this type of cement, which was manufactured without any minor additional constituents in both coarse and fine variants. The coarser product is used in applications where it is important that the removal of water from the concrete, mortar of grout is not inhibited. Pipe spinning is one such application. This type of cement is required to have a specific surface area suitable for the particular application (usually 250–280 m^2/kg Blaine). The finer product is used in processes such as those adopted for the manufacture of aerated concrete blocks where variations in the reactivity of the cement brought about by excessive variations in its specific surface area can adversely affect production rates and product quality.

2.2.6 AIR-ENTRAINING PROPERTIES

Since the late 1940s in North America, much of the concrete likely to be exposed to freezing and thawing and the associated use of de-icers has been protected by air entrainment.[70] Cement manufacturers in that part of the world have therefore made available products which incorporate an air-entraining agent. In the USA this air-entraining agent is required to comply with the relevant ASTM Standard.[71]

These cements are required to have an air content, as assessed using the ASTM Standard mortar, of between 16 and 22 per cent, whereas the non-air-entraining cements must have less than 12 per cent entrained air using the same test procedure. The higher level of entrained air lowers the strength of the test mortar and the minimum requirement for this is generally approximately 80 per cent of that of the equivalent non-air-entraining type. The European cement Prestandard ENV 197-1, through the lack of definition of additive types, permits air-entrained cements under the normal description of common cements. On account of the effect that other variables in the concrete making process (sand content and grading etc.) have on the level of air entrainment, this type of cement is now normally only used on relatively small jobs, with the addition of air-entraining agents to non-air-entraining cements at the concrete mixer being the favoured option in the civil engineering world.

2.2.7 HYDROPHOBIC AND WATER-REPELLENT PROPERTIES

When subject to storage even under moderately humid conditions, Portland cements abstract moisture and carbon dioxide from the atmosphere and partially hydrate. A limited level of moisture/carbon dioxide take-up ('aeration') leads to a reduction in strength-giving properties without the significant development of lumps, a typical situation being where an increase in loss on ignition of 0.5 per cent lowers the 28-day strength by $3\,\mathrm{N/mm^2}$. However, if excessive aeration takes place then, in addition, lumps develop and the cement becomes difficult to disperse in the concrete, mortar or grout. The formation of lumps becomes of greater significance if the cement in question contains relatively high amounts of potassium sulfate, since this combines with the calcium sulfate present to form syngenite ($CaSO_4 \cdot K_2SO_4 \cdot H_2O$). This compound acts as an effective binder of the dry cement particles. In order to alleviate these problems and in some situations to enable cement to be stored as a powder for long periods in the open, up to 0.5 per cent of a saturated fatty acid is interground with the cement clinker and gypsum. This results in a free-flowing hydrophobic powder which has a reduced ability to abstract moisture or carbon dioxide from the air, but which is somewhat difficult to mix with water. In the manufacture of this product attention has to be given to selection of the fatty acid in order to minimise air entrainment. Unsaturated fatty acids are particularly prone to this. India is one of the few countries with a national standard devoted to this type of cement, and this requires 0.1–0.5 per cent of the hydrophobic agent and also introduces a performance test for hydrophobicity.

Generally under the same category as hydrophobic cements are the water-repellent cements produced essentially for the production of mortars used for water-repellent (low suction) renderings and also to minimise efflorescence problems in precast units. These materials are made easier to mix with water by blending the water-repellent material with the cement rather than by intergrinding it with the clinker and gypsum, as is normally the practice with hydrophobic cements.

2.2.8 LOW-ALKALI PROPERTIES

In the early 1940s, in the USA, it was established that certain types of aggregates react with the alkalis in hardened concretes to produce a gel which could, in the presence of moisture, expand and lead to severe cracking. In order to minimise this effect and to permit the continued use of both 'reactive aggregates' and also those about which there were inadequate data, Portland cements (ENV 197-1 Type I and those covered by ASTM C 150-95) were manufactured with a maximum alkali content of 0.60 per cent sodium oxide equivalent $(Na_2O)_e$, where $(Na_2O)_e = 0.658 \times \%K_2O + \%Na_2O$. In many standards a low alkali value is an optional requirement.

In the suite of ASTM Standards is included a performance test for assessing the potential of cements for alkali reactivity using a special grade of Pyrex aggregate, although the acceptability of this test is not universal.[72] The situation regarding the suitability of cements containing secondary materials in low-alkali applications is, in the absence of an internationally agreed performance test, more complex. Details of the situation derived from cement standards as at 1991[11] for different countries and based on alkali levels and composition are summarised in Table 2.17.

It is known[11] that different aggregates can have different demands in respect of alkali requirements and this may have a bearing on the range of values appearing in the various national standards. Generally granulated slags find the greatest favour as secondary materials in connection with reducing the potential for alkali–silica reaction. This is in keeping with published experimental findings.[39]

2.2.9 SEA WATER-RESISTANT PROPERTIES

Some controversy exists internationally regarding the most desirable composition of Portland cements for this purpose. This centres around the optimum level of C_3A. The AFNOR Standard[73,74] refers to recommendations from the Permanent Inter-Ministry Committee for Hydraulic Binders and Admixtures for Concrete and indicates the suitability of the following:

Table 2.17 Summary from different national standards of the requirements to minimise adverse effects from alkali–silica reaction

Max. % $(Na_2O)_e$	Clinker and calcium sulfate (%)	Slag (%)	Pozzolana (inc. fly ash; %)	Others (%)
0.6	95–100	–	–	–
0.9	$\leqslant 50$	$\geqslant 50$	–	–
0.9	40–65	35–60	–	–
1.0	40–80	20–60	–	–
1.0	85	15 slag and/or pozzolana		–
1.0	60–85	15 slag and/or pozzolana		25
1.1	36–50	50–64	–	–
1.3	30–70	30–70	–	–
2.0	15–40	60–85	–	–
2.0	$\leqslant 15$	$\geqslant 85$	–	–

For total immersion zones:

- Portland cements (containing <3 per cent minor additional constituents) and Composite Portland cements containing at least 65 per cent clinker (ENV 197-1 Types IIA-M and IIB-M) with $SO_3 \leqslant 2.5$ per cent; $MgO \leqslant 3$ per cent; $Al_2O_3 \leqslant 8$ per cent; $S \leqslant 0.2$ per cent; $C_3A \leqslant 10$ per cent; $C_3A + 0.27$ (per cent C_3S) $\leqslant 23.5$ per cent;
- blastfurnace slag cements ENV 197-1 Type III/C and Type III/B but with 40–75 per cent slag;
- composite cement similar to ENV 197-1 Type V but with between 25 and 60 per cent clinker, 20–45 per cent fly ash and 20–45 per cent slag;
- calcium aluminate cement;

For tidal zones:

- Portland cements (containing <3 per cent minor additional constituents) with $C_3A \leqslant 5$ per cent;
- ENV 197-1 Type III/B (with >60 per cent slag);
- ENV 197-1 Type III/C;
- calcium aluminate cement.

In the UK, the Code[75] requires that for UK waters, the C_3A content should be within the range 4–10 per cent and specifically states that sulfate-resisting Portland cement to BS 4027 should not be used for reinforced concrete in contact with sea water because it has a maximum C_3A of 3.5 per cent.

Clearly there is little international consensus on the lower level of C_3A and it is difficult to understand the reasoning behind the British Code requirement in respect of BS 4027 cements as there are many examples of satisfactory marine structures in the UK built on concrete made using this cement.

2.2.10 *LEACHING-RESISTANT PROPERTIES*

This class of cement originates from Italy and appears to have been developed to meet a need to minimise the leaching of lime from concrete and mortar. There are a number of types and classes given in the Italian Standards[10] and a test method is available in order to assess the leachability (Table 2.18).

From their compositions it seems evident that the philosophy adopted with these cements is to encourage the lime released from the hydration of the Portland cement clinker

Table 2.18 Italian cement standards – classification of cements by leachability

Type	Degree of leaching resistance	Clinker and calcium sulfate (%)	C_3S in clinker, max. (%)	Slag (%)	Pozzolana (%)
Portland	Moderate	100	40	0	0
Blastfurnace	Moderate	$\leqslant 64$	–	$\geqslant 36$	0
Blastfurnace	High	$\leqslant 50$	–	$\geqslant 50$	0
Blastfurnace	Very high	$\leqslant 30$	–	$\geqslant 70$	0
Pozzolanic	Moderate/high	–	–	–	–
Pozzolanic	Very high	–	–	–	–

component to combine with the slag or pozzolana and thus minimise the amount available for leaching.

2.2.11 NATURAL CEMENTS

These are made by calcining naturally occurring mixtures of calcareous and argillaceous raw materials at temperatures (1000–1200°C) below those required to sinter the product. As such, these cements occupy a position between ordinary Portland cements and hydraulic limes. They have limited application at the present time, although in France a cement of this type known as 'le ciment prompt' is still marketed.

This product is characterised by relatively high early strengths when tested in mortars with a low (1:1) sand:cement ratio (4 N/mm^2 in 15 min and 8 N/mm^2 after 3 h). However, the 28-day strength at 20 N/mm^2 is well below that achieved by normal common cements. It is not used in concrete, but provides an acceptable material for small-scale repair work. Traditional natural cements have the oxide analyses given in Table 2.19.

2.2.12 MASONRY CEMENTS AND ARTIFICIAL HYDRAULIC LIMES

The working properties of mortars used for brick and block laying and for rendering and plastering are important if weathertight structures are to be constructed. An acceptable level of workability may be achieved by increasing the ratio of cement to sand in the mortar. However, such a process leads to high strengths and associated high shrinkage. Site blends of lime and cement have provided a means of achieving the required balance between workability and strength. In order to minimise the need to have additional materials on site, masonry cements were introduced in the first instance in North America. ASTM Standard C 91-95[13] requires that when tested under standard conditions in a 1:3 (by volume) standard sand/masonry cement mortar, the masonry cement should meet requirements for fineness, setting times, autoclave soundness, compressive strength, water retention and air entrainment. There are no compositional requirements. The European Prestandard for masonry cements (ENV 413-1)[5] has requirements for setting times, soundness (le Chatelier expansion), compressive strength, water retention and air entrainment. In the case of the latter, however, restrictions are also placed on the composition for the different types and classes, as is shown in Table 2.20.

As will be noted from Table 2.20, not all masonry cements in the European Prestandard incorporate an air-entraining agent. This is, in the main, in order to accommodate practice in France as all European standards for cement are required to take into account 'all traditional and well-tried products'.

Table 2.19 Analyses of traditional natural cements (per cent)

SiO_2	26.5	24.3
Al_2O_3	9.4	7.2
Fe_2O_3	2.0	5.1
CaO	53.5	33.7
MgO	2.4	20.9
LOI + alkalis	6.2	8.8

Table 2.20 Masonry cements: European Prestandard ENV 413-1 Characteristic requirements

	MC 5	MC 12.5	MC 12.5X	MC 22.5X
Portland cement clinker (%)	$\geqslant 25$	$\geqslant 40$	$\geqslant 40$	$\geqslant 40$
Organic matter (%)	$\leqslant 1$	$\leqslant 1$	$\leqslant 1$	$\leqslant 1$
Air-entraining agent	Yes	Yes	No	No
Air (%)	8–20	8–20	$\leqslant 6$	$\leqslant 6$
Water retention (%)	80–95	80–95	80–95	80–95
Compressive strength (N/mm^2)				
7 days	–	$\geqslant 7$	$\geqslant 7$	$\geqslant 10$
28 days	5–15	12.5–32.5	12.5–32.5	22.5–42.5
Sulfate as SO_3 (%)	$\leqslant 2.0$	$\leqslant 3.0$[a]	$\leqslant 3.0$[a]	$\leqslant 3.0$[a]
Chloride as Cl (%)	–	$\leqslant 0.10$	$\leqslant 0.10$	$\leqslant 0.10$

[a] If the Portland cement clinker content is 55% or more, a maximum of 3.5% is appropriate.

The secondary material in most masonry cements is finely ground limestone, although hydrated lime is also used. The presence of the air-entraining agent not only improves workability, but enhances the freeze–thaw resistance of the mortar prepared from the masonry cement. Some masonry cements contain water repellents.

2.2.13 ROAD BINDERS

These materials are factory-made products supplied ready to use in road bases, sub-bases, capping layers and for soil stabilisation or soil improvement. The present draft European Prestandard is based upon the main constituents being Portland cement clinker (K); granulated blastfurnace slag (S); pozzolanic materials: natural pozzolans, thermally active clays and also shales (P); fly ashes: siliceous (V) and calcareous (W); burnt shale (T) and limestone (L). There are four strength classes, listed in Table 2.21.

Where the road binder contains a minimum of 20 per cent Portland cement clinker, the strength class incorporates an E as a suffix. The draft Prestandard is based upon manufacturers' declared compositions, but the tolerances on these declared compositions are specified as ±10 percentage points of the amount declared to be present if that amount is over 20 per cent (i.e. if the declared amount is 30 per cent, then the tolerance permitted is 20–40 per cent). If the amount declared to be present is between 6 and 20 per cent then the tolerance is ±5 percentage points. The SO_3 is limited to 4.0 per cent or 7.0 per cent for road binders containing burnt shale, calcareous fly ash (only where these materials supply the additional SO_3), and for road binders containing more than 80 per cent granulated blastfurnace slag – provided that these materials meet the requirements of a special soundness test.

Table 2.21 Draft European Prestandard proposals for strength classes of road binders

Strength class	Characteristic compressive strength at 28 days (N/mm^2)
5	5–15
12.5	12.5–32.5
22.5	22.5–42.5
32.5	32.5–52.5

The characteristic requirements are for fineness, with a maximum of 15 per cent coarser than 90 µm, for an initial setting time of 120 min or more, and for a le Chatelier soundness expansion not more than 10 mm.

2.2.14 BUILDING LIMES

The European Prestandard for building limes (ENV 459-1)[7] introduces requirements given in Table 2.22. Although no requirements are given in the Prestandard for reactivity, CL 90 limes for soil stabilisation should reach a maximum temperature of not less than 60°C and all other limes not less than 50°C. The reaction time for 80 per cent conversion of the CaO content capable of being slaked should not be less than 15 min for all ground limes.

Chemical analyses of building limes are given in Table 2.23.

For limes that have been stored in a manner which precludes the uptake of moisture and/or carbon dioxide, the amount of CO_2 in the material may be taken as a measure of the degree of burning which has occurred. The compound composition[76] of hydraulic limes not containing additional hydraulic constituents comprises CaO; $Ca(OH)_2$; α and β $2CaO{\cdot}SiO_2$; $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$; $CaCO_3$; $3CaO{\cdot}2SiO_2$; and α and β $CaO{\cdot}SiO_2$. Where hydraulic limes contain Portland cement as an additional hydraulic material (building limes classified as

Table 2.22 European Prestandard requirements for building limes: ENV 459-1[7]

Type of lime	CL 90	CL 80	CL 70	DL 85	DL 80	HL 2	HL 3.5	HL 5
Fineness max (%):								
Coarser than 90 µm	≤ 7	≤ 7	≤ 7	≤ 7	≤ 7	≤ 15	≤ 15	≤ 15
Coarser than 200 µm	≤ 2	≤ 2	≤ 2	≤ 2	≤ 2	≤ 5	≤ 5	≤ 5
Soundness:								
Pat test[a]	pass	pass	pass	pass	pass	–	–	–
le Chatelier[b], max. expansion (mm)	≤ 20	≤ 20	≤ 20	–	–	≤ 20	≤ 20	≤ 20
Pressed disc[b], max. expansion (mm)	≤ 2	≤ 2	≤ 2	–	–	≤ 2	≤ 2	≤ 2
Max. free water (%)	≤ 2	≤ 2	≤ 2	≤ 2	≤ 2	≤ 2	≤ 2	≤ 1
Mortar tests:								
Penetration (mm)	>20	>20	>20	>20	>20	>20	>20	>20
	<50	<50	<50	<50	<50	<50	<50	<50
Air (%)	≤ 12	≤ 12	≤ 12	≤ 12	≤ 12	≤ 20	≤ 20	≤ 20
Setting time (h)	–	–	–	–	–	$>1 \leq 15$	$>1 \leq 15$	$>1 \leq 15$
Compressive strength (N/mm^2):								
7 days	–	–	–	–	–	–	≥ 1.5	≥ 2
28 days	–	–	–	–	–	2–5	3.5–10	5–15
Quicklime								
Soundness after slaking – pat test	pass	pass	pass	–	–	–	–	–
Yield (dm^3/10 kg)	≥ 26	≥ 26	≥ 26	–	–	–	–	–

[a] For lime putty and hydrated dolomitic limes only.

[b] For building limes other than lime putty and dolomitic limes.

NHL-P in the European Prestandard ENV 459-1), their presence may be established using the method described in BS EN 459-2: 1995.[77]

White and coloured cements, cement paints and oilwell cements are dealt with in chapter 14.

2.3 Manufacture of Portland cement clinker

Portland cement and other types of cements incorporating significant amounts of Portland cement clinker are normally manufactured in established factories (traditionally referred to as 'works'). In many cases these are situated at locations where the locally quarried materials are of suitable quality to enable the kiln feedstock to be produced at an acceptable cost. But in recent years, with the relatively high cost of fuels, consideration has also been given to locations where the raw materials do not contain large amounts of water in order to avoid the extra costs associated with the removal of excess water using additional heat. Another important matter is closeness to a market in order to minimise transport costs. Figure 2.1 shows a modern cement manufacturing plant and highlights the emphasis given to minimising environmental nuisances, while Figure 2.2 illustrates the typical layout of a cement-making works.

Although there is a wide range of hydraulic cements, most rely upon Portland cement clinker as the basis for their strength-giving properties. It is therefore appropriate to discuss in some detail the raw materials and the production techniques adopted in its manufacture. Where secondary materials are introduced into the formulations, these are either added

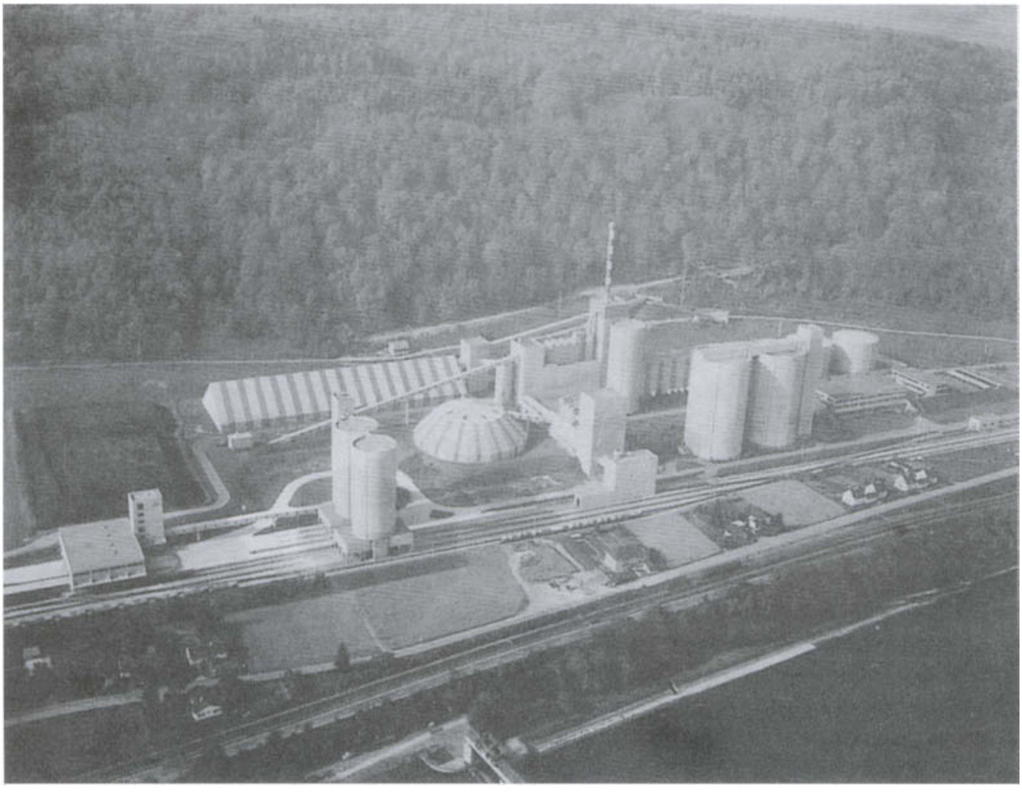

Fig. 2.1 A modern cement manufacturing plant (by courtesy of Cementfabrik Holderbank – Rekingen Works, Switzerland).

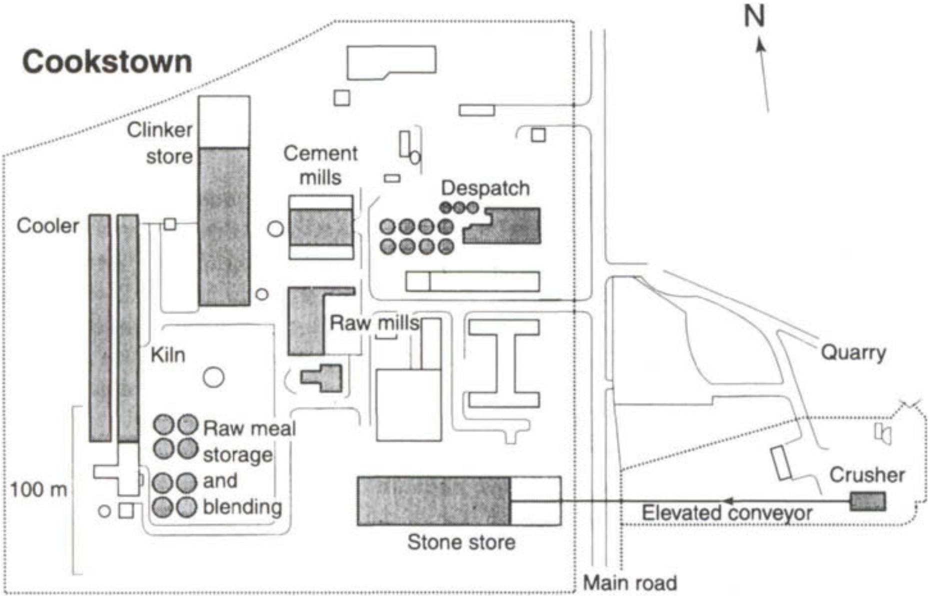

Fig. 2.2 A typical layout for a cement-making plant (after Watson D, Armitage FH, Male CE. Principles of layout design. In: *Process Technology of Cement Manufacturing*, VDZ Congress, 1985, Bauverlag).

Table 2.23 Typical chemical analyses of building limes (per cent)

	Air limes			
	Quicklime CL 90	Hydrated lime CL 80	Dolomitic quicklime DL 85	Hydraulic lime
SiO_2	0.9	0.9	1.0	31.1
Al_2O_3	0.3	0.5	0.3	4.4
Fe_2O_3	0.2	0.2	0.3	2.2
CaO	95.9	71.3	57.5	58.4
MgO	0.3	0.3	37.6	1.1
SO_3	0.5	0.5	–	0.6
CO_2	0.8	3.5	1.0	1.3
K_2O	0.03	0.04	–	–
Na_2O	0.20	0.15	–	–
LOI	0.8	21.4	–	–

Table 2.24 Analysed and calculated calcium silicate contents (per cent)[78]

	Determined using XRD and microscopy	Determined using Bogue formulae based upon oxide analyses
C_3S (alite)	66–82	42–68
C_2S (belite)	2–32	10–36

to the clinker at the grinding stage or blended with the finished cement in the dry state before being tested and stored ready for despatch.

2.3.1 THE PRODUCT

In general terms and as primary objectives, it is necessary for the manufacturer to produce, as economically as possible, a material which is sound (i.e. it does not expand significantly after hardening) and which, when ground with the appropriate amount and form of calcium sulfate to a specific surface area (Blaine) of 300–350 m^2/kg, develops a 28-day strength (when tested using the method given in EN 196-1)[40] of 50–65 N/mm^2. In addition to this, there are also constraints associated with the use of the clinker to prepare cements for special purposes where sulfate resistance, sea water resistance, low alkali release and high early strengths are required.

In order to achieve the primary objectives the clinker should not contain significant amounts (normally over 3%) of uncombined calcium oxide or excessive amounts (not more than 5–6 per cent) of magnesia. It should also contain very little moisture or combined carbon dioxide. In order to ensure the full strength-giving potential, it is necessary for it to contain 70–80 per cent of calcium silicates (calculated on the basis of the Bogue formulae[8]). Of these calcium silicates, over 60 per cent should be as the tricalcium silicate (C_3S) – or since we are dealing with the commercial product which invariably contains an impure form of C_3S it is perhaps better to use the term 'alite'. For similar reasons the dicalcium silicate (C_2S) is perhaps best referred to as 'belite'. For these reasons it is not unexpected that when the calculated calcium silicate content is compared with that measured by X-ray diffraction (XRD) there are some differences, as shown in Table 2.24.[78] The remainder of the composition of the Portland cement clinker comprises compounds which are either necessary in order to achieve the required degree of combination in the course of thermal processing or are uneconomic to remove from the available raw materials. These include:

- 0–16 per cent tricalcium aluminate C_3A;
- 1–17 per cent tetracalcium aluminoferrite C_4AF;
- 0.5–6 per cent magnesia MgO;
- 0.5–3 per cent alkali sulfates Na_2SO_4, K_2SO_4 and other compounds incorporating them;
- 0.2–4 per cent uncombined calcium oxide CaO – free lime.

2.3.2 RAW MATERIALS

Main components

The simplest raw material to use would be one which has exactly the required composition. Materials of this type exist as narrow bands in the chalklands in the UK. However, to base a production unit upon them would involve the rejection of vast quantities of material and in consequence their use is not a commercial, or environmental option. Such a material would require an oxide analysis which approximate to that given in Table 2.25.

In order to maximise the use of raw materials, the simplest step is to combine two materials which are relatively consistent within themselves in order to produce the required feedstock composition. This practice was adopted for many years all over the world, as it

Table 2.25 Ideal composition of raw material (per cent)

	Dry raw material	Clinker made from the dry raw material (assuming no coal ash absorption)
SiO_2	14.0	20.9
Al_2O_3	4.1	6.1
Fe_2O_3	1.6	2.3
CaO	43.2	64.5
Free lime	–	1.0
C_3S (Bogue)	–	55
C_2S (Bogue)	–	18
C_3A (Bogue)	–	12.2
C_4AF (Bogue)	–	7.0

required only the simplest form of control. This usually involved the use of a calcimeter (a device which gave a volumetric measure of the amount of carbonate in a sample) or later through the use of a simple acid–alkali titration. An example is given in Table 2.26.

Situations occur where it is necessary to operate a cement clinker-making plant, but where it is not possible with just two raw materials to achieve the required feedstock composition. In these circumstances, provided that one component has a calcium carbonate content of at least 80–85 per cent, then the appropriate feedstock composition may be achieved by the introduction of other materials. This may also occur, as is described later, when it is necessary to deal with problems associated with alkali build-up in preheater kilns and also when it is desired to lower the alkali levels in the cement clinker produced. Table 2.27 illustrates the situation with a feedstock based upon four components.

The other matter which has to be considered is the amount of flux which is present in

Table 2.26 Cement kiln feedstock based upon two components (per cent)

	Calcium carbonate content			
	Higher	Lower	Feedstock composition	Clinker made from the dry raw material (no coal ash absorption)
Amount of dry material used	25	75		
SiO_2	6.9	15.9	13.7	20.5
Al_2O_3	1.9	4.7	4.0	6.0
Fe_2O_3	0.6	1.9	1.6	2.4
CaO	49.0	41.7	43.5	65.5
$CaCO_3$	87.5	74.5	77.8	–
Free lime	–	–	–	1.0
C_3S (Bogue)	–	–	–	63
C_2S (Bogue)	–	–	–	11
C_3A (Bogue)	–	–	–	11.8
C_4AF (Bogue)	–	–	–	7.3

Table 2.27 Cement kiln feedstock based upon four components (per cent)

	Limestone	Shale	Sand	Iron oxide	Feedstock composition	Clinker made from the dry raw material (no coal ash absorption)
Dry material used	73	22.5	4.2	0.3	–	–
SiO_2	1.4	37.9	95.0	2.7	13.6	20.3
Al_2O_3	0.5	16.5	1.4	6.6	4.2	6.2
Fe_2O_3	0.2	5.1	1.3	84.0	1.6	2.4
CaO	53.7	15.4	1.0	2.7	42.7	64.1
$CaCO_3$	95.9	27.5	–	–	–	–
Free lime	–	–	–	–	–	1.0
C_3S (Bogue)	–	–	–	–	–	57
C_2S (Bogue)	–	–	–	–	–	15
C_3A (Bogue)	–	–	–	–	–	12.4
C_4AF (Bogue)	–	–	–	–	–	7.3

the hottest part of the kiln – known in the industry as the 'burning zone'. This may be calculated[79] for systems where the ratio of alumina to ferric oxide (A/F ratio) is above 1.38 and the amount of magnesia present is no more than 2 per cent, from the oxide analyses using the following formulae:

$$\text{flux at } 1338°\text{C} = 6.1 \times \%Fe_2O_3 + \%MgO + \%K_2O + \%Na_2O$$

$$\text{flux at } 1400°\text{C} = 2.95 \times \%Al_2O_3 + 2.2 \times \%Fe_2O_3 + \%MgO + \%K_2O + \%Na_2O$$

$$\text{flux at } 1450°\text{C} = 3.0 \times \%Al_2O_3 + 2.25 \times \%Fe_2O_3 + \%MgO + \%K_2O + \%Na_2O$$

Where the A/F ratio is less than 1.38 a modified formula is required for the flux at 1338°C:

$$\text{flux at } 1338°\text{C} = 8.5 \times \%Al_2O_3 - 5.22 \times \%Fe_2O_3 + \%MgO + \%K_2O + \%Na_2O$$

Flux levels less than 19 per cent at 1400 and 1450°C usually mean that the extent of the coating which builds up on the refractory lining of the kiln is minimal and that in consequence it may deteriorate more rapidly due to thermal damage. However, variations in the flux generating characteristics of the feedstock can lead to coating being built up onto the refractories and then being removed. When this happens there is a tendency for the coating which is lost to take a few millimetres of the refractory lining with it, which is clearly an undesirable situation. Excessively high flux levels at 1338°C have been associated with the build-up of rings at the point where the feedstock enters the burning zone.

The main raw materials described above may be considered to be the conventional ones used in the manufacture of Portland cement clinker. However, following experimental work in Germany during World War I, Imperial Chemical Industries in the UK brought on to line a process to manufacture both sulfuric acid and Portland cement clinker (the Muller–Kuhne process). The raw materials used to produce approximately 1.25 t of Portland cement clinker and 1.0 t of sulfuric acid were 1.66 t calcium sulfate (in this case natural anhydrite), 0.33 t of coke and coal, 0.13 t of sand and 0.11 t of ash as a source of alumina. The feedstock analysis (per cent) approximated to SiO_2 9.9, Al_2O_3 2.56, Fe_2O_3 1.14, CaO 33.2, SO_3 45.0, active carbon 4.23 and CO_2 0.50. The dried feedstock made from these materials was fed to a rotary cement kiln where sulfur dioxide was evolved in the gases and Portland cement clinker produced as a solid.

It is not only the chemical composition of the main components of the feedstock which is important. The physical form plays an important part in both the quality of the product and the operation of the process. The raw materials come in various degrees of hardness and in the course of comminution do not all achieve the same level of fineness. This is illustrated in Table 2.28. From these results it will be seen from the very high silica ratio of the coarsest fraction that it would be very difficult to react in the limited time the material is exposed to the high temperature zone in the rotary kiln. The 45/90 µm fraction has a very high potential C_3S content which would make it difficult to combine. From their C_3A and C_4AF contents, both these fractions would have a low potential to provide flux. Microscopic examination revealed a high free silica (sand) content in both of the coarser fractions.

Feedstock materials can have the same overall chemical analysis, but due of the different compositions of different size fractions they can require different firing temperatures to provide an acceptable degree of combination. This difference can be as high as 150°C. Thus, in order to achieve the lowest possible temperature in the burning zone of the rotary kiln and through this a lower fuel consumption and a longer refractory life, it is necessary to ensure an adequate level of fineness is achieved in the feedstock. An assessment of the acid-insoluble material in the fraction of the feedstock coarser than 45 µm is often helpful and, if this is mainly free silica, 2.0 per cent is quite sufficient to cause process and quality problems in a market which is highly quality-orientated. However, the most satisfactory approach is to examine the feedstock and the clinker using microscopy. Work using this technique[80] has indicated that in order to achieve an alite size suitable for good strength-giving properties, it is necessary to ensure that any quartz and other acid-insoluble

Table 2.28 Size fractions of different raw materials

	Fraction coarser than 90 µm	Fraction coarser than 45 µm but finer than 90 µm	Total kiln feedstock
SiO_2 (%)	20.0	15.4	13.9
Al_2O_3 (%)	1.3	1.5	3.3
Fe_2O_3 (%)	0.7	0.8	1.7
CaO (%)	43.5	45.3	43.8
Lime saturation factor[a]	0.75	1.00	1.01
Silica modulus[b]	10.0	6.7	2.8
Alumina modulus[c]	1.9	1.9	1.9
Potential C_3S (%)	15	56	48
Potential C_2S (%)	46	2	4
Potential C_3A (%)	2.2	2.6	5.9
Potential C_4AF (%)	2.1	2.4	5.2

[a] $= \dfrac{\%\ \mathrm{CaO}}{2.8 \times \%\ \mathrm{SiO_2} + 1.2 \times \%\ \mathrm{Al_2O_3} + 0.65 \times \%\ \mathrm{Fe_2O_3}}$

[b] $= \dfrac{\%\ \mathrm{SiO_2}}{\%\ \mathrm{Al_2O_3} + \%\ \mathrm{Fe_2O_3}}$

[c] $= \dfrac{\%\ \mathrm{Al_2O_3}}{\%\ \mathrm{Fe_2O_3}}$

materials present should be finer than 45 µm and that the calcite component should be finer than 125 µm. This is illustrated by the quantitative effect that these factors have on the degree of combination achieved in the clinker as shown by the amount of free lime remaining after firing a given temperature.

$$\text{Per cent free lime at } 1400°\text{C} = 0.31\,(\text{LSF} - 100) + 2.18\,(M_S - 1.8) + 0.73\,(\text{Q45}) + 0.33\,(\text{C125}) + 0.34\,(\text{Aq})$$

$$\text{Per cent free lime at } 1500°\text{C} = 0.21\,(\text{LSF} - 100) + 1.59\,(M_S - 1.9) + 0.40\,(\text{Q45}) + 0.22\,(\text{C125}) + 0.08\,(\text{Aq})$$

Or when expressed in terms of the free lime achieved after firing at 1400°C:

$$\text{Per cent free lime at } 1500°\text{C} = 0.54\ (\text{free lime at } 1400°\text{C} - 1.7) + 0.04\,(\text{LSF} - 100) + 0.41\,(M_S) + 0.04\,(\text{C125}) - 0.11\,(\text{Aq})$$

where LSF = 100 (lime saturation factor); M_S = silica modulus; Q45 = per cent quartz found in the material coarser than 45 microns; C125 = per cent residue on a 125 µm sieve; Aq = non-quartz material coarser than 45 µm.

The importance of these matters have been confirmed from plant operations.[81]

Fuels

The cement-making process is relatively fuel intensive, although the end product, concrete when used in a load-bearing structure, has been reported[82] to require only 16 per cent of the energy required for a similar structure built in steel. Gas, oil, liquid waste materials, solid waste materials, petroleum coke and coal have all been successfully used as sources of energy for firing cement-making kilns, either on their own or in various combinations. The fuel selected is governed primarily upon its cost, since fuel costs can amount to as much as 43 per cent of the manufacturing costs.[83]

Natural gas is the simplest fuel to use since it introduces no components which can interfere with the chemistry of the materials. The claims of low flame emissivity may not be such a problem in cement kilns as has been suggested, due to the amount of dust normally found in the burning zone of large modern kilns and the availability of suitably designed burner systems. However, the additional gas volume produced as a result of combustion can lead to a lower unit output. The main problem with oil, and from economic considerations it is normal to use heavy fuel oil in cement kilns, is the sulfur content (normally up to 4 per cent as S), the effect of which will be discussed later. At the present time coal and petroleum coke enjoy a favoured position with regard to cost and are extensively used. The composition of the different coals used to fire cement kilns can vary considerably. Analyses of fuels and ash are given in Tables 2.29 and 2.30.

In most kiln systems the coal ash is incorporated into the feed materials, and in so doing changes the compound composition of the product. In the example given in Table 2.31 the effect of the absorption of 2 per cent coal ash (100 per cent absorption of the ash from an 8 per cent ash coal and a coal consumption of 25 per cent of the clinker) is to lower the tricalcium silicate content from 76 to 64 per cent. This could have the effect of lowering the 28-day strength by 4–5 N/mm^2.

In the example given in Table 2.31 the free lime levels in the two cases are similar. This suggests that the coal ash has been ground sufficiently fine and has been injected sufficiently far into the kiln for it to be incorporated into the raw material feedstock. Coarse ash

Table 2.29 Coal, lignite and petroleum coke analyses

Coal	Water (%)	Ash (%)	Volatiles (%)	Fixed carbon (%)	Calorific value (kcal/kg)	Sulfur (as S) (%)	Chloride (%)
UK bituminous	5.8	5.2	33.8	55.2	7430	1.7	0.15
UK bituminous	13.5	8.9	29.9	47.2	6180	1.7	0.04
UK bituminous	13.2	15.5	27.7	43.6	5700	1.4	0.65
UK low-volatile bituminous	8.8	14.9	15.1	61.2	6580	0.9	0.03
Indian bituminous	8.4	26.1	30.5	35.1	4920	0.5	–
Lignite	15	5	45	56	4830	1.5	0.12
Petroleum coke	8.0	0.3	10.3	81.5	7790	5.2	0.00

Table 2.30 Ash analyses (per cent by mass)[84]

	Bituminous coals			Lignite coals
	USA	England	Germany	Germany
SiO_2	20–60	25–50	25–45	8–18
Al_2O_3	10–35	20–40	15–21	4–9
TiO_2	0.5–2.5	0–3	–	–
Fe_2O_3	5–35	0–30	10–45	2–6
CaO	1–20	1–10	2–4	25–40
MgO	0.3–4	0.5–5	0.5–1	0.5–6
$Na_2O + K_2O$	1–4	1–6	1–5	0.6–3
SO_3	0.1–12	1–12	4–10	1–50
Cl	–	–	0.01–0.28	0.10–0.13
F	–	–	0.005–0.037	–
Zn	–	–	0.002–0.022	0–0.007
Pb	–	–	0.001–0.027	0–0.001

Table 2.31 Effect of 2 per cent ash absorption on composition

	No ash absorption	2% ash absorption
SiO_2 (%)	20.09	20.69
Al_2O_3 (%)	6.43	6.80
Fe_2O_3 (%)	2.30	2.45
CaO (%)	68.61	67.34
Free lime	1.00	1.00
Lime saturation factor	1.05	0.99
Silica modulus	2.30	2.24
Alumina modulus	2.80	2.78
C_3S (%)	76	64
C_2S (%)	0	11
C_3A (%)	13.2	13.9
C_4AF (%)	7.0	7.5

particles and those projected insufficiently far into the kiln can fail to combine, giving higher levels of free lime and additional quality problems. In order to achieve a satisfactory performance, it has been found appropriate to grind coals containing lower amounts of volatile matter somewhat finer. For example, very approximately, if 10 per cent coarser than 90 μm is found to be suitable for a coal with a volatile content of 12 per cent, then it may only be necessary to grind a coal having a volatile content of 28 per cent to 20 per cent coarser than 90 μm. The ignition temperatures of the different forms of coal are also markedly different. At the one extreme, lignite can ignite at just over 400°C, whereas the anthracitic types of coal require ignition temperatures of 700°C. This also reflects the precautions which must be taken in handling these materials, such as drying and grinding in inert gas streams and restricting the size of stockpiles.[85]

Coals containing high (>0.7 per cent Cl) can adversely affect the performance of some types of electrostatic precipitators on wet process kilns.

Other types of solid fuels used to fire cement kilns are such materials as tyres (12.5–18.6 per cent ash, 1.3–2.2 per cent sulfur, 1–2 per cent zinc and having a calorific value of 6450–8000 kcal/kg) and domestic refuse (containing 45–53 per cent paper, 10–13 per cent rags, 8–12 per cent glass, 1–9 per cent metals, 7–9 per cent stones and grit, 4–8 per cent putrescible, 4–6 per cent plastics, 1 per cent rubber and having a calorific value of 2100–2300 kcal/kg), although in the case of the latter the costs associated with the separation of items of metallic hardware can be considerable and the use becomes dependent upon the price the cement manufacturer obtains for handling the material. Rice husks have been used to replace 5–7 per cent of the traditional fuels and, since the ash contains 78–90 per cent of silica, they also provide a very satisfactory means of increasing the silica modulus of the clinker, thus making it possible to reduce the amount of ground sand incorporated into the feedstock. They have ash contents of 18–22 per cent, volatiles of 58 to 62 per cent, fixed carbon 12–18 per cent and calorific values of 3500–4000 kcal/kg.[86]

Fuller's earth from oil recycling is another alternative solid fuel, as are wood chippings from wood processing industries.

A wide range of waste solvents and other organic liquids including chlorinated hydrocarbons have been tested as fuels. These include blends containing alcohols, ketones, xylenes, paraffins, resins, aliphatic and aromatic compounds, waxes, sugars, fats, mineral oils, lubricating oils and hydraulic fluids and can have calorific values from 4400 to 7100 kcal/kg. The level of replacement of more conventional fuels is normally not more than 40 per cent. In order to destroy the most stable of the organic compounds, it has been reported that the following conditions should prevail in the cement kiln: temperature greater than 1200°C, retention time at or above this temperature of 2 s or more, an oxidizing atmosphere, fast quenching of the products of combustion, low chloride levels in the gas stream, low levels of elementary carbon and an absence of catalytic metal chlorides.[87]

Special approval to burn both these types of materials and also such items as tyres is required from the relevant authorities in many countries on account of potential environmental hazards. In the USA, for example, it is necessary to demonstrate a 'destruction and removal efficiency' of 99.99 per cent for one or more of the organic constituents which are more difficult to destroy, and in the case of dioxins the required efficiency is 99.9999 per cent.

Minor components

Care has to be taken to avoid constituents which, even when present in small amounts (<1 per cent), may have an adverse effect upon the performance of the product and/or the production process. The most important of these are probably the alkalis, and in cement technology these are potassium and sodium and are referred to, as are all the elements, as their oxides, K_2O, Na_2O and $(Na_2O)_e$, where the latter is 0.658 (%K_2O) + %Na_2O. As far as the cement itself is concerned, high alkali levels can, in the presence of moisture, give rise to reactions with certain types of aggregates to produce a gel which expands and gives rise to cracking in concretes and mortars. In some countries low-alkali cements (not containing more than 5 per cent secondary materials) are marketed where the alkali expressed as sodium oxide equivalent $(Na_2O)_e$ is maintained at less than 0.60 per cent. An alternative approach is to control the situation by adopting a maximum alkali content in the concrete. When the value for this is 3.0 kg $(Na_2O)_e$ in 1 m^3 of concrete, then a level of 0.65 per cent $(Na_2O)_e$ is often acceptable in the cement used in most general purpose concretes. The alkali content of cements can be maintained at a given level through the careful selection of materials and/or by bleeding high-alkali dusts from the kiln system. Normally sulfate-resisting Portland cements have lower alkali levels than common Portland cements since less of the alkali-containing clays or shales are used in the formulation of their feedstocks. Manufacturers are also able to minimise the potential for alkali–silica reaction by incorporating large amounts (over 50 per cent) of suitable granulated slags into the cement.

Where there is sufficient sulfate present in the clinker, the alkalis are normally present as sulfates. These can be as K_2SO_4, Na_2SO_4, aphthitalite $Na_2SO_4 \cdot 3K_2SO_4$ and/or calcium langbeinite $2CaSO_4 \cdot K_2SO_4$. In the absence of sufficient sulfate in the clinker to maintain the alkalis as their sulfates, the Na_2O is considered to enter the C_3A where it normally increases the reactivity, thus leading to possible setting problems, unless the calcium sulfate added as a set regulator is in the appropriate form. Any K_2O normally enters the C_2S where it again enhances the reactivity to water, but may inhibit its conversion to C_3S. A reducing atmosphere in the kiln is one way of effecting the transfer of alkalis from the sulfate form to the calcium aluminates and silicates.

Higher alkali levels in cements [over ~0.8 per cent $(Na_2O)_e$] when present as alkali sulfates have the effect of increasing the early strengths (~10 per cent) of cements at the expense of their 28 day strength (reductions of 10–15 per cent). When the alkalis are present as calcium langbeinite, a 5–10 per cent reduction in early strength and an increase of the same order at 28 days would not, relative to a cement containing lesser amounts of alkali sulfates, be unexpected. Higher alkali levels are, however, generally considered to be capable of improving the reactivity between Portland cements and granulated slags.

The presence of alkalis in cement kiln systems can have significant effects upon the viscosity of the flux formed in the burning zone. Where the alkalis are present as their sulfates, the viscosity is decreased, thus promoting the formation of C_3S (and in cases of excesses, increasing its crystal size to a point where its hydraulic activity is inhibited). The lower viscosity flux may lead to more dust being formed in the burning zone of the kiln. If the alkalis are not there as their sulfates, the flux viscosity is normally increased and the formation of C_3S inhibited.[88]

Where the kiln is equipped with a high efficiency heat exchanger, such as a cyclone system or a Lepol grate, the presence of alkalis (and sulfates) can have an extremely disruptive effect upon production. From the operational point of view, it is highly desirable for as much as possible of the alkalis to be discharged from the system with the clinker. If this does not take place, some of the alkalis are volatilised in the high temperature part of the kiln and condense in the cooler parts, causing blockages in the heat-exchange systems. Recirculating loads of 150–200 per cent (of the total input) for potassium oxide, 100–150 per cent for sodium oxide and 350–400 per cent for sulfate are not abnormal in kiln systems equipped with high efficiency preheaters. If a sulfate to alkali molar ratio of 1.0 can be arranged throughout the kiln system, then the maximum amount of alkalis can be expected to be discharged from the kiln in the clinker and blockages minimised. If there is an excess of sulfate, then low melting point eutectics based upon alkali sulfates and calcium sulfates form and lead to 'build-up' and blockages. Melting points of less than 800°C are achieved with mixtures of 20 per cent sodium sulfate, 35 per cent calcium sulfate and 45 per cent potassium sulfate, which is equivalent to a ratio of 1.0 part Na_2O, 2.8 parts K_2O, 1.6 parts CaO and 6.0 parts SO_3. If chloride is introduced into the system, then melting points of 100°C lower can be expected. Sulfate-spurrite ($C_2S \cdot CaSO_4$), which is stable within the temperature range 900–1200°C, can also form and has been considered to be associated with the formation of rings in the cement kilns themselves. Ring formation normally increases with an increase in the amount of excess sulfur over that which combines with alkalis. If there is a deficiency of sulfate, then alkali carbonates form and their relatively high volatility and low melting points (850–900°C) can also lead to build-up in preheater systems. Oxidising conditions in the kiln system are particularly important if sulfur is to be maintained in the clinker in order to combine with the alkalis.

The significance of temperatures in the range 800–900°C is that they correspond to those of the material in the vicinity of the transfer from the preheater to the rotary kiln and that the presence of sticky deposits at this point serves to attract dust and to bind it together to form build-up, which in an extreme case can completely throttle the flow of gas and/or solid materials.

From the previous section it will be noted that the effect of the presence of sulfates is intimately connected with those of the alkalis. Sulfur is introduced into the kiln system through the fuel and also with the raw materials. In the case of the latter, it is important from the point of view of the operation of the kiln system to distinguish between that which arrives in the form of sulfates (such as calcium sulfates) and that which enters as sulfides (such as pyrite, marcasite and organic sulfides). The latter can oxidise through an exothermic reaction at 400–600°C, i.e. in a part of the kiln system where there is less calcium oxide available and in consequence the SO_2 released is emitted to atmosphere. On the other hand, the calcium sulfates present do not decompose until 900–1000°C, and the oxides of sulfur produced have more opportunity to react with the alkalis which have been volatilised and also with the CaO which has already been formed at a lower temperature. Whilst the reaction with the alkalis is generally satisfactory for kiln operation, since it increases the chances of the alkalis and sulfate being removed from the kiln in the clinker, it is less satisfactory, as we have seen previously, if significant amounts of the low melting point mixtures of calcium and alkali sulfates form in and around the preheater and lead to blockages.[89]

The full effect of the minor components in the feedstock is rarely felt in isolation and chloride is no exception. Chlorides are introduced into the kiln system with the fuel where that fuel is coal, and with the raw materials, particularly if the clays are of a marine origin. They readily volatilise in the burning zone and condense in the heat exchanger to combine with alkalis and sulfates to form low melting point mixtures. Their effect upon the operation of kilns with cyclone preheaters and gate preheaters is so serious that for the former it is normal practice to limit the total amount of chloride introduced into the process to a maximum of 0.015 per cent of the raw meal feedstock. This low figure effectively means that, assuming the kiln system has no bypass and that there is no chloride input from the raw material, the maximum chloride content acceptable in a good quality coal is about

0.18 per cent. The significance of this can be understood from the fact that generally only something like 20 per cent of the input is retained in the clinker, with the result that a recirculating chloride load of some 400–500 per cent develops in the kiln/preheater system. This high recirculating load is broken by the removal of dust or by the installation and operation of a bypass which removes between 5 and 10 per cent of the gases leaving the kiln before they enter the preheater.

Most standards for Portland cements restrict the amount of chloride present to 0.10 per cent in order to avoid serious problems of reinforcement corrosion in concrete, but with preheater kilns operational problems normally manifest themselves long before this point is reached.

The situation with wet process and dry process kilns without high efficiency preheaters is less critical in respect of chloride input with the greatest problems being associated with the operational efficiency of some types of electrostatic precipitators installed to clean the gases exhausted to atmosphere. Problems of this nature can occur where the total chloride input approaches 0.1, expressed as a percentage of the raw material feedstock.

Where a kiln system has an effective bypass, a deliberate addition of chloride has been used in order to reduce the amount of alkalis present in the clinker. The basis of this approach is that the volatility of the alkali chlorides is greater than that of the sulfates and in consequence the recirculating load within the kiln is increased. The chloride addition can be in the form of calcium chloride or even by firing the kiln with a proportion of a chlorinated solvent.

After alkalis, sulfur and chloride, it is probable that fluorine has attracted most attention as a minor element in cement production. In the early days this was essentially on account of its performance as a mineraliser. Using an addition of 1 per cent calcium fluoride in the feedstock and firing at 1100°C[90] a product containing 33.5 per cent C_3S and 34.5 per cent C_2S was formed, whereas without the calcium fluoride only 55.8 per cent C_2S was formed. At 1200°C, 69.7 per cent C_3S and 13.2 per cent C_2S were formed in the presence of 1 per cent calcium fluoride, against no C_3S and 60 per cent C_2S without the fluoride.

Fluoride additions[91] have the effect of reducing the viscosity of the flux and are reported to form the compounds $3C_2S{\cdot}3CaSO_4{\cdot}CaF_2$ at 900°C, $2C_2S{\cdot}CaSO_4$ at 1050°C and $C_{11}A_7{\cdot}CaF_2$ at 1100°C. The two silicates are unstable above 1100°C and the aluminate above 1297°C. Other workers[92] report the formation of $(C_2S)_2{\cdot}CaF_2$ at 950°C, which breaks down at 1040°C to give C_2S and CaF_2.

Using a feedstock formulated for white cement production and containing 4.38 per cent SO_3 and having a silica ratio of 5.1, it has been possible to show that after 30 minutes firing at 1500°C the free lime is reduced from 3 per cent with no fluorspar present to 1.8 per cent with 0.25 per cent fluorspar and to 0.2 per cent free lime with 0.5 per cent fluorspar.

In the absence of any significant increase in clinker SO_3, up to 0.3 per cent F leads to an increase in strength with some cements, whilst amounts approaching 0.5–0.6 per cent tend to lower strengths. Portland clinkers containing fluorine tend to become pinkish in colour when the addition reaches about 0.2 per cent, and this increases in intensity when the fluorine content reaches 0.5 per cent. Portland cements produced from clinkers containing 0.2 per cent F or more can have slow setting and hardening characteristics at low temperatures (5°C). Unless a deliberate fluorine addition is made, the normal range of fluorine levels in Portland cement clinker is from 0.01 to 0.15 per cent, and strength reductions can be expected if this upper limit is greatly exceeded. However, if additional sulfate is incorporated into the clinker, then higher levels of fluorine can be used to advantage. Table 2.32 presents data[93] for a feedstock containing 6 per cent gypsum and

Table 2.32 Characteristics of Portland (CEM I) cements made from clinkers containing fluorine and sulfate[93]

Clinker				Setting and consistence			Compressive strength (N/mm^2) converted to EN 196-1				
Free lime (%)	K_2O (%)	SO_3 (%)	F (%)	Initial min.	Final min.	Water (%)	8 h	16 h	24 h	7 day	28 day
3.3	1.0	2.9	0.06	90	110	25.3	7.6	20.1	26.0	48.1	59.0
2.0	1.2	3.4	0.10	140	175	31.0	6.1	23.6	34.1	54.8	61.4
1.7	1.4	3.3	0.14	155	205	29.0	4.2	22.4	33.3	57.0	63.9
1.7	1.5	3.6	0.22	170	220	29.5	5.2	25.2	37.7	59.0	69.0
1.6	1.4	3.2	0.39	240	310	27.5	1.9	17.7	30.2	62.8	74.9
1.5	1.2	2.8	0.80	210	260	27.5	2.0	16.5	22.0	64.9	75.5
1.1	1.5	3.9	1.7	540	660	29.5	–	1.8	13.2	53.2	63.6

the clinker ground without extra calcium sulfate to a specific surface area of $450\,m^2/kg$. The clinker has a lime saturation factor of 1.02, a silica ratio of 6 and an alumina ratio of 2.5.

These results show the increase in setting times and the reductions in early strengths obtained with the various fluorine additions. In this work, Moir reported the following phases above 800°C: up to 950°C, K_2SO_4; up to 1020°C, spurrite $2C_2S{\cdot}CaCO_3$; up to 1050°C, $CaSO_4$; 970–1350°C, Klein's compound $C_3A_3{\cdot}CaSO_4$; 1120–1500°C, calcium langbeinite $K_2SO_4{\cdot}2CaSO_4$; 1180–1270°C, $C_{11}A_7CaF_2$; and from 1250°C, C_3S. In later work[94] reference has been made to a clinker produced containing 2.09 per cent SO_3, 0.22 per cent F, 0.49 per cent K_2O and 0.25 per cent Na_2O, and fired at 1350°C rather than 1500°C, thus saving 3 per cent of the fuel. Calcium langbeinite is considered to be the major sulfate-containing phase to crystallise from the flux and acts as an integral retarder.

It has been reported[94] that 92–97 per cent of fluorine, when present at the 0.08 per cent level, is retained in the clinker. There are indications that the use of fluorine as a mineraliser may give rise to the build-up of excessive coating in the kiln and that this may be due to the formation of additional spurrite. The use of a high silica modulus in the feedstock could minimise this problem.

When a feedstock containing barium compounds is converted into clinker, the barium has been found[95] to be distributed between the C_3S, the C_2S, the C_3A and the C_4AF. The C_2S is reported to be capable of incorporating BaO at up to 1.4 per cent of its weight, with the C_3A taking up approximately half of this figure and the C_3S 0.25–0.31 per cent. There is no significant increase in alite size when firing under standard conditions, and as a result BaO is not considered to be a mineraliser. However, possibly due to increased C_2S reactivity, small amounts of barium may increase 28-day strengths, 0.3 per cent BaO by about 20 per cent, 0.5 per cent by 10 per cent and 0.7 per cent causing no increase.

The chromium content (expressed as Cr_2O_3) in Portland cement clinkers is normally in the range 0.002–0.02 per cent, with between 77 and 93 per cent of that fed to the kiln being bonded into the clinker.[84] Most of this chromium is derived from the argillaceous component of the feedstock, from the fuel and in some cases from the refractory bricks used to line the kiln. Some of it is water soluble in the hexavalent form and there have been reports[96] linking this water-soluble chromium to skin dermatitis.

Portland cements can contain between 0 and 30 ppm of hexavalent chromium. In some countries, cements are required to have hexavalent chromium contents less than 2 ppm. This is claimed to be achieved through the patented use of a ferrous sulfate addition (in practice 0.4–0.6 per cent) to the cement,[59] although experience suggests that the effectiveness of this approach may be minimal when the cement is ground at high temperatures in closed-circuit grinding mills which have a high air circulation and also that it may be lost, at least partially, on the storage of the cement.

Returning to the insoluble component of the chromium found in clinkers, nearly half has been found in the alite,[95] and since increasing additions within the range 0–0.4 per cent increase the crystal size of both alite and belite, it may be considered to have some mineralising effect. A 0.4 per cent content in the clinker has been reported to give a 10 per cent increase in 28 day strength, an increase which is probably associated with a reduction in the free lime. In amounts over 0.5 per cent,[88] the free lime is reported to increase as the alite transforms to belite. With over 3 per cent Cr_2O_3 no alite was found in the clinker.

Small amounts of lead are found in clinkers, usually of the order of 0.001–0.02 per cent (expressed as PbO), although in the course of burning domestic refuse at one plant the amount increased from 0.02 to 0.04 per cent. Sprung[84] quotes data for the bonding of lead into the clinker at 59–86 per cent, although in the presence of chloride this figure can be reduced to as low as 4 per cent. Normally, no significant setting or hardening problems are anticipated if the level in clinker is maintained at less than 0.1 per cent.

Although the amount present in Portland cement clinker is normally in excess of that considered to be associated with a minor component, magnesia (MgO) is able to enter the liquid phase to the extent of approximately 5 per cent and in so doing lower its viscosity. However, excessive amounts (usually considered to be over 5 per cent of the clinker as a whole), can crystallise out from the flux as a periclase, the presence of which has been associated with long term unsoundness. Slow-cooled clinkers are particularly vulnerable to this effect. As a result of this, national standards generally accept the less vigorous le Chatelier soundness test where the magnesia content does not exceed 5.0 per cent in the Portland cement clinker and impose the more rigorous autoclave test where the magnesia content exceeds this amount.

Manganese substitutes for ferric oxide in the flux, and where this occurs a reduction in viscosity is experienced. This can lead to the development of excessively large alite crystals which are unhelpful in respect of strength development. Unless special conditions prevail, the amount found in Portland cement clinker is of the order of 0.02–0.14 per cent, as Mn_2O_3. If this level is increased to 0.5 per cent or above, reductions in the early strength-giving properties of the cement can be expected.

The effect of molybdenum has been investigated in connection with the use of tailings from molybdenum–iron ore processing.[97] These tailings contain approximately 50 ppm of Mo and 20 ppm of Cu together with 37–44 per cent SiO_2, 15–19 per cent Fe_2O_3 and 21–24.5 per cent CaO. It was found that the molybdenum entered the flux and reduced the viscosity, thereby lowering the temperature necessary to achieve a given level of combination (free lime). The 28-day strengths increased to a maximum with up to 0.5 per cent molybdenum, but were significantly reduced when 3.0 per cent was incorporated.

The overall view from the work reported on the incorporation of phosphorous compounds (usually derived from the limestone) in Portland cement clinker is that up to 0.3 per cent (or slightly more) of P_2O_5 enters the C_2S and improves its hydraulic properties and can give a modest lengthening of the setting times by perhaps 20 min. This is compatible with the normal range of P_2O_5 contents which are from 0.03 to 0.22 per cent. When higher amounts of P_2O_5 are present, the C_2S is stabilised to an extent that the conversion to C_3S is inhibited. The addition of small amounts of fluorine-containing compounds prevents this effect and permits the formation of C_3S to proceed. When the amount of P_2O_5 present exceeds 1 per cent, it has been reported[98] that 10 per cent of C_3S is lost for each additional 1 per cent of P_2O_5 added.

At the level found in Portland cement clinkers (0.01–0.21 per cent), where it stabilises the C_2S, strontium is not anticipated to present problems either in manufacture or quality. However, in significantly larger amounts (3.7 per cent SrO)[99] make it difficult to reduce free lime due to the conversion of C_3S to $(CSr)_2S$ and free lime: 2.5 per cent has been suggested as a suitable maximum, although this could be dependent upon the quality sought in the product.

Thallium is normally considered to enter cement kiln systems through the use of some types of iron-bearing materials used to correct the chemistry. This element is exceedingly volatile with as little as 5 per cent being bonded in the clinker.[84] In a kiln system a considerable recirculating load develops and, where cyclone preheaters are installed, the maximum amount of thallium condenses at a temperature between 300 and 400°C, which is in the cooler part of the heat exchange system. When present in amounts greater than 0.0005 per cent in the total feed to a kiln system, thallium requires careful assessment in respect of possible environmental problems. Some environmental control authorities place restrictions on the amount of thallium permitted in secondary fuels and in the iron-bearing compounds used to correct the chemistry of the feedstock. In the case of the latter, one authority in a specific instance has adopted a maximum limit of 20 ppm.

The titanium oxide (TiO_2) content of Portland cement clinkers is generally within the range 0.14–0.43%.[84] Additions up to 1 per cent can inhibit early (1–2 days) strength development, but may improve strengths at ages in excess of 3 days.[100] In clinker containing 0.8 per cent TiO_2, 0.35 per cent was found in the alite and much of the remainder in the flux. Alite crystal size increased progressively with 0.2 and 0.4 per cent additions, suggesting mineraliser characteristics.[95]

Vanadium, if present, tends to be found in the alite, the crystal size of which increases with additions up to 0.4 per cent. A 0.2 per cent addition is reported to lead to a 10 per cent reduction in 28-day strength and this could possibly be associated with the increase in crystal size (17.9–24.1 μm). There have been suggestions that the presence of low levels of vanadium compounds (the use of petroleum coke as a fuel can contribute) could lead to a shorter refractory lining life.

Small amounts of zinc (0.01–0.2 per cent) have been reported to increase the reactivity of the C_3A[101] and in consequence lead to possible setting time problems. The presence of up to 0.5 per cent as ZnO does not, however, appear to have a profound effect upon other hydraulic properties.

2.3.3 FEEDSTOCK PREPARATION

Once the components have been selected, the most appropriate method of pulverisation must be established. In many cases this will be decided by the moisture contents.

With chalks and clays with moisture contents over 15 per cent there is often merit in adding water to prepare an aqueous suspension (normally referred to in the industry as 'slurry'). Where the materials are soft it is sufficient to break them down using an attrition device such as a washmill. This comprises a circular tank, the walls of which contain grids or slots. Mounted on a centrally placed plinth is a pivoted arm which rotates in a horizontal plane and to which are attached harrows. The motion of these harrows through the suspension of the lump material in water effects the appropriate degree of breakdown and the fine product flows out through the grids mounted in the walls. Such a piece of equipment serves as a satisfactory method of separating unwanted coarse, harder materials such as flints, and where necessary further classification through hydrocyclones or DSM (Dutch State Mines) sieve bends can be installed to remove other unacceptable coarser components, thus permitting them to be ground in ball mills and returned to the feedstock. Although some degree of control over composition can be achieved at the washmill, it is normally necessary to provide specially designed air-agitated blending tanks to achieve consistently the desired feedstock composition, and once this has been done to prevent the solids from settling out. Slurry produced in this manner can, depending upon the nature of the raw materials and/or the presence of any deflocculants, have water contents of the order of 24–50 per cent. It is expensive to use heat to evaporate large amounts of water from the feedstock, with each 1 per cent requiring of the order of 33 kcal/kg of fuel. In order to avoid this penalty, filtration techniques have been used to reduce the amount of water introduced into the kiln system. Rotary vacuum filters may be used if the filtration characteristics are suitable but, in order to obtain a rigid filter cake which can be handled satisfactorily, it is often necessary to use pressure filtration techniques. These operate at 1–2 MPa and are capable of lowering the moisture contents from over 40 to less than 20 per cent. Filtration times are, however, very dependent upon temperature, being strongly related to the viscosity of the water. They are also dependent upon the degree of flocculation of the materials and a flocculant, such as lime, is sometimes used to make filtration an acceptable economic option. This in itself can cause problems where the filter cake is to be pelletised and fed to a Lepol gate preheater, as its strength can be adversely affected leading to breakdown and excessively high restrictions to gas flow.

Where the raw materials have moisture contents of less than 15 per cent, it is often more economic to dry and grind them at the same time. This is accomplished by passing a flow of hot gases through the ball mills or the vertical spindle mills used for grinding. In most suspension preheater kiln systems, there is sufficient heat available in the waste gases to remove up to 8 per cent moisture in the raw materials. Any moisture in excess of this amount, but less than about 15 per cent, can generally be economically removed by using an external source to boost the heat available.

Where dry powders are produced, it is necessary to blend them to achieve a similar degree of uniformity as that achieved with the feedstock produced in the form of slurry. This is usually carried out in large silos fitted with air agitation at the bottom and designed to operate with a higher air pressure on any one quadrant at a given time such that the entire mass of powder is turned over and effectively blended.

Once the basic composition of the feedstock has been established, it is normal to effect the necessary control using oxide analyses derived from the use of X-ray fluorescence equipment. The results obtained from such a method are in terms of the elements themselves, but it is convenient for the manufacturing process to express these as oxides, bearing in mind that most are not, of course, present in the raw materials in that form.

The principle parameters used for control purposes are the lime saturation factor (LSF), the silica ratio (or modulus), the alumina ratio (or modulus) (all defined earlier in section 2.3.2) and the potential C_3S calculated from the oxide analyses using the Bogue formulae (see section 2.4.2). The LSF is particularly important in feedstock preparation as it provides a means of preventing compositions being used which contain more lime than it is possible to combine with the silica, alumina and ferric oxide present. A given potential C_3S level

Table 2.33 Methods of achieving a given C_3S level

C_3S (Potential) (%)	LSF	Silica ratio	Alumina ratio	Flux at 1450°C (%)
59.6	1.00	1.0	0.7	40.6
59.5	1.00	1.5	1.5	38.6
60.7	1.00	2.0	3.0	26.2
58.3	0.95	2.0	1.0	25.7
60.2	0.95	3.0	2.0	19.1
59.8	0.90	5.0	0.7	11.9
60.5	0.90	10.0	3.0	6.8

can in theory be achieved in a variety of ways, as is illustrated in Table 2.33. However, in terms of compositions which could be effectively fired in the kiln, only those with flux values in the range 19–26 per cent need to be considered further.

In general terms, the LSF and the silica ratio determine the content of silicates, and the alumina ratio the amount of C_3A present and also the flux level. Changes in the flux composition and amount can have serious effects on the ability of the coating which forms on the refractory lining of the kiln to remain in place and protect this lining. With modern blending systems, four or more components and X-ray analysis, a standard deviation on the LSF of 0.01 and of 0.04 on the silica ratio should be possible, although over the longer term, deliberate changes to compensate for variations in the ash content of the fuel may increase these figures.

Where only two components are available for the feedstock preparation and control is essentially through the use of calcium determinations, the standard deviations can be expected to be higher particularly in respect of the silica ratio. This need not always be a matter of too much concern since in some instances an increase in silica ratio will be accompanied by a reduction in LSF, thereby maintaining a similar combinability, temperature and C_3S levels.

The aspect of fineness of the feedstock has been dealt with earlier.

2.3.4 PYRO-PROCESSING

Only a very small proportion of Portland cement clinker is manufactured these days in shaft kilns. This is essentially because outputs per unit are generally low (up to 500 t/day), whereas single rotary kiln units have been quoted as producing 8000 t/day or more. The quality of the product made in shaft kilns is normally more variable than that made in rotary kilns.

The selection of a particular type of rotary kiln system is influenced essentially by the raw materials available, the fuel consumption, the output required and the capital investment available. The general situation is illustrated in Table 2.34.

Figures 2.3–2.5 illustrate the main types of kiln systems adopted for the manufacture of Portland cement clinker.

The rotary kiln itself consists of a cylindrical tube fitted at suitable intervals with tyres which run on pairs of rollers. The speed of rotation is normally in the range 1.0–3.5 rev/min and the tube is inclined to the horizontal at between 1 in 20 and 1 in 30. Virtually all kilns in operation today incorporate heat exchangers to recover as much as possible of the heat produced to raise the temperature of the feedstock to the 1450–1500°C required to produce

Table 2.34 Parameters influencing the selection of a rotary kiln system

Process	Wet	Semi Wet	Semi Dry	Dry Preheater	Dry Precalciner
Kiln length (m)	40–232	40–90	24–75	40–95	54–110
Kiln diameter (m)	2.4–6.6	3.6–6.0	2.3–6.0	2.8–6.0	3.5–5.9
Output (t/day)	100–3350	400–3000	100–2400	200–3500	1500–8500
Feedstock moisture (%)	24–48	17–22	10–15[a]	≤8[b]	≤8[b]
Fuel consumption (kcal/kg clinker)	1000–2200	900–1200	800–950	800–950	800–950

[a] Additional heat needed also to dry raw materials.
[b] Additional heat needed above 8%.

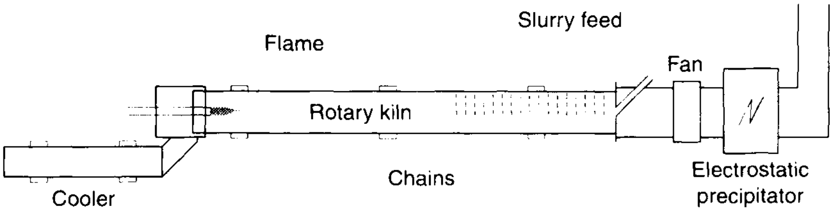

Fig. 2.3 Wet process (shown here with a rotary cooler).

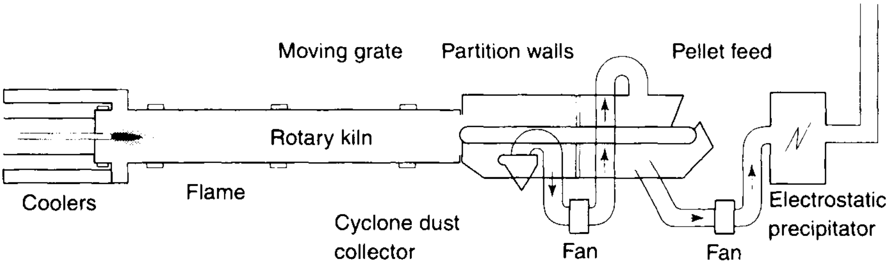

Fig. 2.4 Semi-wet/dry process (shown here with a planetary cooler).

Portland cement clinker. In the wet-process and in some of the long dry-process kilns this takes the form of chains hung from the shell and exposed to the gas stream. These chains may be attached to the kiln shell at one end only (curtain chains) or looped and attached to the shell at both ends (Festoon chains). Essentially, they abstract heat from the gas stream and transfer it by conduction to the feedstock as the kiln rotates. Using this approach it is possible to lower the temperature of the gases from a wet-process kiln to the order of 150–180°C. This is important as in a given wet kiln system, 50°C in the exit gases relates to 60 kcal/kg in fuel consumption.

In order to achieve greater fuel savings, more sophisticated heat exchangers have been introduced. One of these is what is known as the semi-dry process and as such employs the Lepol gate. This is a moving grate upon which a dry feedstock made into pellets through the addition of water provides a bed through which the hot gases from the kiln make two passes. In so doing their temperature is reduced to between 120 and 180°C. This combined

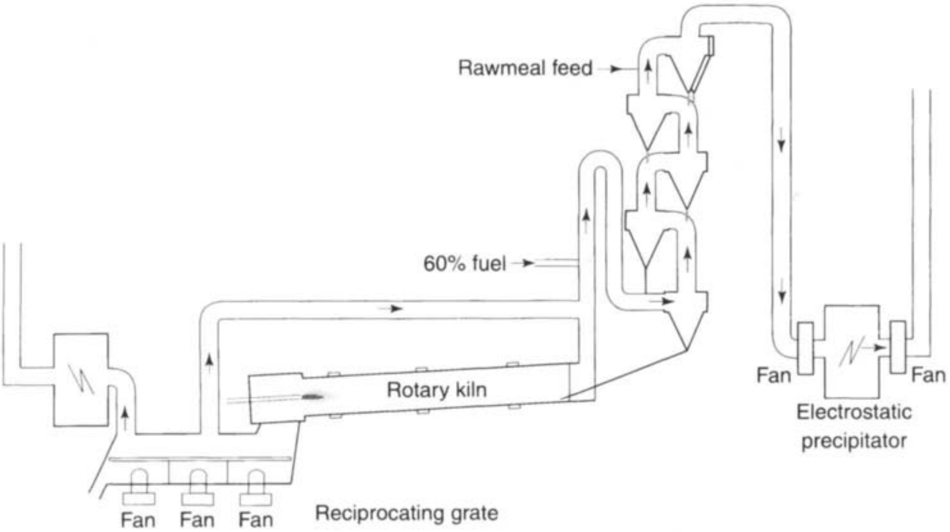

Fig. 2.5 Dry-process precalciner (shown here with a separate duct conveying hot air from the cooler).

with a pellet moisture content within the range 10–15 per cent leads to an attractively low fuel consumption. However, in considering this it should not be forgotten that perhaps an additional 50–90 kcal/kg may be necessary to dry the raw materials. For stable operation it is necessary to master the complexities of the double gas pass through the Lepol grate. This is particularly important if the feedstock tends to form dense, low-strength friable nodules. Such nodules are liable to explode in the course of their passage between the higher and lower temperature zones of the grate. When this happens, the material forming the bed becomes less permeable and the gas flow through the grate is restricted with the result that less air becomes available for combustion. It is then necessary to reduce the fuel input in order to avoid reducing conditions in the kiln and generating carbon monoxide, which brings with it the danger of explosions in the electrostatic precipitator used to de-dust the gases emitted to atmosphere. Since an inadequate amount of heat is then being introduced, it becomes necessary to reduce the amount of feedstock entering the kiln in order to ensure that it receives the necessary amount of heat to complete the conversion to the calcium silicates and aluminates. The design of the grate chamber does not render it easy to remove alkali build-up. There are also many points where air can leak into this type of heat exchanger. Only a limited amount of fuel can be introduced in the vicinity of the grate and thus precalcining, as practised on suspension preheater kilns, is not an option.

The Lepol grate has been adapted to handle filter cake which has been made into pellets in a process known as the semi-wet process. Filter cake has also been fed into converted wet process kilns with some benefits in output and fuel consumption.

Probably the most important development has been the introduction of cyclone heat exchangers. Depending upon the moisture content of the raw materials and hence the amount of heat required from the kiln system for drying purposes, between one and five cyclones in series are used to transfer the heat in the gas stream to dry the powdered feedstock.

These cyclones are mounted in a tower above the feed end of the kiln. The feedstock is introduced into the inlet of the uppermost cyclone where the gas temperature is of the order of 500°C. A high proportion of this powder is then discharged from the bottom of the cone of this cyclone into the gas stream entering the next lower cyclone. The gas temperature here is of the order of 700°C. In a similar manner the powder is discharged into the inlet to the next lower cyclone where the gas temperature is approximately 850°C. Then the powdered feedstock is discharged into the inlet to the bottom cyclone where the gases have a temperature of about 1050°C. Finally, the bottom cyclone discharges into the kiln itself. In the course of this heat exchange operation the temperature of the powder is increased from ambient to about 850°C with some decarbonation taking place. At the same time the gas temperature is reduced from about 1050°C to about 350°C. Gas at this temperature can be fed to a grinding/drying mill system and is capable of removing up to 8 per cent moisture in the raw materials.

The precalciner kiln system sets out to achieve almost complete decarbonation of the feedstock in the cyclone preheater before it reaches the kiln itself. Since the decarbonation reaction is highly endothermic (of the order of 450 kcal/kg), this involves introducing about 60 per cent of the total fuel required by the kiln system into the preheater. A number of items of equipment are available to achieve this objective, some specifically designed for use with low-grade fuels. With this type of operation it is normal to duct surplus hot air from the grate cooler used to cool the clinker produced by the kiln. The cyclones in the preheater are, apart from the upper, low-temperature ones, lined with bricks.

The inside of the rotary kiln is lined with refractory bricks having a thickness between 175 and 250 mm. The quality of brick installed varies with the conditions prevailing in the kiln. At the feed inlet end of a dry-process kiln and for the first 15–20 per cent of the kiln length where the material temperatures are of the order of 850–950°C, a fireclay brick of 60 per cent silica and 40 per cent alumina having a cold crushing strength of 25 MPa is normally satisfactory. Special insulating bricks have been used in this part of the kiln, but due to their lower strengths they tend to wear rather more quickly and the associated loss of thickness can reduce their effectiveness in providing insulation. The next 20 per cent of the kiln length is normally lined with a brick having 55 per cent or more alumina and less than 40 per cent silica, followed over the next 15–20 per cent by a basic brick containing over 55 per cent magnesia and less than 15 per cent chromium oxide and 10–15 per cent alumina. In the high-temperature (or burning) zone where material temperatures reach 1450–1500°C, a brick containing more than 85 per cent magnesia and less than 15 per cent alumina is often used. Such a brick should have a cold crushing strength in excess of 40 MPa. The thermal conductivity of these bricks is considerably higher than those used in the colder parts of the kiln. The bricks containing 40 per cent alumina having a thermal conductivity of 0.9 kcal/(m h °C) at 350°C compared with 3.1 for the bricks containing 85 per cent or more magnesia. It is important to ensure that the cooling zone between the burning zone and the cooler is lined with bricks having a relatively high resistance to abrasion and those containing 55 per cent magnesia and less than 15 per cent chromium oxide have been used successfully for this purpose.

The bricks installed in the burning zone have the shortest life. This can be as short as 3 months for large-diameter kiln operating with variable and difficult materials to well over a year with smaller kilns burning well-controlled feedstock of low variability. A great deal depends upon the stability of the coating of clinker which attaches itself to the bricks. Excessive flexing of the kiln tube due to excessive wear on the tyres can also damage the brickwork. There are many advantages in operating kilns which have diameters within the range 4.2–4.5 m. At this size, ring formation is generally less troublesome than on the smaller diameter kilns, but the curvature is not reduced excessively such that the keying of the bricks and the maintenance of coating is a problem.

A 4.2 m diameter kiln operating with a conventional four-stage cyclone preheater can be expected to produce 1300 t of Portland cement clinker over a 24 h period. If a similar diameter kiln is fitted with a precalciner then an output of 3000 t/day can be expected.

In kiln systems, apart from those fitted with precalcining facilities, the full heat input is introduced into the rotating part of the kiln and the greater part of the highly endothermic decarbonation of the feedstock takes place in the kiln itself. In a wet-process kiln the heat required to evaporate the water in the slurry is also introduced at this point. The result is very high gas velocities, which in turn means that much larger diameter kilns are required for a given output. Thus, a wet-process kiln capable of 1100 t/day may have a diameter of 4.4 m whereas the equivalent output dry-process cyclone preheater kiln (without a precalciner) would have a diameter of only 4.0 m. The heat source (or sources in the case of precalciner kilns) is normally coal, petroleum coke, oil, gas and/or various waste materials discussed earlier. In the case of the solid fuels they are ground in a mill swept with hot air (or in the case of some high volatile fuels in an inert gas) usually drawn from the kiln hood (preheater in the case of an inert gas) or from the surplus air available from a grate cooler. In some plants the pulverised fuel is conveyed direct from the coal mill into the kiln (direct firing) and in other cases it is ground, collected in cyclone and fabric filter systems and transferred into a hopper to be subsequently fed at the appropriate controlled rate into an air stream and into the kiln. There have been considerable developments over recent years in the design of the pipe which actually projects the ground fuel and the air into the rotary kiln to produce the flame. Some of these developments have been brought about by the desire to reduce the amount of the oxides of nitrogen produced in the combustion process. Whereas previously open pipes were used, there are now multi-channel burners which can introduce the fuel at a different velocity to that of the air streams. In order to achieve the highest strength-giving potential in the Portland cement clinker, it is desirable to operate with a short, relatively intense flame in order to provide a rapid rise in temperature in the feed as it approaches the burning zone, since this is considered[102] to produce alite in the most desirable form.

Various forms of closed-loop control have been used in the operation of cement kiln systems. On simple wet and dry kilns the air/gas flow through the kiln has been controlled by maintaining a given level of suction in the kiln hood (the interface between the cooler and the kiln) through the adjustment effected on a damper placed before the induced draft fan at the inlet end of the kiln. Having stabilised this loop, then the coal feed is linked to continuously measured oxygen in the kiln exit gases. Thus, when the measured oxygen increases, additional coal is fed to the kiln in order to maintain a constant heat input. In this way variations in both coal quality and feed rate can be minimised.

The speed of the grate in a grate cooler has been successfully incorporated in a closed loop with the undergate pressure in one of the hot end compartments. In this loop the objective is to maintain a given amount of air into the undergrate compartment. However, if the clinker becomes finer it causes a higher restriction in the bed sitting on the grate, thus reducing the air flow to the cooler and kiln. When this happens, the additional pressure is sensed and the grate speeded up, thereby thinning the bed, lowering the restriction and permitting the required amount of air to reach the kiln.

With the Lepol kilns, the continuous measurement of the pressure drop between the hot and cold sections of the Lepol grate has been linked to the fans in order to minimise the bursting of nodules caused by gas of excessive temperature flowing under the wall between the two sections of the grate.

With the development of computer control, it has become possible to link a number of these loops together and produce comprehensive control systems for material flow and combustion control. This has been greatly assisted by the development of continuous measurement of the nitrogen oxide content of the kiln exit gases. This measurement for a given kiln provides a good second-order measure of the temperature in the burning zone.

2.3.5 CLINKER COOLERS

Having raised the temperature of the Portland cement clinker to 1450–1500°C in order to achieve the required level of combination, it is important to recover as much heat as possible and to return it to the process. To do this, the hot clinker is passed through a cooler. However, a high rate of clinker cooling between the temperature of the burning zone and about 1200°C is important if the best strength-giving properties are to be achieved. Microscopic examination of clinkers which have been slowly cooled from 1450 to 1200°C often reveal a situation where the alite has effected a partial transformation into belite and free lime. The C_3A exhibits a tendency to crystallise from the flux in a form which is more reactive and which may lead to setting problems. There is also a danger with clinkers relatively high in magnesia that this can crystallise from the flux as periclase and lead to long-term unsoundness.

Coolers take three main forms. The rotary cooler, which was much favoured for the smaller wet process kilns, takes the form of an inclined rotating tube fitted with lifters through which the clinker and air for combustion in the kiln pass in a contraflow configuration. The main problems with this type of equipment are associated with the maintenance of an effective seal at the hot end, the size required when used with the larger dry process kilns and the need to raise the level of the kiln and the preheater to permit the clinker to fall by gravity into the cooler inlet. Heat recovery is not very effective with as much as 30 per cent being lost through the shell.

The planetary cooler consists of a series of tubes (usually 10) which are attached to the kiln shell and rotate with it. These suffer from the same problems of relatively low heat recovery as the rotary coolers, but do not require the kiln to be constructed at such an elevated level. However, their popularity has declined over recent years on account of the improvements which have been possible with the grate coolers and also because they are not readily compatible with precalciner kiln systems which require a supply of hot air from the cooler to be made available at the preheater tower. Grate coolers comprise a series of horizontal or slightly inclined reciprocating perforated plates which move the clinker forward in the form of a bed whilst cooling air is forced through the underside. The early grate coolers suffered from many problems associated with the failure of the grate plates, which invariably required a kiln to be shut down in order to rectify the problem. They have a disadvantage in that a considerable amount of electrical power is required to drive the fans which force the air through the clinker bed. They also need something like 3.0–3.5 kg of air to cool 1 kg of clinker. Since in a preheater kiln only 1.5 kg per kg clinker of air is needed in the kiln in order to burn the amount of fuel required, there is a problem of discharging this excess air to the atmosphere. Before this is done, the often not inconsiderable amount of dust it contains has to be removed. Due to the temperatures involved this is not an inexpensive operation. The use of some of this excess air in the precalciner and/or in drying the raw materials has reduced the magnitude of this problem.

2.3.6 HEAT BALANCE

Since fuel costs represent a major part of the cost of producing cement, it has always been important for manufacturers to establish where waste is occurring. This is carried out by

Table 2.35 Heat balances associated with different types of rotary kiln systems[103]

	Lepol kiln		Suspension preheater kiln		Wet-process kiln	
Heat input						
From fuel		829		858		1378
From raw materials		28		39		11
From cooling air	(20°C)	0	(14°C)	−5	(12°C)	−7
Total input		857		892		1382
Heat expenditure						
Theoretical heat requirement for clinker burning[a]		385		396		389
Evaporation of water	(11.9%)	122	(0.41%)	4	(39.2%)	565
Exit gas losses	(120°C)	78	(314°C)	184	(212°C)	224
Dust losses	(2.48%)	5	(12.1%)	5	(8.5%)	3
Radiation and convection losses		106		154		86
Losses at the cooler		115		109		84
Unaccounted for		46		40		31
Total expenditure		857		892		1382

[a] The 'theoretical heat' is calculated by the formula proposed by zur Strassen:

$$Q = 2.2\,\mathrm{At} + 6.48\,\mathrm{Mc} + 7.646\,\mathrm{Ct} - 5.1165\,\mathrm{S} - 0.59\,\mathrm{F}$$

where Q = heat of reaction in kcal/kg, and the following are expressed as percentages of the lost free meal feedstock: At = per cent Al_2O_3, Mc = per cent MgO, Ct = per cent CaO, S = per cent SiO_2, and F = per cent Fe_2O_3 + per cent P_2O_5.

striking a balance between the amount of heat put into the kiln system and that which can be accounted for from measurements made during process operation. Table 2.35 illustrates this for three different types of kiln system. The data presented illustrate the considerable amount of heat required to evaporate the water in the wet process. The lower cooler losses in this process reflects the ability to use more of the hot air from the cooler as a result of the greater amount of fuel available for burning in this type of kiln. The exit gas losses are higher in the suspension preheater process, but this heat is available to dry the raw materials as necessary. In the Lepol kiln the amount of heat required from a separate generator to dry the raw materials is not shown in this heat balance.

In normal Portland cement clinkers about 500 kcal/kg is required to remove the carbon dioxide from the calcium carbonate present, where just over 100 kcal/kg is recovered from the exothermic reaction which results from the formation of alite and belite.

2.3.7 *REACTIONS IN THE KILN SYSTEM*

These are illustrated in Figure 2.6. On the left-hand side is the feedstock comprising, in this case, calcite ($CaCO_3$), quartz (SiO_2), clay minerals (SiO_2–Al_2O_3–H_2O) and iron oxide (Fe_2O_3). Up to a temperature of about 700°C, activation of the silicates through the removal of water and changes in the crystal structure takes place. Within the temperature range 700–900°C, decarbonation of the calcium carbonate occurs, together with the initial combination of the alumina, ferric oxide and of activated silica with lime. From 900 to 1200°C, belite forms. Above 1250°C and more particularly above 1300°C, the liquid phase

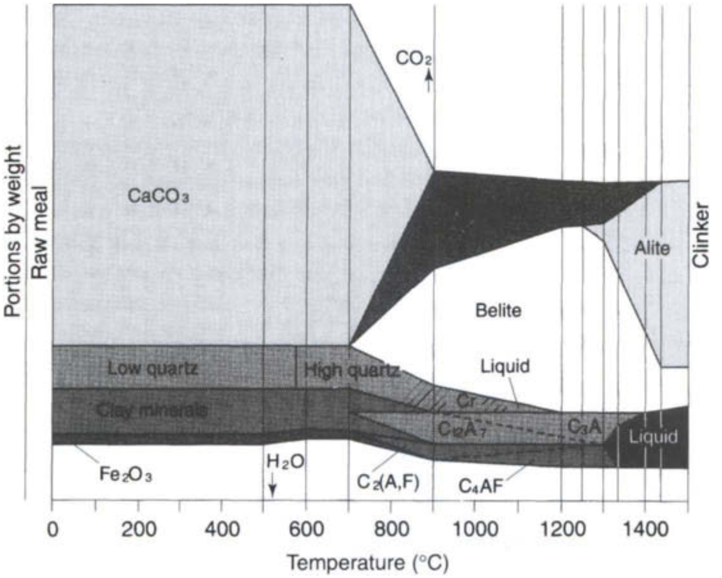

Fig. 2.6 Reactions taking place during raw-meal burning to clinker (reproduced by courtesy of KHD Humboldt Wedag AG).

appears and this promotes the reaction between belite and free lime to form alite. During the cooling stage (right-hand side of the diagram) the molten phase goes to a glass or, if cooling is slow, the C_3A crystallises out and in extreme cases the alite dissolves back into the liquid phase and reappears as secondary belite. Not shown on Figure 2.6, alkali sulfates condense out as a separate phase during the cooling process.

When the sulfuric acid process is adopted, the principle role of the carbon present is to reduce some of the calcium sulfate to calcium sulfide. This calcium sulfide then reacts with the remaining calcium sulfate to produce sulfur dioxide gas, this latter reaction being promoted by the reaction of the lime produced with the silica and the alumina in the added sand and ash. If too much carbon is added then too much calcium sulfide is produced and survives in the clinker. If too little is added then some of the calcium sulfate remains in the clinker. Overall this process was a very sensitive one to operate and did not always produce Portland cement clinker of the highest quality. The gases leaving the kiln had an SO_2 content of 9 per cent and a temperature of about 730°C. Despite this, the overall fuel consumption was relatively low at about 950 kcal/kg of clinker; a typical oxide analysis for Portland cement clinker made using this process was:

SiO_2(%)	21.70	LSF	0.975
Al_2O_3(%)	5.54	Silica ratio	2.82
Fe_2O_3(%)	2.15	Alumina ratio	2.58
CaO(%)	67.10	C_3S(%)	65
SO_3(%)	1.00	C_2S(%)	14
Free lime(%)	0.80	C_3A(%)	11.0
		C_4AF(%)	6.5

The maximum level acceptable to the manufacturer for S was 0.05 per cent, for SO_3 1.5 per cent and for free lime 1.5 per cent.

Building limes are manufactured on both shaft kilns and on rotary kilns. In the case of the shaft kilns, the size grading of the feedstock (usually between 50 and 150 mm) is important if an adequate supply of the air required for the efficient combustion of the fuel is to be present. For manufacture by rotary kiln it is possible to process smaller sized material or slurry, although considerations of fuel economy favour the former. When manufactured using lump or coarse granular material, it is important that there is low variability in the chemical composition of the raw materials used to produce the feedstock since blending of materials having significantly different chemical compositions is not a realistic option. With the high-calcium limes there is a considerable interest in high purity materials because, in addition to their use in the building industry, they are also used extensively in the chemical industry and in water treatment applications. Thus, it is not unusual for manufacturers to produce a common high-quality quicklime suitable for subsequent processing to meet the needs of all these applications. To do this the firing of the simpler types of shaft kilns using natural gas is often adopted. Many of the earlier simple shaft kilns have now been replaced by the parallel-flow regenerative shaft kilns.[104] These consist essentially of two or three interconnected vertical shafts. The operation of the two-shaft version is as follows. A measured amount of the fuel is introduced down pipes into the upper part of one of the shafts and is burnt using combustion air flowing in the same direction. The heat so generated decarbonates the measured amount of the limestone which has been introduced into the top of the shaft. The gases produced from the combustion of the fuel then pass up the second shaft and transfer much of their residual heat to the bed of limestone there. The process is then reversed and the fuel is injected down pipes into the preheated limestone in the second shaft. Typical cycle times are of the order of 30 min and the fuel consumption of this type of shaft kiln when producing high-calcium limes is about 1000 kcal/kg as opposed to 1600 kcal/kg for the older and simpler type of shaft kiln. It also often permits a greater level of control to be achieved over the reactivity of the product.

The manufacture of high-calcium lime on rotary kilns also permits a high level of control to be achieved over product reactivity, but at the cost of higher fuel consumptions – over 1800 kcal/kg for the simpler type of kiln and 1350 kcal/kg for the kiln with a multi-stage suspension preheater.

2.3.8 CLINKER TESTING AND CONTROL

The key to making a cement of good and consistent quality depends essentially on the control which can be applied to the preparation of the feedstock to the kiln system. For this to be effective it is necessary to have a number of components, each having low variability and which can be brought together in controlled proportions. Where a given raw material is known to vary in its composition, it is helpful to build stockpiles where the material in question is crushed and then spread out in layers and where recovery is carried out in a manner which blends the layers together. The sampling carried out at the various stages in the blending process has to take in to account the need for very large sample sizes where the particle size of the raw material is large (as in quarried limestone). Chemical analysis expressed as oxides is normally carried out using X-ray fluorescence equipment and computers provide a useful means of making the calculations necessary to produce the desired feedstock analysis and also to make any necessary corrections.

If the chemical and physical condition of the feedstock to the kiln is not correct, it can lead to a variety of problems. If there is large change in LSF and/or alumina and silica moduli, then a change in the amount and the properties of the flux can be expected and can bring with it a loss of the coating which is normally in place on the refractory lining in the burning zone of the kiln. If the failing is an increased LSF, it may be impossible for an appropriate amount of the lime to be combined with the silica and alumina present, with the result that the free lime will be high and the cement produced from the clinker unsound.

If the LSF is lower than that required, there will be a tendency to overheat the clinker, giving rise to low levels of free lime but large alite crystals. The result may be a decrease in strength, although in this case a substantial increase in the fineness to which the cement is ground may help to maintain this. If the alkalis or the tricalcium aluminate are too high, there is little that can be done other than to segregate the clinker in question and to use it for another class of cement. It is important to establish that the components in the clinker are combined to an adequate degree. This can be achieved by the determination of the free lime, i.e. the lime that is left over after the formation of the calcium silicates and the calcium aluminates, etc. An alternative approach is to measure what is known as the 'litre weight'. This is a bulk density measurement obtained by sieving out between two sieves, not greatly different in mesh size, a portion of the clinker which is reasonably representative of the whole. The mass of a given volume of this can be related to the free lime, with lower litre weights being equated to higher levels of free lime. When using this test it is desirable to monitor the results obtained using the free lime test as changes in the amount and type of flux present can change the relationship.

2.3.9 ENVIRONMENTAL CONSIDERATIONS

A Portland cement manufacturing plant producing 1000000 tonnes each year and using the dry process will handle over 1.5 million tonnes of dry powder feedstock and this material may have to be moved through three or more potentially dust-generating transfer points. The clinker and cement produced will also have to undergo a similar treatment. In addition over 100000 tonnes of coal and 50000 tonnes of gypsum will have to be handled. During the year the kiln system could be expected to generate over 1.5 billion cubic metres of gases.

The potential for dust emissions both at low level and at high level is therefore not inconsiderable. Fortunately, the type of dust emitted to the atmosphere is normally a nuisance rather than harmful to health.

Stringent regulations prevail to limit the dust emitted from the kiln systems and these have been reduced with the passage of time as the technology of arrestment has developed. In the UK[105] the situation for the kilns is summarised as

	Pre-1967	1967–1974	1974	1979	1998
Maximum emission of particulate matter (mg/m^3)	460	460–230	230	100	50

The cubic metre volume referred to is calculated to 0°C, 101.3 kPa (1 atmosphere) with no correction for water vapour or oxygen.

In 1998 the maximum emission for clinker coolers is expected to be 100 mg/m^3 and for other operations including cement grinding 50 mg/m^3. The above figures refer to non-continuous monitoring. Where continuous monitoring is adopted, then the emission values are considered to comply with the requirements if 95 per cent of the hourly average readings for each 24 h period do not exceed the emission limit values and the peak hourly average value does not exceed 1.5 × the limit values.

In addition to particulate emissions, advances in measurement techniques have brought with them consciousness of the presence of other components in the kiln gases, and there are now maximum limits for sulfur dioxide of 750 mg/m^3 and for nitrogen oxides expressed as NO_2 of 1800 mg/m^3 for wet-process kilns, 1500 mg/m^3 for semi-wet and for semi-dry kilns and 1200 mg/m^3 for dry process kilns. Where cement kilns are used for the incineration of wastes, the standards contained in the relevant Guidance Notes (5/1)[105] should apply to the portion of the exhaust gases attributable to the burning of the waste. This latter document sets maximum limits for volatile organic compounds (20 mg/m^3), hydrogen chloride (10 mg/m^3), hydrogen fluoride (2 mg/m^3), dioxins (1 mg/m^3), cadmium, thallium (together 0.1 mg/m^3), mercury (0.1 mg/m^3), antimony, arsenic, chromium, cobalt, copper, lead, manganese, nickel, tin and vanadium (1.0 mg/m^3). In addition, lower levels for particulate emissions (20 mg/m^3) and for sulfur dioxide (50 mg/m^3) also prevail.

Electrostatic precipitators are the normal method used to clean the gases emitted from the kiln systems. They take the form of a series of vertical plates spaced between 25 and 40 cm, and in between these plates are a series of wires. A potential difference of 30–70 kV is generated between the negatively charged wires and the plates. This corona discharge ionises that part of the gas which is in the vicinity of the wires and the negative ions produced charge the dust particles, inducing them to migrate to the positively charged plates. The negatively charged dust particles release their charge onto the surface of the plates, where they settle to form a slowly growing layer. At predetermined intervals the plates are rapped and the compacted layer of dust becomes detached and falls into the hopper situated below the precipitator. A smaller amount of dust becomes positively charged and migrates to the negatively charged wires, which also have to be rapped at intervals in order to keep them clean.

The velocity at which the particles migrate is directly proportional to the particle diameter, and thus in order to remove the finest particles large units are necessary. This is reflected in the cost and a unit to remove 99.9 per cent of the particulates can cost over five times that of a unit to remove only 90 per cent.

In addition to this, it is often necessary with dry-process kilns to condition the gases such that they have a temperature of the order of 150°C and a dew point of 50–60°C in order to achieve adequate precipitation. To do this requires a conditioning tower into which finely atomized water is introduced into the gas stream.

Electrostatic precipitators are now commonplace on cement grinding mills as these often have water injected into the outlet chamber for cooling purposes, and this can cause blinding of fabric filters often used for small, local dust collection purposes on a cement plant.

Whilst there has been a considerable concentration of effort and money in dealing with high-level emissions – including the construction of tall chimneys having efflux velocities in excess of 15 m/s – it is often the low-level emissions from items such as material handling which can provoke many complaints, and these are not easy to contain.

Noise is another form of pollution with which a cement manufacturer has to contend. At a distance of 1 m from its shell, a ball mill may emit noise at 115 dB (A), a compressor 120 dB (A) and a high-pressure fan 128 dB (A). Although distance can have a significant attenuating effect, it is often necessary to install substantial structures to lower the noise level to the 65 dB (A), which in some localities is demanded at the plant boundary and the 35 dB (A) required at night in some residential locations.

In situations where it is necessary to blast the raw materials restrictions apply in many cases regarding the amount of vibration permitted. This is normally assessed in terms of its velocity. A maximum of 2 mm/s is considered appropriate for ruins and dilapidated buildings. 8 mm/s for undamaged buildings in a technically sound condition, and 10–40 mm/s for well-stiffened and braced structures.

Overall, it has been estimated[106] that the cost of environmental protection equipment can amount to 20 per cent of the capital cost of a new cement manufacturing plant.

2.4 Production of cements

2.4.1 CEMENT GRINDING

Once the Portland cement clinker has been manufactured it is normally fed to a store to effect a measure of blending and also to allow it to cool to ambient temperature. The latter operation is desirable because most of the clinker coolers associated with kiln operation are unable to lower the temperature below 50–80°C, and even at this temperature the amount of heat introduced into the grinding process is unwelcome.

At most manufacturing plants the ball mill is used to grind the clinker and, since the production rate is directly related to the amount of electrical energy supplied, the power of the electric motor used to turn the mill is a first-order measure of the output achieved. Mills vary in their power input from as little as 200 kW up to 10000 kW.

An efficient mill system grinding a Portland cement (without secondary components) to a level of fineness required for a 42.5 strength class[4] can be expected to consume of the order of 30 kWh/t, and on this basis the mills cited above should be capable of producing 6–7 and 333 t/h, respectively.

The ball mill in its simplest form consists of a tube rotating about a horizontal axis. The inside is normally divided into at least two chambers separated by slotted diaphragm(s). This division enables the mill to operate with at least two different size gradings of grinding media (usually balls). Such an arrangement is necessary because the clinker normally fed to the mill to be ground can contain lumps as large as 60 mm in diameter. These large lumps require a larger ball size (90–100 mm) to break them down. At the same time, balls as small as 13 mm in diameter are needed to grind the material to the fineness required in the more rapid-hardening cements. If such a wide range of ball sizes were to be placed into one chamber, the smaller balls would move to the inlet end and the larger balls to the outlet end, thus making effective grinding impossible. By segregating the ball sizes through the use of diaphragms the larger balls can be kept at the inlet end of the mill and the smaller balls at the outlet. It is possible to achieve a similar effect in a single chamber through the use of classifying liner plates in the mill. These are plates with a wedge-type profile with the tapered part of the wedge facing the mill inlet. These are effective in dealing with ball sizes within the range 60–13 mm, and it is normal practice where larger clinker particle sizes have to be dealt with to introduce a separate chamber accommodating 90–60 mm diameter media.

In order to achieve efficient grinding it is necessary for the media to cascade over each other as the mill rotates. This means that the rotational speed must be kept below the critical point where the media are held against the mill shell by centrifugal force. This 'critical speed' is defined as 42.3 divided by the square root of the internal diameter of the mill (in metres), and the rotational speed of most mills is kept within 65–80 per cent of the critical speed.

The volume of grinding media used in the mill is normally established at a level which either gives the lowest specific power consumption (kWh/t of product) or gives the maximum output. In the case of the latter, it is often decided by the maximum amount of power available from the motor. However, subject to the motor power available, a good starting point would be 30 per cent of the internal volume of the mill taken up with the grinding media. A useful relationship between mill power, media loading speed and rotational speed is given by the following formula:

power to the motor (kW) = $D.A.W.N.$

where D = internal diameter of the mill (m); A = a constant for a given mill system, usually about 0.245; W = the mass of the grinding media in tonnes; and N = the rotational speed of the mill (rev/min).

Only 1–2 per cent of the electrical energy supplied to the ball mill is used in actually fracturing the particles. This means that in the course of the grinding operation a not inconsiderable amount of heat is produced, and one of the principle problems associated with cement grinding is to remove the heat. In the case of small output mills (up to 900 kW) fed with cold clinker it is possible to achieve an adequate degree of cooling by spraying water on to the mill shell. However, with larger mills the ratio of shell surface to heat input decreases and other methods have to be adopted. One of the most satisfactory is to spray water into the outlet chamber of the mill and to use the latent heat of vaporisation to remove the heat. This requires good control facilities and also sufficient ventilation to prevent the water hydrating the cement and causing a loss in its strength-giving properties. Other methods which are used, often in conjunction with water injection, are to introduce a classifier into the milling system. This involves using the mill to produce a relatively coarse product (having, say, a Blaine specific surface area of 270 m^2/kg) and to use the classifier to separate out a product of the required fineness. The power required to produce a coarse product is less and hence the heat introduced is also less. In addition, the movement of the hot cement in an elevator and through the classifier, particularly if it is air swept, can effect a considerable degree of cooling. In this type of mill system –known as a closed-circuit mill – the coarse material produced in the classifier is fed back to the feed end of the ball mill. Closed-circuit grinding is necessary when large mills are required to produce finely ground cements and also in situations where there is a significant difference in the hardness of the Portland cement clinker and any secondary material incorporated into the cement. Grinding cement in a closed-circuit mill system generally produces a narrower particle grading in the cement than that produced from a mill system without a classifier (an open-circuit mill) and this in turn leads to a higher water demand in the mortar or concrete produced from that cement. The higher water demand means that, for a given cement content, lower strengths are produced.

The emphasis placed upon grinding temperatures is associated with the effect that this has upon the calcium sulfate (gypsum rock) added to the clinker, in amounts normally between 3 and 8 per cent, to retard the hydration of the tricalcium aluminate and to optimise the strength-giving properties of the calcium silicates.

If the calcium sulfate is added in the form of gypsum, it can become dehydrated at grinding temperatures of the order of 115–130°C or above, and can be present in a form which when mixed with water forms a supersaturated solution with respect to gypsum and from which secondary gypsum precipitates to provide a structure having some rigidity. This has the effect of stiffening the concrete or mortar and making it necessary to add additional water and thereby lower the strength-giving properties. This is known as 'false set' and should be distinguished from 'flash set', which results in cements which have insufficient sulfate present effectively to stop the hydration of the tricalcium aluminate to the hydrate rather than to ettringite. Flash set is accompanied with the release of considerable amounts of heat whereas it is sometimes possible with false set (as its name implies) to break down the structure developed through vigorous mixing. Some of the problems with false setting can be alleviated by replacing some of the gypsum added to the cement by natural anhydrite. Other problems associated with the calcium sulfate addition arise when the clinker contains a relatively high SO_3 content. As most cement specifications contain a requirement for a maximum SO_3 level, the amount of calcium sulfate which can be added is restricted, and in that situation must be in a form where the solubility is sufficient to prevent the formation of the tricalcium aluminate hydrate rather than ettringite.

Other problems occur when the reactivity of the tricalcium aluminate is reduced through the uptake of moisture and/or carbon dioxide.[107] In this case it may be unable to react sufficiently rapidly to remove enough sulfate from the aqueous phase to prevent the precipitation of secondary gypsum, although when in its original (unaerated) state this situation prevails.

The pre-eminence of the ball mill has been challenged by the vertical spindle (or roller) mill on the grounds that it is capable of a lower power consumption per unit mass of product (kWh/t). However, the particle grading produced from such a mill tends to be narrower than the ball mill and products made in this way tend to suffer from relatively high water demands when made into concrete or mortar. More work on this approach would appear to be required before any benefits can be realised.

Another development is the introduction of the 'roller press' (otherwise known as high-pressure material-bed comminution)[108] to disintegrate the clinker. This involves the use of two rollers turning at a peripheral speed of between 0.9 and 1.8 m/s and with a gap between them of 8–30 mm. The pressure developed on the particles exceeds 50 MPa, and claims have been made that the clinker is 'activated' by the very intensive stressing which occurs as a result of the passage through the rollers. It has been suggested that, provided the product from the roller press is operated in closed circuit with a disintegrator and a classifier, a ball mill may become unnecessary. If this is done, power savings of 45 per cent have been claimed.[109] However, despite this, the normal application of the roller press is in conjunction with a ball mill, taking advantage of the smaller feedstock size to use it in the single chamber configuration. Power savings of 30 per cent have been claimed.

2.4.2 CEMENT TESTING AND CONTROL

The principal test carried out at the cement mill is the fineness test, generally as the specific surface area, but also in terms of the content of coarse particles if it is possible to feed this information back to make a correction, i.e. where closed-circuit grinding is installed. It is also important to ensure that the SO_3 content is at the required level, and this can be controlled through the addition of gypsum rock. Where secondary materials are incorporated by intergrinding, it is necessary to arrange that the grinding process adopted does not overgrind one component at the expense of the other. This may occur where there is a significant difference in the hardness of the materials. For example, if the slag is much harder than the clinker, the latter may be ground excessively fine, whereas for some purposes it is more important that the slag component should be more finely ground. Where limestone is used as a secondary material, the fact that it is normally softer than the clinker renders it suitable to correct shortcomings in respect of the particle grading and lower the water demand of the cement when used in concrete or mortar. Where fly ash is used as the secondary material, the carbon can act as an effective grinding aid (taking us back to the practice adopted many years ago where coal was used to remove the coating from a badly coated grinding mill), but this is accompanied with the development of a distinctly dark colour in the cement produced. In this situation, it is not unusual to add the fly ash to the separator of a closed-circuit mill system and thereby avoid the full effect from the intergrinding and the dispersion of the carbon particles, as well as any danger of breaking the spherical fly ash particles which may result in a reduction of the beneficial effect which some fly ashes may have on workability.

In order to achieve the optimum performance it is important to match the fineness of the clinker and the secondary material(s). It is also necessary to have available methods of analysis which can be used to assess the amount of secondary material present. Control of the temperature of the cement in the grinding circuit is also important if false setting characteristics are to be avoided.

Where the strength-giving properties of the cement need to be carefully controlled, small corrections are often possible by adjustments to the fineness at the cement mill. However, the most important strength test requirements are those at 28 days,[110] and a great deal of cement (perhaps 500000 t at a very large works) can be produced before a 28-day strength result becomes available. It is therefore usual to monitor and to control production using rapid X-ray methods, having over a period of time related these to the strength-giving properties of the cement produced at a particular manufacturing plant. A typical flow sheet for a cement plant illustrating the sampling points (s) is given in Figure 2.7.[111] Recent developments in European certification of cements require, in addition, sampling at the point of despatch.

A number of factors enter into this and, leaving on one side the minor constituents, they include the C_3S, C_3A, silica modulus, LSF, free lime, SO_3, specific surface area, amount of material coarser than 32 or 45 μm, loss of ignition, and alkalis.

The compound compositions of Portland cements containing no secondary materials

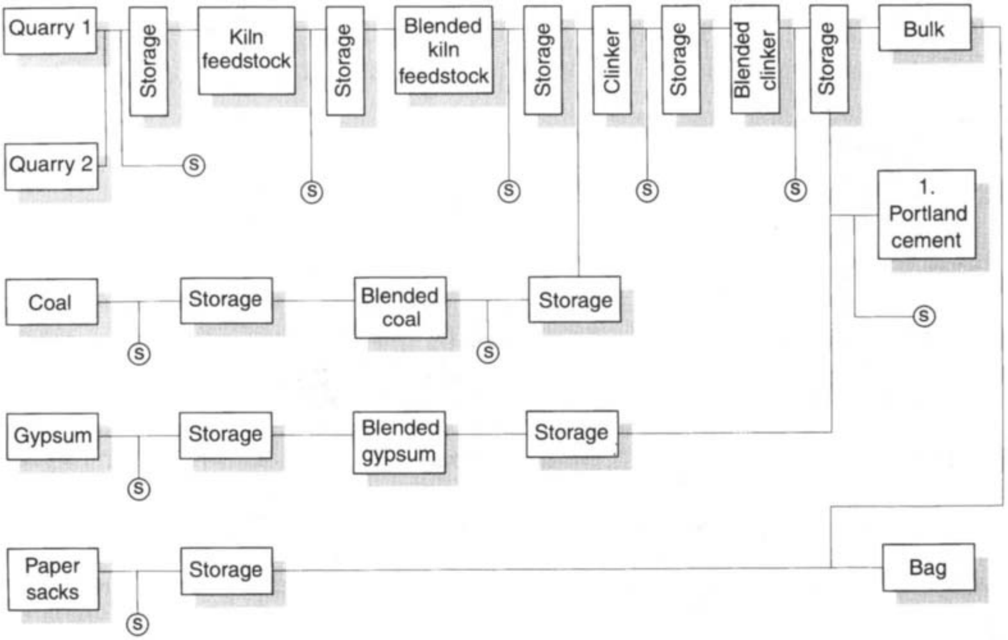

Fig. 2.7 A typical flow sheet for a cement plant illustrating the sampling points (s). (Source: Evans, Ref. 111.)

and having an alumina/ferric oxide ratio equal to or more than 0.64 may be calculated from the oxide analyses as follows:[8]

$$
\begin{aligned}
\%\ \text{tricalcium silicate } (C_3S) = {} & (4.071 \times \%\ \text{CaO}) - (7.700 \times \%\ \text{SiO}_2) \\
& - (6.718 \times \%\ \text{Al}_2\text{O}_3) - (1.430 \times \%\ \text{Fe}_2\text{O}_3) \\
& - (2.852 \times \%\ \text{SO}_3)
\end{aligned}
$$

$$\%\ \text{dicalcium silicate } (C_2S) = (2.867 \times \%\ \text{SiO}_2) - (0.7544 \times \%\ C_3S)$$

$$\%\ \text{tricalcium aluminate } (C_3A) = (2.650 \times \%\ \text{Al}_2\text{O}_3) - (1.692 \times \%\text{Fe}_2\text{O}_3)$$

$$\%\ \text{tetracalcium aluminoferrite } (C_4AF) = (3.043 \times \%\ \text{Fe}_2\text{O}_3)$$

The results from these calculations can be presented in two different ways, notably as 'potential' values which do not take into account any free lime present and also, perhaps more realistically, allowing for the free lime present. In the case of the latter, it is normal to deduct the percentage of free lime from the CaO percentage before it is used in the formula for the C_3S. These formulae do not adequately cover the distribution of the SO_3 between the alkalis and the calcium present, neither do they correspond exactly with the compound compositions as measured using X-ray diffraction (see section 2.3.1). The relative significance of these assessments will be different for different works and also, in some cases, different for different kiln systems and milling systems at a given works because it is not only the quantity present, but also the crystal size, extent of impurities present and the reactivity.

A well-equipped works laboratory and trained staff are necessary in order to control production and to make realistic estimates of the 28-day strength at the time the product is manufactured, bearing in mind the cost constraints considered to be important by some critical users (section 2.2.2).

For many years the technical and scientific personnel employed by the cement manufacturers have had both the integrity and the authority to maintain a high degree of product quality. However, present-day trends bringing with them the potential for interference from commercial interests has made it helpful, in some instances, to have support from external agencies. The Standard BS EN 29002 (ISO 9002)[112] dealing with quality systems and the monitoring of the implementation of this as part of quality assurance schemes has assisted in this respect, particularly where those carrying out the external inspections have a working knowledge of the cement-making process. On the downside, however, this has only been achieved at the expense of a considerable increase in what many view as unnecessary paperwork and attention to matters of no real significance.[113]

In the European Community, the Construction Products Directive effectively makes it necessary for manufacturers to obtain permission to use an EC marking in order to market their products. Although the exact position is not as yet (1996) clear, it would seem probable that this will involve some form of certification by an external body or bodies.[114]

2.4.3 STORAGE AND PACKAGING

Ground Portland cement, provided that it is sufficiently cool, may be fed directly to a storage silo. If it requires cooling, then it can be passed through a cement cooler, usually a vertical cylinder inside which the cement is lifted by a screw and brought into contact with a water-cooled shell.

Storage silos vary in size from several hundred tonnes to 14000 t or more. Care must be taken when operating these installations to avoid lump formation as this can block the discharge devices. Lump formation is considered[115] to occur when the water released from the gypsum during the grinding process diffuses from the relatively hot inner part of the silo to the cooler walls where it serves to hydrate the cement. Replacement of part of the gypsum by natural anhydrite is claimed to minimise this problem.

When cement is stored in paper sacks under high humidity conditions (>90 per cent relative humidity) for some time, lump formation can ocur. This may be associated with potassium sulfate present reacting with gypsum to form syngenite $K_2SO_4 \cdot CaSO_4 \cdot H_2O$. Higher levels of free lime in the cement inhibit this reaction by preferentially taking up moisture. Syngenite can also lead to stiffening problems when the cement is made into a paste.[116]

The formation of lumps is made worse if the powders are stored under pressure, i.e. at the bottom of a stack of sacks. Paper sacks containing plies of polyethylene-coated paper (10 g of polyethylene film per m^2 of paper) or polyethylene film itself are used[117] to minimise the uptake of moisture vapour and to extend the storage life of packed cement. It is also possible to minimise the syngenite problem by the addition of water to the cement grinding mill. The objective here is to form the syngenite in the mill, where it is ground and is less effective in binding the cement particles together than it is when formed *in situ*.

In 1989 the world cement production amounted to 1145 Mt/year with the following distribution between continents: Europe 24.8 per cent, China 18.1 per cent, Asia (apart from China, Japan and USSR) 17.5 per cent, USSR 12.2 per cent, America (apart from USA) 8.9 per cent, Japan 7.1 per cent, USA 6.1 per cent, Africa 4.6 per cent and Oceania 0.7 per cent.

The proportion despatched in sacks or in bulk varies from country to country, with the proportion being moved in bulk in Europe in 1989 varying from 37 per cent in Portugal to 91 per cent in Finland. Cement usage in Europe varies from 863 kg/head of population in Switzerland and 734 in Italy to 320 in the UK and 266 kg/head in Denmark.

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3

Cement Components and Their Phase Relations

Donald E. Macphee and Eric E. Lachowski

3.1 Introduction

Since the last edition of this book was published, considerable advances have been made in the development of techniques and instrumentation for the characterisation of minerals and multi-component oxide systems. Such techniques include differential thermal analysis (DTA), differential scanning calorimetry (DSC) and crystallography, but probably the most significant advances have been in electron optics and related methods. These have permitted the compositional characterisation of microcrystalline phases by electron probe microanalysis (EPMA) and analytical electron microscopy (AEM) and have revealed that many 'simple' cement compounds are compositionally very complex. This has implications for mineral distribution calculations such as that of Bogue and has resulted in various modifications to them.

The complexity of cement mineralogy has its origins in the thermodynamic relationships existing between compounds during the manufacture of cement. The multi-component cement clinker reflects combinations of phases which are mutually compatible under cement kiln conditions, and the existence of these phase combinations, in principle, can be interpreted in relation to equilibrium or pseudo-equilibrium phase diagrams of pure oxide systems even though the raw materials themselves are not pure oxides.

A series of chemical reactions proceeding over a range of temperatures describes the conversion of raw materials to cement clinker. As for all chemical reactions, those involved during the manufacture of cement represent the drive to minimise free energy in the system. Phase diagrams are schematic representations of the thermodynamic properties of systems, reflecting equilibrium, or near-equilibrium, conditions as a function of temperature (and sometimes pressure). This chapter, therefore, examines equilibrium phase diagrams of some chemical systems with particular relevance to the manufacture of cement.

3.2 Phase diagrams

3.2.1 BINARY DIAGRAMS AND THE PHASE RULE

The basis of all phase diagrams is the phase rule, $P + F = C + 2$. where P represents the number of coexisting phases, F the number of degrees of freedom remaining in the system and C the number of components. A 'phase' is defined as any part of the system which is physically homogeneous and bounded by a surface so that it is mechanically separable from other parts of the system. In terms of the phase rule, the number of 'components' C is defined as the *smallest* number of independently variable chemical constituents necessary and sufficient to express the composition of each phase present. For example, although there are three elements present in calcium silicates, Ca, Si and O, all compositions can be expressed in terms of CaO and SiO_2. Therefore $C = 2$ for the 'binary' CaO–SiO_2 system. These and other components important in cement making are discussed in some detail later. The number of 'degrees of freedom', F, is the number of intensive variables (e.g. pressure, temperature, composition) that can be altered independently and arbitrarily without bringing about the disappearance of a phase or the appearance of a new phase. When $F = 0$, the system is said to be 'invariant' and all properties are fixed. For $F = 1$, the system is 'unvariant' and the specification of one variable, e.g. temperature, automatically defines all others, and so on. The significance of this approach will become more evident as examples are discussed. A reduced form of the phase rule is applicable when 'condensed' systems are being considered. In these, the vapour pressures of phases are low compared with atmospheric pressure and so the removal of pressure as an intensive variable reduces the phase rule to $P + F = C + 1$. Only temperature remains as an additional variable. In certain cases, however, for example in systems involving Fe(II) and Fe(III), phase equilibria can be sensitive to gas partial pressures and thus the extended phase rule should be applied.

The phase diagram for a simple binary system A–B without any binary phases is shown in Figure 3.1. Compositions may be expressed as either mole per cent or weight per cent. At low temperatures a physical mixture of A and B is represented. Where two or more phases coexist, they are said to be 'compatible'. In this case the compatible phases are A and B. The mixture melts 'congruently' to give a melt of the same composition at point e, the 'eutectic' point. A liquid coexisting with either A or B results at all other positions on the horizontal line aeb. This line is the 'solidus' and represents the boundary below which only solids can exist. The curves linking the melting points of A and B through the eutectic represent the 'liquidus', above which no solids can appear. The shape of the liquidus is defined by the cooling characteristics of melts over a range of compositions in the system A–B and it is to be noted that the melting temperature of A is reduced by B and vice versa.

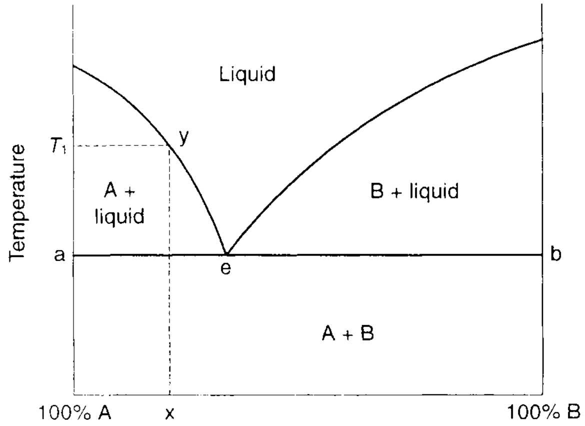


Fig. 3.1 Simple binary system A–B showing no intermediate compositions.

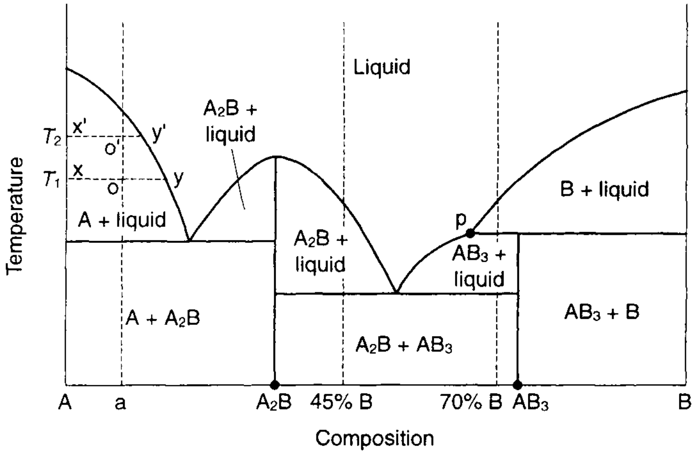


Fig. 3.2 The binary system A–B containing two binary phases, A_2B and AB_3.

The diagram is suitably labelled to indicate the combination of phases coexisting within any particular 'phase field', a region within boundary lines in the phase diagram. If a melt of composition x is cooled to the liquidus temperature at y, crystals of A appear in the 'primary phase field of A' (so named because A crystallises first on cooling). On further cooling, the *liquid* becomes progressively richer in B until at the eutectic temperature, both A and B crystallise. At any point within the primary phase field of A, crystals of A and a liquid phase coexist ($P = 2$). For a binary system, $C = 2$ and so by application of the condensed phase rule, $F = 1$ for this phase field. Either temperature *or* composition need be specified to define completely the system within the phase boundary as follows. A construction line drawn horizontally at the specified temperature (e.g. T_1), will intersect the liquidus at y. This automatically defines the liquid composition at x, read from the composition axis; the coexisting solid is A at any point within this phase field. Similarly, compositional information allows temperature to be defined. At e, three phases coexist, solids A and B, and liquid. Application of the phase rule gives $F = 0$, an invariant condition; composition and temperature are fixed. Thus the eutectic point is an invariant point.

Binary phases can be introduced without too much complexity. Figure 3.2 contains a similar eutectic system to that in Figure 3.1, in this case limited by the compositions of A and the binary phase A_2B. A_2B melts congruently (to give a melt of the same composition) but the other binary phase, AB_3, melts 'incongruently' to give B and a liquid of composition corresponding to the 'peritectic', p, an invariant point. Note that the peritectic characteristically lies outwith the range of compositions between B and AB_3. Again all phase fields except that corresponding to the liquid are two-phase ($F = 1$) and, as before, solid and liquid compositions can be read from the diagram given the appropriate temperature information. The cooling behaviour in the region of the peritectic is slightly more complicated than in the region of the eutectic. For example, at a composition corresponding to about 70 per cent B, the liquid cools to give B + liquid initially. On further cooling to the peritectic temperature, B is consumed as AB_3 crystallises to coexist with a liquid phase. In comparison, at a composition corresponding to about 45 per cent B, the A_2B crystallising at the liquidus temperature is stable to room temperature.

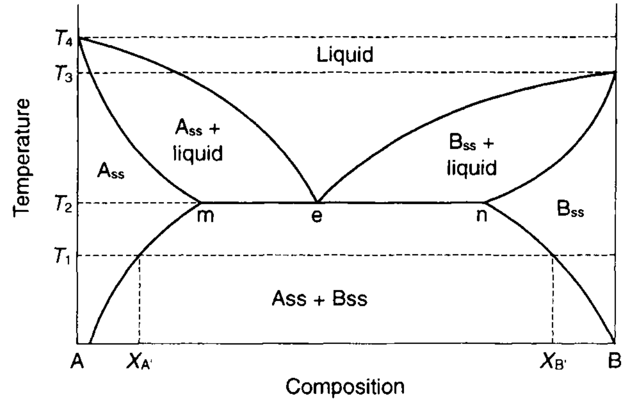


Fig. 3.3 Binary system A–B showing partial solid solution (adapted from Ref. 1).

It may be of interest to know the relative amounts of phases present in a particular mixture. Any of the two-phase regions in Figure 3.2, for example, can be analysed for mix composition by the use of the 'lever rule'. In this context, mix composition is used to define the relative amounts of the phases in a two-phase mixture, whereas bulk composition and phase composition are used to define the overall proportioning of components in the bulk, and of components in the phases, respectively. The lever rule can be used as follows.

In the two-phase region A + liquid (Figure 3.2), the ratio of A to liquid at temperature T_1 and at a bulk composition corresponding to a is given by oy/ox. Thus, as temperature increases to T_2, the same ratio can be seen to reduce (comparing o′y′/o′x′ to oy/ox). This is consistent with expectations, i.e. as temperature increases, more solid melts. The principles of the lever rule may be used generally in phase diagrams and its implications to specific systems will be discussed where appropriate below.

In many cases, solubility of one solid phase in another can occur. This is common in geological systems, e.g. the plagioclase feldspars, where $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$ define the end-members of a series of intermediate compositions resulting from varying degrees of solubility of one phase in the other. Only partial solubilities are observed in cement-related systems and their effect on phase diagrams is illustrated in Figure 3.3, which is a modification of Figure 3.1. The maximum solubility of B in A is represented at point m. The 'solid solution' labelled A_{SS}, is single phase ($P = 1$) because the matrix (A) has B *dissolved* in it. Note that the extent of solubility increases with temperature up to the solidus section 'men', above which solubility diminishes due to the increasing presence of liquid. The situation for B_{SS} is similar with maximum solubility defined at n. As before, compositions can be read from the base axis of the diagram given appropriate temperature information; for example, at temperature T_1, the compositions of A_{SS} and B_{SS} are x_A' and x_B' respectively.

So far, it is evident that much information can be derived from even relatively straightforward diagrams. It is important therefore that some reliability can be placed in their construction. Whilst experimental studies are always the more direct means of defining the shape of a liquidus or position of a eutectic, for example, some element of modelling is often employed to extrapolate or complete an intermediate portion of the diagram, e.g. between two or more experimental data points. Beyond this, the equilibrium

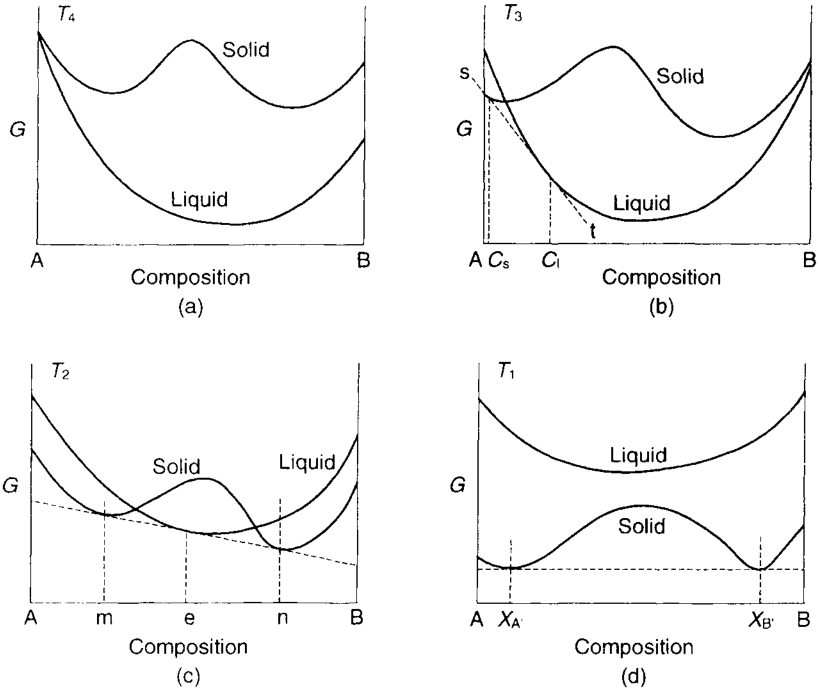
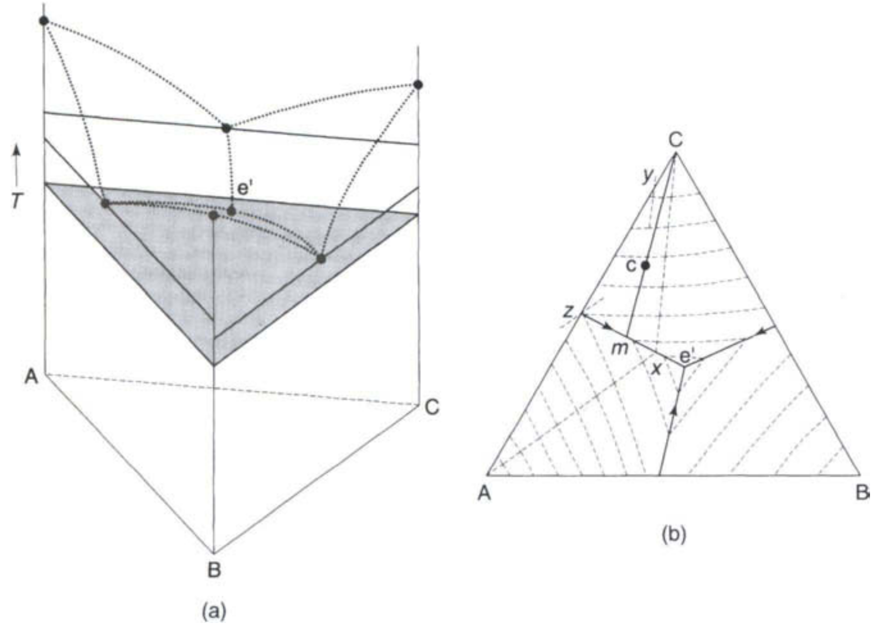


Fig. 3.4 Isothermal free energy curves for the system A–B shown in Figure 3.3 (adapted from Ref. 1).

nature of phase diagrams permits the use of free energy data to define or confirm important positions on the diagram[1] as illustrated by Figure 3.4 using Figure 3.3 as a reference. We recall that the derivative of Gibbs free energy with respect to composition ($\delta G/\delta n$) is μ, the chemical potential. For a solid to be in equilibrium with a liquid, $\mu_{\text{liquid}} = \mu_{\text{solid}}$, so that the gradients of the respective isothermal free energy curves will be the same. In Figure 3.4(*a*), the solid and liquid curves have a common tangent only at the composition A, and at the melting point of A, T_4. In Figure 3.4(*b*), the common tangent, s–t, intercepts the liquid and solid curves at compositions corresponding to the liquid, C_l and solid, C_s, respectively. The compositions of solid and liquid can be equally derived from the composition axis of Figure 3.3 for temperature T_3 as described previously. Figure 3.4(*c*) illustrates the situation at the eutectic temperature, T_2, where the common tangent intercepts the liquid and solid curves at three points representing solid, liquid and eutectic mixture composition. Solid solution compositions at temperature T_1 are then readily derived from Figure 3.4(*d*).

3.2.2 TERNARY DIAGRAMS

Ternary diagrams represent three-component systems and are conveniently presented as triangular diagrams where each side corresponds to an individual binary system. However, in three dimensions the diagram is more complex with surfaces emerging



(a)

(b)

Fig. 3.5 Alternative representations of the ternary system A–B–C.

(Figure 3.5(*a*)) rather than lines as in the binary system. A convenient way of expressing detail in the complete system is by the use of isothermal contour lines (broken lines in Figure 3.5(*b*)); arrows on the bold phase field boundary lines indicate the direction of falling temperature. However, it is easier and often more relevant to discuss isothermal sections of the complete diagram, particularly for subsolidus properties or, as is useful in some cases, a vertical section between two compatible phases. We shall therefore focus on isothermal sections, an example of which is illustrated in Figure 3.5(*a*) (shaded section). But first, some explanation of interpreting compositions from ternary diagrams will be given. Each edge of the ternary diagram between pairs of end-members is a binary system in its own right, as is a vertical section between two compatible phases, and has all the normal properties of a binary system. Additionally, the components can participate to provide ternary or three-component phases where the fractional contribution of all components must add up to unity, e.g. a phase with the composition A_3BC_2 has 50 per cent A, 16.7 per cent B and 33.3 per cent C. On the diagram, this composition can be fixed in several ways, but the simplest and often most convenient way is to plot the composition using percentages of only two of the components; the third is automatically fixed by the geometry of the diagram. It can be seen that ternary phases lie within the boundary of the diagram, illustrating the contribution of each of the components in the phase composition.

The cooling characteristics of phases in the ternary system can be described in a similar way to that previously discussed for binary systems. In addition to the binary eutectics located on the binary edges of the diagrams in Figure 3.5, a 'ternary eutectic' is shown at e′. This occurs at the minimum temperature on the liquidus 'surface'. The cooling behaviour within such a system is illustrated by example in Figure 3.5(*b*) for composition

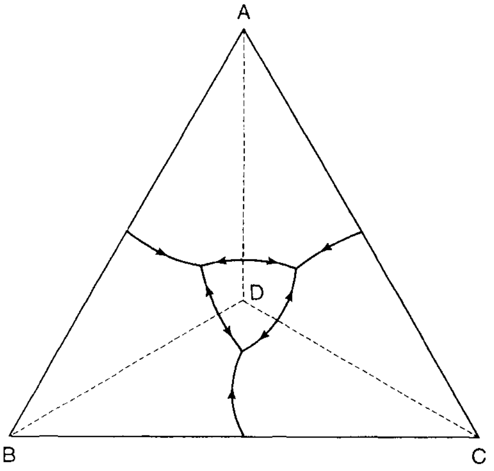


Fig. 3.6 A ternary system A–B–C containing a congruently melting ternary phase D.

c. Solid C crystallises in its primary phase field at c and the liquid composition alters in the direction cm where A crystallises at m. Further cooling causes compositional changes in the liquid along me′ resulting in all solids (A, B and C) coexisting at the eutectic temperature.

It is convenient to use Figure 3.5(*b*) to illustrate the application of the lever rule in ternary systems. As before, it may be of interest to know the amount of any phase present at a particular temperature, x, for a fixed bulk composition, c. Construction lines xA and xC can be drawn to construct the triangle xAC. By translating the line xC such that it passes through the original composition, c, an intersection y on the line AC can be found. Similarly, point z can be located by translating line xA. The relative amounts of A, C and liquid can now be determined from the line portions yC, zA and yz, respectively. Clearly, maximum liquid content occurs at point c, and decreases as the system cools in the direction cme.

Figure 3.6 shows a congruently melting ternary phase, D (a compound of A, B and C), and its influence on the shape of the liquidus surface. There are four primary phase fields, one for each of the solids, A, B, C and D. The phase field boundaries again indicate the direction of falling temperature. Note that the temperature maximum on each boundary corresponds to its intersection with the line drawn between the pure component A, B or C and the ternary phase D. As in binary systems, pure phases correspond to local temperature maxima so that in Figure 3.6 a dome-like shape exists above composition D. Temperature minima are observed at each of the ternary eutectics (intersections of phase field boundaries) and at the binary eutectics. The cooling behaviour may be deduced from analogy with the previous example. For an incongruently melting phase, E, a peritectic diagram (Figure 3.7) is applicable. In this case, E does not lie within its own primary phase field and the peritectic, p′, does not correspond to a temperature minimum (note the analogy with binary systems).

There are certain limitations in expressing systems containing more than three components in two dimensions. For example, a four-component or 'quaternary' system takes the form of a trigonal pyramid. The faces of the pyramid are isothermal sections

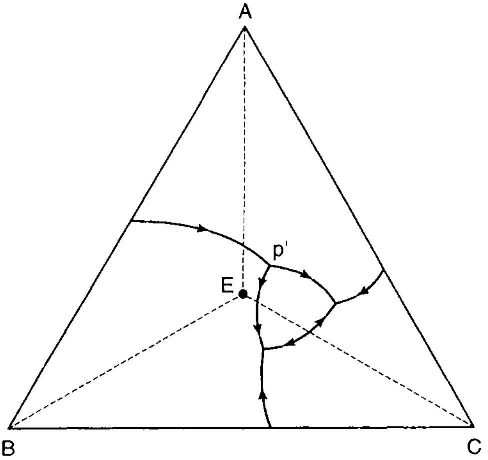


Fig. 3.7 A ternary system A–B–C containing an incongruently melting ternary phase E.

(see below) of ternary diagrams and the edges are isothermal sections of binary diagrams. Within the pyramid lie compositions which can be represented by physical mixtures of components, binary, ternary and quaternary phases. Compatibility relations are analogous to those in binary and ternary systems (see below), taking the form of solid tetrahedroids. These diagrams can be treated in an analogous way to those of binary and ternary systems. In the general case, quaternary diagrams can contain liquidus information, but in view of the complexity in presentation and discussion of such diagrams, these will not be discussed in detail here. A useful visualisation of the three-dimensional nature of quaternary diagrams can be viewed from stereoscopic images or solid models.

3.2.3 ISOTHERMAL SECTIONS

Figure 3.5(*a*) illustrates the concept of an isothermal section (shaded plane) as related to a ternary diagram. Figure 3.8 provides an example showing the simplified three-component subsolidus assemblages in another hypothetical A–B–C system. Compatibility relationships are easily recognised. For instance, A, A_2B and ABC would comprise the assemblage of phases within the region bounded by lines connecting the compositions of A, A_2B and ABC in the diagram. This area is called a 'compatibility triangle' where only these phases can coexist. Each triangle can be treated as a miniature phase diagram so that compositions of physical mixtures within its boundary can be expressed in terms of the phases at its vertices. For example, one could apply the lever rule as illustrated above to determine mix composition within this phase field.

The use of isothermal conditions also greatly simplifies quaternary diagrams. Note that it is not uncommon to see subsolidus compatibility relationships and crystallisation pathways superimposed on the same diagram. The latter gives a general description of the system over a range of temperatures whereas the compatibility relationships usually correspond to isothermal conditions, normally ambient. Examples can be seen in Figures 3.6 and 3.7, each of which illustrates three subsolidus compatibility regions separated in

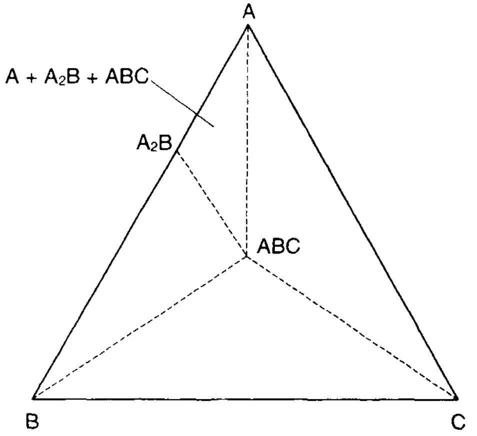


Fig. 3.8 Hypothetical ternary system A–B–C showing subsolidus compatibilities.

this case by the broken construction lines, e.g. A + B + D, A + C + D and B + D + C underlying the primary phase fields in Figure 3.6. Conventionally, such phase field boundaries are denoted by solid lines.

3.2.4 ISOPLETHIC SECTIONS

Another useful representation of multi-component diagrams is the isoplethic section which is a view of a section of the diagram taken at a fixed percentage of a particular component. Figure 3.9 shows a 5 per cent A isopleth from the diagram for the system A–B–C–D. Figure 3.9(*b*) represents a plan view of Figure 3.9(*a*). Such a diagram simplifies the representation of primary phase fields and their use will be discussed further when the CaO–Al_2O_3–SiO_2–MgO system is described below (Figure 3.20).

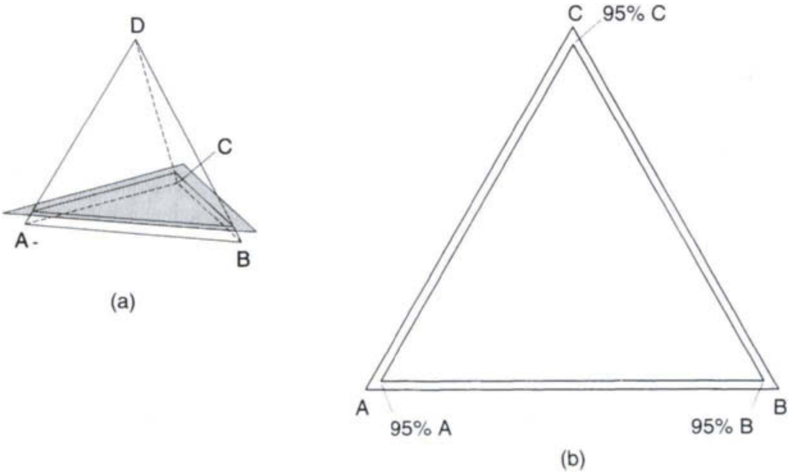


Fig. 3.9 Isoplethic section of a quaternary system.

3.2.5 GENERAL RULES FOR INTERPRETING PHASE DIAGRAMS

More complex ternary diagrams than those that have been discussed can occur, but application of the same general principles will indicate their significance and will allow the crystallisation path of any bulk composition to be deduced. The general rules governing crystallisation paths in ternary diagrams which have been utilised in the foregoing examples can be briefly summarised as follows:

- When one solid phase only is present, the crystallisation path lies within a primary phase field and is given by the prolongation of a line drawn from the composition of that solid through the original mix composition. This is necessarily a direction of falling temperature.
- When two solid phases are present, the crystallisation path follows the boundary line between the primary phase fields of the two solids in the direction of falling temperature. For a given point on the boundary curve considered, the mean composition of the total solid separated as the system cools to that point is given by the intersection of the line drawn through the point on the boundary curve and the original mix composition with the line joining together the composition of the two solids present. The composition of the instantaneously crystallising solid at any point is given by the intersection of the tangent to the boundary curve at that point with the same composition line (i.e. between the compositions of the two crystallising solids) or its prolongation. If this line has to be extended beyond the composition of one of its end-members before an intersection occurs, then one solid is redissolving and the other separating out. This occurs in the case of peritectics and the crystallisation path leaves the boundary line and enters an adjoining primary phase field. This is a consequence of the above intersection occurring outside the compatibility triangle of interest.
- When three solids are present together, the liquid composition must be at a eutectic or peritectic (invariant point). In the former case, the mix will go solid at this point. In the latter case the mix will go solid at this point if the original mix composition is such that it falls within the triangle formed by joining together the compositions of the three solids coexisting at this point. If this is not the case, one solid will entirely disappear by redissolving (peritectic reaction) and the crystallisation path then follows a boundary curve to another invariant or eutectic point.

The assumption is made in tracing such crystallisation paths that equilibrium between solid and liquid is always maintained. All too often in real systems, this is not the case leading to fractionation, which will be discussed later. The path followed by a solid mix on heating is, with the same assumption of equilibrium, the exact reverse of the crystallisation path on cooling.

3.3 Oxide components of cements

Having outlined the important features of phase diagram interpretation using hypothetical systems, attention can now focus on their application to cement-related systems. Where necessary, additional interpretations of features in certain diagrams are given. The phases present in cement may be considered to be compounds of a number of

Table 3.1 Abbreviated nomenclature commonly used in cement chemistry

C	CaO	S	SiO_2	A	Al_2O_3	M	MgO	H	H_2O
T	TiO_2	F	Fe_2O_3	f	FeO	N	Na_2O	K	K_2O
$\bar{C}$	CO_2	$\bar{S}$	SO_3	P	P_2O_5				

simple oxides, and it is customary to describe their formulae in these terms, e.g. Ca_3SiO_5 becomes $3CaO \cdot SiO_2$. This nomenclature may be further abbreviated to C_3S in line with the general scheme used widely in ceramic sciences and given in Table 3.1. However, it is important to note that these formulae have no chemical significance except when read in the context described above. For example, C_3S has no identifiable CaO or SiO_2 in its structure. In general, these simple oxides are not present in cement clinker (with the occasional exception of small amounts of CaO). Thus the following data on physical properties of the simple oxides are provided only for completeness as they define the end-member components of the more complex systems to be discussed below. Of more relevance are the properties of the cement clinker phases which will be discussed in more detail.

3.3.1 *CHARACTERISTICS OF OXIDE COMPONENTS*

The physical properties of the important oxide components of cements are summarised in Table 3.2. Other features are described below.

CaO (lime) is quantitatively one of the most important components of cement and is normally introduced during cement making from limestone, principally calcite, $CaCO_3$, which decarbonates from about 680°C. Some properties depend on calcination temperature, e.g. specific gravity varies between 3.25 and 3.38 and reactivity with water reduces with increasing temperature. Both properties are related to active surface area, diminished by sintering at high temperatures. CaO has the NaCl structure (face-centred cubic).[2] Similarly, the reactivity of MgO (periclase) with water is influenced by calcination temperature. It too has the NaCl structure[3] and is normally introduced to cement as an impurity in the limestone source or in the clay or shale raw feed. Slow hydration of MgO in cements is deleterious, causing unsoundness, and limits acceptable MgO content of cements to typically less than 1.0 per cent.

Silica, SiO_2, exists naturally in the pure state as different crystalline 'polymorphs' (e.g. α-quartz, cristobalite and tridymite) and as impure, poorly crystallised or amorphous minerals (e.g. opal and flint). Figure 3.10 shows the relationship between the different polymorphs and is effectively a phase diagram of a one-component system. Note that the complete phase rule, $P + F = C + 2$ is applicable to this diagram. At atmospheric pressure, with the exception of the α- (or low) quartz to β- (or high) quartz transformation at 573°C, reactions are sluggish and much metastable behaviour is observed (Figure 3.10).[11] Rather than as the oxide, SiO_2 is introduced to the cement in the aluminosilicate minerals of the shale or clay component of the kiln feed and combines with CaO during the clinkering process to give the impure calcium silicates, alite and belite, which are structurally related to C_3S and β-C_2S, respectively. These minerals comprise the bulk of the hydraulically active material in Portland cement clinker.

Aluminium oxide occurs in nature as α-Al_2O_3 (corundum). An ill-crystallised polymorph, γ-Al_2O_3, may arise in kilns on the heating of substances such as bauxite and

Table 3.2 Physical data on the principal oxide components of cements

					Unit cell parameters (a, b, c in Å)						
Oxide	Polymorph	Melting point (°C)	Specific gravity	Space group	a	b	c	α	β	γ	n
CaO[2]		2614	3.25–3.38	Fm3m	4.8106	–	–	90.00	–	–	1.838
MgO[3]		2852	3.58	Fm3m	4.2110	–	–	90.00	–	–	1.735
SiO_2	α-quartz[4]	1710	2.651	$P3_221$	4.913	–	5.405	90.00	–	120.00	$\omega = 1.544$ $\varepsilon = 1.533$
	β-quartz[3]			$P6_222$	4.9977	–	5.460	90.00	–	120.00	
	Tridimite[5]		2.26		9.88	17.1	16.3	90.00	–	–	$\alpha = 1.471–1.479$ $\beta = 1.472–1.480$ $\gamma = 1.474–1.483$
	Cristobalite[6]		2.33	$P4_12_12$	4.9732	–	6.9236	90.00	–	–	$\omega = 1.487$ $\varepsilon = 1.484$
Al_2O_3	Corundum[7,8] (α-alumina)	2050	4.0–4.1	$R\bar{3}c$	4.7588	–	12.992	90.00	–	120.00	$\omega = 1.765–1.776$ $\varepsilon = 1.752–1.768$
Fe_2O_3	Haematite[9]	1350	5.26	$R\bar{3}c$	5.0356	–	13.749	90.00	–	120.00	$\omega = 3.22$ $\varepsilon = 2.94$
FeO	Wustite[10]	1372	6.062	Fm3m	4.37	–	–	90.00	–	–	2.32

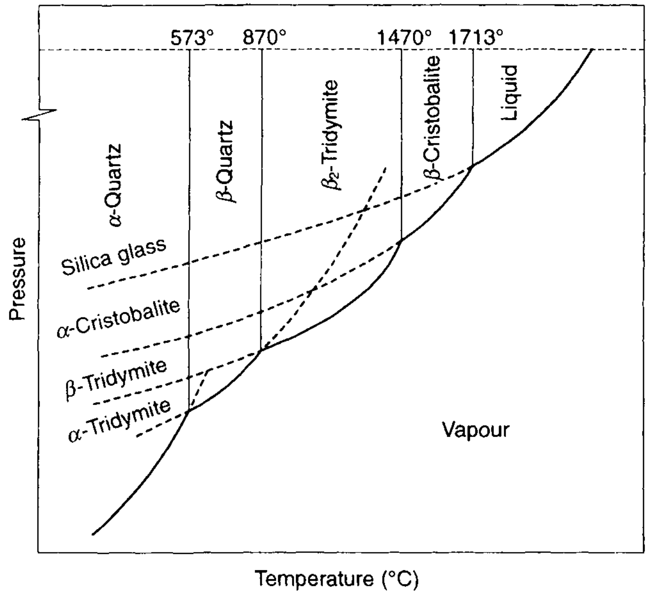


Fig. 3.10 Equilibrium phase diagrams for SiO_2 (adapted from Ref. 11). Metastability indicated by broken lines.

clays at approximately 900°C.[12] So-called β-Al_2O_3 is not a polymorph of Al_2O_3 and is in fact a sodium aluminate.[13] Iron oxides in Portland cements are derived from clay and shale and in high-alumina cements are derived from the bauxite feed. Their compositions are influenced by the prevailing redox conditions; Fe(II) exists in wustite and Fe(III) in haematite. Mixed oxidation states exist in the spinel phase, Fe_3O_4. Fe_2O_3 is not stable at liquidus temperatures, even in air.[14]

3.4 Cement-related systems

3.4.1 SYSTEMS CONTAINING MAJOR COMPONENTS

The system CaO–SiO$_2$

The phase diagram for this system (Figure 3.11)[15] contains four binary compounds, CS, C_3S_2, C_2S and C_3S. All but C_3S_2 undergo phase transitions, which are discussed below. Some polymorphs are omitted from the diagram for clarity. Physical and crystallographic data on these phases are presented in Tables 3.3 and 3.4.

Calcium metasilicate, CS, exhibits three modifications. The high-temperature form, α-CS or pseudowollastonite, occurs rarely in nature whilst the two β-polymorphs, parawollastonite and wollastonite, are reasonably common. CS has a primary phase field, melting congruently at 1544°C, the transition between the β- and α- forms occurring at 1125°C.

Rankinite, C_3S_2, melts incongruently at 1464°C. A related phase, kilchoanite, previously thought to be a polymorph of rankinite contains essential water.[16]

Neither the calcium metasilicates nor rankinite are appreciably hydraulic and are not found in Portland cement clinkers.

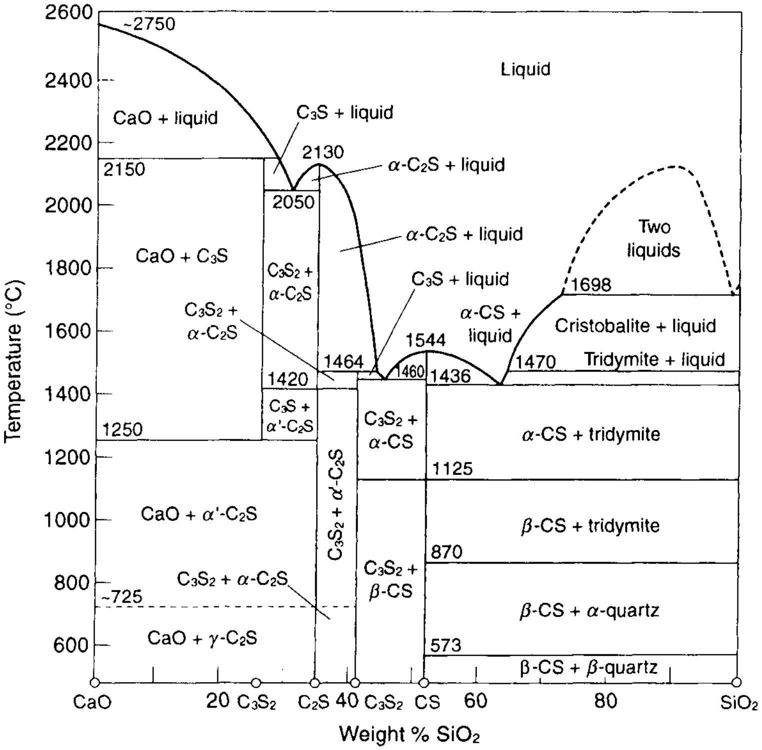


Fig. 3.11 Equilibrium phase diagram for the CaO–SiO_2 system (source: Ref. 15).

Calcium orthosilicates. Dicalcium silicate is an important constituent of Portland cement clinker (comprising 20–40 per cent by weight of the phases present). It exhibits a number of polymorphs, classified by Bredig,[17] the hydraulically important polymorph in Portland cement being β-C_2S. This also appears in slags, refractories and belite cements. On cooling from elevated temperatures, α-C_2S passes through a number of closely related polymorphs α', α'_L and α'_H[18] (the latter two formerly were not distinguishable from α') before transforming to the β-form at 630°C. The transformation at lower temperature to the γ-modification is accompanied by a volume increase responsible for the well-known phenomenon of 'dusting'. These phase transformations are summarised in Figure 3.12. γ-C_2S is non-hydraulic, but fortunately β-C_2S can be stabilised to low temperature by quenching or by formation of solid solution with a large number of oxide impurities[19] which dissolve at high temperature in the α or α' phases.[20] Examples of impurities include boric oxide, phosphorus pentoxide and magnesia. This means that it is belite, the impure form of β-C_2S, which is present in cement clinker. Pure β-C_2S is not an equilibrium phase under normal atmospheric conditions,[21] and therefore its existence is not reflected in the equilibrium CaO–SiO_2 diagram (Figure 3.11).

The most abundant phase of Portland cement clinker is alite, an impure form of tricalcium silicate (C_3S). Although a 'lower limit of stability' exists for C_3S at about 1250°C, the decomposition to CaO and C_2S on cooling is kinetically restricted and the compound exhibits a number of metastable modifications in the temperature range between room temperature and 1100°C.[30] Of these, the highest temperature, and only thermodynamically stable polymorph (metastable below 1250°C), designated R (for

Table 3.3 Physical and optical data for binary phases in the CaO–SiO_2 system

Phase	Polymorph	Name	Melting/ transformation point (°C)	Specific gravity	Space group	Unit cell parameters (*a*, *b*, *c* in Å) *a*	*b*	*c*	α	β	γ	*n*
$CaO\cdot SiO_2$	α-CS[22]	Pseudowollastonite	1544	2.912	P1	6.82	6.82	19.65	90.4	90.4	119.3	1.610, 1.611, 1.654
	β-CS[22]	Wollastonite	1125	2.88	P1	7.371	7.894	7.037	95.32	90.02	102.9	1.620, 1.632, 1.634
	β-CS[23]	Parawollastonite 2M	1125	2.91	$P2_1/a$	15.429	7.325	7.069	90.0	95.38	90.0	1.618, 1.630, 1.632
$3CaO\cdot 2SiO_2$[24]		Rankinite	1464	2.998	$P2_1/a$	10.614	8.914	7.847	90.0	120.08	90.0	1.640, 1.644, 1.650
$2CaO\cdot SiO_2$	α-C_2S		2130	2.94	$P6_3/mmc$	9.571	–	7.307	90.0	–	120.0	
	α′-C_2S	High	1435		Pmcn[25]	5.593	18.95	6.86	90.0	–	–	
		Low			Pmcn	11.84	18.95	6.84	90.0	–	–	
	β-C_2S		670	3.313[26]	$P2_1/n$[27]	9.297	6.756	5.502	90.0	94.59	90.0	
	γ-C_2S		735	2.97	Pcmn[28]	5.080	6.758	11.22	90.0	–	–	

Table 3.4 Physical and crystallographic data on pure tricalcium silicate polymorphs[29]

Polymorph	Melting/ transformation temp. (°C)	Structure	*a*	*b*	*c*	α	β	γ
R	2070[31]	Rhombohedral	7.15	–	25.56	90.00	90.00	120.0
M_{III}	1060	Monoclinic	33.08	7.03	18.50	90.00	94.12	90.00
M_{II}	1050	Pseudohexagonal	7.13	7.14	25.13	90.00	90.00	120.06
		Orthorhombic	12.34	7.14	25.13	90.00	90.00	90.00
M_I	990	Pseudohexagonal	7.12	7.14	25.42	89.95	90.13	120.08
		Monoclinic	14.23	7.14	25.42	90.00	90.13	90.00
T_{III}	980	Triclinic	14.23	14.29	25.41	89.94	90.15	120.05
T_{II}	920	Triclinic	14.20	14.28	25.36	90.00	90.17	120.04
T_I	600	Triclinic	14.14	14.28	25.29	90.10	90.21	120.02

rhombohedral), melts incongruently at 2070°C to give CaO and liquid (see Figure 3.11) and, on cooling, undergoes reversible polymorphic transformation below 1100°C to monoclinic (and orthorhombic) and then triclinic modifications. The monoclinic polymorph, M_{III}, has a transient existence over a small range of temperature,[31] its stability being due to the impurity level, notably of MgO, in the structure. The cooling sequence is as follows:

$$R \xrightarrow{1060°C} M_{III} \xrightarrow{1050°C} M_{II} \xrightarrow{990°C} M_I \xrightarrow{980°C} T_{III} \xrightarrow{920°C} T_{II} \xrightarrow{600°C} T_I$$

All polymorphs have very similar structures mainly related by small distortions as the C_3S structure endeavours to accommodate crystallographic strain as it is cooled below its limit of stability (Figure 3.11). For this reason, the M and T polymorphs can be described in terms of pseudohexagonal unit cells.

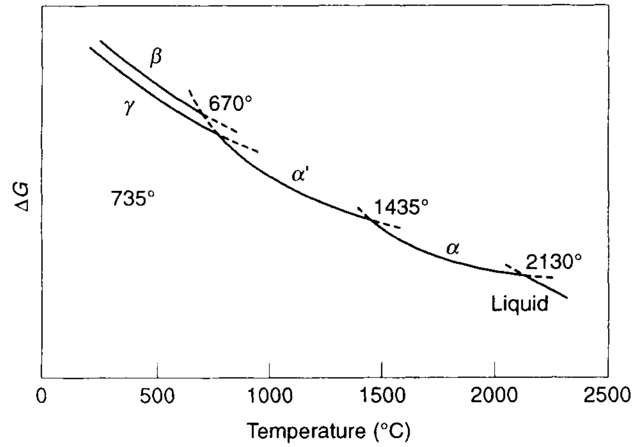


Fig. 3.12 Relative free energies of C_2S as a function of temperature (source: Ref. 21).

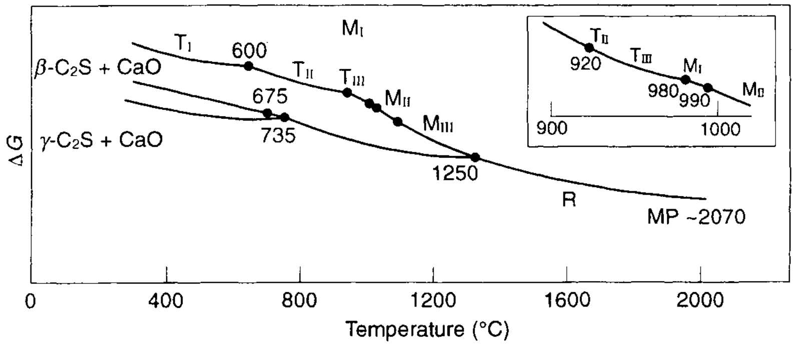


Fig. 3.13 Relative free energies of C_3S as a function of temperature (adapted from Ref. 33).

This is another case where thc equilibrium phase diagram does not fully represent the situation for actual clinkers. In most clinkers, usually the M_I or M_{III} phases are present at room temperature;[32] this is highly dependent on impurity content and heating and cooling history, e.g. 0.8 per cent MgO stabilises M_{III} whereas increasing SO_3 content favours M_I. Consequently, zoned M_I–M_{III} crystals are often found in Portland cements. A relative free energy diagram[33] (Figure 3.13) illustrates the differences between the equilibrium and non-equilibrium pathways.

The system CaO–Al_2O_3

The rapid decrease in liquidus temperature brought about by the addition of Al_2O_3 to CaO should be noted (Figure 3.14) and is significant in reducing the burning temperatures

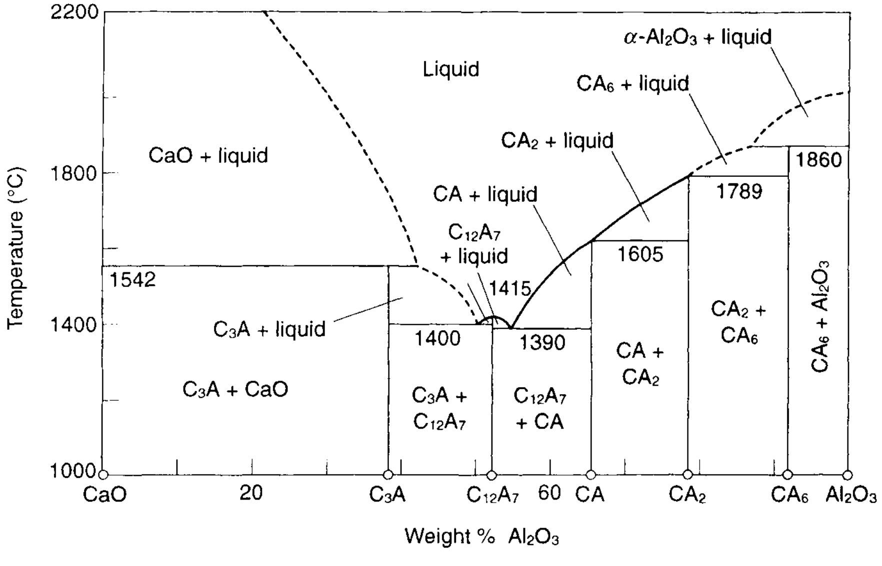


Fig. 3.14 The system CaO–Al_2O_3 in air of ordinary humidity (source: Ref. 38).

Table 3.5 Physical and optical data for binary phases in the $CaO–Al_2O_3$ system

Phase	Melting transformation point (°C)	Specific gravity	Space group	Unit cell parameters (a, b, c in Å)						
				a	b	c	α	β	γ	n
C_3A[41]	1539	3.028	Pa3	15.263	–	–	90.0	–	–	
$C_{12}A_7$[42]	See text	2.70	$I\bar{4}3d$	11.982	–	–	90.0	–	–	1.608
CA[43]	1602	2.96[44]	$P2_1/c$	8.698	8.092	15.208		90.014		
CA_2[45]	1762	2.90	C2/c	12.868	8.879	5.440		106.75		
CA_6[46,47]	1830	3.84	$P6_3/mmc$	5.5579	–	21.905			120	1.79, 1.807

required for cement making to economic levels. It also has implications for the performance of lime-based refractories. This system contains the stable phases C_3A, CA, $C_{12}A_7$, CA_2 and CA_6.

$C_{12}A_7$ was thought to be stabilised by essential water,[34] but more recent studies[35] have shown that the water can be removed at 1350°C, below its melting temperature (1374°C in dry air). Absorption of water into the structure is at a maximum at 900°C, giving a composition of formula $11CaO \cdot 7Al_2O_3 \cdot Ca(OH)_2$. The hydroxide ion may be replaced by chloride or fluoride.[36] Although the phase melts incongruently in dry air,[37] congruent melting at 1415°C is observed in normal atmospheres[38] as represented in Figure 3.14.

C_3A melts incongruently at 1542°C. It is cubic in the pure state; the two crystallographic modifications often referred to in the literature, i.e. orthorhombic and monoclinic, are stabilised by about 6 per cent Na_2O.[39] With the exception of $C_{12}A_7$, all the other phases also melt incongruently as indicated in Figure 3.14. Physical and crystallographic data on these phases are presented in Table 3.5. Of significance to aluminous cements are the phases CA and $C_{12}A_7$, but CA_2, CA_6 and α-Al_2O_3 may be present in those with a high alumina content.[40] All binary phases in the $CaO–Al_2O_3$ system except CA_6 are hydraulically active at room temperature. However, C_3A is the most important of these phases in Portland cements, heavily influencing the initial set characteristics due to its rapid hydration, which requires retardation, normally by gypsum addition.

3.4.2 TERNARY SYSTEMS

The usefulness of equilibrium phase diagrams of binary systems to the interpretation of cement manufacturing reactions is extremely limited. In fact, ternary diagrams are similarly restricted, also due to the presence of metastable phases, but they are somewhat more useful because the additional component brings about a closer approximation to the relevant chemistry. From a quantitatively significant viewpoint, the $CaO–Al_2O_3–SiO_2$ and the $CaO–Al_2O_3–Fe_2O_3$ are the most relevant ternary systems.

The system $CaO–Al_2O_3–SiO_2$

A large number of ternary phases are present in this system (Figure 3.15[48]) but it is mixtures of the lime-rich binary phases represented in this system which are most important to cements; 90 per cent of Portland cement is made up of binary phases in this three-component system. Although cement manufacture may take place at 1400–1450°C, a slightly higher temperature for the Fe-free $CaO–Al_2O_3–SiO_2$ system is required to

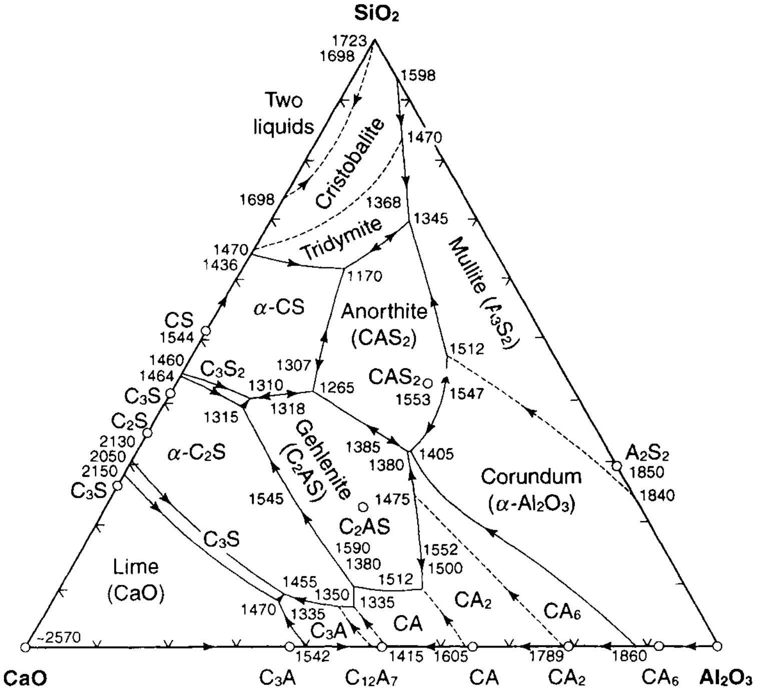


Fig. 3.15 The system $CaO-Al_2O_3-SiO_2$ (source: Ref. 48).

provide a comparable situation for discussion. Thus the 1500°C isotherm of the portion relevant to cement manufacture is expanded and presented in Figure 3.16.[49] A typical bulk composition of Portland cement is represented by the point c in Figure 3.16 and lies within the phase field bounded by lines connecting C_3S, C_2S and a liquid phase of composition L_c. This means that the equilibrium phase assemblage at the burning temperature will consist of a liquid phase (containing the aluminous component), C_3S and C_2S.

However, the final phase assemblage obtained on cooling may be rather more complex than the phase diagram suggests. This is due to fractionation, a condition arising due to the slow rate of reaction between solids and between liquid and solid phases. Thus, non-equilibrium conditions are established because high-temperature assemblages are effectively 'frozen-in' as the clinker experiences relatively rapid cooling. According to the subsolidus diagram (Figure 3.17), composition c should crystallise to yield C_3S, C_2S and C_3A. The diagram also shows that a melt of bulk composition L_c (transposed from Figure 3.16 to Figure 3.17), considered in isolation from the solid, would crystallise on cooling to give C_2S, C_3A and $C_{12}A_7$. In practice all four phases, including C_3S, are observed. The phase rule predicts only three indicating that effectively two metastable equilibria are observed in this particular case due to fractionation. This again illustrates the need for caution when using equilibrium phase diagrams to deduce phase assemblages in the manufacture of cement.

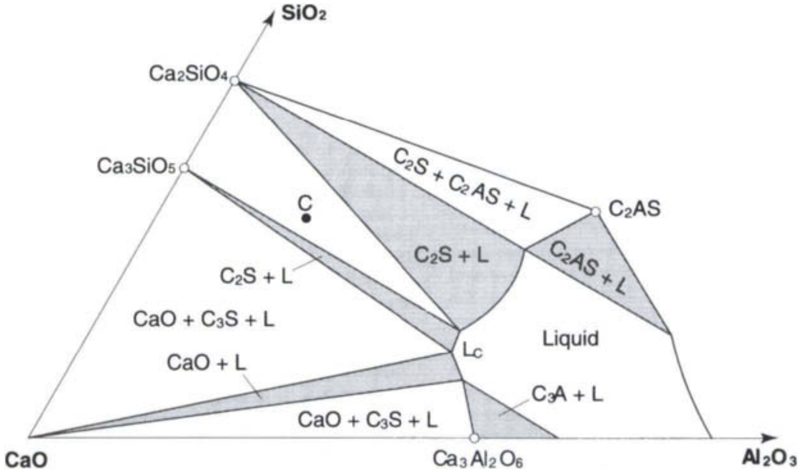


Fig. 3.16 Isothermal section (1500°C) of a portion of the $CaO-Al_2O_3-SiO_2$ system relevant to cement making (adapted from Ref. 49).

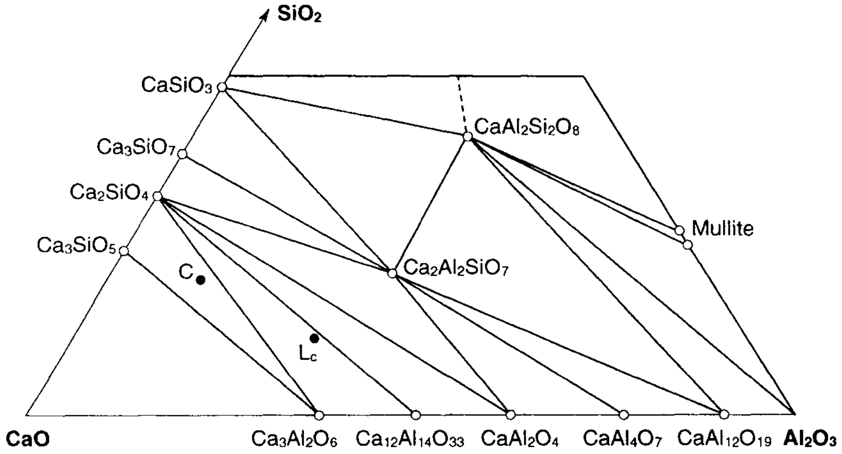


Fig. 3.17 Subsolidus diagram of the portion of the $CaO-Al_2O_3-SiO_2$ system shown in Figure 3.16 (adapted from Ref. 49).

The system $CaO-Al_2O_3-Fe_2O_3$

In this system the phase of most significance to Portland and aluminous cements is brownmillerite, the only ternary phase in the system. It is considered to have the composition $Ca_2(Al_xFe_{1-x})_2O_5$ where x is between 0.48 and 0.7; if CaO is also present, x is fixed at 0.48,[50,51] giving a composition close to C_4AF. This phase is commonly known as ferrite, which in real cements contains a number of other ions in solid solution. Solid solution formation is not restricted to this phase as Figure 3.18 shows. Fe^{3+} also dissolves in C_3A, $C_{12}A_7$ and CA up to levels of about 4.5 per cent at 1325°C, expressed as Fe_2O_3. This is shown by the hatched lines.

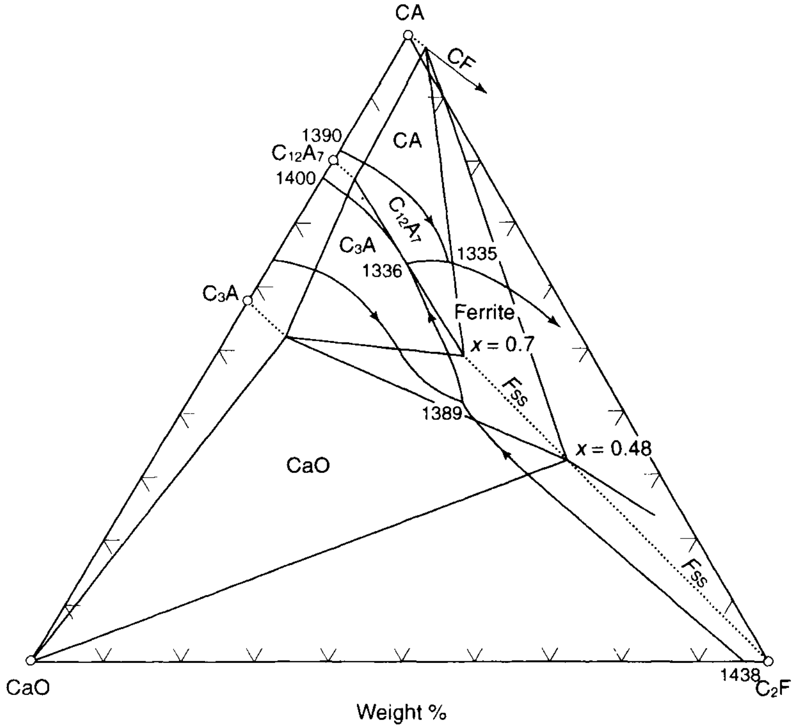


Fig. 3.18 The system $CaO–Al_2O_3–Fe_2O_3$ (source: Ref. 54). Solid solutions are indicated by hatching. F_{SS} refers to solid solution in the ferrite phase.

Some level of uncertainty in this system is evident from the discontinuous representation of certain primary phase field boundaries. Complications arise because the oxidation state of the iron in the more iron-rich regions of the diagram is variable, depending on temperature and oxygen partial pressures.

Quaternary system $CaO–Al_2O_3–Fe_2O_3–SiO_2$

This system (Figure 3.19(*a*)) is of most relevance to cements, with more than 95 per cent of the composition of Portland and aluminous cements coming from compounds containing calcium, aluminium, silicon and iron oxides. Representation of this quaternary system in two dimensions presents certain difficulties owing to its complexity and the unavoidable superimposition of phase fields. Fortunately, it is acceptable and appropriate for only the portion of the $CaO–Al_2O_3–Fe_2O_3–SiO_2$ system relevant to Portland cements to be presented. The less congested $CaO–C_{12}A_7–C_2S–C_4AF$ subsystem is shown in Figure 3.19(*b*), updated from Lea and Parker's studies[52,53] by Taylor (Ref 54, pp. 45–50) and based on modifications by Swayze,[55] Newkirk and Thwaite,[50] Welch and Gutt,[15] Gutt,[56] Majumdar[51] and Sorrentino and Glasser.[57] Invariant points are also identified and the associated data are partially reproduced in Table 3.6.

Note that Figure 3.19(*b*) is not an isothermal diagram and also that certain features of ternary diagrams are transformed in quaternary diagrams to accommodate the geometry

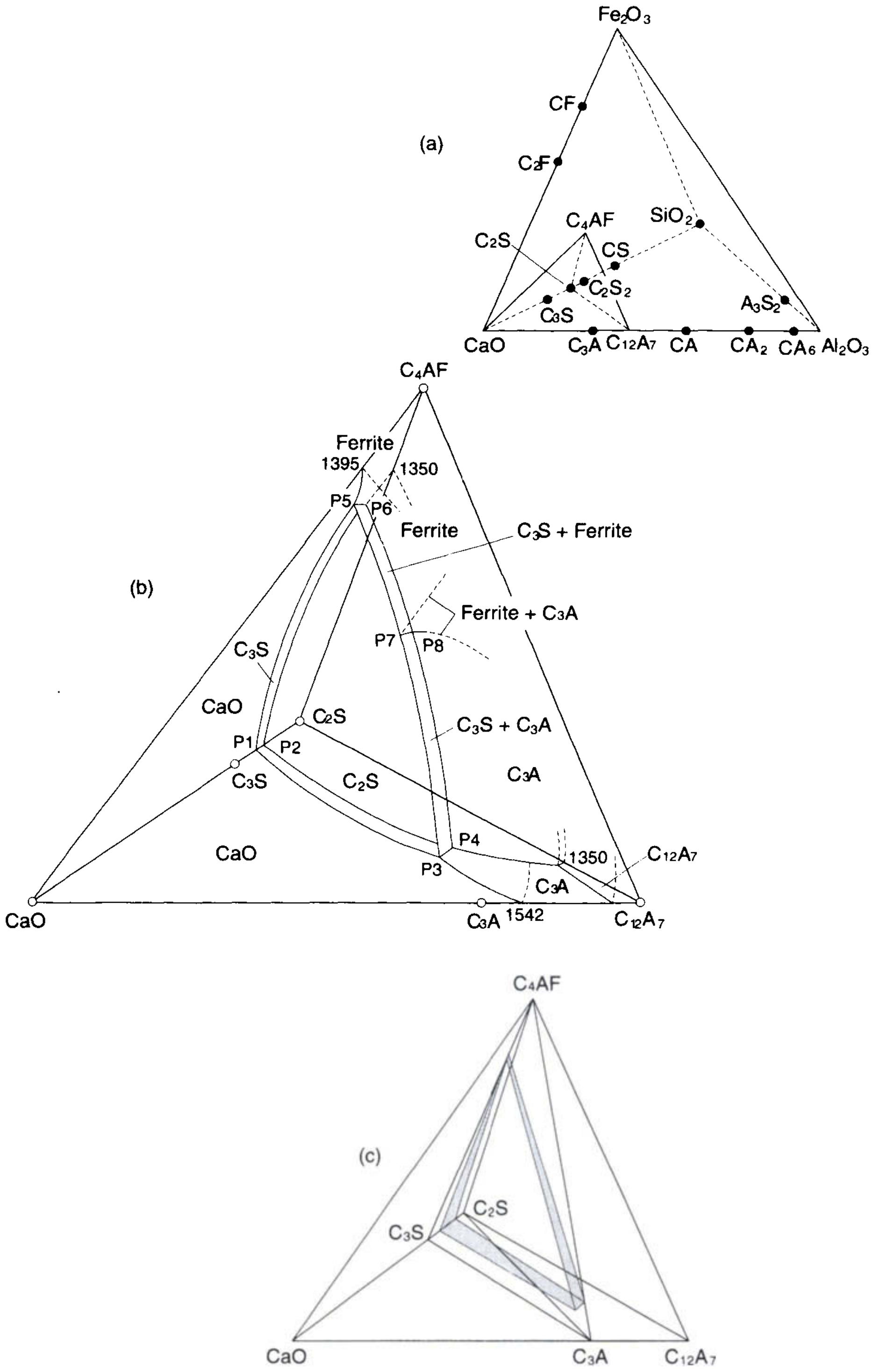


Fig. 3.19 Subsolidus quaternary diagrams of (a) the $CaO–Al_2O_3–SiO_2–Fe_2O_3$ system, (b) the $CaO–C_4AF–C_2S–C_{12}A_7$ subsystem (source: Ref. 54) and (c) the $CaO–C_4AF–C_2S–C_{12}A_7$ subsystem with the primary crystallisation field of C_3S superimposed over the three compatibility tetrahedra.

Table 3.6 Invariant points involving C_3S in the $CaO-Al_2O_3-Fe_2O_3-SiO_2$ system and in the same modified by 5 per cent MgO

Point	Solid phases in addition to C_3S	Liquid composition (weight %) CaO	Al_2O_3	Fe_2O_3	SiO_2	MgO	x in ferrite phase[b]	Type of point[a]	Temp. (°C)
P1	CaO	71.5		–	28.5	–	–	P	2150
P2	C_2S	69.5	–		30.5	–	–	E	2050
P3	$CaO + C_3A$	59.7	32.8	–	7.5	–	–	P	1470
P4	$C_2S + C_3A$	58.5	32.9	–	8.6	–	–	P	1455
P5	CaO + ferrite	52.8	16.2	25.4	5.6	–	0.50	E	1347
P6	C_2S + ferrite	52.4	16.3	25.5	5.8	–	0.50	P	1348
P7	$CaO + C_3A$ + ferrite	55.0	22.7	16.5	5.8	–	0.50	P	1341
P7	$CaO + C_3A$ + ferrite	53.9	21.2	19.1	5.8	–	0.44	P	1342
P7	$CaO + C_3A$ + ferrite + MgO	50.9	22.7	15.8	5.6	<5.0	0.47	P	1305
P8	$C_2S + C_3A$ + ferrite	54.8	22.7	16.5	6.0	–	0.50	?	1338
P8	$C_2S + C_3A$ + ferrite	53.5	22.3	18.2	6.0	–	0.57	P	1338
P8	$C_2S + C_3A$ + ferrite + MgO	50.5	23.9	14.7	5.9	<5.0	0.67	P	1301

Source: Ref. 54, by permission.

[a] P = peritectic; E = eutectic.

[b] x in formula $Ca_2(Al_xFe_{1-x})_2O_5$.

imposed by the additional component, i.e. isotherms and phase field boundaries become surfaces and phase fields become volumes. Figure 3.19(*b*) shows that there are no quaternary phases in this subsystem. Therefore, *at equilibrium*, any mix composition will crystallise four phases, their identity depending on in which subsolidus compatibility tetrahedron the bulk composition lies. The three subsolidus compatibility volumes are schematically shown in Figure 3.19(*c*) with the primary crystallisation field for C_3S superimposed (shaded edges). Since it is desirable when making Portland cement that the C_3S content is optimised and the free lime content of the product minimised, this diagram can therefore be used to provide a guide to achieving the above condition as follows.

The feature highlighted in the diagram (Figure 3.19(*b*)) and shaded in Figure 3.19(*c*) is the primary phase *volume* of C_3S, which is represented by a thin slice intersecting both the $CaO-C_2S-C_4AF$ and the $CaO-C_2S-C_{12}A_7$ boundary faces but not the $CaO-C_{12}A_7-C_4AF$ face. It lies between the primary phase volumes of CaO and C_2S. For bulk compositions lying within this volume, C_3S would be the first phase to crystallise from a melt. Should the bulk composition lie in the CaO or the C_2S primary phase volumes, then CaO or C_2S, respectively, would be the first crystallised phases. Figure 3.19(*c*) shows that the boundary on the CaO-rich side of the primary crystallisation field for C_3S barely intersects the $CaO-C_3S-C_3A-C_4AF$ tetrahedron, so that CaO crystallisation can be avoided if the bulk composition is kept to the CaO-poor side of that boundary.

Using a simultaneous equation approach, Taylor[54] has presented the following expression permitting the calculation of CaO content at any point on the plane defined by connecting C_3S, C_4AF and the invariant point P3 (Figure 3.19(*b*) and Table 3.6):

$$CaO = 2.80\ SiO_2 + 1.18\ Al_2O_3 + 0.65\ Fe_2O_3$$

where CaO, SiO_2, Al_2O_3 and Fe_2O_3 represent weight percentages of oxides. The ratio

$CaO/(2.80\ SiO_2+1.18\ Al_2O_3+0.65\ Fe_2O_3)$ is called the lime saturation factor (LSF). Values greater than unity indicate the likely presence of free lime in the cement clinker. Typical values for Portland cement are in the range 0.92–0.98.[54]

3.4.3 SYSTEMS CONTAINING MINOR COMPONENTS

The systems so far described have been presented as idealised, compositionally simplified cement systems. Raw feed composition and production processes lead to a more complex situation because the equilibria discussed above may be strongly influenced by the presence of minor concentrations of impurities. A prime example is the stabilisation of β-C_2S to ambient conditions as already described. It should be recalled that the four surfaces of a quaternary system each represent a ternary system, the edges of which describe three binary systems. The properties of these binary and ternary systems are therefore expressed within the more complex quaternary system so that information on characteristics such as melting temperatures or phase field boundaries will also be present in the quaternary (or higher order) systems. Within the bulk (below the surfaces) of these four-component diagrams, however, influences of the other components on features of the three- and two-component subsystems can be significant.

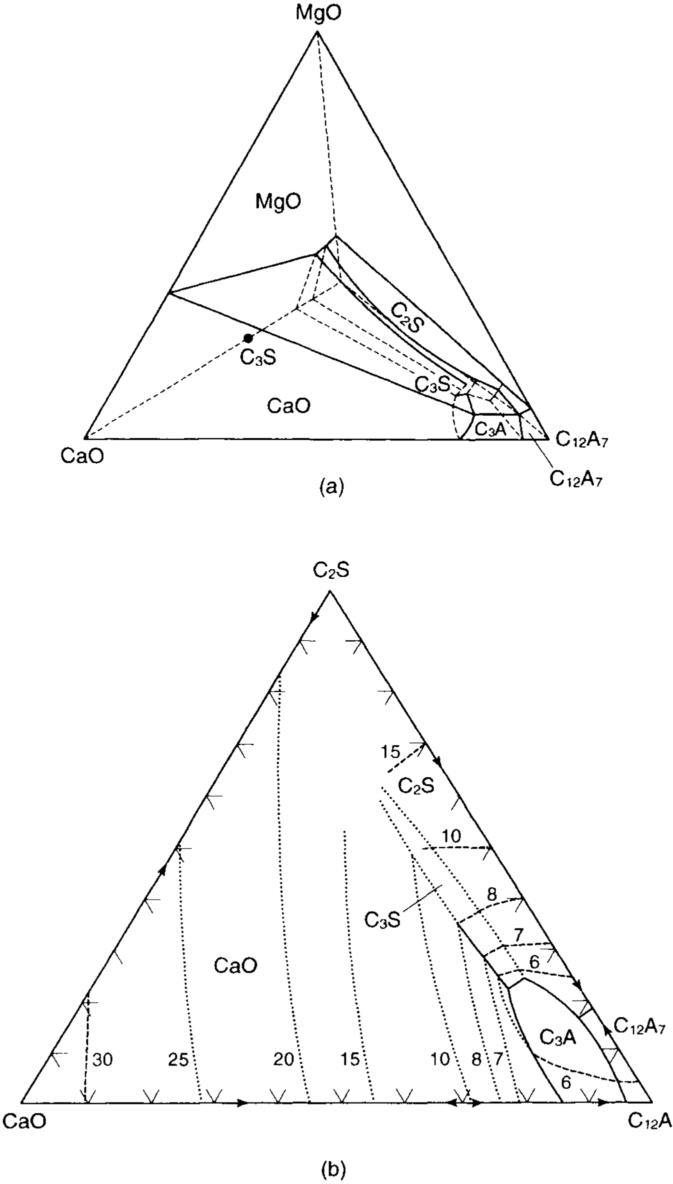
The principle can be illustrated using a ternary system, e.g. CaO–Al_2O_3–SiO_2 system, in which small amounts of Al_2O_3 are dissolved in C_3S. In this case, although Al_2O_3 is a major component of cement, it is a minor constituent of C_3S. It influences the stability of certain otherwise metastable C_3S polymorphs[58] and can be considered to affect the $C_3S \rightarrow C_2S$ transition temperature. The effect on the ternary diagram as compositions move away from the binary face to accommodate Al_2O_3 addition may be visualised by considering the transition temperature at 1250°C (Figure 3.11). As the level of dissolved impurity increases, the transition temperature falls to ambient; C_3S is observed at room temperature in either the M_I, M_{III} or T_{II} polymorphs. The volume of the resulting stability field for C_3S is increased while that for C_2S is decreased thus reflecting the changing stabilities of phases in this part of the system.

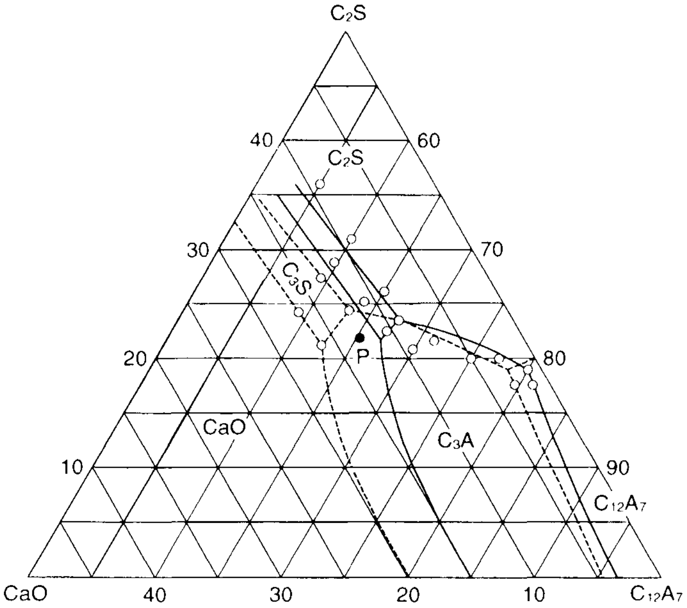
This is an important aspect of phase equilibria in cement systems and the role of minor components is discussed more fully below. While these components may be considered individually, illustrating some important compositional and stability-related properties, the impact of multiple components deserves special consideration (e.g. the competing influences of SO_3 and MgO in the stabilisation of M_I and M_{III} polymorphs of C_3S[59]) and will also be discussed where relevant.

The system CaO–MgO–Al_2O_3–SiO_2

A number of binary, ternary and quaternary phases containing MgO exist in this system but, with the exception of those phases containing magnesium in solid solution, only free MgO (periclase) is important in cement clinker. The distribution of MgO in clinker has significance for the properties and appearance of hydrating cement. Free MgO in cement is undesirable due to slower hydration kinetics and subsequent deleterious expansion in the hardened paste. Phase relations in this system therefore have an important bearing on defining conditions for cement manufacture.

Originally, McMurdie and Insley[60] presented a quaternary diagram for the CaO–C_5A_3–C_2S–MgO system but this was later modified to incorporate $C_{12}A_7$, the revised composition for C_5A_3 (Figure 3.20(*a*)). The very large primary phase volume of MgO suggests that in the CaO-rich portions of the diagram, relatively low MgO contents will be sufficient to saturate the liquid phase and the solid phases (by solid solution formation in, for example, C_3S and β-C_2S) in MgO. McMurdie and Insley determined the position of the critical divariant surface, which marks the limits of the MgO primary phase volume, and found it to be approximately parallel to the CaO–$C_{12}A_7$–C_2S plane. The projection in Figure 3.20(*b*), effectively looking down from the MgO apex, can therefore be used to represent the MgO levels required to saturate the liquid (and the appropriate solids); the saturation MgO content is expressed as contours (not to be





(c)

Fig. 3.20 Equilibrium diagrams for (a) the quaternary subsystem CaO-$C_{12}A_7$ C_2S MgO, (b) a projection of the same subsystem, looking down from the MgO apex, and showing the MgO levels (as contours) required to saturate the liquid with MgO (source: Ref. 20) and (c) an alternative representation showing the effect of 5 per cent MgO (solid lines) on the position of phase field boundaries (adapted from Ref. 60).

confused with isotherms). The figure shows that in the portion of the diagram relevant to cement compositions, less than 6 weight per cent is sufficient to crystallise MgO. Figure 3.20(*c*) alternatively shows the influence of 5 per cent MgO on the positions of the primary phase field boundaries, illustrating the important influence that impurities can have on phase relations in cement systems. In this case it can be seen that a shift in bulk composition may be required to avoid crystallisation of free lime where this would not occur in the MgO-free system, e.g. at point P. Even at 5 per cent, MgO is still observed[61] indicating that bulk compositions must contain lower MgO contents to limit free MgO in the cement product.

Effect of MgO on the CaO–Al_2O_3–Fe_2O_3 SiO_2 system

The influence of MgO on the CaO–Al_2O_3–SiO_2 system discussed above extends into the CaO–Al_2O_3–Fe_2O_3–SiO_2 system where crystallisation temperatures and compositions of the liquid and ferrite phase (which can contain appreciable MgO) are affected. Swayze[55] presented the 5 per cent MgO isopleth of this system and modifications to this diagram[54] have led to the data presented in Table 3.6 on invariant points involving MgO. In addition to changes in the positions of invariant points, the larger effect from MgO comes from solid solution formation which alters the properties, in particular, of the ferrite phase.

Solid solution is a general phenomenon in cement phases, often causing shifts in the positions of fields of stability, as has been seen above, but in the case of ferrite the substitution of Mg^{2+} for Fe^{3+} causes oxygen vacancies, the resulting electronic transitions producing a darkening of the colour.[62]

Effect of SO_3 and alkalis (Na_2O and K_2O)

The bulk of the oxide components passing through a cement kiln are essentially non-volatile. However, some have appreciable vapour pressures at clinkering temperatures: this leads to vaporisation–condensation cycles which have important implications for clinker phase compositions. Amongst the important volatile components in the kiln is sulfur, introduced either in the raw feed or in the fuel. The presence of free oxygen in the kiln favours oxidation of sulfur (although reduced species may also be present) and an equilibrium between SO_3 and SO_2 is readily established. Some of this is absorbed by free CaO to give a $CaSO_4$ content in the clinker. Alkalis also undergo evaporation–condensation in the kiln and it is suspected that the transport of sulfur is enhanced by the presence of alkalis. In most clinkers the K_2O and Na_2O are in excess of the equivalent amount of SO_3, and K_2O is usually more abundant than Na_2O.[63]

The $CaO–Al_2O_3–SiO_2–SO_3$ system holds significant interest in relation to the synthesis of calcium sulfoaluminate (CSA) cement. This represents an important and potentially low-temperature cement with rapid setting and good strength development. In Portland cements, poorly hydraulic calcium sulfosilicate, $C_5S_2\bar{S}$, may be observed under abnormal conditions (i.e. in kiln rings) and we have already noted that SO_3, as a minor component, can influence the polymorphism of alite. High levels of SO_3 can completely suppress C_3S formation[64] but this can be reversed by the presence of fluoride (0.5 per cent as CaF_2). This will stabilise C_3S in a system containing up to 10 per cent SO_3.

Phase equilibria in part of the system $CaO–Al_2O_3–SiO_2–Fe_2O_3–MgO–CaSO_4–K_2SO_4$ were studied by Kaprâlik *et al.*[65] in relation to calcium sulfoaluminate clinker manufacture. Three seven-phase subsolidus (950°C) assemblages were identified in the relevant part of this system as follows:

- $MgO–CaO–C\bar{S}–C_4AF–C_5S_2\bar{S}–C_4A_3\bar{S}–C_2K\bar{S}_3$
- $MgO–CaO–C_3A–C_4AF–C_5S_2\bar{S}–C_4A_3\bar{S}–C_2K\bar{S}_3$
- $MgO–C_2S–C_3A–C_4AF–C_5S_2\bar{S}–C_4A_3\bar{S}–C_2K\bar{S}_3$

The persistence of MgO indicated that it is unreactive in this system. In oxidising conditions, Fe_2O_3 is taken into C_4AF and small amounts of alkali can cause significant changes in the phase composition of the sulfate phases $C_4A_3\bar{S}$ and $C_5S_2\bar{S}$. Such compositional effects are illustrated by the relative stabilities of Ca-langbeinite, $C_2K\bar{S}_3$ and $C_4A_3\bar{S}$ which depend on $K_2O/CaSO_4$ ratios.

Phosphates

The phosphate contents of Portland cement clinkers are normally low (around 0.2 per cent as P_2O_5) although higher levels may be experienced where phosphate is present in significant levels in the raw materials. Figure 3.21[66] shows that up to about 0.5 weight per cent (as P_2O_5) can be accommodated in the structure of C_3S (giving C_3S'' on the diagram) before it decomposes at higher phosphate levels to give a solid solution between C_2S and phosphate, and free lime. These products have less satisfactory cementing characteristics. While previous work[67] had indicated complete solubility between C_2S

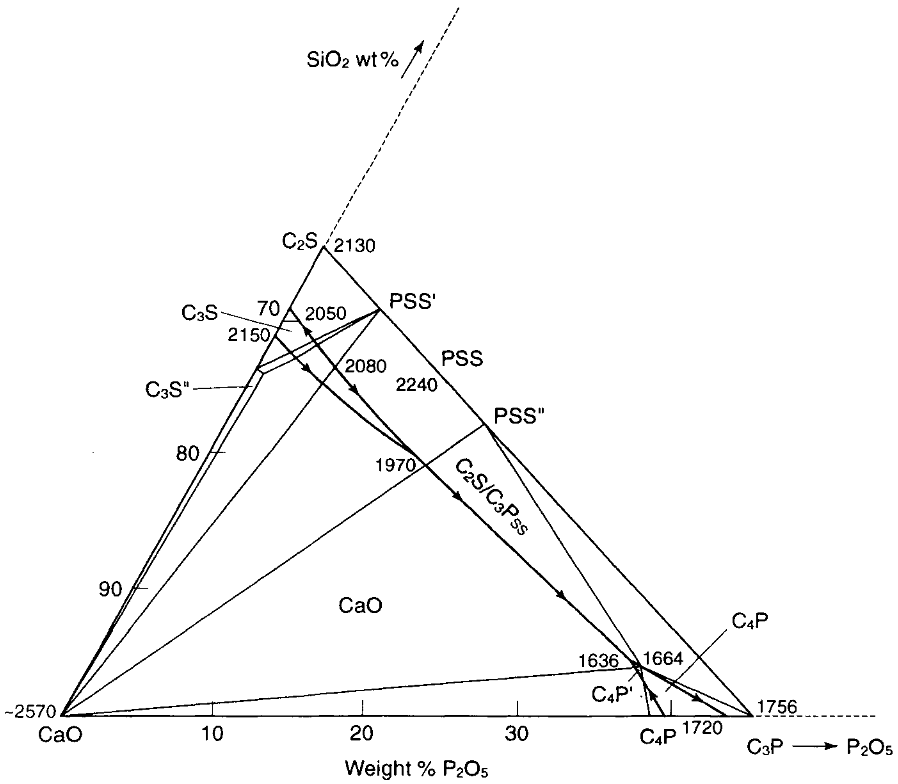


Fig. 3.21 Phase diagram of the system CaO–C_2S–C_3P (source: Ref. 66). ━ = phase boundary; — = compatibility join at 1500°C; PSS = phosphate solid solution at maximum liquidus temperature; PSS′ = limiting phosphate solid solution at 1500°C; PSS″ = limiting phosphate solid solution at 1500°C; C_3S'' = C_3S solid solution with Ca^{2+} and PO_4^{3-} ions; C_4P' solid solution with Ca^{2+} and silicate ions.

and C_3P at 1500°C, later work showed the presence of a miscibility gap, limited by positions PSS′ and PSS″ on the figure. The phase diagram shows a number of other solid solutions in addition to the parent phases, C_3S, C_3P, C_4P and C_2S. It can be seen that although the primary crystallisation field for C_3S extends to 13 weight per cent P_2O_5, it becomes increasingly narrow towards its maximum limit so that the compositional constraints for the crystallisation of C_3S (or C_3S'') become more stringent. Also, it should be noted that the nearer the bulk composition tends towards the limit of C_3S stability, the less C_3S can be expected in the clinker. This situation is normally avoided by careful mix proportioning. Consequently, other features such as those appearing in the C_4P region of the diagram are less relevant in cement manufacture.

The presence of fluoride in phosphatic limestones can have an important influence on the phase equilibria discussed above because coupled substitutions of phosphate and fluoride can occur in C_3S. Consideration of the CaO–P_2O_5–CaF_2 system would show that fluorapatite [3(C_3P)·CaF_2] forms a compatibility with C_3S with up to 2 mole per cent of fluorapatite being dissolved in the C_3S structure at 1905°C. This corresponds to a C_3S composition having up to 1.16 per cent P_2O_5.

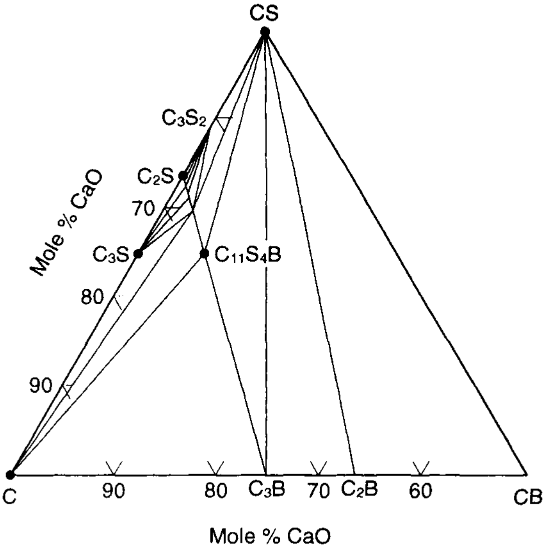


Fig. 3.22 Subsolidus phase relations for a portion of the $CaO–SiO_2–B_2O_3$ ternary system (adapted from Ref. 69).

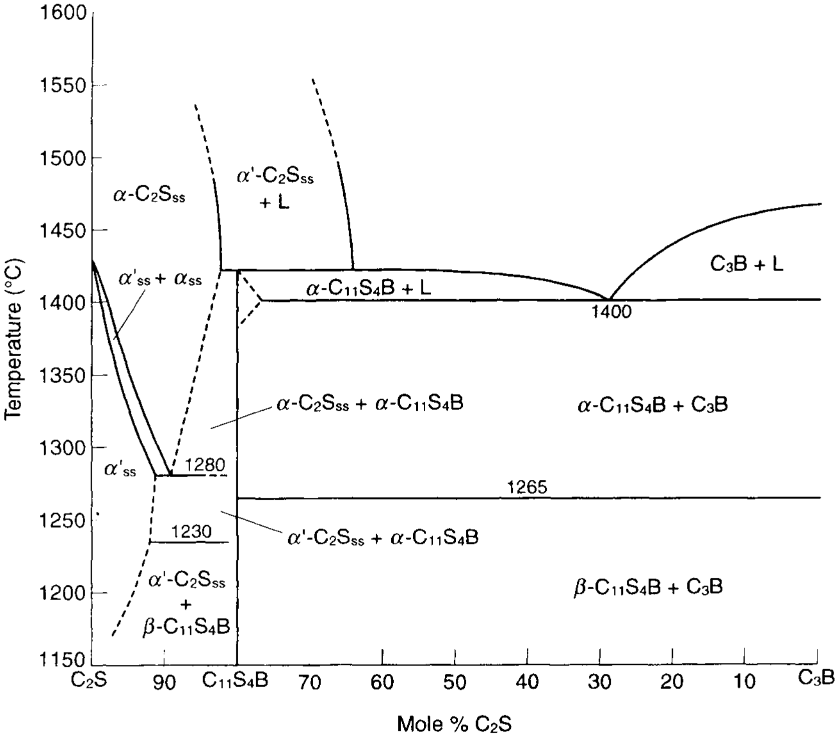


Fig. 3.23 The pseudo-binary system $C_2S–C_3B$ (adapted from Ref. 69).

Borates

Calcium borates have been shown to be useful fluxing agents in cement manufacture because they lower the viscosity and surface tension of the melt. Their influence on the stabilities and compositions of the calcium silicates can be estimated from the phase diagram for the ternary system $CaO–SiO_2–B_2O_3$. This system was first studied by Flint and Wells[68] and the subsolidus phase diagram, later modified by Fletcher and Glasser,[69] is shown in Figure 3.22. The diagram shows that borate is dissolved only in C_2S, the nature of the solution being further illustrated by considering the $C_2S–C_3B$ binary join (Figure 3.23). This diagram shows the existence of the binary phase $C_{11}S_4B$, and the solid solution of boric oxide in C_2S polymorphs in the temperature range 1150–1500°C is illustrated. These solutions give compositions of the general formula $Ca_{2-0.5x}(SiO_4)_{1-x}(BO_3)_x$, where the value of x defines the polymorph which is stabilised (i.e. γ, β, α or α').

Titanium oxide

The titanium oxide content of Portland cements (0.2–0.3 per cent) is primarily associated with the C_4AF phase, but in aluminous cements, where TiO_2 contents are

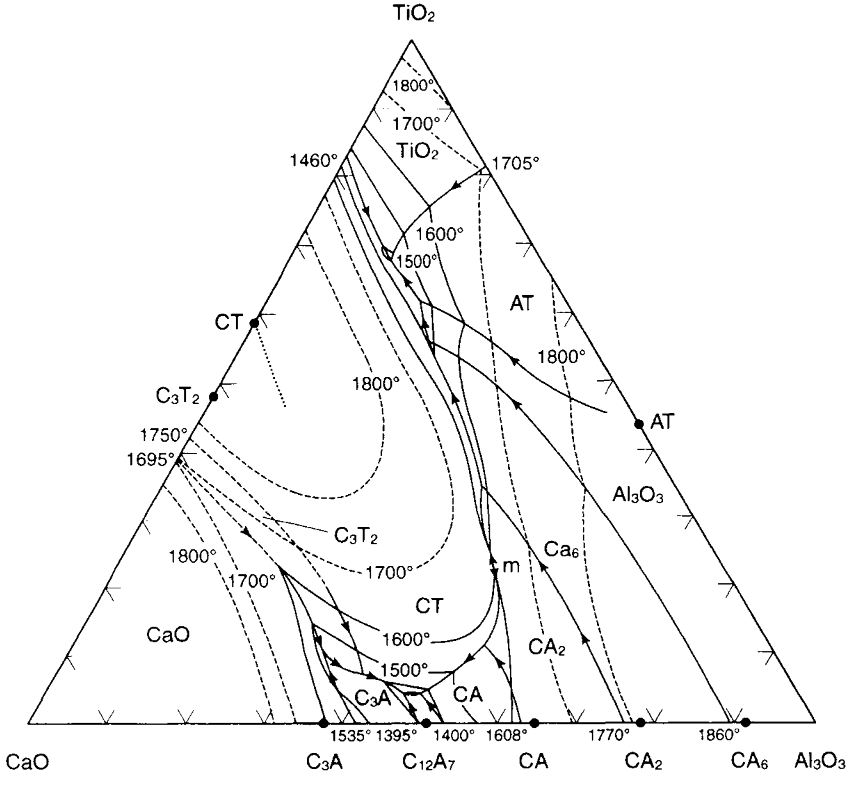


Fig. 3.24 Equilibrium phase diagram of the system $CaO–Al_2O_3–TiO_2$ (source: Ref. 70).

usually higher (1.5–2.0 per cent), the high solubility of titanium in calcium aluminate liquids leads to the crystallisation of a perovskite phase (ideally $CaTiO_3$). The perovskite primary phase field extends to within a few weight per cent of the CaO–Al_2O_3 binary edge of the CaO–Al_2O_3–TiO_2 system[70] (Figure 3.24) in the vicinity of the $C_{12}A_7$ primary phase field. The diagram also shows that the perovskite phase can tolerate approximately 10 weight per cent of Al_2O_3. The substituted perovskite is compatible with most of the calcium aluminates at subsolidus temperatures and may appear in Portland cements with more than a few per cent TiO_2. This phase cannot however be distinguished by XRD from C_3A.

Fluorides and fluorosilicates

Fluoride may be present due to the raw materials or as a deliberate addition as a fluxing agent. It can have a strong accelerating influence on the formation of C_3S and C_2S and has a deleterious effect on the strength development of their hydrates. It also stabilises α- and α'-C_2S, but only in the presence of C_3S; this is attributed to the liberation of free lime due to the substitution of F^- for O^{2-}[71] C_3S itself undergoes solid solution formation with CaF_2, with about 0.74 per cent (as F^-) being dissolved. However, XRD shows that the resulting solid solution has the structure of alite. The relevant portion of the CaO–SiO_2–CaF_2 system, modified from the version of Gutt and Osborne,[72] is shown in Figure 3.25 and features C_3S, C_2S and the ternary phases $2C_2S{\cdot}CaF_2$ and $Ca_{5.5}Si_2O_9F$ (equivalent to $C_{10}S_4{\cdot}CaF_2$). The latter was formerly described as $3C_3S{\cdot}CaF_2$ but Perez-Mendez *et al.*[73,74] revised this composition on the basis of structural determination and proposed the general formula $Ca_{6-0.5x}Si_2O_{10-x}F_x$. However, levels of fluoride in single crystals were found to be much lower than previously supposed. They also suspected that the phase may indeed be metastable.

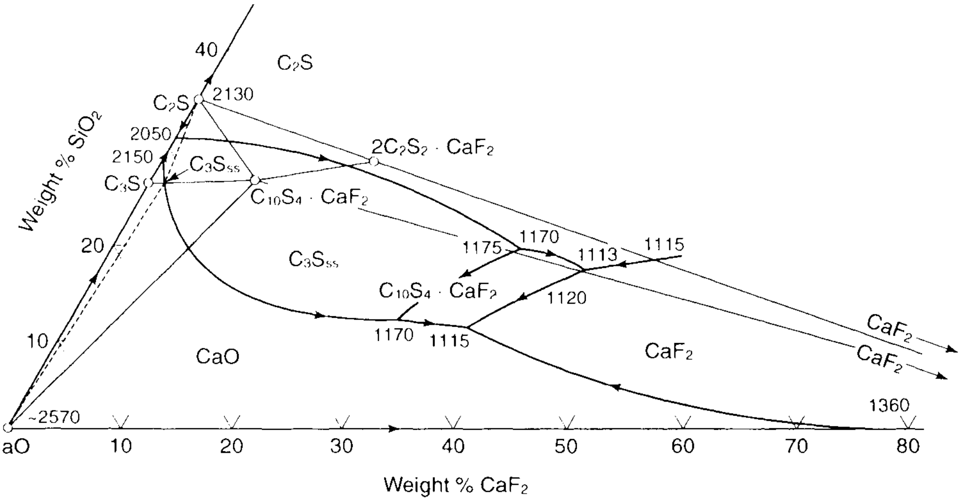


Fig. 3.25 The portion of the CaO–SiO_2–CaF_2 system relevant to Portland cement (adapted from Ref. 72).

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4

The Constitution and Specification of Portland Cements

C. David Lawrence

4.1 Introduction

The British Standard BS 6100 (*Building and civil engineering terms*, Part 6. Section 6.1, Binders: 1984) uses the term 'binder' to cover all building cements and plasters. A hydraulic binder is a finely ground substance which sets and gradually hardens when formed into a paste with a limited quantity of water, due to chemical reactions between the cement and the water to form a stone-like material. The cement continues to harden under water. An active hydraulic binder is a cement that hardens without the addition of an activator, such as lime. Portland cement is the most commonly employed active hydraulic binder; the name 'Portland cement' was first patented in 1824 by Aspdin, although his product was formed at a much lower temperature than the modern cement and its main component was dicalcium silicate rather than tricalcium silicate. The resemblance of the hardened product to Portland stone is said to be the origin of the name for this cement.

Hydraulic binders are normally employed with aggregates (natural sand and gravel or crushed rock) to form workable material (fresh concrete and mortar), which may be poured into moulds, compacted by vibration and then allowed to harden before demoulding. Building blocks may be formed by a combination of pressure and vibration, in which case a drier mix is employed which is self supporting immediately after pressing. Cement grout, composed of cement–water paste without sand additions, is employed to encapsulate prestressed steel wires in preformed ducts in order to prevent steel corrosion. They are also used in other situations, for example, to stabilise poor natural rock formations and to fill joints in structures. They may contain fine aggregate in the mix in order to reduce drying shrinkage and limit temperature rises due to the exothermic nature of cement hydration. For masonry mortars used to form bonds between bricks and building blocks, a cement–sand or cement–hydrated lime–sand mix is employed having a high water/cement ratio. Special masonry cements are available, containing added clay or finely ground limestone to allow high water/cement ratios to be employed without resulting in bleeding. Water-resisting renders for existing walls require a somewhat different mix of Portland cement–hydrated lime–graded sand, having a coarser sand and lower water/cement ratio.

The cementing action of Portland cement derives largely from the chemical reaction of components tri- and dicalcium silicate with water (hydration). The hydration products from the reacting cement gradually fill the spaces between aggregate particles to give a continuous matrix, thereby producing a relatively impermeable composite which is strong in compression. The calcium silicate hydration products have limited solubilities in water and this forms the basis of their durability. A fundamental property of hydraulic cements is that they set and generate strong materials when stored under water. Compressive strength is used as a means of categorising cement quality. The European Standard describes test methods which have been adopted:

- BS EN 196-1: 1995. *Determination of strength.*
- BS EN 196-3: 1995. *Determination of setting time and soundness.*

The initial setting time of a cement is determined by monitoring the repeated penetration of a 1.13 mm diameter needle into a fresh cement paste pat of standard consistence (using the Vicat apparatus); failure to penetrate beyond a chosen point is taken as the time of initial setting. A cement paste of standard consistence is one that allows a 10 mm diameter plunger (loaded to a standard degree) to penetrate a standard depth into the paste surface. The composition of the paste (water content) is modified until the required degree of resistance is obtained (ASTM C 191-92, ASTM C 204-94, BS EN 196-3: 1995) in arriving at a standard consistence.

Although water in excess of that required for complete hydration of the cement may be employed in the concrete mix, in order to make the fresh concrete sufficiently workable for proper placing and compaction, too large an excess must be avoided since ultimate strength is inversely related to the overall water/cement ratio. An external supply of liquid water must remain available to the cement after setting, during the initial hardening period, if the full potential of the cement is to be realised, since the hydration reaction is virtually stopped if relative humidities fall below about 95 per cent.

The importance of packing density in hydraulic cement systems is well documented: the greater the density of packing, the greater the strength after hydration. In the extreme, a high-pressure (e.g. 300 MPa) moulding of unhydrated Portland cement produces hardened cement of very low porosity and very high strength after hydration: at an equivalent water/cement ratio of about 0.1, compressive strengths over 450 MPa have been reported. A substantial increase in solid volume occurs during the hydration of Portland cement, but these products are stable under water in spite of containing a large fraction of unhydrated Portland cement. This observation illustrates the virtual impermeability of the hydration product towards ingress of additional water, which would allow hydration to continue and result in uncontrolled expansion.

The common sources of lime employed in the manufacture of Portland cement are limestone and chalk (calcium carbonate), while the chief sources of silica are clays or shales. The latter are aluminium silicates which also contain some combined iron, and free silica as quartz. When a mix of these materials in the proportions of 3 4 parts of carbonate to 1 of aluminium silicate, depending on their composition, is heated to about 1450°C, partial melting and chemical combination occur. The resulting clinker is made up of two calcium silicates (Ca_2SiO_4 and Ca_3SiO_5), which comprise about 80 per cent of the total mass, together with tricalcium aluminate ($Ca_3Al_2O_6$) and aluminoferrite solid solution ($xCa_2Al_2O_5 \cdot yCa_2Fe_2O_5$). The composition of the aluminoferrite solid solution in Portland cement is commonly assumed to be $Ca_4Al_2O_5 \cdot Fe_2O_5$, i.e. x/y is assumed to be close to unity.

The ratios of oxygen to the other elements in the clinker thus produced are those found in the common oxides, so that it is usual to consider a composition as if made up of oxides. Iron is assumed to be present in the hexavalent state, as Fe_2O_3. Lower valency iron compounds can be present if the kiln is run under reducing conditions. This situation is normally avoided as it can lead to a reduction in the quantity of alite formed; however, the production of white Portland cement sometimes requires reducing conditions in order to achieve the required degree of whiteness.

By using the cement chemist's abbreviations ($C \equiv CaO$, $S \equiv SiO_2$, $A \equiv Al_2O_3$, $F \equiv Fe_2O_3$, $\overline{F} \equiv CaF_2$, $\overline{S} \equiv SO_3$) it is possible to simplify the writing of formulae for these compounds, since they may be derived by the simple addition of oxide formulae. For example, the formation of tricalcium silicate may be represented by:

$$3CaO + SiO_2 = Ca_3SiO_5 \tag{4.1}$$

or by

$$3C + S = C_3S \tag{4.2}$$

The other principal compounds present in ordinary Portland cement clinker become C_2S, C_3A and C_4AF.

Minor elements in the as-dug raw materials, such as sodium, potassium, magnesium, manganese and titanium, may enter into solid solution in the crystal structures of the major phases. The C_3S and C_2S in industrial clinker differs somewhat from the simple compositions implied by these formulae, and they are often referred to as alite and belite, respectively, names originating from the early examinations of polished sections of clinker under the optical microscope. The crystal structures for these phases may be equilibrium forms at high temperatures that have been stabilised by the presence of impurities (depending on the rate of quenching employed).

Portland cement is produced from clinker by grinding with approximately 5 per cent natural gypsum (usually composed of a mixture of calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$, and anhydrite, $CaSO_4$), in order to regulate the setting time of the cement. Portland cement is ground until more than 90 per cent passes through a 90 μm sieve. The total sulfate level, expressed as the equivalent percentage of sulfur trioxide (SO_3), is limited by the cement standards, including any sulfate already present in the clinker (mostly as alkali metal sulfate).

The free lime in Portland cement, as CaO, must be limited or unsoundness, i.e. expansion, may result during hydration. Important minor components in Portland cement are alkali metal oxides, some of which enter the crystal structures of all the phases, but the majority is present as readily soluble sulfate or hydroxide.

4.2 Chemical analysis of Portland cements

Procedures for the chemical analysis of cements are given in several Standards

• BS EN 196-7: 1992.	Methods of taking and preparing samples of cement.
• BS EN 196-2: 1995.	Chemical analysis of cement.
• BS EN 196-21: 1992.	Determination of the chloride, carbon dioxide and alkali content of cement.
• ASTM C 114-88.	Chemical analysis of hydraulic cement.

Considerable effort has been devoted to the development of more rapid and improved schemes of analytical procedures. Titrimetric methods for estimating the main constituents of cements are becoming almost universally employed. Most of these methods are based on the use of the complexing reagent EDTA (ethylenediaminetetraacetic acid, usually used as the disodium salt). This reagent has the property of forming soluble octahedral complexes with many metal ions, selectively being achieved through the control of pH and by masking interfering elements by suitable reagents. CaO, MgO, Al_2O_3 and Fe_2O_3 are determined using this reagent at different pH values.[1] Silica is determined in the latest British Standard by the traditional method of treating with hot strong HCl containing NH_4Cl to dissolve other species, followed by filtration and ignition. Sulfate is determined by the well-tried technique of precipitation with acidified $BaCl_2$ solution, and weighing the dried precipitate. Flame photometry is applied to the determination of alkali metals (BS EN 196-21: 1996.), by measuring the intensities of the visible light emission lines at radiation wavelengths of 589 and 768 nm, and reading off the concentrations from calibration plots. Chloride content is determined by reacting the digested sample with silver nitrate solution and back titrating with ammonium thiocyanate. Carbon dioxide is determined by releasing from the cement with concentrated phosphoric or sulfuric acid and entraining in a gas stream of nitrogen through absorption trains of alkali followed by drying tubes of $Mg(ClO_4)_2$.

Spectrophotometric methods are now widely employed for the estimation of the minor elements in cement,[2,3] particularly TiO_2, Mn_2O_3 and P_2O_5. In many rapid schemes of analysis, SiO_2 is determined as the yellow silicomolybdate, or sometimes after reduction to molybdenum blue. Aluminium and iron can also be determined by spectrophotometry. Flame photometry[4,5] is virtually the only method now used to estimate the alkalis in cement; provided precautions are taken to eliminate interferences from other elements (particularly calcium), only simple equipment is required for these determinations. With a more sensitive spectrophotometer flame, estimations can be extended to strontium[6] and magnesium.[7] Manganese can also be determined by this method.[8]

The technique of atomic absorption spectrophotometry makes possible the accurate determination of the major elements present in cement. In this technique, a cement solution is atomised in a flame, and the energy absorbed from a spectral lamp for each element to be determined is measured in turn. Very little chemical separation is required. Elements which have been determined in cement by this method include Si, Al, Fe, Ti, Mn, Ca, Mg, Sr, Na, K and Li.[9] Most of the newer rapid methods for the analysis of cement include provision for the estimation of SO_3, usually titrimetrically or turbimetrically; the latter method is widely used in cement works practice. Fluorine is usually separated by steam distillation or pyrohydrolysis, and then estimated titrimetrically or colorimetrically.[10,11] Spectrographic analysis is particularly useful for the determination of elements present in cement in only small amounts, but this technique has also been employed for the major elements with an accuracy better than 4 per cent.

4.2.1 X-RAY FLUORESCENCE SPECTROSCOPY

X-ray fluorescence spectrometry is a non-destructive instrumental method of qualitatitive and quantitative analysis for chemical elements based on measurement of the intensities of their X-ray spectral lines emitted by secondary excitation. The primary beam taken from an X-ray tube irradiates the specimens, exciting each chemical element to emit secondary spectral lines having wavelengths characteristic of that element and intensities related to its concentration. The secondary radiation is analysed by means of a crystal rotated in the plane of the radiation and its intensity measured using a detector.

It is proposed to include this method of analysis in the UK alternative procedures to parts of BS EN 196-2. The method is intended for the determination of the total major oxides of BS ENV 197 Type CEM 1 cement. X-ray fluorescence spectroscopy is being increasingly employed, particularly where large numbers of cement analyses are required, including cement works control.[12,13]

In order to avoid mineralogical and particle size effects, the cement sample is fused with a mixture of lithium tetraborate ($Li_2B_4O_7$) and lanthanum oxide. The resultant melt is cast to form a glass bead suitable for introduction into an X-ray fluorescence spectrometer. The intensities of the fluorescent X-rays of the required elements are measured and the chemical composition of the cement is determined by reference to previously established calibrations. These have been selected to cover narrow compositional ranges so that, together with the use of lanthanum oxide as a heavy absorber, matrix effects are minimised. The cement sample is ground to pass a 150 µm sieve after any metallic iron has been removed by the use of a magnet. A 1 g sample is mixed thoroughly with 9 g of freshly ignited lithium tetraborate and 1 g of freshly ignited lanthanum oxide. The dry powder is transferred to a 50 mL fusion dish made from an alloy of platinum (5 per cent gold) and placed in a furnace at 1100°C for 10 min together with the mould. Casting moulds made from the same alloy are designed to give circular beads of a diameter within the range 35–40 mm, and thickness exceeding the critical depth for the element lines used in the analysis. The melt is transferred to the mould and allowed to cool, and the bead is then removed from the mould. The flat base of the bead is presented to the X-ray beam for analysis.

4.2.2 *TYPICAL AND AVERAGE COMPOSITIONS OF PORTLAND CEMENTS*

A view of the composition of Portland cements, including data from a number of countries throughout the world, is obtained from the plots of frequency of distribution of chemical composition given in Figures 4.1–4.3.[14] Data are expressed as average, minimum and maximum values for a wider range of chemical parameters in Tables 4.1 and 4.2. The tables include minor and trace elements.

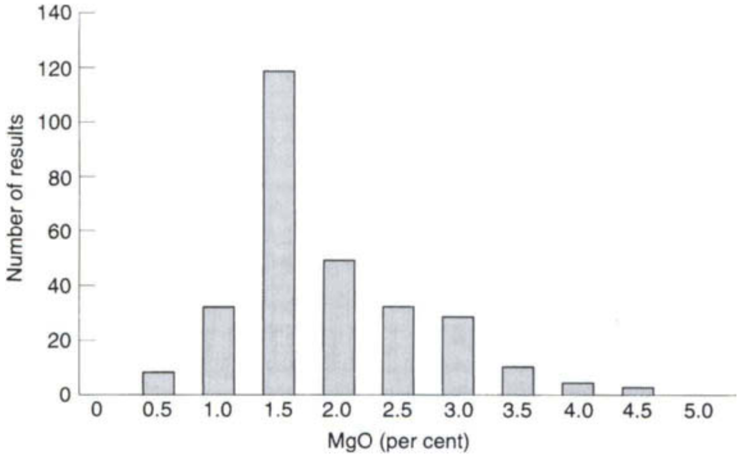

Fig. 4.1 Frequency distribution of percentage MgO in Portland cements.

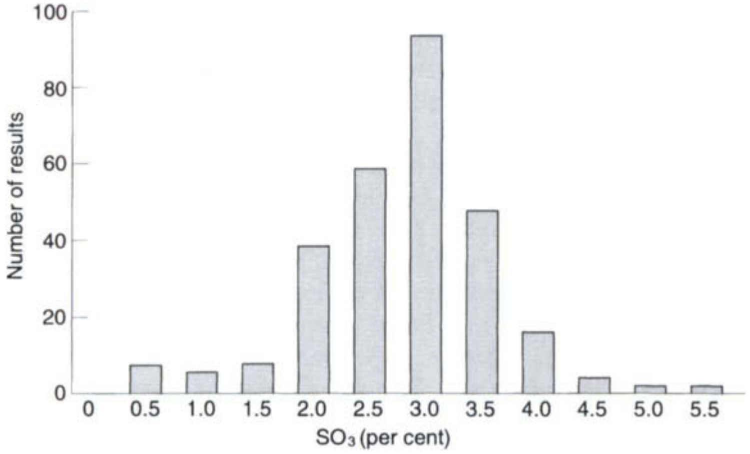

Fig. 4.2 Frequency distribution of percentage SO_3 in Portland cements.

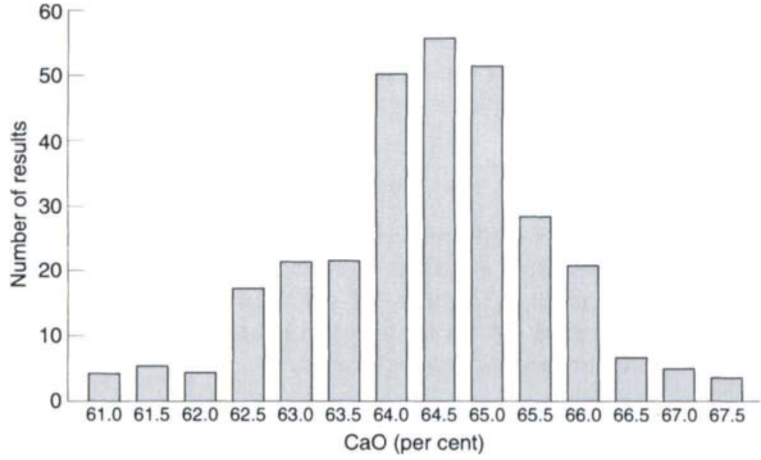

Fig. 4.3 Frequency distribution of percentage CaO in Portland cements.

4.3 Alkali content

Portland cement concretes are naturally alkaline because Portland cement reacts with water to produce solutions which are saturated with $Ca(OH)_2$, but there are also present in Portland cement small and variable percentages of Na_2O and K_2O as minor components in the cement minerals or as sulfates, which readily form NaOH and KOH solutions as the cement aluminate and ferrite hydrate to absorb the sulfate ion. These highly alkaline solutions are able to react with certain aggregates which contain a reactive form of silica, to give a gel which is able to absorb water and swell, thus generating a pressure which can crack the concrete (alkali–silica reaction, or ASR). The quantity of gel thus formed may be limited either by the alkali or by the reactive silica contents of the concrete. In some circumstances the gel may swell and cause cracking if extra water

Table 4.1 Summary of chemical data for a selection of Portland cements

Component	Minimum	Average	Maximum	Number of samples
SiO_2 (%)	18.4	21.02	24.50	284
Fe_2O_3 (%)	0.16	2.85	5.78	284
Al_2O_3 (%)	3.10	5.04	7.56	284
CaO (%)	58.10	64.18	68.00	284
MgO (%)	0.02	1.67	7.10	285
SO_3 (%)	0	2.58	5.35	280
Na_2O (%)	0	0.24	0.78	263
K_2O (%)	0.04	0.70	1.66	280
Equivalent alkali (%)	0.03	0.68	1.24	280
Free lime (%)	0.03	1.243	3.68	132
Chloride (%)	0	0.016	0.047	15
Sr(mg/kg)	0	532	19195	191
Zn(mg/kg)	0	22	321	191
Ti(mg/kg)	0	1059	4196	288
P(mg/kg)	0	389	2139	288
Mn(mg/kg)	0	315	2366	288

Table 4.2 Trace metal contents of a selection of Portland cements (mg/kg)

Trace metal	Minimum	Average	Maximum	Number of samples
Mercury	0.001	0.014	0.039	21
Selenium	0.62	–	2.23	6
Thallium	0.01	1.08	2.68	32
Cadmium	0.03	0.34	1.12	42
Lead	1	12	75	82
Antimony	0.7	–	4.0	2
Silver	6.75	9.20	19.90	93
Arsenic	5	19	71	54
Nickel	10	31	129	85
Barium	91	280	1402	94
Beryllium	0.32	1.13	3.05	93
Chromium	25	76	422	94

becomes available at a later date. Other forms of alkali–aggregate reaction have been identified.

Alkali–silica reaction has been observed in the UK and has been widely reported in other parts of the world. It takes the form of an overall expansion of the concrete, with the surface layers put into tension, giving rise to tensile cracking where the surface layers fail to expand to the same extent. Exudation of a syrupy liquid or gel takes place at the surface of the concrete. This gel can be observed to fill the pores and microcracks within the structure. An attempt has been made to use the crack pattern visible on sawn sections to diagnose causes of failure.[115] Examples of crack patterns for delayed ettringite expansion, thermal expansion of the aggregate, drying shrinkage, etc., are presented, as well as those for alkali–silica reaction.

The presence of alkali silica gel is not in itself sufficient evidence that any observed expansion has been caused by ASR. Usually, substantial quantities of gel are required before disruption takes place. It should be noted that expansions resulting from the occurrence of alkali–reaction can be readily reduced by the inclusion of a small percentage of reinforcement steel, the expansive force generated by the formation of alkali silica gel being relatively small. It was reported[15] that the application of an external compressive stress of 4 MPa was sufficient to prevent expansion and the inclusion of 0.5 per cent reinforcement steel reduced expansion by approximately 55 per cent. In full-size reinforcement concrete members, cracking is observed to follow the direction of the main reinforcement bars.

4.3.1 PORE FLUID COMPOSITION

It is believed that ASR usually occurs where the alkalis in the cement are readily soluble in the associated aqueous phase, and much work has been published on the composition of the pore fluid within hardened cement pastes and mortars.

Early work[16] using extracts of pore solution from fresh pastes before setting, indicated that NaOH and KOH were the major components after about 1 day of hydration, rather than $Ca(OH)_2$, and that silicate and aluminate concentrations were extremely low. The concentrations of sulfate fell rapidly in the first minutes, from supersaturation with respect to $CaSO_4 \cdot 2H_2O$, then remained stable at the saturation level for $CaSO_4 \cdot 2H_2O$ for several hours. The sulfate concentration then fell suddenly to very low levels, indicating that the gypsum had been completely combined with aluminate or ferrite. The sulfate ion concentration tended to rise slowly in the period 1–6 months after reaching very low levels after 1–2 days of hydration. Alkali levels continued to rise for the duration of the experiment.

Later, Longuet[17] described the composition of pore fluids expressed from Portland (CPA) and slag cement (CLK) pastes (water/cement = 0.5) at pressures of 350 MPa, after storage periods of up to 2 years at 20°C (Figure 4.4). The alkali contents (per cent) of the two Portland cements were 1.16 K_2O, 0.29 Na_2O and 1.21 K_2O, 0.24 Na_2O, and those of the two slag cements were 0.41 K_2O, 0.20 Na_2O and 0.39 K_2O, 0.20 Na_2O. Alkali levels rose sharply in the first 28 days, but then reached a slowly rising plateau and remained thereafter approximately constant for at least 2 years. Alkali concentrations were about five times greater for the Portland cement than for the slag cement pastes.

These results have been extended by analyses of pore solutions squeezed from set pastes and mortars.[18] For example, the principal dissolved ions in the pore solutions expressed from a range of mortars (water/cement = 0.485) as measured between 1 week and 6 months, were hydroxyl and alkali metal. Values of pH measured directly on the expressed solution varied from 13.4 to 14.0. Concentrations of alkalis ranged from 6 to 279 mmol/L for sodium and from 75 to 857 mmol/L for potassium.

A mathematical model linking alkali metal ion levels in the Portland cement and the levels dissolved in the pore solution has been developed which shows that a large percentage of the sodium and potassium ion in the Portland cement ends up in the pore solution; typically, 40–60 per cent of the Na^+ and 50–70 per cent of the K^+ are present in the pore solution.[19]

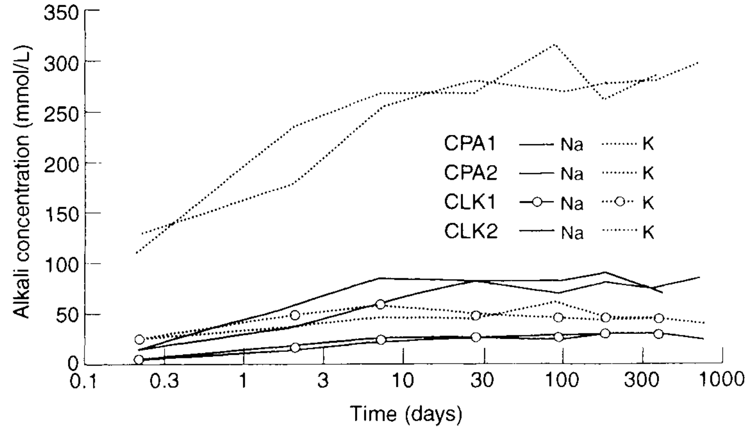

Fig. 4.4 Pore fluid alkali levels for Portland and slag cement pastes, w/c = 0.5 obtained by Longuet.[17]

In principle, pore fluid composition (alkali content) can be affected by period and type of storage, aggregate and sand type (in particular its reactivity towards alkali), binder type and binder composition (in particular its alkali content), the mix proportions (water/cement ratio) and sample preparation procedure. It may also be affected by uncontrolled deviations from the techniques nominally adopted. For example, the moisture state of the specimen and the level of carbonation are factors that are very likely to have a large influence on the composition of the pore fluid expressed from the specimen. Because of the inherent difficulties associated with the technique, the validity of published data must be considered in some detail. Relatively few laboratories have become expert in squeezing pore fluid from hardened cementitious products, and reservations exist concerning its general adoption.

Assessments of the technique from the point of view of its reproducibility and reliability have been made by Tritthart.[20,21] The reproducibility of the procedure for 3 month old cement pastes (Portland cement, fly ash, slag), made with a water/cementitious ratio of 0.6, and rotated to prevent bleeding, has been reported. Coefficients of variation lie, mainly, between 1 and 10 per cent (Table 4.3).

Table 4.3 Variability of hydroxyl ion concentration measurement from pore fluids from 3 month old cement pastes[20]

	Laboratory 1 (mol OH^-/L)		Laboratory 2 (mol OH^-/L)		Laboratory 3 (mol OH^-/L)	
Cement		Chloride contaminated		Chloride contaminated		Chloride contaminated
Portland	0.569 ± 0.063	0.633 ± 0.020	–	0.638 ± 0.011	–	0.570 ± 0.007
Slag	0.401 ± 0.007	0.581 ± 0.040	0.412	0.629 ± 0.009	–	0.550 ± 0.008
Fly ash	0.266 ± 0.048	0.379 ± 0.004	0.265	0.367 ± 0.018	0.270	0.340 ± 0

The report tabulates average and standard deviations for the whole experiment: Portland cement, 0.610 ± 0.035; slag cement, 0.600 ± 0.038; fly ash cement, 0.359 ± 0.020. Pore fluids expressed from pastes after 7 and 28 days sealed cure at 38°C gave repeat analyses for $K^+ + Na^+$ concentrations which were usually within 5 per cent, as were analyses of pore fluids expressed at three pressures: 0–200, 200–560 and 0–560 MPa.[21] Up to an age of 28 days, the pore fluid composition from pastes was similar to that from the corresponding mortar (both ASR reactive and non-reactive sands were examined). A good reproducibility was reported by Page and Vennesland[22] for paste samples examined in triplicate.

The volume of pore fluid that can be expressed is small (1–5 mL) and becomes smaller with increased period of cure and increased aggregate content. The difficulty of the procedure is therefore least for cement pastes at early ages, and these systems have received most attention. The effect of binder type and alkali content for cement pastes has been examined in some detail for these systems.

A factor which has been introduced[23] is the increased concentration of pore fluid solutes due to the chemical withdrawal of liquid water during the continued hydration of the cement; Barneyback and Diamond recommend that pore fluid concentrations should be recalculated to the original water content in order to separate chemical absorption from the physical increase in solute concentrations anticipated from this reduction in solvent volume in the pore fluid.

It is apparent that a number of mechanisms are in operation. Processes that may be expected to result in an increased alkali concentration in the pore fluid are the release of alkali by the Portland cement, giving a rapid production of readily soluble alkali hydroxide and sulfate; release of alkali from any secondary binder present, thus adding to the pore fluid concentration during a subsequent period of slower hydration; and a general increase in degree of hydration during the initial hardening process causing a reduction of the liquid water content and consequently a gradual increase in the concentration of the solutes present. Reductions in the pore fluid concentration may be caused by simple dilution of the Portland cement by the secondary binder, leading to a reduction in the immediate pore fluid alkali concentration; i.e. the absorption of alkali by the cement hydrates, resulting in a reduction in pore fluid concentration (this absorption is claimed to be enhanced by a reduction in lime/silica ratio of the C-S-H by reaction of siliceous pozzolanas with Portland cement).

It is observed that pore fluid alkali levels for plain Portland cement usually show a steady rise in concentration with period of storage. Erratic behaviour and late decreases in concentration may be due to problems with the technique or to genuine late pozzolanic activity of the secondary binder present. For fly ash pastes, the evidence points either to a steady rising, or near constant alkali concentration, although there is some evidence for a steady decline. Alkali levels in pore fluid are consistently much below those for Portland cement pastes, in spite of a high total alkali in the fly ash binder. Only unusually low-alkali Portland cements showed increased alkali levels in the pore fluid with fly ash replacements, except where unusually high-alkali fly ash was being considered. The net result may be a level of alkali in the pore fluid that is roughly in line with the view that fly ash is acting as a diluent of the Portland cement[24–26] (Figure 4.5). For slag cement pastes, most investigations find that alkali levels reach a constant value well below the level for the corresponding Portland cement,[25–27] although high-alkali fly ashes produce increased alkali concentrations in the pore fluid. For microsilica pastes, a rapid decline in alkali concentration, beginning at an early age, even when the microsilica contains a

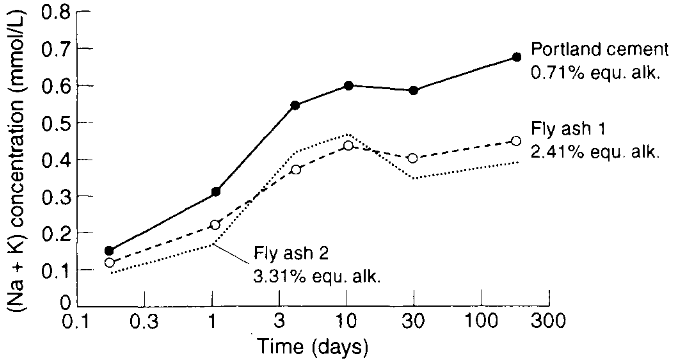

Fig. 4.5 Pore fluid alkali concentration for Portland and fly ash cement pastes, water/cementitious ratio = 0.4.[24]

substantial amount of alkali, usually occur[22,28] but at least one investigation found little or no reduction either in the initial or the long-term alkali level when microsilica is incorporated.[26]

Page and coworkers[29] have devised a technique for extracting pore fluid from concrete 100 mm cube specimens by fracturing the concrete, then collecting samples of mortar and expressing pore fluid from the crushed samples. The technique is named the 'crush-sectioning' procedure. The aggregate was a quartzite with a maximum size of 10 mm. The effect of carbonation on the pore fluid composition was reported: carbonation reduced the alkali metal ion concentrations in the pore fluid and caused a progressive decline in both K^+ and Na^+ concentrations as the carbonated surface was approached. The use of alkali-reactive aggregates usually results in a progressive reduction in hydroxyl ion concentration in the pore fluid.

4.4 Optical examination of Portland cement clinker

The methods for the determination of refractive indices and other optical properties under the microscope afford a useful method of identification. A mineral grain immersed in a liquid of the same refractive index as itself almost or entirely disappears from view, but if the liquid is of different refractive index the mineral grain stands out, surrounded under suitable conditions of illumination by a thin band of light known as the Becke line. If the mineral is of higher refractive index than the liquid and the objective is racked downwards from the point of good focus, the band of light shifts outward towards the liquid. By using a series of liquids of varying refractive indices, the refractive index of a mineral grain may be determined.

4.4.1 PREPARATION AND EXAMINATION OF POLISHED SURFACES

An important method that has been used to examine cement clinker and concretes is that commonly used in metallography, in which a polished and etched surface is examined by reflected light. The sample is first mounted in a plastic resin, then ground flat by successively finer grades of carborundum powder on rotating steel laps, and polished on cloth or metal or paper-covered plastics laps with polishing powders such as rouge, diamond powder or freshly ignited magnesia. When polishing Portland cement clinker, it is advisable to use alcohol or another inert liquid for the final stage of polishing. Alternatively, a lap impregnated with 0.25 µm diamond dust may be used for all stages, following the first levelling of the surface.[30] The surface of a thin section can also be polished, making it possible to identify the minerals by their optical properties under transmitted light and to compare the etch properties of the same grain under reflected light. A thin section, about 20 µm thick, is first prepared, but without a cover glass. A cork or wood support is temporarily cemented to the back of the slide with shellac and the slide is cut so that it only extends to about 6 mm beyond the actual section. The top surface is then polished, preferably on a diamond-impregnated lap at not too high a speed.

4.4.2 ETCHING METHODS

The etch reagent is poured into a small watch glass and the polished specimen is rapidly immersed, polished surface down, care being taken to avoid trapping air bubbles on the surface. The watch glass is gently rocked during the etching period. The specimen is then removed and rinsed, in alcohol if the etch reagent is made up in alcohol, otherwise in water. Many of the etch reactions depend on the formation of a thin film on the surface of the crystals which produces interference colours. Care has to be taken not to scratch this film in drying the specimen. The best method is to dab gently on lens-cleaning tissue or a soft cloth. Where the etch acts by removal of a surface film, the surface is not harmed by gentle wiping. A method sometimes used is to expose the surface to hydrofluoric acid vapour. The specimen is placed face down over a lead or platinum crucible half-filled with acid. A wide-range of etching fluids is described by Barnes and Ghose.[30]

When an unetched specimen of Portland cement clinker is examined, two constituents, appearing white against the grey groundmass, are differentiated owing to their high reflectivity. The commoner is $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, which occurs as small needle- or spear-shaped crystals. The other constituent, MgO, is rare. It tends to occur as squares or triangles, often rounded at the angles. Free CaO may also be seen in unetched specimens, being darker in colour than the groundmass, and often scratched owing to its relative softness. If the specimen is buffed, the free CaO will be pitted. Free CaO is etched after about 2 s by distilled water, appearing pitted and displaying interference colours.

$3CaO \cdot SiO_2$ and free CaO are etched by immersing the specimen for 3 h in a mixture of equal volumes of ethylene glycol and absolute alcohol. Another method, which is quicker and therefore in some respects more convenient, is to immerse the specimen for 10 s in a 10 per cent solution of magnesium sulfate in water, followed by a rapid wash in water and then alcohol before drying. A disadvantage is that the reagent also etches the groundmass, but this ceases to be a difficulty with experience. $2CaO \cdot SiO_2$ is etched to a blue or red colour (depending on the time of etching) by holding the inverted specimen over a crucible containing hydrofluoric acid (40 per cent solution) and allowing the vapour to come into contact with the polished surface. About 10–20 s will bring about the blue stage, somewhat longer etching producing the red colour. At this later stage, differentiation of the groundmass also occurs, whilst $3CaO \cdot SiO_2$ is etched to a straw colour.

In a useful general etching method, the specimen is immersed in distilled water for 5 s, washed in alcohol and then immersed in a 0.25 per cent solution of nitric acid in alcohol. The surface is finally washed in alcohol and dried by blotting. The acid colours the calcium silicates, while the water affects mainly the $3CaO \cdot Al_2O_3$ and some glass compositions, the $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ remaining unattacked. There is some doubt as to the effect on glass, possibly[31] glass compositions of high iron content are not etched, while those of low iron but high alumina content are etched by this reagent. Etching KOH solution is claimed to etch successfully the high-iron glass, but not the crystalline ferrites.[32]

A typical polished surface of Portland cement clinker, etched with water followed by 0.25 per cent nitric acid in alcohol, is shown in Figure 4.6(a). Large prismatic crystals of $3CaO \cdot SiO_2$, etched light grey, together with rounded, darker, striated crystals of $2CaO \cdot SiO_2$ may be seen. The groundmass is principally $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ with a little grey interstitial matter that is probably glass. One crystal of $3CaO \cdot SiO_2$ encloses a small triangular crystal of MgO. Figure 4.6(b) shows a polished surface etched with hydrofluoric acid vapour. The $3CaO \cdot SiO_2$ occurs as irregular prismatic grains, light grey in colour. The $2CaO \cdot SiO_2$ is darker and occurs in three types: large rounded and striated crystals, irregular masses 'fingered' at the edges, and groups of small dots. The latter have been formed by exsolution during crystallisation of the glass. The groundmass is crystalline, the light grey matter being $3CaO \cdot Al_2O_3$ and the white being $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$.

4.4.3 PREPARATION OF THIN SECTIONS OF PORTLAND CLINKER

A small chip of material may be obtained by breaking a piece of clinker with a hammer, or breaking a thin slice formed using a diamond saw. The diamond saw consists of either a slow-running soft iron disc which has diamond dust pressed into its rim, or a fast-running resin-bonded diamond saw. As the material to be cut is hydraulic, water cannot be used as a lubricant but liquid paraffin or ethylene glycol are suitable.

With porous materials, such as Portland cement clinker, it is necessary to impregnate with resin. Even with a dense material, setting in resin is a convenient method of obtaining a specimen which can be handled easily and marked for identification. Moreover, it is convenient to slice through the impregnated specimen, keeping one cut face for preparing a thin section and using the other for polishing and etching. The material, whether a slice, lump or about six small chips, is placed in a glass specimen tube of 20 mm diameter in a desiccator fitted with a two-holed rubber bung in the cap, through one hole of which a separating funnel fitted with a tap is inserted, while the other is used for evacuating. The desiccator is held evacuated for 1 h and then resin is run into the specimen tube from the funnel until the sample is covered. The specimen tube and contents are then removed and heated in an oven for 4 h at 50°C, followed by 24 h at 100°C. Cold-setting epoxy resins may also be used, according to the makers' instructions. The hardened resin, containing the specimen, is removed from the tube by breaking the glass.

The next stage is to grind the specimen until one flat surface of sufficient area is obtained. A rotating metal lap can be used for this grinding with 60 min carborundum, and then 120 min carborundum, as abrasive. When the surface is judged to be flat, it is cleaned of all grinding powder and is then ready for final polishing. This is done by hand on a glass plate, using 4F carborundum powder, or on a plastics plate, using 0.25 μm diamond dust. Some workers prefer to use diamond impregnated laps for all stages. When a perfectly even surface is obtained, the specimen is cleaned well and left to dry. It is then ready for mounting.

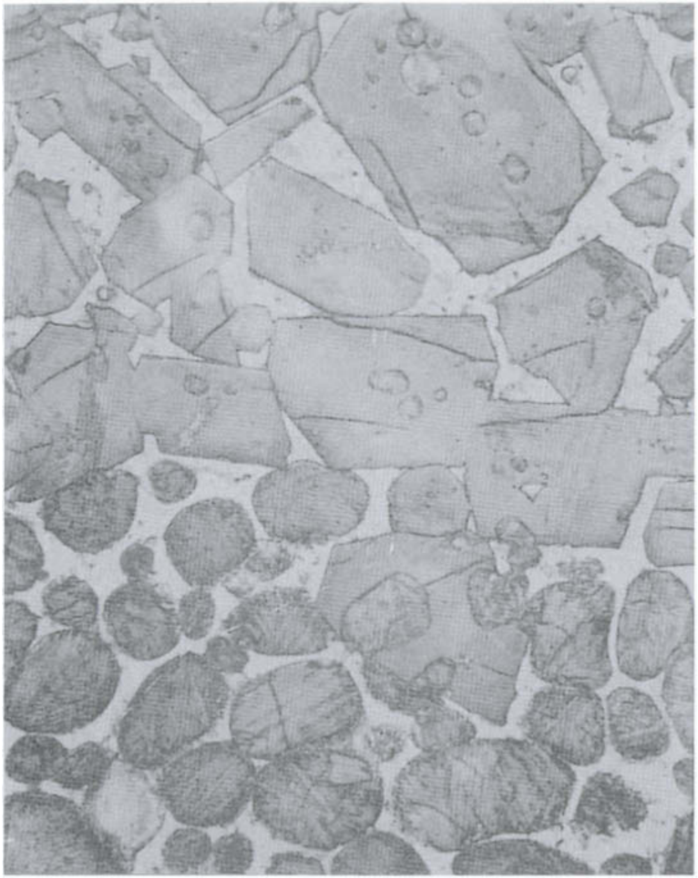

Fig. 4.6(a) Polished surface of Portland cement clinker, etched with water followed by 0.25 per cent HNO_3 in alcohol (×360).

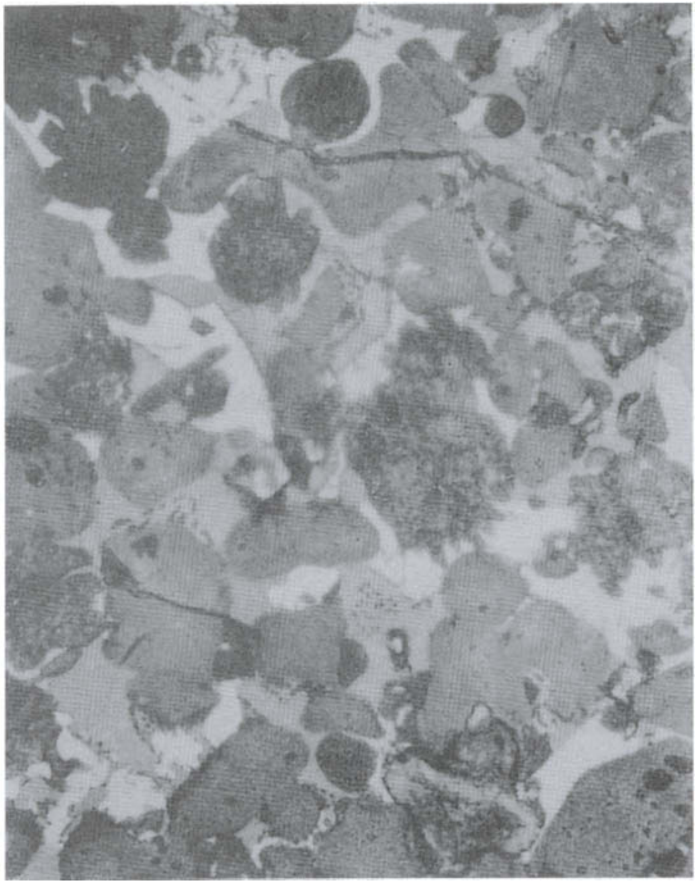

Fig. 4.6(b) Polished surface of Portland cement clinker, etched with HF vapour (×360).

To mount the specimen, a hotplate maintained at 100°C is required. A 25 x 75 mm glass microscope slide is placed on the hotplate, and a small quantity of filtered Canada balsam is placed on the microscope slide and left to 'cook'. The state of the cooked balsam is critical and it should be tested at frequent intervals. A small drop of the cooking balsam is taken on the end of a needle and pressed against the thumb nail; when it shatters on slight pressure, the balsam is cooked sufficiently. When the balsam is judged to be ready for mounting, the specimen is lowered into the balsam, polished face downwards, and then removed from the hotplate and pressed to remove any entrapped air bubbles. It is then left to cool. Various synthetic substitutes for Canada balsam (e.g. Lakeside 70°C) are available and are easier to use. The cooking temperature may be higher, perhaps 140°C. A thermosetting resin has been suggested.[30]

The mounted specimen is now ready for final grinding. This is done on the metal lap, using coarse 60 min and 120 min carborundum powder. The section is ground until it is just transparent, great care being required to keep the thickness of the thin section even and not to break away the surrounding layer of balsam, since this is the only protection for the edges of the now thin section.

When the section is just transparent, it is cleaned of all grinding powder and the final grinding carried on by hand, as described above. As the section becomes thinner, repeated examinations on a petrological microscope are made. The grinding is brought to an end when the minerals give the desired interference colours under crossed nicols. It is usual to make sections ~20 μm thick; this is the thickness which will cause $3CaO \cdot SiO_2$ to have white-grey polarisation colours.

A cover glass should be placed on top of the finished section for protection. This can be done by applying a small blob of Canada balsam (or substitute) to a thin cover glass whilst on a hotplate; the finished slide is also placed on the hotplate and the cover glass placed on top of the specimen, balsam side down. When all the balsam has covered the specimen, the slide is removed from the hotplate and finally pressed into position and then left to cool. The time the slide is on the hotplate while mounting the cover glass is sufficient to fix the balsam. When cool, the surplus balsam may be removed by a solvent, such as methylated spirits or benzene. The section is then ready for examination on the petrological microscope.

4.4.4 PORTLAND CEMENT MINERALS

Photomicrographs by transmitted light are shown in Figures 4.7 and 4.8. Figure 4.7(a) shows a clinker composed almost entirely of white prismatic grains of tricalcium silicate with scattered brown interstitial matter. Figure 4.7(b) shows a central mass of darker, rounded dicalcium silicate grains and some white tricalcium silicate towards the edge of the picture. The dicalcium silicate grains are surrounded by, and set in, the dark brown interstitial matter; they appear much darker in the photomicrograph than the tricalcium silicate owing to their much higher light absorption. When examined visually under the microscope, the contrast does not appear so definite, but there is a marked difference in transparency between the tri- and dicalcium silicates. The former are transparent and white or occasionally a pale green colour, depending on the thickness of the thin section. Figure 4.8 shows the interstitial matter particularly clearly differentiated from the primary crystals.

There is usually no difficulty with microscopic measurements[33,34] in identifying $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$, although the former may have reaction rims and the latter

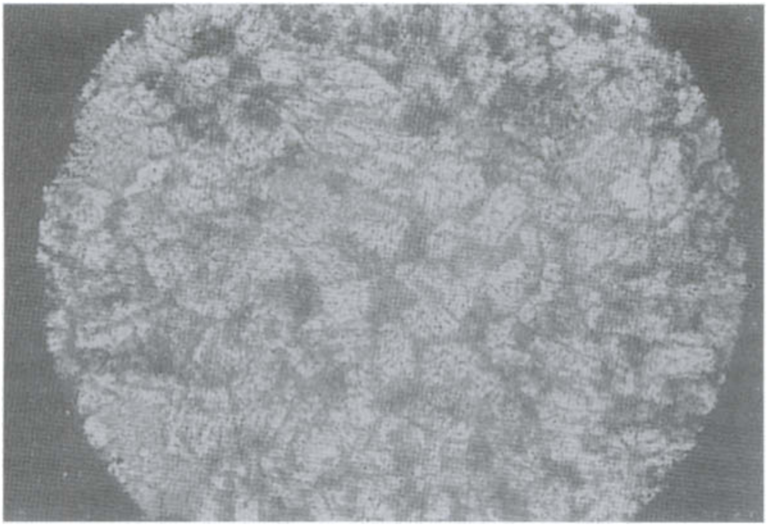

Fig. 4.7(a) Thin section of Portland cement clinker showing prismatic tricalcium silicate (×235).

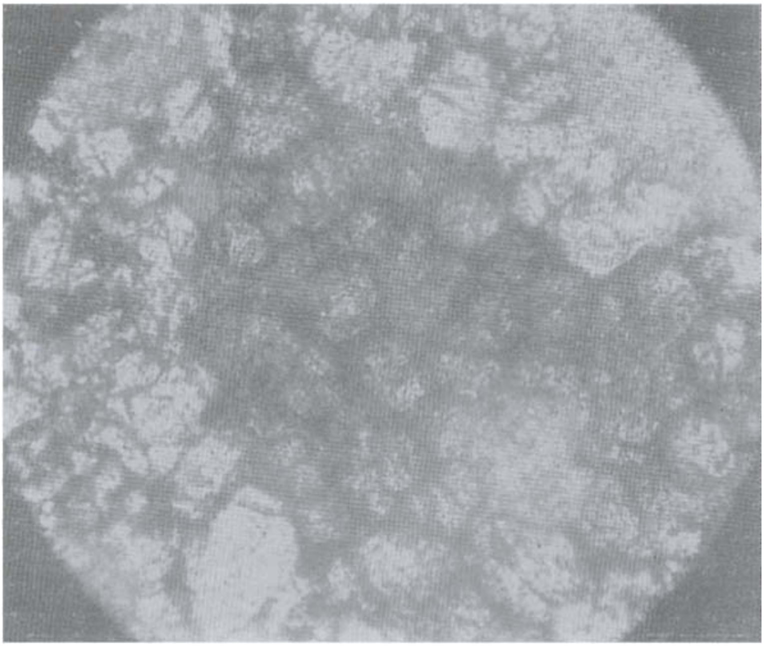

Fig. 4.7(b) Thin section of Portland cement clinker showing dicalcium silicate in centre and tricalcium silicate in outer part (×235).

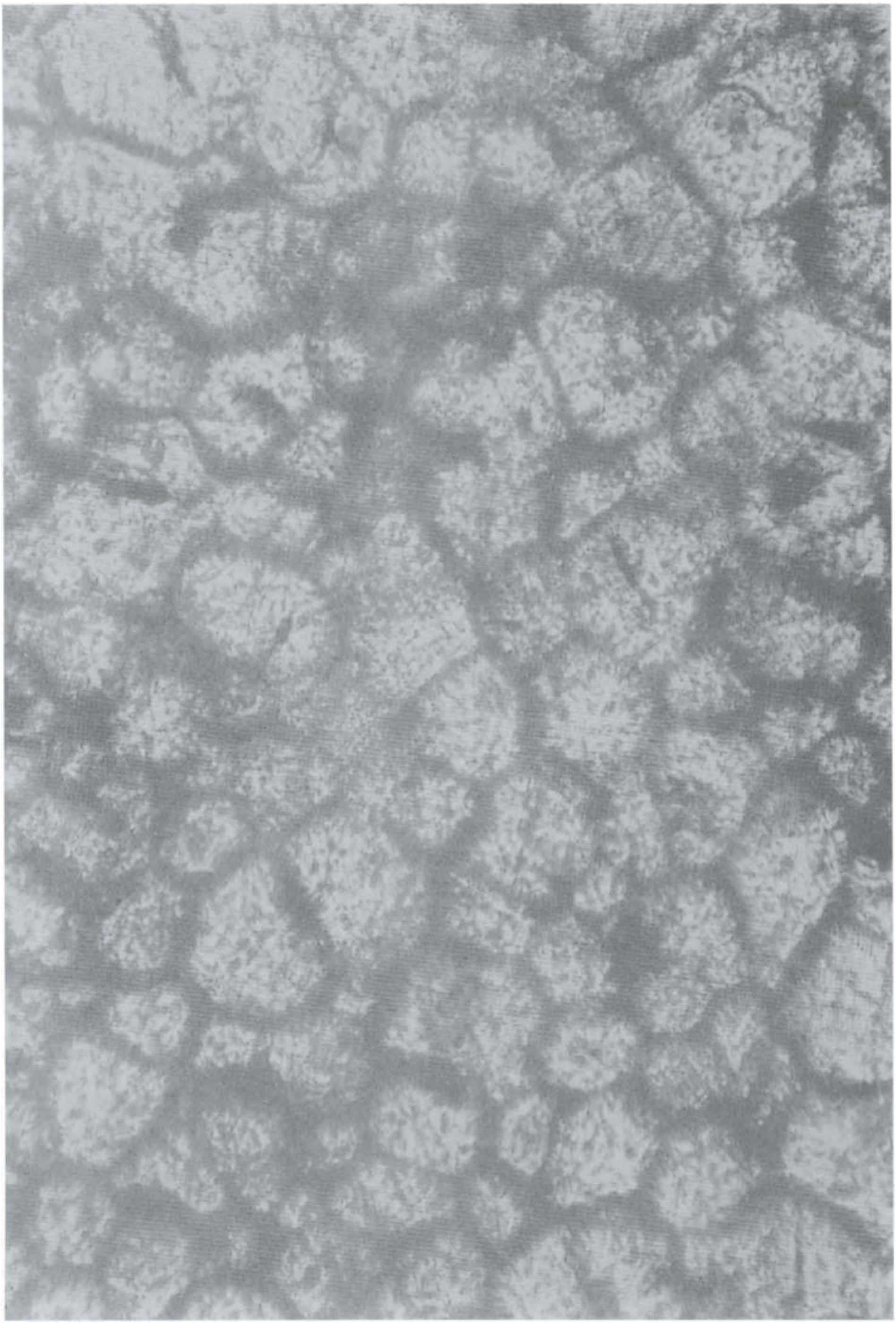

Fig. 4.8 Thin section of Portland cement clinker showing large primary crystals and well-differentiated interstitial material (×350).

may be underestimated when very small secondary crystals are present. In slowly cooled or in quenched clinker, the interstitial compounds can also be measured with some accuracy, but at intermediate rates of cooling, the scale of crystallisation of the interstitial matter may be too small for accurate work. With synthetic clinker, containing only CaO, Al_2O_3, SiO_2 and Fe_2O_3,[31] very good agreement with the Bogue formula was obtained when the clinkers were fully crystallised. When alkalis and MgO were present, the measured $3CaO \cdot SiO_2$ level rose above the calculated value.

The size of silicate crystals, and the general appearance of the section, vary considerably with different cements and manufacturing processes. In some clinkers the $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$, and sometimes the CaO, are aggregated together – compare (a) and (b) in Figure 4.7 – and if the section is examined under low power, these aggregations can often be seen to be relics of coarser particles of the raw meal; if the particle was originally calcite, a clump of $3CaO \cdot SiO_2$ with possibly a core of free CaO is seen; if siliceous, the relict is usually $2CaO \cdot SiO_2$. Clinkers differ greatly in their porosity, and skins and cores are sometimes visible, which may suggest the action of ash or changes in kiln conditions.

The largest crystals of $3CaO \cdot SiO_2$ or $2CaO \cdot SiO_2$ are about 40 µm, while an average size would be 15–20 µm. Tricalcium silicate in thin sections shows grey to white interference colours under crossed nicols. The optic axial angle is low, especially when Al_2O_3 is present in solid solution, but is raised by increasing Fe_2O_3 contents. The clinker mineral is always impure, but it can only be distinguished with certainty from pure $3CaO \cdot SiO_2$ by X-ray methods. In polished surfaces, $3CaO \cdot SiO_2$ is specifically etched by ethylene glycol or magnesium sulfate solution; in some clinkers, the edges of the crystals can be seen to be corroded and converted to $2CaO \cdot SiO_2$ by reaction with the liquid during cooling.

Dicalcium silicate rarely shows any crystal form, appearing as rounded grains which in transmitted light show yellow interference colours in a section of normal thickness (~0.025 mm). The crystals frequently show polysynthetic or inversion twinning, which is particularly clear in the polished and etched surface. The powder X-ray diagram, even after concentration of the $2CaO \cdot SiO_2$ fraction, usually only shows lines corresponding to the β form.[35] The α' form may be detected in clinkers that are usually high in K_2O, or containing P_2O_5. A small amount of the α or α' form, insufficient to show by X-rays, could be present,[36] but the optical properties of all three modifications are so strongly affected by solid solution that detection by optical means is very difficult. The optic axial angle found in the clinker mineral is often much smaller than that quoted for 'pure' β-$2CaO \cdot SiO_2$, but the refractive indices and birefringence support the X-ray findings. Three types of β-$2CaO \cdot SiO_2$ have been distinguished, according to their appearance in the polished etched specimen.[37] It has been shown that these arise from the conditions of formation and that the braided appearance of $2CaO \cdot SiO_2$ clinker is paralleled in the mineral, larnite. A small amount of $2CaO \cdot SiO_2$ is sometimes found dispersed in the interstitial material as tiny rounded dots (see Figure 4.6); this has crystallised from the liquid or glass during cooling.

Free CaO occurs in clinker as aggregates or single grains, rounded in shape and frequently as large as the $2CaO \cdot SiO_2$ grains. It is not easily distinguished in thin sections but is readily seen in the polished surface, being soft and easily scratched. It is readily etched by water or moist air, and then appears dark and, when over-etched, pitted. In powdered clinker or cement, free CaO is readily detected under the microscope by White's test. It can be determined quantitatively by analysis or by X-ray methods.

MgO, or periclase, is not affected by the etches commonly employed and always appears bright in the polished surface. It is found in association with all the other clinker constituents and tends to exhibit rectangular or triangular forms. It is hard and, if the surface is lightly polished on a cloth, it stands out in relief. The interstitial material is frequently difficult to resolve by microscopic examination. $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, or the corresponding ferrite solid solution, is recognised in this section by its reddish colour, birefringence and pleochroism. It is usually prismatic in form. An estimate of the position of this compound in the ferrite solid solution series can be made either by measurement of the reflectance in polished specimens or, more reliably, by measurement of the angles of the (200) or (202) reflections in the powder X-ray pattern.[35] The composition of the ferrite can vary from $6CaO \cdot 2Al_2O_3 \cdot Fe_2O_3$ to $6CaO \cdot Al_2O_3 \cdot 2Fe_2O_3$, but the median value is fairly close to $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The ferrite phase in reflected light appears very bright and is not etched by the reagents commonly used.

In order to obtain a quantitative estimate of the amount of the various phases present, one of the many forms of integrating micrometer stage may be employed. The thin section, or polished specimen, is carried on a slide which can be traversed along a given line by one of a number of micrometer screws. Each component is assigned to a definite screw and provision is made for spanning gaps in the specimen. The specimen is scanned in a regular manner, the stage being moved so that each screw measures the total intercepts on the crosswires corresponding to its assigned constituent. The volume percentages of the constituents are thus obtained. In applying the method to Portland cement clinker, difficulties arise because of the high magnification which has to be employed and because of doubtful identification, particularly of interstitial matter. The 'point counter' system has many advantages. Here the stage is moved a definite distance by operating any one of a number of electrical contacts. Each contact is assigned to a definite compound and as soon as the area on which the crosswires intersect is identified, the corresponding switch button is pressed, and the stage automatically moves on.

4.4.5 CLINKER STRUCTURE

The view has been held that it is necessary to break the crystals of the cement compounds in grinding, and to expose a fresh surface before they can hydrate rapidly. On this theory, a clinker in which the crystals of the silicates are small has been considered not to produce as good a cement as one composed of larger crystals. Little evidence seems to be available to support this opinion.[38–41] There is some evidence that the strength is higher with alite crystals of 15 µm than of 40 µm dimensions, and with an increasing diameter/thickness ratio. A more correct explanation may be that in clinkers with an Al_2O_3/Fe_2O_3 ratio above ~ 1.7, the alite crystals react with the liquid during cooling, unless this is rapid, and become coated with dicalcium silicate. Unless this is broken away during grinding, it might be expected to slow down the hydration of the alites.

The opinion also exists fairly widely that a Portland cement can be overburnt. Thus, in the test of the litre-weight of the clinker, which is often used in the control of cement burning, it has been found, at various works, that there is an optimum value and that harder burnt clinker, giving a higher litre-weight, does not give the highest strength. Some results showed a lower strength for the extreme case of a cement melted, compared with one clinkered, as did other laboratory tests at less extreme temperatures. However, the effect can probably be attributed more to differences in cooling conditions than in the burning temperature, and that, at the higher temperature in the furnace used, there was a longer cooling zone at temperatures conducive to more perfect crystallisation. Some work on tricalcium silicate, in which an optimum burning temperature of 1500°C was found, with a reduced activity at higher temperatures, supports these conclusions. In contrast, in other studies fusion at 2000°C improves both strength and soundness.[42] High contents of free CaO and MgO could be tolerated because they crystallised from the fused mix as very small grains which were uniformly distributed.

For certain mix compositions of high lime content, an undue increase in burning temperature can also result in free CaO becoming a phase in equilibrium with the clinker liquid. Though this should be recombined on cooling, the rate of solution of the lime crystals may be too slow for this to occur.

4.4.6 COLOUR OF PORTLAND CEMENT CLINKER

The normal greenish black colour of Portland cement clinker may be considerably changed if reducing conditions exist locally at any point in a kiln, even though the general atmosphere is an oxidising one. The production of clinker with a black external shell and a yellow or brown interior has been ascribed to partial reduction of the iron, followed by a subsequent reoxidation which has not penetrated beyond the surface. It should be noted in this connection, that even in an oxidising atmosphere, some dissociation of ferric oxide may occur at clinkering temperatures; reoxidation occurs during cooling, but may not necessarily be complete, and FeO contents from a trace to 0.45 per cent have been reported. Overburning has been found to give a clinker that is black on the surface and deep yellow inside, and this has been ascribed to the increases in the ferrous oxide content.

The rate of cooling also affects the colour,[43] and quenched clinkers tend to be more brownish yellow owing to the decrease of the amount of crystalline iron compound present, and its replacement by glass. The ferrite crystals darken as the amount of MgO in the cement increases, but if rapid cooling occurs, the glass is still yellowish brown. Dark brown colours can be produced[44] in commercial production, by slow cooling in a reducing atmosphere from immediately below the clinkering temperature. The presence of manganese oxide also gives a brown colour to cement. Provided the atmosphere contains oxygen, the substitution of divalent Mg^{2+} or Zn^{2+} for trivalent Al^{3+} or Fe^{3+} in the aluminoferrite phase results in oxygen vacancies in the structure,[45] and a colour change from yellowish brown to dark grey. High Si^{4+} or Ti^{4+} substitution causes the aluminoferrite to remain yellowish brown even in the presence of oxygen.

4.5 Mineral separation techniques

Portland cement clinker, as ordinarily prepared, is not a homogeneous substance, but a rather fine-grained mixture of several solid phases. It is therefore difficult to draw any conclusions from a study of its chemical reactions alone, since these may involve more than one constituent, and the only methods capable of yielding trustworthy results are those which enable us to deal with the individual constituents separately. The conditions have a close parallel with the study of igneous rocks. It would be impossible to determine the structure of a granite by observing its gross behaviour towards reagents. The reactions with the quartz, feldspar and mica would be superimposed and confused, and the resulting action would give only a meaningless average. A number of methods are available for overcoming these difficulties, such as mineral separation after crushing, optical examination of the crushed material or of thin section or of polished and etched surfaces, the use of X-rays, and electron microprobe analysis.

A rock may be crushed to such a degree of fineness as to release the constituent crystal grains and the powder thus obtained can be suspended in liquids of suitable densities, bringing about a separation of the light and heavier minerals. In skilled hands, the method is capable of giving very accurate results. It has been applied to cements, but with less success, as the close intermixture and friable character of the constituents render a separation impossible until the whole has been reduced to a fine powder, when the particles no longer settle satisfactorily after suspension in heavy liquids. An improvement may be obtained by effecting the separation of the crushed material by centrifugal or magnetic means, but even then a clean separation has not been effected. Microscopic examination of the crushed material shows that many of the grains are composed of one constituent, but that attached to their edges there may remain fragments of a second constituent, thus rendering a perfect separation impracticable. Such partially successful separations, using chemical or physical methods, can be a useful preliminary to X-ray examination since the intensity of the reflections obtained for a given constituent will be enhanced.

Tricalcium silicate grows to a larger size than any other constituent, and separation of enough material for analysis by centrifuging a graded clinker powder in heavy liquids has been achieved. Partial hydration[35] of a clinker left the slowly hydrating $2CaO \cdot SiO_2$ as a residue after acid extraction of the set cement. Many workers have used an alkaline solution of a dimethylamine salt to dissolve the silicate phases, leaving a concentration of other constituents. A solution of salicyclic acid in methanol has also been used to dissolve the calcium silicate phases from Portland cement.[46–49] The cement specimen must first be ground to a particle size less than 5 μm in an agate ball mill, with cyclohexane as a grinding aid. Other organic acid solutions have been proposed.[46] These methods, or alkaline ammonium citrate or acetic acid,[50–52] have been used to intensify the X-ray reflections from the ferrite phase in order to obtain its composition from the *d*-spacings. A solution of KOH containing sucrose is recommended as a dissolution medium which removes the calcium aluminate phases.[49] These solubility methods depend on differences in the rate of solution of the various compounds and require, therefore, a suitable choice of the extraction conditions. A bar magnet has also been used to separate the ferrite phase.[53]

4.6 X-ray analysis

In general, crystalline materials belonging to the crystallographic systems of higher symmetry, such as the isometric, tend to give strong patterns containing relatively few lines, while materials of lower crystal symmetry give weaker patterns and a greater number of lines. A further complication arises from the fact that very high-resolution X-ray spectrometers will break down what is apparently a single strong reflection into a series of closely spaced weaker lines. This occurs with the impure forms of $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$, which are found in cement clinker and, furthermore, the positions of these complex reflections vary with the nature of the impurities present. X-ray analysis is, therefore, an operation requiring much skill and experience, especially when, as is the case with Portland cement, reflections from different minerals coincide or overlap.

The principle is similar to the powder method employing a photographic film, but the specimen is flat. It is automatically rotated and the diffracted energy is measured by a

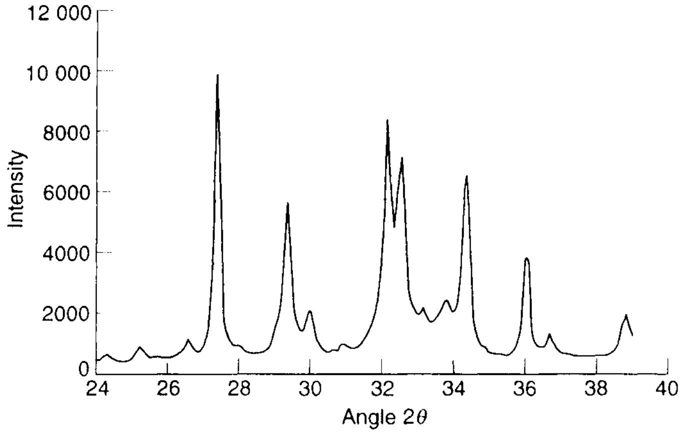

Fig. 4.9 X-ray diffraction analysis of unhydrated cement, ES3982.

Geiger or other counter. The result appears either as a trace of diffracted energy versus the angle turned by the specimen, or as total counts at predetermined angular positions. In either case, the diffracted energy for a selected reflection is compared with that of a standard preparation of the substance to be estimated. To check the intensity of the incident X-ray beam, an internal standard, such as Si or TiO_2, may be mixed with the sample, or a separate check run may be made with an external standard, usually α-Al_2O_3.

An X-ray diffraction trace for a Portland cement is recorded in Figure 4.9. The diffraction trace includes two peaks at 27.45 and 36.11° 2θ due to rutile (TiO_2) which was added as an internal standard before grinding (20 per cent addition).[54]

4.6.1 ESTIMATION OF COMPOUND CONTENT BY X-RAY DIFFRACTION

Quantitative X-ray powder diffraction analyses have been carried out routinely in a number of laboratories. In one system, a Siemens fully automatic diffractometer system, with monochromated copper K-α radiation, operating at 40 kV and 30 mA, was used to collect the diffracted intensity data, using a fixed-time step-count procedure over the angular range of 24 to 39° 2θ, at an interval of 0.05° per step. Rutile was used as an internal standard, and was added at the rate of one part to five parts of cement (or primary standard) by mass. All materials were ground to a particle size of less than 5 μm, by milling in an agate ball mill, with cyclohexane as a grinding aid. Powder specimens for the diffractometer were made by loading the sample holder from the back before pressing into a compact so as to limit the effects induced by preferred orientation.

Diffracted X-ray intensity was measured by counting photons for 20 s at each angle 2θ, i.e. for 261 angular positions between 24 and 39° 2θ.[54] It is necessary to take account of the solid solutions exhibited by the four major phases in Portland cement by making a qualitative choice of the particular standard phase to be employed in the analysis by comparing the fine structure exhibited in the diffraction patterns. Two hundred and sixty-one linear equations are set up using the selected primary standards obtained on

Table 4.4 Quantitative X-ray diffraction analysis of cements listed in Table 4.5

Code	Alite	Belite	High-temperature C_2S	C_3A, cubic	C_3A, orthorhombic	Ferrite	Gypsum	Hemihydrate	Anhydrite	Calcite
ES3982	64.0	14.5	2.0	0	3.5	9.5	0	1.5	0	2.5
ES3984	66.5	11.0	4.0	0	3.0	9.5	1.0	1.0	0	1.5
ES4037	65.0	14.0	0	0	7.0	6.0	5.0	1.5	0	0
ES3986	61.0	18.0	3.5	0.5	2.5	10.0	0	0	0	1.5
ES3988	59.0	18.0	3.5	0	2.5	10.0	0	0.5	0	2.5
ES3990	59.5	17.0	3.0	1.0	2.0	9.5	3.0	0.5	0	2.0
ES3992	65.0	13.5	2.5	3.5	2.5	7.5	0	0.5	0	2.5
ES3994	66.0	13.0	2.5	3.5	2.5	7.0	0	0	0	2.5
ES3996	63.5	12.0	4.0	2.5	2.5	6.5	4.0	0.5	0	1.5
ES4031	64.5	18.0	0	8.0	2.0	5.5	0	1.0	0	0
ES4036	61.0	19.0	0	3.5	8.0	6.0	0.5	1.5	1.5	0
ES4044	78.0	6.0	0	0	3.5	10.0	0	0	1.5	0
ES3753	65.0	12.5	3.5	0	5.5	9.5	0.5	0	2.0	1.0[a]
ES4144	65.0	15.0	0	1.0	9.0	7.5	1.5	1.0	0	0
ES4174	54.5	26.0	2.5	6.5	0	6.0	0	1.0	0	2.0[b]

[a] $Ca(OH)_2$.
[b] Quartz.

Table 4.5 Chemical analysis of cements examined (main components; per cent)

Code	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	LOI[a]	Na_2O	K_2O	Na_2O eq.
ES3982	20.9	2.80	4.32	62.8	2.14	4.19	0.90	0.32	1.02	0.99
ES3984	21.3	2.82	4.36	63.3	2.15	3.30	0.75	0.31	0.99	0.96
ES4037	20.0	2.19	4.82	62.7	2.61	4.14	1.31	0.41	0.83	0.95
ES3986	21.4	2.91	4.09	63.0	2.64	3.02	0.89	0.41	0.78	0.92
ES3988	21.0	2.85	4.01	62.4	2.60	3.93	0.95	0.42	0.77	0.93
ES3990	20.8	2.82	3.97	62.1	2.58	4.55	1.01	0.40	0.77	0.91
ES3992	20.3	2.28	5.08	63.3	2.70	3.23	0.96	0.44	0.86	1.00
ES3994	20.0	2.24	4.99	62.8	2.66	4.12	1.10	0.37	0.85	0.93
ES3996	19.8	2.22	4.93	62.5	2.63	4.80	1.10	0.38	0.85	0.94
ES4031	19.9	2.15	5.91	65.0	1.22	3.41	0.65	0.28	0.95	0.91
ES4036	20.9	2.04	5.08	64.4	1.76	2.98	1.21	0.20	1.12	0.94
ES4044	20.3	3.02	4.88	63.4	2.13	3.21	1.23	0.40	0.86	0.90
ES3753	20.5	3.20	4.82	62.3	2.62	2.82	0.93	0.44	1.16	1.20
ES4144	20.0	2.44	5.47	62.3	2.66	3.83	0.95	0.28	0.81	0.81
ES4174	21.5	2.72	5.37	63.5	1.56	2.50	1.12	0.17	0.76	0.67

[a] LOI – loss on ignition.

synthesised or separated pure cement minerals (alite, belite, C_3A, etc.), and then the best values for the proportions of the primary standards in the unknown cement are obtained by the method of least squares. Examples of the results of this procedure are recorded in Table 4.4 for cements listed in Table 4.5.

4.7 Calculation of the proportion of constituent minerals

If the analytical composition of a cement is known, together with the compounds which have been formed during burning, it is clearly possible to calculate the amounts of these compounds which are present in the cement. This calculation is universally known as the Bogue calculation. The results of the work on the constitution of Portland cement have shown that it consists essentially of the compounds $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$, a ferrite close to $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, MgO and a little free CaO. To these must be added the gypsum introduced during grinding to control the setting time of the cement. The minor components, such as TiO_2, Mn_2O_3, K_2O and Na_2O, do not normally amount to more than about 2 per cent, and it is usual to ignore them in calculations of the potential compound composition of a cement. The word 'potential' is used because it is assumed in any such calculation that the cement is entirely crystalline, and that no glass remains in the clinker after cooling.

The compound composition of a Portland cement can be calculated as follows.[55] The SO_3 content is first considered and the equivalent amount of CaO required to form $CaSO_4$ is calculated. This, together with the free-lime content of the cement as obtained by estimation, are subtracted from the total lime content. The remaining lime, together with the cement of SiO_2, Al_2O_3 and Fe_2O_3 are now divided up to give the compounds $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, $3CaO \cdot Al_2O_3$, $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$. The amounts of CaO and Al_2O_3 required to combine with the Fe_2O_3 to form $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ are derived and the content of this compound obtained. The remaining alumina is now calculated to $3CaO \cdot Al_2O_3$. The CaO remaining after subtraction of the amounts used in forming the above two compounds is finally allotted to the silica and the contents of $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ calculated. The method is best illustrated by an actual calculation, remembering that the molecular proportions of the various oxides in the different compounds are as follows.

The theoretical compound or mineral content of a clinker may be derived from the chemical analysis, using equations based on the chemical phase diagram for the system $CaO–SiO_2–Al_2O_3–Fe_2O_3$. Although the method does not usually provide results which are in close agreement with directly determined mineralogical proportions (measured by X-ray diffraction analysis), it is adopted for cement standards throughout the world. The American Standard ASTM C 150-94 (Portland cement) gives formulae (originally derived by R.H. Bogue at the National Bureau of Standards, Washington) to calculate the mineralogical composition from the chemical analysis:

$$\%\ \text{Tetracalcium aluminoferrite}\ (C_4AF) = 3.043(\%\ Fe_2O_3) \qquad (4.3)$$

$$\%\ \text{Tricalcium aluminate}\ (C_3A) = 2.650(\%\ Al_2O_3) - 1.692(\%\ Fe_2O_3) \qquad (4.4)$$

$$\%\ \text{Dicalcium silicate}\ (\beta\text{-}C_2S) = 2.867(\%\ SiO_2) - 0.7544(\%\ C_3S) \qquad (4.5)$$

$$\begin{aligned}\%\ \text{Tricalcium silicate}\ (C_3S) = {} & 4.071(\%\ CaO) - 7.600(\%\ SiO_2) - 6.718(\%\ Al_2O_3) \\ & - 1.430(\%\ Fe_2O_3) - 2.852(\%\ SO_3)\end{aligned} \qquad (4.6)$$

where the % CaO and % Al_2O_3, etc. terms being the mass percentages of the component oxides.

In deriving the above formulae, the following steps are assumed:

1. All the SO_3 present is combined with CaO to give $CaSO_4$, and the equivalent CaO $= 0.70(\%\ SO_3)$, is subtracted from the total CaO present.

2. All the Fe_2O_3 present is combined as $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ and the quantities of $Al_2O_3 = 0.64(\% \ Fe_2O_3)$ and $CaO = 1.40(\% \ Fe_2O_3)$ are subtracted from the appropriate totals.
3. The remaining Al_2O_3 is combined as $3CaO \cdot Al_2O_3$ and a further quantity of $CaO = 1.65(\% \ Al_2O_3)$ is subtracted from the total remaining CaO.
4. The SiO_2 combines initially with CaO to form $2CaO \cdot SiO_2$, giving a provisional dicalcium silicate figure. The CaO combining with $SiO_2 = 2.87(\% \ SiO_2)$ is subtracted from the total CaO figure and the remaining CaO is then combined with part of the $C_2S = 4.071(\% \ CaO)$ to form C_3S.

These equations are based on the understanding that chemical equilibrium is established at the clinkering temperature, and is maintained throughout the critical cooling period and, more importantly, the chemical compositions of the phases are as stated. The errors which this introduces are exacerbated by formation of minor compounds (e.g. alkali metal sulfates) and by solid solutions in both the major and minor components. For example, magnesia and alumina are taken up by the silicates, and silica is absorbed by the aluminoferrite. For these reasons the Bogue composition is referred to as the potential chemical compound composition.

There is a wide agreement that the Bogue calculation gives seriously incorrect results, especially for alite and $3CaO \cdot Al_2O_3$ contents.

4.7.1 MODIFIED BOGUE CALCULATION

The Bogue calculation has been refined by Taylor[56] by utilising more realistic phase compositions (derived from averaged microanalytical data), with the result that the calculated mineralogical composition is more nearly representative of the true mineralogical composition, as determined by quantitative X-ray diffraction analysis. The assumption that average phase compositions are realistic for a wide range of clinker formation conditions may be questioned (section 4.8).

Various other corrections to the Bogue calculation have been proposed, but none of these have yet received any general acceptance, but with the information now becoming available from electron microprobe analysis, it is possible that some corrected compound compositions might eventually be agreed for use in the Bogue calculation.

4.7.2 DEVIATION OF COMPOUND CONTENT FROM CALCULATED VALUE

The effect of the various compositional factors discussed above in causing deviations from the Bogue formula can only be assessed qualitatively and not calculated quantitatively. The broad effects are summarised in Tables 4.6 and 4.7.

The $3CaO \cdot Al_2O_3$ content of the plant clinkers was always lower than the Bogue value, by up to 10 per cent in extreme cases, and to a lesser extent below the results from the modified calculation. Only in the case of the slowly cooled samples did the $3CaO \cdot Al_2O_3$ content approach the Bogue value. The content of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ in plant clinkers approached the Bogue value for clinkers of Al_2O_3/Fe_2O_3 ratio up to about 2, but was low at higher ratios. The amount of glass determined microscopically tended to be lower than that given by the heat of solution method but, for most of the plant clinkers, the discrepancy was only a few per cent. The free MgO found was less than the total present, to an extent that increased with the rate of cooling, as would be expected from its solubility in the glass.

Table 4.6 Chemical analysis of Portland cements included in Table 4.7

Cement	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	Free lime	Na_2O	K_2O	TiO_2
10	19.37	3.98	5.74	63.33	1.43	2.76	0.64	0.39	0.30	0.30
11	21.04	2.36	5.48	64.37	1.20	2.35	2.24	0.26	0.67	0.34
12	20.49	2.55	5.40	65.02	1.32	2.40	0.94	0.33	0.52	0.32
13	21.73	2.32	4.84	64.59	1.32	2.55	2.02	0.23	0.65	0.25
14	19.64	2.41	5.53	64.43	1.88	2.81	2.64	0.21	1.45	0.30
15	21.42	2.39	5.11	65.14	0.71	2.82	1.15	0.26	0.49	0.30
16	21.28	1.78	4.88	65.06	0.93	2.74	2.21	0.20	0.69	0.30
17	19.83	2.21	6.89	63.98	1.98	2.65	1.58	0.19	0.68	0.40
18	19.65	2.72	5.32	64.32	1.04	2.98	1.34	0.27	0.66	0.38
19	20.80	2.30	5.54	63.87	1.22	2.71	2.21	0.29	0.56	0.22
20	21.02	2.34	5.77	64.25	1.23	2.67	2.34	0.27	0.50	0.25
21	20.96	1.84	4.85	63.80	1.06	3.00	3.19	0.22	0.94	0.28
22	23.04	1.96	4.65	63.82	1.49	2.42	2.03	0.18	0.62	0.42
23	21.31	2.27	5.30	64.99	1.09	2.42	1.72	0.22	0.73	0.36
24	21.60	2.49	4.37	65.21	1.05	2.46	1.47	0.15	0.54	0.32
25	21.86	2.47	4.48	65.77	1.08	2.13	0.78	0.15	0.66	0.34

Table 4.7 Comparison of the analysis of Portland cements for compound content by Bogue and X-ray methods

Cement	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	Alite	Belite	C_3A	Ferrite
10	56	14	8	12	4.7	54	18	8.8	15
11	46	25	11	7	4.0	54	15	15	5
12	58	15	10	8	4.1	61	17	10	8
13	47	27	9	7	4.3	57	23	8.2	4.9
14	54	16	11	7	4.8	76	5.3	8.8	7.3
15	59	15	9	7	4.8	62.4	18.8	9.3	4.9
16	51	23	10	6	4.7	70.6	10.9	9.9	2.7
17	54	15	13	7	4.5	58.3	16	12.3	5.6
18	59	12	9	8	5.1	61.1	15.2	8.7	6.3
19	54	17	10	7	4.6	54.9	20.5	11	6.1
20	50	22	10	7	4.6	54.9	21	11.2	5.7
21	48	23	9	6	5.1	60.7	19.5	7.8	4.5
22	41	34	9	6	4.1	46.7	30.2	8.6	6.3
23	61	13	9	7	4.1	65.9	15.9	8.2	5.3
24	63	14	6	7	4.2	57.3	21.2	5.1	7.2
25	64	13	7	7	3.6	58.6	22.4	5.2	7

Comparison of the compound composition of cements by Bogue analysis and by modern X-ray analysis shows that the percentage of alite is usually considerably larger than the corresponding Bogue C_3S, and that the X-ray C_3A is substantially less than the corresponding Bogue value (Table 4.7).

4.8 Electron microprobe analysis

The composition of individual phases in Portland cement clinker can be determined by modern methods.[57,58] Two main types of instrumentation have been employed: the classical electron microprobe (EPMA), using a crystal spectrophotometer to analyse the characteristic X-rays from each element excited by the narrow electron beam of the electron microscope; and SEM-EDS (energy-dispersive spectrometer) where a scanning electron microscope is fitted with a solid-state detector (Si(Li)) for the secondary characteristic X-rays. Electron column instruments attached with wavelength-dispersive or energy-dispersive spectrometers may be used for the analysis of Portland cement clinkers.[59,60] Each system requires a standardisation procedure in which a material with known composition is analysed during the determination and a ratio of characteristic X-ray intensity from the specimen and standard is recorded. Corrections are applied for the differences in absorption, scattering and secondary fluorescence between the specimen and the standard.[30,61] The specimen is mounted in resin and a highly polished surface is presented to the electron beam. This surface is coated with an electrically conducting layer, usually carbon.

For comparison with the analytical data collected on real clinkers, the nominal analyses assumed in the Bogue procedure are presented in Table 4.8. The range of compositions (Tables 4.9–4.12) found for the silicate phases in Portland cement clinker have been published in a number of papers.[59,62–67] Alkalis are always present in amounts varying from <0.2 per cent $Na_2O + K_2O$ up to ~1.5 per cent. Titanium oxide is commonly present to the extent of 0.1–0.4 per cent TiO_2 and may rise to 1.5 per cent in aluminoferrites. MgO occurs in amounts up to 2 per cent in alites and up to about 1 per cent in belites; there up to about 1.5 per cent in the aluminate phase but much more occurs in aluminoferrites, where >5 per cent has been reported. High-iron clinkers, used in sulfate-resisting Portland cement and oilwell cements have been analysed,[68] and gave an average MgO content of 4.2 per cent; the aluminoferrite compositions varied considerably within a single clinker, and deviated from the proposed average value,[56] especially at high MgO contents. Over 5 per cent SiO_2 can occur in both aluminates and aluminoferrites.

Comparisons of analyses from real clinkers with the assumed Bogue values indicate that CaO levels in both alites and belites are somewhat lower than Bogue values. CaO levels in aluminoferrites are similar to the Bogue values but considerably lower than Bogue values in the aluminate phase Levels for Al_2O_3 are similar to Bogue in aluminoferrites and considerably less in the aluminates. Levels for Fe_2O_3 are much less than Bogue values for the aluminoferrite. Na_2O may be moderate in alite, belite and aluminoferrite, but higher in aluminates. K_2O may be high in belite but only moderate in alite. MgO may

Table 4.8 Composition of the Portland cement clinker compounds used in the Bogue formula (per cent)

	C_3S	C_2S	C_3A	C_4AF
CaO	73.684	65.116	62.264	46.159
SiO_2	26.316	34.884	0	0
Al_2O_3	0	0	37.736	20.981
Fe_2O_3	0	0	0	32.860

Table 4.9 Analyses of alites

Component	Range	Average or typical	Reference
Fe_2O_3	0.06–4.48	0.95	63
		0.4	66
	0.4–1.7		62
	0.4–1.5		64
	0.63–1.52		67
		0.7	56
Al_2O_3	1.39–9.24	3.48	63
		1.0	66
	1.0–1.8		62
	1.1–2.7		64
	0.6–1.14		67
		1.0	56
CaO	60.89–76.99	69.50	63
		72.6	66
	69.3–72.4		62
	69.0–72.7		64
	69.34–73.3		67
		71.6	56
MgO	0.14–1.51	0.74	63
		0.6	66
	0.5–2.1		62
	0.5–1.4		64
	0.46–2.05		67
		1.1	56
Na_2O	0.2–1.19	0.67	63
		0	66
	<0.1–0.3		62
	0.1–0.3		64
	0.02–0.25		63
		0.1	56
K_2O	0.05–0.86	0.23	63
		0	66
	<0.1–0.3		62
	0.1–0.3		63
	0.1–0.34		67
		0.1	56

be >1 per cent in alite but somewhat less in belite, and very high in aluminoferrite (5 per cent) and ~1 per cent in aluminates.

The proposed compound compositions to be used in the modified Bogue calculation[56] are within the range of published values. However, the relatively wide range of compositions found in practice seems to detract from this theoretical approach to the determination of phase composition.

Table 4.10 Analyses of belites

Component	Range	Average or typical	Reference
Fe_2O_3	0.06–2.54	0.995	63
		0.8	66
	0.07–2.3		62
	0.3–1.8		64
	0.93–1.74		67
		0.9	56
Al_2O_3	1.39–5.85	3.73	63
		2.1	66
	1.7–2.8		62
	1.4–3.1		64
	0.96–1.92		67
		2.1	56
CaO	55.39–66.78	62.00	63
		63.2	66
	62.2–66.4		62
	60.3–64.4		64
	59.70–64.20		67
		63.5	56
MgO	0.07–1.06	0.34	63
		0.3	66
	0.2–0.8		62
	0.4–0.8		64
	0.23–1.10		67
		0.5	56
Na_2O	0.25–1.38	0.59	63
		0	66
	0.1–0.8		62
	0–1.1		64
	0.06–0.35		63
		0.1	56
K_2O	0.10–3.49	0.98	63
		0.9	66
	0.3–1.9		62
	0.6–1.3		64
	0.53–2.86		67
		0.9	56

Table 4.11 Analyses of aluminoferrites

Component	Range	Average or typical	Reference
SiO_2		3.8	66
	1.8–3.1		62
	2.0–5.5		64
	2.5–4.55		67
		3.6	56
Fe_2O_3		19.6	66
	20.8–26.7		62
	19.4–26.2		64
	18.67–30.63		67
		21.4	56
Al_2O_3		22.1	66
	20.2–24.4		62
	17.3–22.9		64
	13.70–23.16		67
		21.9	56
TiO_2		1.6	66
			62
	0.5–1.8		64
	0.40–1.73		67
		1.6	56
CaO		47.4	66
	47.4–50.0		62
	45.5–50.7		64
	45.95–51.75		67
		47.5	56
MgO		3.9	66
	1.9–3.2		62
	2.3–5.4		64
	1.6–3.3		67
		3.0	56
Na_2O		0	66
	0.1–0.3		62
	0–0.9		64
	0.05–0.20		67
		0.1	56
K_2O		0.3	66
	0.1–0.2		62
	0–0.3		64
	0.05–0.85		67
		0.2	56

Table 4.12 Analyses of aluminates

Component	Range	Average or typical	Reference
SiO_2		4.2	66
	3.1–4.3		62
	3.5–5.6		64
	3.67–6.60		67
		3.7	56
Fe_2O_3		5.0	66
	5.2–8.3		62
	2.9–7.1		64
	4.3–6.60		67
		5.1	56
Al_2O_3		31.3	66
	28.7–31.8		62
	26.4–35.0		64
	21.65–34.2		67
		31.3	56
TiO_2		0.2	66
			62
	0–0.4		64
	0.03–0.40		67
		0.2	56
CaO		56.0	66
	51.5–58.3		62
	52.3–58.7		64
	48.10–61.20		67
		56.6	56
MgO		1.4	66
	0.8–1.5		62
	0–2.1		64
	0.55–1.15		67
		1.4	56
Na_2O		0.9	66
	0.3–4.6		62
	0.2–4.0		64
	1.10–2.25		67
		1.0	56
K_2O		0.6	66
	0.2–0.8		62
	0.3–0.8		64
	1.40–3.85		67
		0.7	56

4.9 Grinding of Portland cement

Cement is produced by grinding clinker with calcium sulfate (either the 'as-dug' natural material or a chemical industry by-product, widely used in Japan, for example), usually in a tube mill. This is divided into two or three chambers by slotted partition walls, termed diaphragms, which permit the forward movement of the cement but keep the size graded, with hard steel balls separated in order to reduce the energy lost by cushioning (fine particles reduce the impact of the balls on the coarser material). Milling is continuous and the fineness of the cement depends on the rate at which clinker and gypsum are introduced. A large mill, 4.6 m in diameter and 14 m long, drawing 4500 kW, would contain ~280 t of steel balls with diameters ranging from 90 mm in the first chamber down to 15 mm in the last chamber. A mill may operate either on open circuit, that is with the product going direct to a storage silo, or on closed circuit with air going through the mill (two or three volume changes per minute) taking the cement to a separator (classifier) from which coarse material is returned for further grinding. Air sweeping the mill carries the product to a classifier. Such a system has the advantages of reducing cushioning and of enhancing cement quality by reducing the residue on a 45 μm sieve for a product with a given specific surface.

The mill must not rotate above the effective critical speed producing a centrifuging action. The shell of the mill is protected by liner plates which may have a rippled profile to optimise lifting, since slippage of the media is another way in which energy is lost. Efficiency is rated in terms of the surface area produced per unit of electrical energy consumed, although in everyday running the residues on 90 and 45 μm sieves are also monitored to detect any fall in mill performance occurring, for example, as a result of media wear. Energy consumption is approximately linear up to about 300 m^2/kg, above which it increases progressively per unit increase in surface area as cushioning becomes more serious. This effect is reduced by the division of the mill into chambers. The energy consumption of a cement mill is usually compared to a 'standard energy requirement' of 1.15×10^4 m^2/kWh for a hypothetical standard clinker.

The grinding media are steel balls of different size distributions optimised with respect to the granulometry of the clinker and the desired fineness of the cement. The finer the cement, the smaller the size of grinding media used. In an open-circuit grinding system, the clinker and gypsum (and possibly other mineral admixtures) are fed into the mill and pass straight through, leaving the mill as finished cement. For a fineness in excess of what corresponds to a Blaine surface area of 320 m^2/kg, it is necessary to use grinding aids to avoid agglomeration of the cement on the grinding media and on the interior parts of the mill.

The wall of a ball mill lifts the media and powder as it rotates, and at a certain height they fall to grind the material. The difficulty in grinding clinker is comparable to that for flint, and energy consumption is considerable. A power consumption in the range 35–40 kWh/t is typical for ordinary Portland cement within the surface area range 300–340 m^2/kg. For rapid-hardening cement (surface area >400 m^2/kg) consumption is in excess of 50 kWh/t. Large modern mills are equipped with internal water sprays since cement prepared at too high a temperature is more susceptible to delayed stiffening or false set. The water used must only cool evaporatively and a target material temperature of ~115°C is usual. An air-cooled heat exchanger may be employed to cool the product, which is usually conveyed pneumatically to a storage silo.

Typical power consumptions for grinding cement with a surface area of 320 m^2/kg of 31.1 kWh/t (of cement) for open and 28.7 kWh/t for closed-circuit milling have been reported.[69] However, the separator in the second system consumed 2.2 kWh/t, so that the overall saving was negligible. On the other hand, in grinding to rapid-hardening cement fineness (400–450 m^2/kg) they observed a typical saving of 1–2 in ~55 kWh/t with closed-circuit equipment. This also has the advantage of producing a cement with a lower residue on a 45 μm sieve which is beneficial to cement quality. Almost all large mills now installed (2000 kW and above) are operated on a closed circuit, and a cooler in the system is desirable, since a major part of the energy consumed is converted into heat. Cooling of the mill is achieved either by sweeping the mill with large amounts of cold air, or by evaporating water from the internal parts of the mill.

In the grinding process, only a small fraction of the energy absorbed (1–2 per cent) is used for increasing the specific surface of the material to be ground, most being dissipated as heat. A small increase in this percentage of useful work would be expected to increase grinding efficiency significantly; major developments in the cement industry have been successfully carried out in this area.

Two developments have succeeded in reducing the power consumption of a mill to between 20 and 30 kWh/t.[70,72] These are the vertical roller mill finish grinder and the roller press pregrinding system. The vertical grinding mill was not introduced earlier because the particle size distribution produced was too steep, so the water requirement was too high. The grinding mechanism of the roller mill is to press and grind the materials between the roller and table, as opposed to the ball mill where most of the energy is wasted as thermal or sonic energy generated by the collision between balls. The behaviour of the ground cement has been shown to be related to the type of grinding equipment employed.[78]

A mill is designed on the basis of the throughput required, using data for clinker grindability determined in the laboratory. The ideal way to grind a material would be to break each crystal or aggregate of crystals, separately by simple cleavage. The energy consumed is then the surface energy plus that lost to the fragments and the media as heat. However, those milling systems which most efficiently keep the particles separated for grinding, such as the roller or vertical spindle mill, are also the most susceptible to wear, and with a hard abrasive material like clinker, this produces maintenance problems. Consequently, although a ball mill wastes energy in multiple impacts (cushioning), ease of maintenance makes it predominant in cement grinding.

For the grinding of clinker to form cement, a number of different systems cover most cases seen in practice.

A conventional closed circuit with a ball mill and a high-efficiency separator.

Pregrinding with a roller press and subsequent finish grinding in a ball mill. The production of the finer particles takes place in the roller press and the main role of the ball mill is to disintegrate the flakes of agglomerated material coming out of the press and to grind the coarser particles. This system is typically preferred for the uprating of existing ball mills, and throughput capacities may be increased by 50 per cent.[71] The system will usually be arranged for the recycling of part of the pressed slabs to the roller press (that part subjected to lower pressures, at the end sections of the rollers).

Semi-finish grinding with a roller press operating in closed circuit with a separator, and finish grinding in a ball mill. The material coming from the press is disagglomerated in the bottom module of the separator, and the coarser part is recycled to the roller press. The finer particles are carried upwards to the top separator where the final separation takes place after mixing with the ball mill discharge; the reject from the top separator is suitable for grinding with small grinding media in a one-compartment mill which ensures optimum ball mill performance. In this way the separation of fines from the roller press prevents overgrinding in the ball mill.

Finish grinding with a roller press operating in closed circuit with a separator. As far as energy saving is concerned, the finish-grinding roller press is attractive but there are a number of drawbacks: the maximum output will be lower than the conventional grinding system; the cement produced will have characteristics somewhat different from those of a cement produced in a conventional cement grinding plant; in particular, the particle size grading is wider in this system, and less dehydration of the gypsum occurs.[70]

Finish grinding with the vertical roller mill in closed circuit incorporating a high-performance separator. The vertical roller mill is widely used in the grinding of raw materials and solid fuel, but its use for finish grinding has been prevented for three reasons: the particle size distribution of the product is too steep, leading to too high a water demand; the degree of dehydration of the gypsum is smaller than with a conventional grinding mill, because the temperature and residence time in the mill are lower; and a problem of vibration generation arose where hard materials were to be ground.[69] These problems have been overcome by automatic particle size control of the milling, using on-line laser diffraction particle size distribution analysers; by maintaining the temperature of grinding at about 120°C to allow appropriate dehydration of the gypsum; and by modifying the shape of the space between the roller table and the roller.

One way of increasing the efficiency of a mill system is to introduce a separator. In the separator the material from the grinding mill is split into a fine and coarse fraction. The coarser particles are returned to the mill for further grinding. Only the finely ground particles leave the mill system as finished cement.

The efficiency of a separator depends on its ability to produce a narrow grain-size interval, and to disperse agglomerates of smaller particles. Separators act by imposing combinations of centrifugal forces and air flow drag on the material. By installing highly efficient separators in existing grinding plants, increases of up to 30 per cent in production have been obtained.

4.9.1 CLINKER GRINDABILITY

The grindability of clinker depends on its chemistry and on the conditions it experiences in burning. Hard burning and high melt contents resulting from a low silica ratio increase initial grindability since they result in a clinker with low porosity. However, after most of the aggregates of crystals have been broken, the fracture properties of the individual phases dominate the rate of increase in fineness. Hardness is less important than brittleness and, since $3CaO \cdot SiO_2$ cracks more readily than $2CaO \cdot SiO_2$ in a microhardness measurement, it is considered that clinkers with a high lime saturation factor are ground more readily than those with a low lime saturation factor.

The specific power consumption for grinding clinker increases when the amount of fine material increases. The production of fine grained or dusty clinker is avoided by ensuring that strong nodules of clinker are formed by agglomeration in the kiln. The requirement is met when 90–95 per cent of the void space is filled with liquid melt, which means that between 15 and 25 per cent by mass of the charge must be melted.[75] Two properties of the melt are decisive in determining the rate of agglomeration of the clinker and the strength of the resulting nodules, namely its surface tension and its viscosity. It has been observed that increasing content of SO_3 in the feed results in a more dusty clinker, and this has been ascribed to the decrease in melt surface tension associated with increased K_2SO_4 levels.

The grindability of a clinker is related to the packing density of the individual clinker mineral grains suspended in the clinker melt. Due to their elongated habit, alite crystals pack less densely than the belite crystals, resulting in a clinker which is easier to grind. The grindability of a clinker sample sintered to a density of $3000\,kg/m^3$ is determined by its fracture energy and the size of the microcracks present.[73] The number and size of the latter can be related to the cooling regime experienced by the clinker. The measured fracture energies using notched sintered prisms of clinker lie in the range 12–20 Jm^2. From measurements of the impression made in each clinker phase by a Vickers microindenter, and the size of the cracks radiating from the indentation, values for a brittleness index have been calculated: $3CaO \cdot SiO_2$, 4.7; $3CaO \cdot Al_2O_3$, 2.9; $2CaO \cdot SiO_2$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, 2.0.

The particle size distribution produced when a material is ground becomes wider as the material becomes easier to grind. During the intergrinding of cement constituents of differing grindability, the particle size distribution of the material which is harder to grind becomes narrower, the easier the other component is to grind. Conversely, the particle size distribution of the material which is easier to grind becomes wider the harder the other component is to grind.[74] The properties of cements with several main components are influenced to a critical extent by the particle size distributions of the components. In spite of the greater fineness required, slag cements do not normally have higher water demands than a Portland cement of the same standard strength. As a rule, interground limestone Portland cements of the same strength require less mixing water than Portland cement in spite of their greater fineness.

4.9.2 GYPSUM ADDITIONS TO PORTLAND CEMENT CLINKER

'Gypsum', while not a raw material in the kiln feed, is used in Portland cement to regulate set and is added to clinker at a level of about 5 per cent, the gypsum rock being generally used in the state in which it is received. Calcium sulfate produced as a chemical by-product in other industries has also been employed.

An addition is calculated to produce the optimum performance from the points of view of strength development and water demand for the cement. It may contain anhydrite, clay, quartz and calcite as impurities, at levels which vary widely with source. Deposits may be mined or quarried; separation of the purest material is necessary for white cement. A material too rich in anhydrite (greater than about 70 per cent) is unsuitable because this mineral dissolves too slowly in water to be the principal set retarder.

The amount of calcium sulfate added depends on the target sulfate level for the cement and therefore also on the sulfate in the clinker. The latter is derived from the sulfur in the raw materials and fuel. Any K_2O or Na_2O in the kiln feed combines preferentially with sulfur to form sulfates. Any excess of sulfur over that required to combine with available alkalis combines with calcium, and the double salt ($2CaSO_4 \cdot K_2SO_4$) may be formed. In the hottest zone of the kiln, the sulfates may volatilise and, in part, be chemically reduced to form sulfur dioxide. These substances are then captured by the incoming feed and recycled. Thus a balanced cycle develops involving entry with the feed to the kiln and loss from it either as a constituent of the clinker or in the combustion gases.

In order to minimise the risk of producing a false setting cement, milling should not be carried out at too high a temperature. Mill temperature is limited by supplying the mill with cool clinker, by cooling the recirculating air and, in some cases, by using an internal water spray. This must do no more than cool evaporatively, of course, and the flow of water is controlled by monitoring the loss on ignition of the cement as it leaves the mill.

4.9.3 SPECIFIC SURFACE AREA

The fineness of cement is a major factor influencing its rate of hydration, since the hydration reaction occurs at the interface with water. The surface area of Portland cement is usually measured by an air permeability method (BS EN 196-9: 1992. *Determination of fineness*). Portland cement is usually ground to a surface area in the range 300–350 m^2/kg and rapid-hardening Portland cement to 400–550 m^2/kg.

Blaine

A standard method of determining the specific surface of cement in many countries is based on the principle of resistance to air flow through a compact of the cement, developed by Rigden and by Blaine. A constant volume method makes use of the fact that the time, t, required to pass a fixed volume of air through a compact bed of cement, 12.7 mm diameter and 15 mm in depth, of standard porosity is related to the specific surface of cement by a simple relationship:

$$S_w = K\sqrt{t} \tag{4.7}$$

where K is a constant for an apparatus. The pressure steadily decreases as air flows through the specimen. A reference cement with standardised specific surface area, originating in the National Institute of Standards and Technology (NIST), near Washington, USA, is used to calibrate the apparatus.

The European Standard EN 196, Part 6 (*Method of testing cement: Determination of fineness:* 1989) is applicable for the determination of specific surface area of cements in the UK. Two methods are given, a sieving method (suitable for checking and controlling the production process) and the above air permeability method.

Lea and Nurse

The air permeability method of Lea and Nurse gives an absolute value of specific surface area, utilising the accurately measured dimensions of the larger cement compact, but it is now no longer used although still included in the Standard. In the Lea and Nurse apparatus, dry air is passed continuously at constant pressure, first through the compacted cylindrical bed of cement (25 mm diameter, 10 mm deep) and then through a length of capillary tubing. The relationship between the surface area, S_w, and the measured resistance to flow of a cement powder bed for a specific surface in the range in which laminar flow occurs is given by the Carman–Kozeny equation:

$$S_w = \frac{N}{\rho(1-\epsilon)}\sqrt{\frac{\epsilon^3 A \Delta p}{\eta Q L}} \tag{4.8}$$

where A, L and ϵ are the bed cross-sectional area, thickness and porosity; η is the Stokes viscosity of air and Q its rate of flow; ρ is the density of the powder and Δp the drop in pressure across the compact bed; N is a dimensionless constant dependent on the units chosen.

A manometer is used to measure the drop in pressure across the bed of cement (h_1), while a second manometer measures the drop across the capillary (h_2) and acts as a flowmeter. The relationship between the specific surface area and a manometer reading is

$$S_w = \frac{K}{\rho}\sqrt{\frac{h_1}{h_2}} \tag{4.9}$$

where K is a constant depending on the dimensions of the apparatus.

The density of the cement is determined by the displacement of kerosine, using a vacuum pump to ensure complete displacement of air, or by use of an air displacement apparatus. Densities of Portland cement usually lie in the range 3050–3250 kg/m^3. The mass of cement used to form the bed in the apparatus is adjusted to produce a bed with a porosity of 0.475.

Wagner

Another method of determining the specific surface area of cement is described in the American Standard ASTM C 115. The cement is dispersed in kerosine and a column of the suspension is allowed to settle, the intensity of light transmitted being measured as a function of time and depth below the surface of the column. In this standard the results are used to determine the specific surface areas, although they could provide a particle size distribution. Because this Wagner procedure assumes that all particles with a diameter <7.5 µm have an average diameter of 3.8 µm, it gives a lower specific surface than an air permeability method.

4.9.4 PARTICLE SIZE DISTRIBUTION

Particle size distributions for powders that have been produced by crushing forces can be represented by the Rosin–Rammler distribution;[76] if the mass percentage oversize, R, is obtained for a range of sizes X (by sieving, for example), then a plot of R against X gives the cumulative percentage oversize curve. According to the Rosin–Rammler theory, a plot of $\log(\log(100/R))$ against $\log(X)$ results in a straight line (Deutsche Normen 66 145: 1976, *Graphical representation of particle size distribution*).

The experimental techniques employed to determine particle size distribution are those applicable generally to powders: sieving; sedimentation in a non-aqueous liquid, such as ethanol; using an Andreasen pipette or a sedimentation balance; the Coulter counter; and light extinction and scattering methods. The principles of these methods are discussed by Allen;[76] gravitational sedimentation and the Coulter counter are described in BS 3406. In the last few years, automated methods of determining particle size distributions, involving the measurement of the low-angle scattering of light, have become available, and are increasingly used in the cement industry. These methods use the fact that a light beam is scattered through a range of angles, dependent on particle size. Measurement of the distribution of light intensity close to the original beam is made possible by employing a laser, and the results can be converted to a particle size distribution.

Intergrinding of two components

In general, the particle size distribution produced by grinding a material is wider, the easier the material is to grind. During the intergrinding of cement constituents of differing grindability, the particle size distribution of the material which is harder to grind becomes narrower the easier the other component is to grind. Conversely, the particle size distribution of the material which is easier to grind becomes wider, the harder the other component is to grind.[74]

Composition of different size fractions for Portland cement

The compositional differences of the different particle size fractions for one particular commercial Portland cement produced during the 1970s are recorded in Tables 4.13 and 4.14. There is a clear tendency for sulfate to concentrate in the finest fractions, as would be expected since most of the sulfate would be present in the easily ground gypsum

Table 4.13 Particle size distributions of a Portland cement (Coulter counter) and the cement classified into five graded fractions by air elutriation

	Mass percentage of size less than the indicated diameter					
Diameter (µm)	Original cement 0	Size fraction 1	Size fraction 2	Size fraction 3	Size fraction 4	Size fraction 5
Nominal size fraction	Initial grading	< 7 µm	7–15 µm	15–24 µm	25–40 µm	> 45 µm
90						99
80						90
70	94					75
60	82				99.5	59
50	71				96	37
45					92	
40	60				87	13
35					73	
30	46			99.6	50	2
25			99	96	28	
20	30		96	83	11	0.2
17.5				66		
15		99.2	89	45	3	
12.5			80	23		
10	14	96	72	8	0.5	
9		94	51			
8		90	39			
7.5				3		
7		80	27			
6		63	17	1		
5	5	43	9			
4		24	2			
3	2	8				
2		0.2				

Table 4.14 Composition of original Portland cement and its classified size fractions

	Percentage composition by mass					
Component	Original cement 0	Size fraction 1	Size fraction 2	Size fraction 3	Size fraction 4	Size fraction 5
Size fraction	Initial	< 7 μm	7–15 μm	15–25 μm	25–45 μm	> 45 μm
SiO_2	22.39	17.44	20.08	22.00	23.31	23.73
Insoluble	0.30	1.03	0.62	0.30	0.17	0.15
Fe_2O_3	2.37	2.12	2.16	2.24	2.33	2.48
Al_2O_3	3.90	3.36	3.55	3.65	3.92	4.30
CaO	64.22	57.39	62.05	64.68	65.49	65.10
MgO	1.09	1.25	1.13	0.98	0.96	0.95
SO_3	2.42	9.23	4.79	2.40	1.26	0.83
Loss 0–105°C	0.03	0.93	0.54	0.36	0.30	0.07
Loss 105–590°C	1.24	4.48	2.73	1.23	0.50	0.57
Loss 590–1000°C	0.69	0.97	0.83	0.96	0.80	0.50
Na_2O	0.15	0.15	0.14	0.13	0.11	0.11
K_2O	0.62	0.86	0.62	0.55	0.56	0.54
P_2O_5	0.18	0.14	0.17	0.18	0.18	0.18
TiO_2	0.30	0.21	0.23	0.24	0.28	0.30
Mn_2O_3	0.09	0.09	0.09	0.10	0.10	0.08
Free CaO	2.65	6.30	4.24	2.56	1.35	1.55
SrO	0.13	0.13	0.14	0.14	0.13	0.13
Bogue composition						
$CaSO_4$	4.1	15.7	8.1	4.1	2.1	1.4
C_3S	45	24	42	52	51	44
C_2S	31	32	26	24	28	35
C_3A	6.3	5.3	5.8	5.9	6.5	7.2
C_4AF	7.2	6.5	6.6	6.8	7.1	7.5
Quantitative X-ray diffraction analysis						
Alite	50	37	49	53	43	44
Belite	32	23	23	24	40	38
C_3A	5.1	3.9	4.2	4.9	5.5	5.7
Ferrite	4.7	4.1	4.3	5.1	5.8	6.4
CaO	1.5	2	1	1	1.5	1.5
$CaSO_4$	–	15.4	6.5	2.5	0.5	0.5
K_2SO_4	–	1.5	1	1	1	1
Physical characteristics						
Density (kg/m^3)	3100	2880	2980	3560	3120	3160
Specific surface (m^2/kg)	373	1490	738	305	141	80

addition. Free lime is also concentrated in the finest fraction, together with loss on ignition and acid-insoluble matter. There are smaller tendencies for concentration in the finest fractions for potassium, sodium and magnesium. Both CaO and SiO_2 are depleted in the finest fraction and the ratio of C_3S to C_2S reaches a maximum in the intermediate particle size range.

4.9.5 WATER DEMAND FOR PORTLAND CEMENTS

The water demand of a cement is the amount of water required to form a paste of standard consistence. When the paste is cast into the standard shallow container, 40 mm in depth, standard consistence is defined as one which allows a flat-ended plunger, 10 mm in diameter and weighing 300 g, to penetrate to between 7 and 5 mm from the bottom of the container.

The fluidity of a cement paste of given water/cement ratio may be measured; the smaller the water demand, the greater the fluidity for a given water/cement ratio. The British Standard test for plasters may be used for cements: an open brass cylinder, 50 mm in height and 30 mm in internal diameter, is placed on a glass plate and filled with freshly mixed paste (plaster or cement), and then the cylinder is raised allowing the paste to flow across the plate; the diameter of the resulting pat (in millimetres) gives a measure of the fluidity of the paste (Table 4.15).

Sulfate-resisting Portland (SRP) cements tend to show lower water demands and greater fluidities than do ordinary Portland cements.

Effect of proportions and activities of the main clinker minerals on water demand and fluidity

Slow cooling during clinker production results in an increased reactivity, due to the production of larger crystal sizes for C_3A, and consequently larger water demand.[77]

Effect of sulfate type and content on water demand

At the optimum calcium sulfate level, the early hydration products of the C_3A form ettringite which deposits as a fine-grained material on the clinker surface. This hydration product does not bridge the water-filled gaps between particles of clinker, and the paste becomes only slightly stiffer due to initial hydration during the early period.[74] Two cements produced from the same clinker to two different specific surface areas, show very different levels of water demands and setting times.

It is argued that the quantity of sulfate in solution should be adjusted to the level of activity of C_3A in order to optimise fluidity: if there is too little sulfate present, then, in addition to ettringite, platy crystals of calcium aluminate hydrate or calcium monosulfoaluminate hydrate are formed. If there is too much sulfate, then secondary gypsum is formed during early hydration of the hemihydrate present. Both additional hydration products result in reduced fluidity and increased water demand and may lead to premature setting.

Table 4.15 Fluidity of cement–water pastes for a range of Portland cements

Cement	C_3S	C_2S	C_3A	C_4AF	Na_2O	K_2O	Surface Area (m^2/kg)	Fluidity (mm)
D9	55	28	8	5	0.18	0.58	426	161
D10	56	14	8	12	0.39	0.90	356	163
D11	62	17	10	6	0.26	0.67	291	168
D14	76	5	9	5	0.21	1.45	372	133
ES924	63	20	1	11	0.30	0.32	433	176
ES1192	57	30	0.4	9	0.13	0.49	300	137
ES1216	59	24	2	11	0.31	0.60	372	182

The solubility behaviour of the sulfate agent depends on the form in which it is present in the cement.[79] Gypsum dissolves relatively slowly; hemihydrate and soluble anhydrite dissolve much faster, and in much greater quantities. Natural anhydrite dissolves substantially more slowly. The high temperatures and relatively long residence time in the ball mill ground product produce almost complete dehydration of the gypsum. A high sulfate concentration at the start of hydration can therefore be obtained easily. Different conditions prevail in the high-pressure grinding rolls: the temperature is much lower and the residence time is much shorter. Consequently, dehydration of the gypsum is much reduced and, if a fast dissolution of sulfate is required, hemihydrate must be added before grinding.

Fineness of grinding

In addition to the form of the sulfate, the fineness of grinding and the distribution of the sulfate will affect the water demand. The optimum percentages of calcium sulfate hemihydrate required in a hemihydrate–anhydrite mixture are much higher for the more finely ground cement. A sufficiently homogeneous distribution can only be achieved by sufficiently high fineness of grinding. With ball mill grinding, the sulfate becomes concentrated in the finest fraction, and is distributed homogeneously throughout the cement. On the other hand, when grinding by high-pressure rolls, the sulfate agent is often not sufficiently finely ground and an adequately homogeneous distribution in the cement is not always achieved.

The fluidity of cement mortars and the water demand of fresh concretes reach optimum levels at intermediate additions of gypsum.[80] It has been deduced[81] that the activity of C_3A is influenced by the stressing of crystal lattices that accompanies fine grinding. This conclusion was drawn from a series of tests in which Portland cement was ground either conventionally in a ball mill or in high-pressure grinding rolls. The water demand of the ball milled cement was 27 per cent and of the high-pressure ground cement was 32.5 per cent, at the same specific surface area (350 m^2/kg). It was argued that a significant increase in C_3A activity had occurred; however, the observed differences in water demand were shown to be the result of differences in the rates of interaction between the calcium sulfate agent present and the C_3A in the two systems.[82]

In addition to the particle size distribution of the cement, a further factor affecting the water demand is the extent of the gypsum dehydration.[70] In roller mills, the grinding temperature remains low and as a consequence most of the gypsum remains as gypsum, and results in a higher water demand. The uneven distribution of gypsum produced by the roller mill would also result in local setting and again cause increased water demand. A relationship has been found between the mill outlet temperature and the water demand, such that the water demand for normal consistency fell from 30.5 to 29 per cent as the mill outlet temperature increased from 90 to 130°C.

Effect of alkali content on water demand

Alkalis affect the reactivity of the C_3A present in a cement: the higher the K_2O bound in the crystal lattice, the greater the reactivity and the greater the concentration of rapidly soluble sulfate required to control the setting and fluidity reduction.[83] If the same quantity of potassium is added as sulfate, there is no increase in activity. In contrast to K_2O, the absorption of Na_2O into the lattice reduces the activity of the C_3A,[83] while neither alkali present as sulfate affects the rate of hydration of the aluminate or the water demand.

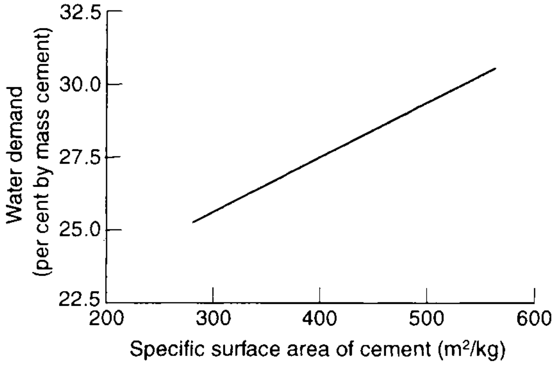

Fig. 4.10 Relationship between water demand and specific surface area of Portland cement.[78]

Investigations of the effect of alkali additions on the rheological properties of cement pastes[84] has shown that the plastic viscosity values were unaffected, but the yield stress values were much higher for high-alkali cements than for low-alkali cements.

The presence of alkali sulfates in clinker can also affect the bleeding of cement pastes. Bleeding is the development of a layer of water at the top surface as a result of the sedimentation of the cement particles. Both the bleeding rate and bleeding capacity of cement pastes decreased with increased amounts of water-soluble alkalis.[85]

Effect of specific surface area on water demand

The relationship between specific surface area and the water demand is presented in Figure 4.10. It was found that the water demand increased significantly as the specific surface area increased.[78]

Effect of particle size distribution on water demand

The surface area and the particle size distribution have a major effect on strength, setting time and more particularly on water demand.[78,86] For equal specific surface area, cements with a narrower particle size distribution have a higher proportion of fine particles, and thus an increasing proportion of fine particles is completely hydrated and a higher strength is obtained. The increased water demand with narrowing particle size range largely arises from the need to fill the voids between cement particles with water, in order to make the paste fluid, and a narrower particle size range inevitably leads to an increase in void content and consequently an increased water demand.

4.10 Unsoundness in Portland cements

Unsoundness may be attributed to the presence of free CaO and MgO in the clinker. The effect of free lime on the expansion of 1:1 sand:cement prisms is illustrated in Figure 4.11.[87]

The European Standard BS EN 196-3: 1995 (*Determination of setting time and soundness*) contains the relevant procedure for the UK. In the test, a cement paste of standard consistence is formed and cast into a small cylinder mould, 30 mm in diameter

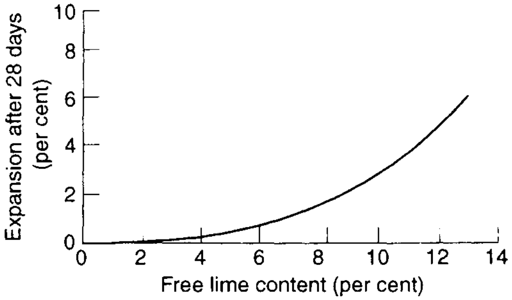

Fig. 4.11 Relationship between free lime content and expansion (water immersion at 20°C).

and 30 mm in height with glass end-plates. The flexible metal cylinder mould is split along its length at one point, and any expansion is magnified by the relative movement of 150 mm arms soldered to the mould on either side of the split.

The cement is allowed to harden under water at 20 ± 1°C for 24 h, then the temperature of the water bath containing the cement paste is raised to 100°C for 1 h and then cooled. Divergence of the arms indicates the tendency for the cement to unsoundness. Expansions must not be greater than 10 mm. If the expansion is greater, aeration of the cement for 7 days should be carried out in a specified manner, and the repeated expansion test result should be less than 5 mm. Unsoundness may be due to the presence of an undue quantity of free lime in the cement (>2 per cent), or to a high MgO content present as the free oxide.

The soundness of a cement is tested mainly by two methods, the autoclave test (ASTM C 151-93a) and the le Chatelier boiling water test. In the autoclave test, cement paste bars (25.4 x 25.4 mm in cross-section) are cured for 24 h at room temperature, their lengths measured and then placed in an autoclave which is raised to a steam pressure of 2 ± 0.07 MPa (216 ± 2°C) and held for 3 h (Table 4.16). The expansion of the bars is

Table 4.16 Effect of fineness and storage on the soundness of cement

MgO in clinker (%)	2.5	3.5	5.0
Periclase in clinker (%)	0.5	1.2	2.6
	Autoclave expansion (%)		
	Cement fineness 300 ± 5 m^2/kg		
Fresh	0.23	0.35	4.10
Stored	0.20	0.30	3.30
	Cement fineness 390 ± 5 m^2/kg		
Fresh	–	–	0.75
Stored	–	–	0.65
	Cement fineness 520 ± 5 m^2/kg		
Fresh	–	–	0.47
Stored	–	–	0.33

obtained after cooling and placing under water. A range of expansions from 0.11 to 0.94 per cent is mentioned in the Standard, and a standard deviation of 0.024 per cent applies throughout this range.

In the le Chatelier test, the expansion of a cement paste is determined after it has been kept at 100°C for 1 h. Both unsoundness due to free CaO and to MgO are detected and assessed in the autoclave test, while the le Chatelier test only fully accounts for the unsoundness due to free CaO.[88]

The autoclave test is a more severe test than the le Chatelier test: cements with 5 per cent MgO passed the le Chatelier test provided their free CaO was low, while all plain Portland cements with this level of MgO failed the autoclave test.[88] The autoclave test is influenced by the C_3A level, the expansion increasing as the potential C_3A increases.[89]

4.10.1 FREE LIME CONTENT

Free, or uncombined, calcium oxide usually occurs to a small extent in Portland cement clinker, and in the ground cement. In a fresh clinker it is entirely present as calcium oxide, but in the ground cement a considerable proportion of the total free lime is usually found to be present as calcium hydroxide. This is due to hydration of the free calcium oxide during grinding of the clinker by moisture contained in the added gypsum, or by combined water released from the gypsum owing to the relatively high temperature developed in the grinding mill. Clinker is often stored for a long period before grinding and may absorb some moisture. Free lime may be detected qualitatively in the ground clinker by the use of White's reagent, a solution of 5 g phenol in 5 mL of nitrobenzene to which two drops of water are added. A few milligrams of the cement or of the finely powdered clinker, are placed on a microscope slide, a drop of White's reagent added, and then a cover glass pressed lightly down. The slide is examined under crossed nicols with a microscope fitted with polarising and analysing nicols. A 16 mm, or higher power, objective should be used. If appreciable amounts of free lime are present, long needles of high birefringence are observed within a few minutes of preparing the slide, at first radiating from the small particles in which free lime is present, and gradually spreading over the slide. Although the crystals, which consist of calcium phenoxide, develop rapidly if much free lime is present, the slide should be allowed to stand 1 h to detect traces. The test is sensitive and will detect <0.1 per cent free lime in a cement. After standing for a long period, there is some indication of attack by the reagent on other constituents of the cement, but this is so slow that it does not interfere with the test. Both free calcium oxide and hydroxide are detected by this test.

A quantitative estimation of the total free calcium oxide and hydroxide in a cement can be made by the extraction method of Lerch and Bogue, which makes use of the solubility of lime in a solvent consisting of one part by volume pure glycerol to five volumes absolute alcohol. The presence of some moisture accelerates the initial rate of solution of the lime; too much may cause attack on the cement compounds, but comparative trials carried out by the ASTM[90,91] showed little difference between the results with glycerols containing 0.5 and 5 per cent water. The alcohol is preferably anhydrous (99 per cent) ethyl alcohol, but anhydrous alcohol denatured with 5 per cent anhydrous methyl alcohol is permitted. The indicator used is 0.18 g phenolphthalein in

2160 mL of the mixed solvent. If the glycerol–alcohol solvent is acidic to the indicator, an addition of a dilute solution of NaOH in absolute alcohol is made until a slight pink colour occurs and, if alkaline, of the standard ammonium acetate solution. This solution, which is used for titrating the lime dissolved in the estimation, is prepared by dissolving 16 g dry crystalline ammonium acetate in 1 L of absolute, or anhydrous denatured, alcohol. It is standardised as follows: 0.1 g of freshly ignited CaO is placed in a 200 mL Erlenmeyer flask and 60 mL of the glycerol–ethyl alcohol solvent added, and the CaO is dispersed by shaking. A reflux condenser is fitted and the mixture is boiled for 5–20 min. It is titrated while still nearly boiling with the ammonium acetate solution. The container is replaced, the boiling is continued for 5–20 min and the mix is titrated again. This process is continued until the free CaO content does not increase by more than 0.05 per cent after 2 h boiling.

The free-lime estimation is carried out by weighing 1 g of finely ground cement into a flask, adding 60 mL of the solvent, and proceeding as in the standardisation of the ammonium acetate solution. The free CaO content of the cement is calculated as follows:

$$\%\ \mathrm{CaO} = \frac{100EV}{w} \tag{4.10}$$

where E = equivalence of standard ammonium acetate solution in grams of CaO per millilitre, V = millilitres of ammonium acetate solution required and w = weight of sample taken.

The method estimates free CaO present both as the oxide and hydroxide. Free MgO, burnt at kiln temperatures, does not react or affect the results.

Various other methods, or modifications of the alcohol–glycerol and ethylene glycol methods, have been proposed, but the only one that need concern us is that of Franke.[92,93] This method makes use of an acetoacetic ester–isobutyl alcohol solvent, and is included in the American Standard ASTM C 114. The pure ester attacks the cement compounds but the isobutyl alcohol reduces the pH and retards their reaction. About 0.05–0.1 g of cement, depending on its free lime content, is placed in a 200 mL Erlenmeyer flask fitted with a ground glass joint and a reflux condenser with calcium chloride and soda-lime guard tubes; 3 mL acetoacetic ester and 20 mL isobutyl alcohol are added and the mixture is boiled for 1 h. After cooling, the solution is filtered through a hirsch funnel (porcelain filter disc) under vacuum, the filter and flask is washed with 20 mL isobutyl alcohol and the calcium in the filtrate is determined.

It will be noticed that the above methods give the total free calcium oxide and hydroxide in a cement and do not differentiate between the two. An approximate determination of the calcium hydroxide present in a fresh cement, and hence, by subtracting it from the total free calcium oxide and hydroxide, of the free calcium oxide, may be obtained by an additional estimation[94] of the water combined as calcium hydroxide.

The small proportion of combined water in a fresh cement may be present either in calcium hydroxide or in hydrated cement compounds and gypsum. On heating the cement, the water combined in the hydrated cement compounds, other than calcium hydroxide, is mostly lost below 350°C, while that combined in calcium hydroxide is lost almost entirely between 350 and 550°C. The loss of water from a fresh cement over the range 350–550°C may, after a small correction, be used as a measure of the calcium hydroxide content. The correction is due to a small loss of water occurring between 350 and 550°C from the hydrated cement compounds. With set cements, it is found, that the loss of water from the hydrated cement compounds at 550°C is about 1.09 times that at 250°C. This factor is rather variable (between 1.07 and 1.12), but when the loss at 350°C is low, as in fresh cements, the error introduced is fairly small. The method cannot, for this reason, be applied satisfactorily to hydrated cements in which the loss at 350°C is large. The calcium hydroxide content is calculated as follows; ~5 g of the cement is heated for 30 min at the stated temperatures. If loss on heating at 350°C = x_1 and loss on heating at 550°C = x_2, then loss due to decomposition of calcium hydroxide = $x_2 - 1.09\,x_1$. This loss multiplied by the ratio of the molecular weight of CaO to H_2O, 56/18, gives the calcium hydroxide content in terms of CaO. The method is probably only correct to about ±0.5 per cent CaO.

Calcium hydroxide in a cement can also be determined by differential thermal analysis, or by thermogravimetric methods.[95,96]

4.10.2 MAGNESIA CONTENT

Free MgO in Portland cement can be determined by a method developed by Taylor and Bogue, in which the free oxide is extracted by treatment with a solution of ammonium nitrate in anhydrous alcohol and glycerol. The MgO forms a double salt, according to the equation:

$$MgO + 4NH_4NO_3 = Mg(NO_3)_4(NH_4)_2 + 2NH_3 + H_2O \tag{4.11}$$

Aqueous solutions of ammonium nitrate attack magnesia present in compounds, or in the glass, of the cement and are therefore unsuitable. The estimation is carried out in the same way as for free lime, using 1 g of the cement, ground to pass a 300-mesh sieve, and adding 4 g ammonium nitrate to the 50 mL absolute alcohol–10 mL glycerol mixture. The mixture is boiled gently on a steam bath or hot plate for 1–5 min until evolution of ammonia ceases. The solution is filtered, the residue is washed with hot absolute alcohol and the magnesia in the filtrate is determined. X-ray analysis can also be used provided that more than about 0.5 per cent MgO is present.

Magnesia is a relatively unimportant constituent in most Portland cements, averaging only about 1.5 per cent MgO in British cements, but in some foreign cements it may rise to 3–4 per cent. MgO that is not incorporated in the clinker phases occurs as periclase at room temperature. Microscopic examination reveals its presence in clinkers with MgO contents from about 2.0 per cent upwards. Magnesium that is combined within the main phases of the clinker does not give rise to unsoundness. Specifications in all countries place a maximum limit, usually 4–6 per cent, on the permissible content of MgO because higher contents lead to long-term unsoundness. This arises from the very slow hydration, accompanied by expansion, of free MgO crystals (periclase) when these are above a certain size.

$$\begin{array}{ccccc} MgO & + & H_2O & = & Mg(OH)_2 \\ \text{periclase} & & \text{water} & & \text{brucite} \\ 11.2 & & 18.0 & & 24.3 \quad \text{molar volumes} \end{array} \tag{4.12}$$

Mg^{2+} can substitute for Ca^{2+} in alite, the substitution limit rising from 1.6 per cent MgO at 1450°C to 2 per cent at 1550°C. Belite can incorporate much smaller amounts of MgO in its crystal lattice, up to 0.5 per cent. Ferrite can incorporate up to 4.4 per

Table 4.17 Electron probe microanalysis of clinkers containing about 2 per cent MgO

Phase	MgO content
Alite	1.3 ± 0.2
Belite	0.6 ± 0.2
Calcium aluminate	2.0 ± 0.5
Calcium aluminoferrite	4.5 ± 0.5

Table 4.18 Effect of MgO grain size on soundness of cement

Grain size of periclase (mm)	Percentage of periclase which causes cracking
0.03–0.06	1.0
0.015–0.03	1.2
0.005–0.015	2.0
<0.005	6.0

cent MgO according to Midgely.[97] C_3A has been reported to be able to incorporate up to 2 per cent MgO. Table 4.17 gives electron microprobe analyses of clinkers containing 2 per cent MgO.[88]

The above levels of magnesium substitution are much lower than the solubilities of MgO in the liquid melt at equilibrium with these solids (5–5.5 per cent), so the maximum uptake of MgO in a clinker depends on the percentage of liquid melt formed at the clinkering temperature. The uptake of MgO into the liquid melt increases rapidly with rising temperature and crystallisation of MgO should occur (i.e. secondary periclase form) during cooling from around 1450°C during manufacture where MgO levels are between 2 and 5 per cent. In industrial clinkers, the MgO takes the form of octahedral or rounded grains (0.001–0.005 mm in diameter) in the matrix, and the MgO grain size influences the percentage MgO that results in unsoundness (see Table 4.18). Very finely crystalline periclase may also be present within the alite grains.[98] Primary periclase is formed in the burning of the clinker, during the thermal decomposition of magnesium-containing carbonates.[99] It can partly dissolve in the melt as the temperature rises but some may remain in the final clinker. The distribution of MgO is influenced by the fineness of grinding of the raw feed and the degree of homogenisation. The crystal size and quantity of primary MgO increases as the burning temperature is increased up to about 1400°C, but at this temperature periclase can begin to dissolve in the liquid melt.

4.10.3 EFFECT OF SPECIFIC SURFACE AREA

The expansion of mortar bars under water at 20°C is affected by the free lime content of the cement and by its specific surface area (Figure 4.12); the finer the grinding of the cement, the smaller is the expansion due to CaO hydration.[87]

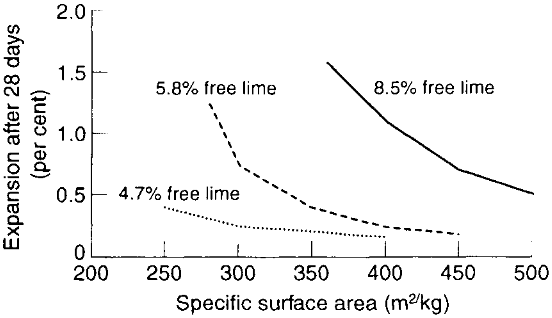

Fig. 4.12 Effect of specific surface area on expansion.

Expansions have been reduced by incorporating sodium, magnesium or calcium chloride with the cement, or by adding 0.4 per cent CaF_2 to the clinker raw feed. The calcium fluoride reduces the size of the periclase grains formed. The unsoundness of cements containing high levels of periclase can be removed by the addition of 50–70 per cent blastfurnace slag, or by intergrinding trass. An addition of 15–30 per cent fly ash is sufficient to eliminate the unsoundness of cements containing 8–15 per cent MgO.

Unsoundness has proved a problem in some countries where the magnesium content of cements is about 3–4 per cent, but under some conditions of burning, higher magnesia contents can be tolerated. Thus cements have been obtained which were sound and had satisfactory strengths,[100] with MgO contents of up to 6.5 per cent, and similar instances have been quoted in later investigations in the USA. It has also been claimed that still higher contents can be tolerated in cements of high iron oxide content[101-103] or to which pozzolanas have been added.[104,105]

4.10.4 EFFECT OF SULFATE CONTENT

The ASTM C 452-89 test (*Potential expansion of Portland cement mortars exposed to sulfate*) employs mortars (cement:sand:water = 1:2.75:0.485) and the Portland cement sulfate content is increased to 7 per cent SO_3 by mass of cement by adding gypsum. The mortar prisms are stored under distilled water and the expansion noted after 28 days. Data have been reported using this test that demonstrate a good correlation between the Bogue C_3A content and expansion.[106,107] Slag cements are expansive when used in this test but fly ash and silica fume blends are not.

The effects of added gypsum on Portland cement mortars and concretes have been investigated.[108] Where excess SO_3 is present, the pattern is one of increasing expansion with increasing initial period of cure. For SO_3 additions above a certain minimum, a common expansion curve versus time is obtained. The maximum SO_3 addition which causes nominally zero further expansion after 2 days curing is adopted as the optimum SO_3 addition for the cement. This definition of optimum sulfate content corresponds with that proposed by Lerch[109] and also with the sulfate level for minimum shrinkage on subsequent drying. A statistical analysis of the data allows the maximum SO_3 which causes zero further expansion to be expressed in terms of the cement fineness F and Bogue composition.

$$(SO_3)_{2d} = 0.035 \cdot F^{0.34} \cdot (\%\ C_3A + \%\ C_4AF) \tag{4.13}$$

The reaction between sulfates and aluminates in Portland cement is one which is used in the commercial production of expansive grouts and concretes. Type S expansive cements are formed from high-C_3A Portland cement clinker and excess calcium sulfate.

4.10.5 DELAYED ETTRINGITE EXPANSION

Hardened Portland cement concrete that has been subjected to either high-temperature heat cure or high-temperature excursions (temperatures up to 100°C in each case) may suffer deterioration (expansion and cracking). This problem is thought to result from the late formation of crystalline ettringite within the hardened concrete. A characteristic feature of concrete suffering from this problem is the development of 'uniform' rims of ettringite (10–50 µm thick) around selected aggregate or sand particles.[110–112] The problem has not been observed with fly ash or slag cement concretes.

Expansion of the order of 1 per cent have been obtained reproducibly in the laboratory for mortar and concrete specimens. An induction period where no expansion occurs is found which may last for up to 1 year. Expansion then gradually occurs over a further period of several months, eventually reaching an ultimate level, after which the concrete remains fairly stable. Deep cracking of the specimens occurs when expansions approach the 1 per cent level, especially for concrete specimens.

Experimentally, the sulfate concentration in the pore fluid rises during curing at elevated temperatures, depending on the temperature of curing, and then slowly falls during subsequent storage at room temperature. It is postulated that aluminate ions are absorbed by the calcium silicate hydrate gel during heat curing of Portland cement. At elevated temperatures, a certain fraction of the aluminate gradually becomes firmly combined as hydrogarnet but the remainder is available after subsequent cooling to form calcium sulfoaluminate hydrates within the cement gel. The reduction in the amount of available aluminate allows a relatively high sulfate concentration in the pore solution to be maintained immediately on cooling and results in conditions favourable to the formation of ettringite rather than calcium monosulfoaluminate.

It is possible that a slow diffusion of the components of ettringite from within the cement paste to growing macrocrystals of ettringite determines the character of the delayed expansion. The very long induction time before expansion commences is a consequence of the extended time required for sufficient ettringite components to diffuse to the nucleation sites. The expansive process results from ettringite crystal growth to give macrocrystalline ettringite. On this basis, delayed ettringite expansion is distinctly different from ordinary sulfate attack.

The main observation giving rise to this hypothesis is that usually cement pastes do not appear to expand while mortars and concretes do, assuming that the cement used is expansive under the heat-cure conditions employed. Also, aggregate type has a large influence on subsequent expansion. This supports the view that nucleation sites (or microcracks) at the cement paste–aggregate interface may be necessary before expansive processes can begin. Cement pastes do expand if microcracking has been allowed to take place during heat cure.

The main observation casting doubt on this view is the uniformity of the bands of ettringite surrounding the aggregate particles, suggesting that the cement paste fraction has expanded away from the aggregate, i.e. that the expansive process is taking place within

Table 4.19 Coefficients of determination (r^2) for expansions after 100, 400, 800 and 1600 days' water storage versus single cement parameters, subsequent to curing at 100°C for 3 h

	Correlation with expansion after increasing time			
Single cement parameters	100 days	400 days	800 days	1600 days
Total SO_3	0.273	0.424	0.414	0.423
CaO	0.198	0.401	0.444	0.468
MgO	0.190	0.406	0.451	0.475
Na_2O	0.286	0.566	0.570	0.597
K_2O	0.063	0.079	0.072	0.079
Soluble Na_2O	0.062	0.204	0.194	0.183
Soluble K_2O	0.016	0.077	0.081	0.086
Combined Na_2O	0.289	0.495	0.515	0.549
Combined K_2O	0.066	0.013	0.006	0.008
Soluble SO_3	0.098	0.086	0.081	0.084
Alite	0.042	0	0.001	0.001
C_3A	0.060	0.143	0.146	0.136

the cement paste fraction. It has been observed that sometimes this band surrounding the aggregate is empty or filled with calcium hydroxide, again indicating that the process is one of expansion leading to a gap developing at the paste–aggregate interface which subsequently (and incidentally) usually becomes filled with crystal growth.

An alternative view is that expansion is determined by the absorption of moisture from the environment, the long times involved before expansion being a consequence of the very slow diffusion of additional moisture into the dense mortars. The actual mechanism of expansion is then similar to that for simple sulfate attack. However, a successful theory has not been established from the large number of hypotheses suggested for this expansive process; it could be the result of simple ettringite crystal growth, or ettringite crystal swelling from some partially dehydrated form of ettringite, or a form of colloidal imbibition of water by finely divided ettringite. It seems clear that expansion is associated with the presence of ettringite, however.

On this basis, the differences in expansiveness shown by cement pastes, mortars and concretes are the result of differences in rates of diffusion of moisture through these materials, coupled with the high sensitivity of the expansive process to moisture levels in the systems. In support of these views, it is observed that small specimens expand more rapidly than larger specimens.

Whatever the precise mechanism of expansion, there is a degree of correlation between Portland cement composition and a tendency to show expansion (Table 4.19). Fifty-five Portland cements were examined by forming them into standard mortar prisms, 40 × 40 × 160 mm in dimensions, and then heat curing at 100°C for 3 h while under water, and then cooling under water to room temperature. Both fineness of grinding and total sulfate level are found to be significant and to correlate positively with expansions. The sulfate content probably determines the quantity of ettringite being produced in a given cement, and therefore the total expansion. Fineness of grinding affects the rate of hydration and possibly the degree of interaction between aluminate and silicate hydrates. Among the components of clinker composition which appear to correlate positively with expansion are MgO content and combined Na_2O.

4.11 Use of compound content in cement specifications

The specifications for Portland cement in many countries contain some clauses relating to the composition. Some limitation is often placed on the lime content with the object of ensuring that the cement does not contain excess lime over that which can combine with the acidic oxides and thus liable to show unsoundness. It is true that a separate specific test for soundness is always included, but it has usually been considered that an additional safeguard is provided by limiting the lime content. With the continued demand for cements of higher earlier strength, it has been necessary for manufacturers to raise the lime content, and the specification limits have been progressively raised to enable this to be done.

4.11.1 AMERICAN CEMENT STANDARDS

Standard chemical requirements are set out in Table 4.20. The American Standards make extensive use of the chemical composition of cements and set out the Bogue calculation for compound content in great detail (ASTM C 150).

In addition, there are ASTM methods (C 265-64) for determining the amount of water-soluble sulfur trioxide in a cement paste at 24 h after mixing, and for the determination of the optimum SO_3 content for highest strength. Neither of these tests is a specification requirement.

Some specifications limit the content of matter insoluble in dilute acid, e.g. to 1.5 per cent in the British, 0.75 per cent in the ASTM and up to 3 per cent in other national specifications. The loss on ignition is also usually controlled, the maximum permitted under the British specification being 3 per cent for cements in temperate climates and 4 per cent in tropical climates. The ASTM limit is 3 per cent, except for Type IV where it is 2.5 per cent. Limits in other countries, e.g. Germany, go up to 5 per cent.

Table 4.20 Chemical specifications for Portland cements, ASTM C 150-94

	Cement type				
	I and IA	II and IIA	III and IIIA	IV	V
SiO_2 minimum (%)		20.0			
Al_2O_3 maximum (%)		6.0			
Fe_2O_3 maximum (%)		6.0		6.5	
MgO maximum (%)	6.0	6.0	6.0	6.0	6.0
SO_3 maximum (%)					
When C_3A is 8% or less	3.0	3.0	3.5	2.3	2.3
When C_3A is >8%	3.5		4.5		
Loss on ignition (%)	3.0	3.0	3.0	2.5	3.0
Insoluble residue (%)	0.75	0.75	0.75	0.75	0.75
C_3S maximum (%)				35	
C_2S minimum (%)				40	
C_3A maximum (%)		8	15	7	5
($C_3A + C_4AF$) maximum or solid solution ($C_4AF + C_2F$) maximum, whichever is appropriate (%)					25

Table 4.21 Nomenclature and compositions of cements defined in the European Standard BS ENV 197-1: 1992

Cement	Designation		Clinker	S	D	P	Q	V	W	T	L
CEM I	Portland cement	I	95–100								
CEM II	Portland slag cement	II/A-S	80–94	6–20							
		II/B-S	65–79	21–35							
	Portland silica fume cement	II/A-D	90–94		6–10						
	Portland pozzolanic cement	II/A-P	80–94			6–20					
		II/B-P	65–79			21–35					
		II/A-Q	80–94				6–20				
		II/B-Q	65–79				21–35				
	Portland fly ash cement	II/A-V	80–94					6–20			
		II/B-V	65–79					21–35			
		II/A-W	80–94						6–20		
		II/B-W	65–79						21–35		
	Portland burnt shale cement	II/A-T	80–94							6–20	
		II/B-T	65–79							21–35	
	Portland limestone cement	II/A-L	80–94								6–20
		II/B-L	65–79								21–35
	Portland composite cement	II/A-M	80–94	6-20							
		II/B-M	65–79	21–35							
CEM III	Blastfurnace cement	III/A	35–64	36–65							
		III/B	20–34	66–80							
		III/C	5–19	81–95							
CEM IV	Pozzolanic cement	IV/A	65–89		11–35						
		IV/B	45–64		36–55						
CEM V	Composite cement	V/A	40–64	18–30		18–30					
		V/B	20–39	31–50		31–50					

Table 4.22 Definitions of strength classes in ENV 197

Strength class	Compressive strength (MPa)		
	2 days	7 days	28 days
32.5	–	> 16	32.5–52.5
32.5R	≥10	–	32.5–52.5
42.5	≥10	–	42.5–62.5
42.5R	≥20	–	42.5–62.5
52.5	≥20	–	≥52.5
52.5R	≥30	–	≥52.5

4.11.2 EUROPEAN CEMENT STANDARDS

- BS ENV 197-1: 1992. *Cement – composition, specification and conformity criteria.*
- DD ENV 197-1: 1995. *Common cements.*

The European Prestandard has now been adopted by the European Committee for Standardisation (CEN); cement types are outlined in Tables 4.21 and 4.23. There are five main types but Type II is subdivided into seven divisions, making 11 different types of cement, but most of these 11 binder types can be specified with different proportions of Portland cement clinker, giving 25 different cements in all. Each of these can be obtained in three strength classes, being the characteristic compressive strength after 28 days hydration in Megapascals (32.5, 42.5 and 52.5; Table 4.22), which may be high early strength (R) or ordinary, totalling 150 cements in all. Crushing strength is measured using mortar prisms, 40 x 40 x 160 mm in dimension, in accordance with the specification set out in BS EN 196-1: 1996. An additional strength class is included in the Standard for use in the UK, that of 62.5N.

The values in Table 4.21 refer to the cement nucleus, excluding calcium sulfate and any additives. All cements, apart from Portland–composite cement, can contain up to 5 per cent minor constituents, which may be filler or one of the other main components unless they are included as a main constituent of the cement.

The usual addition of calcium sulfate is required for all binder types in order to regulate the setting time. The maximum permitted level for SO_3 is generally 3.5 per cent, except that type CEM III may contain up to 4.0 per cent. Other binder types in the strength class 42.5R may also contain up to 4.0 per cent SO_3. Cement type CEM II/B-T and CEM III/C may contain up to 4.5 per cent SO_3. These limits are characteristic values rather than absolute maxima, and may be exceeded by up to 0.5 per cent SO_3 in 10 per cent of the samples taken.

OPC (BS 12: 1989) is similar to CEM I, 42.5 strength class; RHPC (BS 12: 1989) is similar to CEM I, 42.5R strength class; CFPC (BS 12: 1989) is similar to CEM I, 32.5R strength class.

4.11.3 BRITISH CEMENT STANDARDS

Many countries place no limit on the lime content of Portland cement. The ASTM specification (C 150-94) does not limit the lime content for ordinary (Type I) and rapid-

Table 4.23 Identification of the main constituents of European cements, other than Portland cement clinker

Notation	Designation
S	Granulated blastfurnace slag
D	Silica fume
P	Pozzolana, natural
Q	Pozzolana, industrial
V	Fly ash, siliceous
W	Fly ash, calcareous
T	Burnt shale
L	Limestone
M	Composite, two or more of the above

hardening (Type III) Portland cement, but for modified (Type II), low-heat (Type IV) and sulfate-resisting cement (Type V) there are composition requirements as in Table 4.20.

Active hydraulic binders (UK)

The British Standard specification for Portland cement has been modified to align it more closely with the developments in Technical Committee 51 of the European Committee for Standardisation (CEN). A range of strength classes can now be specified, which include the performance ranges of the old Ordinary Portland and Rapid-Hardening Portland cements. The MgO content should not exceed 5.0 per cent and the SO_3 content should not exceed 3.5 per cent, in general; if the level of C_3A (Bogue) is less than 3.5 per cent, the proportion of SO_3 should not exceed 2.5 per cent.

Portland cement Portland cement (BS 12: 1996) is a factory-produced binder general-purpose Portland cement made by grinding Portland cement clinker together with a controlled amount of calcium sulfate ($\leq$3.5 per cent SO_3) and up to 5 per cent additional inorganic mineral, e.g. fly ash or limestone. Portland cement clinker consists of not less than 66 per cent of calcium silicates ($3CaO \cdot SiO_2 + 2CaO \cdot SiO_2$). The ratio CaO/SiO_2 shall not be less than 2.0. The maximum MgO level is 5 per cent in the Portland cement clinker component. Although a specified fineness or specific surface area is no longer included in the Standard, fineness data (BS EN 196-21) and more detailed chemical analyses can be made available on request. Compressive strengths shall conform to the European Standard ENV 197-1 and shall be measured according to BS EN 196-1: 1995. The initial setting time (BS EN 196-3: 1995) shall not be less than 60 min in general, and not less than 45 min for cement strength classes 52.5N and 62.5N. The expansion determined in the test for unsoundness (BS EN 196-3) shall not exceed 10 mm.

Sulfate-resisting Portland cement Sulfate-resisting Portland cement (BS 4027: 1996) is made by burning normal raw materials to which iron oxide is added, to reduce the alumina ratio to about 0.7. An addition of siliceous material is made to maintain the silica ratio. The content of C_3A in the resulting clinker is usually of the order of 1 per cent when calculated by the Bogue formula, $\% \, C_3A = 2.65A - 1.69F$ (Al_2O_3 and Fe_2O_3 determined by BS EN 196-2: 1995), and the composition of the aluminoferrite approaches C_6AF_2. It is usually ground more finely than ordinary Portland cement. The maximum permitted C_3A is 3.5 per cent (Bogue calculation). Fineness data and more detailed chemical analyses can be made available on request. Provision is made for a low-alkali (<0.6 per cent equivalent Na_2O, equal to % Na_2O + (62/94)·% K_2O) sulfate-resisting Portland cement in this standard. The general chemical, strength, soundness and setting time requirements set out in BS 12 for Portland cement are applicable; the SO_3 level should not exceed 2.5 per cent. Note that no minor mineral addition is permitted for this Portland cement.

Sulfate-resisting Portland cements were developed in Germany and Canada during the 1930s and differ primarily from ordinary Portland cement in having a low calculated content of tricalcium aluminate. This may be achieved either by using raw materials of low alumina content or by adding iron oxide in order to produce a low ratio of Al_2O_3/Fe_2O_3, i.e. about unity or less. It is not usual for this ratio to fall below 0.64, corresponding to the compound $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The strength requirements for sulfate-resisting Portland cement are the same as for ordinary Portland cement in the British specifications, and slightly lower in the ASTM specifications.

White cement White cement is manufactured from especially pure chalk or limestone, with china clay (low in iron) and white sand as sources of silica. It is otherwise covered by the requirements of BS 12. Such an unreactive mix requires power-consuming sand grinding, and very high clinkering temperatures (~1600°C).

Quick-setting cements Quick-setting cements and cements which set with a high water/cement ratio are available on a limited scale in the UK. They are produced either by intergrinding Portland cement clinker with a special clinker rich in $C_{12}A_7$, and suitable retarders, or by using a clinker containing Klein's compound ($3CA \cdot CaSO_4$ or $C_4A_3 \cdot SO_3$). Cements which are expansive or shrinkage compensated can be obtained by intergrinding Klein's compound with anhydrite and Portland cement clinker. The latter acts as a source of lime so that ettringite formation occurs with a degree of expansion, depending on the proportions used.

Oil well cements Oil well cements are based on coarsely ground sulfate-resisting Portland cement clinker with one or more retarders (gypsum or lignosulfonates) to give the extended thickening time necessary for pumping a cement grout at high temperatures and pressures. The amount and type of retarder is dependent on the oil well depth.

Controlled fineness Portland cement Controlled fineness Portland cement (BS 12: 1996), a category of Portland cement, is included in this edition of BS 12, having an unspecified fineness that is to be agreed between the cement manufacturer and the customer. This cement is primarily intended for use in the manufacture of fibre-cement board, where a calendering machine is used to deposit successive layers of cement/fibre from a dilute slurry onto a porous fabric belt. A coarsely ground cement allows easier extraction of the excess water in the deposited layers.

Low-heat Portland cement Low-heat Portland cement (BS 1370: 1979) is usually only manufactured to meet an individual, very large order. A low lime saturation is employed to reduce the C_3S content and a lower limit for surface area is specified, since employing a cement which is too coarsely ground to reduce the rate of heat evolution would yield concretes prone to bleeding and segregation. Heat of hydration is limited to 250 kJ/kg at an age of 7 days and 290 kJ/kg at 28 days. Chemical composition limits are defined in terms of the moduli:

$$\frac{1.0\ \%\ \mathrm{CaO} - 0.7\ \%\ \mathrm{SO_3}}{2.4\ \%\ \mathrm{SiO_2} + 1.2\ \%\ \mathrm{Al_2O_3} + 0.65\ \%\ \mathrm{Fe_2O_3}} < 1.0 \tag{4.14}$$

and

$$\frac{1.0\ \%\ \mathrm{CaO} - 0.7\ \%\ \mathrm{SO_3}}{1.9\ \%\ \mathrm{SiO_2} + 1.2\ \%\ \mathrm{Al_2O_3} + 0.65\ \%\ \mathrm{Fe_2O_3}} > 1.0 \tag{4.15}$$

The maximum SO_3 content should not exceed 3.0 per cent. The specific surface must be greater than 325 m^2/kg.

Low-heat Portland cement was developed in the USA soon after 1930 for use in mass concrete construction, such as dams, where the temperature rise caused by the heat evolved on hydration can become excessively large. A form of cement with a heat evolution intermediate between that of low-heat and the average ordinary Portland cement, but with a rate of strength development nearly comparable to the latter, was introduced in the USA in about 1934 as a compromise to avoid some of the difficulties that had arisen in concreting with low-heat cement in cold weather.[113,114] Later, this cement first called 'modified' cement, and subsequently Type II cement, was adopted for some other types of constructional work on account of its supposed superior durability to ordinary Portland cement. It is defined in the ASTM specification as being for use for concrete exposed to moderate sulfate action, or where moderate heat of hydration is required. The method of control used in the specification is based on a limitation of composition and compound content. Its manufacture spread later to many other countries, although with the introduction of other methods of concrete cooling, its use has now declined.

Low-alkali Portland cement The observation that certain aggregates are sensitive to attack by alkalis and that these occur much more widely than was previously thought has led to the increasing availability of low-alkali cements (<0.6 per cent equivalent Na_2O, equal to % $Na_2O + (62/94) \cdot$ % K_2O). In the UK the requirement can be met by sulfate-resisting Portland cements.

Latent hydraulic binders (UK)

Pulverised-fuel ash This is covered by the British Standard BS 3892: Part 1: 1993 (*Specification for pulverised-fuel ash for use with Portland cement*). The solid waste product extracted from power station flue gases by electrostatic precipitation is selected and, where necessary, processed. An upper limit is placed on SO_3 level of 2.0 per cent. The American Standard ASTM C 618-87 (*Specification for fly ash and raw or calcined natural pozzolan for use as a mineral admixture in Portland cement concrete*) recognises two types of fly ash: Class F, the type normally met in the UK and produced by burning anthracite or bituminous coal, and Class C, produced by burning lignite or sub-bituminous coal which may contain a lime content greater than 10 per cent CaO. A maximum level of 4 per cent SO is placed on Class F fly ash, and 5 per cent SO_3 on Class C fly ash.

Ground granulated blastfurnace slag This is covered by BS 6699: 1992 (*Specification for ground granulated blastfurnace slag for use with Portland cement*). Selected blastfurnace slag, a by-product from the manufacture of pig iron, is quenched from the molten state, and finely ground (maximum SO_3 2.0 per cent). The equivalent American standard is ASTM C 989-88 (*Specification for ground granulated blastfurnace slag for use in concrete and mortars*).

Silica fume, ASTM C 1240-93 Silica fume for use in hydraulic cement concrete and mortar; minimum SiO_2 85 per cent.

Composite hydraulic binders (UK)

Portland blastfurnace cements (BS 146: 1996) These are represented by factory cement (granulated blastfurnace slag comprises 6–35 per cent of the total composite binder) and Blastfurnace cement (BC) containing selected Portland cement clinker (complying where appropriate with BS 12 cement clinker) and selected granulated blastfurnace slag; either interground or blended after separate grinding; the SO levels are brought to an optimum value by including calcium sulfate in the formulation (maximum 3.5 per cent SO_3). Two types of Portland blastfurnace cement are included in the standard: Portland slag cement (6–35 per cent blastfurnace slag) and Blastfurnace cement (36–65 per cent blastfurnace slag).

High-slag blastfurnace cement (HSBC) (BS 4246: 1996) This is composed of factory cement (granulated blastfurnace slag 50–85 per cent of total composite binder containing selected Portland cement clinker, complying where appropriate with BS 12 cement clinker) and selected granulated blastfurnace slag; either interground or blended after separate grinding. The SO_3 level is brought to an optimum value by including calcium sulfate in the formulation (maximum 3.5 per cent SO_3).

Supersulfated cement (BS 4248: 1982) This is a factory cement, a composite binder containing a high level of granulated blastfurnace slag (minimum 75 per cent of the total composite binder) ground or blended with a Portland cement clinker and a controlled increased proportion of calcium sulfate (minimum 4.5 per cent SO_3). This binder is not currently available in the UK.

Portland pulverised-fuel ash cements (BS 6588: 1996) These comprise factory cement (fly ash 6–35 per cent of total composite binder) formed by blending or intergrinding Portland cement clinker (complying where appropriate with BS 12 cement clinker) with pulverised-fuel ash. This class of cement is subdivided into A 6–20 per cent fly ash and B 21–35 per cent fly ash. The SO_3 level is adjusted to an optimum value by incorporating calcium sulfate in the formulation (maximum 3.5 per cent SO_3).

Pozzolanic pulverised-fuel ash cement (BS 6610: 1996) A factory cement (fly ash 36–55 per cent of total composite binder) formed by blending or intergrinding Portland cement clinker (complying where appropriate with BS 12 cement clinker) with ground pozzolana (fly ash). The SO_3 level is adjusted to an optimum value by incorporating calcium sulfate in the formulation (maximum 3.5 per cent SO_3).

Portland limestone cement (BS 7583: 1996) A factory cement (limestone 6–20 per cent of total composite binder) formed by blending or integrating Portland cement clinker (complying as appropriate with BS 12 clinker) with ground limestone. The SO_3 level is adjusted to an optimum value by incorporating calcium sulfate in the formulation (maximum 3.5 per cent SO_3).

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5

The Burning of Portland Cement

Fredrik P. Glasser

5.1 Introduction

When the last revised edition of this book was published in 1970, the foundations of the physics, chemistry and mineralogy of clinkering had been laid. The purpose of this chapter is to update and supplement this information. Reference will be made to older papers, pre-1970, where relevant but the older literature will not be comprehensively reviewed. Where literature references are given, priority is reserved for source papers and to recent reviews which provide in-depth coverage as it is not practicable to cite every relevant paper.

During the burning of cement, the raw materials are combined into the characteristic phases which we associate with the product termed 'Portland cement'. The coexistence and nature of compounds in a Portland cement content comprise a distinctive synthetic product which is termed 'clinker'. The constituent phases of cement clinker occur rarely in nature, hence the unique nature of the synthetic material. Nevertheless, the synthetic material develops in response to the principles of chemical thermodynamics. Three processes are essential for production of a satisfactory clinker:

1. the correct chemical composition of the mix;
2. an appropriate physico-chemical state of the raw constituents, such as fineness and homogeneity;
3. the temperature and duration of burning and the conditions of clinker cooling.

During the past few decades, several important process changes have occurred. Briefly, changes to production technology include:

- Improved grinding methods and closer control of particle size distribution of the raw meal.
- The tendency, where practical, to incorporate appropriate by-product materials as part of the kiln feed. These may include additives which are incorporated into clinker, such as slags, fly ash and mill scale, or combustible wastes such as rubber tyres, used hydrocarbon oils and solvents.
- The widespread use of dry or semi-dry process kilns, in conjunction with suspension preheaters, to improve fuel economy.
- Stricter environmental controls leading, for example, to limits on the chromium content of clinker and on dust emissions from kiln stacks, at the baghouse, etc.

While these changes reflect on plant practice and influence the design of new plant as well as upgrading or replacement of older plant, many features of cement production remain essentially unchanged. We recognise that:

- It is essential to approach a phase equilibrium, or very nearly an equilibrium, at clinkering temperatures. Previous processing of raw materials, including selection, blending and preliminary pyro-processing have as their objective the attainment of a high-temperature equilibrium as rapidly as possible, with minimal expenditure of energy at all stages and optimisation of the overall energy budget.
- The mineralogical state of the clinker attained at peak firing temperature becomes thermodynamically unstable as the clinker is cooled. Nevertheless, it is highly desirable to control the sequence of phase changes occurring during cooling. The phase transformations encountered during cooling vary greatly in their kinetics; some are virtually non-quenchable, especially on an industrial scale, while others are readily inhibited, even at relatively slow cooling rates characteristic of large-scale production processes. In general, the quenched phases stable at high temperature are preferred to the low-temperature phases.
- Despite the extensive chemical changes occurring, including loss of water, CO_2, etc., and the rather thorough mineralogical reconstitution which occurs during clinkerisation, the microstructural features of clinker still reflect, in part, the microstructure, mineralogy and granulometry of the raw materials, the kiln design, the nature of the fuel source and the kiln atmosphere, as well as the thermal profiling of the clinkering process.

Cement chemical shorthand ($C = CaO$, $A = Al_2O_3$, $S = SiO_2$, $M = MgO$, $F = Fe_2O_3$, $f = FeO$, $\bar{S} = SO_3$) will be used, often interspersed with full formulae and, where appropriate, mineral names, e.g. C_2AS = gehlenite = $Ca_2Al_2SiO_7$. Minor substitution, e.g. Fe^{3+} for Al^{3+}, often occurs without explicit mention. Mineral names, which imply a structure type rather than a specific chemistry, are especially useful in this context.

5.2 Methods for the determination of clinker phase composition

5.2.1 SURVEY OF METHODS

The phase content of clinker greatly influences its properties and it is therefore important to anticipate its mineralogy and, where appropriate, determine it directly. Various direct and indirect methods have been used to determine phase content: Table 5.1 gives a survey of the principal methods in use. These methods will be developed subsequently.

5.2.2 CALCULATION OF PHASE COMPOSITION

Historically, the Bogue calculation was one of the first practical fruits of phase equilibrium studies of the $CaO-Al_2O_3-Fe_2O_3-SiO_2$ system. It recognised that cements were comprised mainly of four phases, having the idealised compositions Ca_3SiO_5, Ca_2SiO_4, $Ca_3Al_2O_6$ and $Ca_2(Fe_{2-x}Al_x)O_5$. The compositions of the phases could be related to bulk composition by solving a series of simultaneous equations, construction of which was based on the relevant known phase equilibria in portions of the $CaO-Al_2O_3-Fe_2O_3-SiO_2$ system. A great utility of the Bogue calculation is that it is not necessary to have an actual clinker on which to perform measurements; various proportions of raw materials, each of known

Table 5.1 Principal methods for the determination of Portland cement clinker composition

Method	Applications area
Direct methods	
X-ray powder diffraction	Relates X-ray reflection intensity to phase content
Optical microscopy	Requires polished and etched thin section of clinker
Scanning electron microscopy with analysis	Closely related to optical microscopy; more expensive but also capable of automation; more versatile since chemical differences can also be measured
Supplementary methods	
Selective dissolution	Chemical free-lime determination is a widely used example; other methods are occasionally used. Requires judicious selection of reagents
Thermal analysis	Determination of thermally active phases in mixtures, e.g. gypsum content by thermogravimetry
Indirect methods	
Bogue calculation	Converts chemical analysis to potential phase composition; does not actually require measurements on a clinker, so useful for trial calculations
Hybrid methods	
Modified Bogue-type calculation	Uses Bogue-type calculation but additionally incorporates experimentally determined corrections, e.g. for chemically determined free lime, Ca contained in residual anhydrite, and solid solution corrections, using realistic formulae

composition, can be converted by straightforward calculation to a potential phase composition, thereby enabling proposed mixes to be evaluated for cementitious potential, in terms of their final mineralogy. Of course, Bogue was sufficiently familiar with clinkering technology to be aware that equilibrium might not be fully attained in the course of burning and introduced an optional correction factor to allow for the content of free, chemically uncombined lime: other commonly occurring departures from equilibrium could also be catered for in order to reconcile potential and actual phase contents. However, the principal use of the calculation was to indicate the potential composition of the batch, rather than its actual composition.

Despite its apparently firm theoretical foundation, the Bogue calculation has not escaped criticism. Some of these criticisms arise from a failure to appreciate the nature of its underlying assumptions, while others have a more factual basis. For example, direct experimental methods applied to the quantitative determination of clinker mineralogy have tended to suggest that the Bogue calculation systematically underestimates the alite content of clinker. Gutteridge concluded this by X-ray diffraction,[1] Odler by microscopy and X-ray diffraction[2] and Kristman by reflected light microscopy;[3] Aldridge came to the same conclusion using results of a cooperative study, based on microscopic examination of selected clinker which was independently analysed in six laboratories.[4]

Taylor reviewed these differences and presented a revised basis for the Bogue calculation.[5] It takes into account modern data on element fractionation into Portland cement clinker phases, using data collected from a number of sources. Table 5.2 indicates the average compositions of cement clinker phases which, it is suggested, approximate those encountered in 'real' clinkers. In the absence of specific analyses of the constituent phases, these compositions are recommended for use. In most cases, the amount of non-essential oxides contained in solid solution in the principal clinker phases is considerably less than the maximum values recorded in the literature but, as noted, this is not unexpected.

Some trends in element distribution are evident. Amongst the silicate phases, MgO concentrates in alite whereas Al_2O_3 and K_2O are preferentially concentrated in belite. Overall, ferrite is the host for much of the MgO and especially TiO_2; Na_2O concentrates in the aluminate. Although a clinker may contain overall only a few weight per cent of the minor components, their unequal partition amongst the major phases is partially responsible for the departures observed in practice from idealised Bogue calculations. Also, data obtained from real clinkers enable selection of a more realistic ferrite phase composition; the C_4AF composition, often assumed as the basis for a Bogue calculation, may not be correct. If an incorrect composition is used, it gives unrepresentative values of the alumina partition which, in turn, will affect calculation of C_3A as well as ferrite contents. The use of more sophisticated phase compositions, derived from real clinkers, will thus give a more reliable estimate of potential phase composition. Unusual clinkers, having abnormal contents of minor elements, may still cause problems but the bulk of clinker compositions will probably be amenable to treatment by the modified Bogue calculation and enable a convergence between calculated and observed phase compositions to be achieved.

Table 5.2 Composition (weight per cent) of the phases in Portland cement clinker

Phases	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
Silicates								
Alite[a]	0.1	1.1	1.0	25.2	0.1	71.6	0.0	0.7
Belite[b]	0.1	0.5	2.1	31.5	0.9	63.5	0.2	0.9
Aluminate								
[c]	1.0	1.4	31.3	3.7	0.7	56.6	0.2	5.1
[d]	0.6	1.2	28.9	4.3	4.0	53.9	0.5	6.6
[e]	0.4	1.0	33.8	4.6	0.5	58.1	0.6	1.0
Ferrite								
[f]	0.1	3.0	21.9	3.6	0.2	47.5	1.6	21.4
[g]	0.1	2.8	15.2	3.5	0.2	46.0	1.7	29.8

[a] For a clinker with 1.65% MgO and 2.8% Fe_2O_3. More generally, MgO in alite = 0.667%, MgO in clinker, up to a maximum of 2%. Fe_2O_3 in alite = 0.25%, Fe_2O_3 in clinker, up to a maximum of 1.1%; % CaO = 71.6 − 1.4 (% MgO in alite − 1.1): the composition should be normalised to 100%.

[b] Also contains 0.1% SO_3. SO_3 in belite tends to be highest in clinkers with high $SO_3/(Na_2O + K_2O)$ ratios.

[c] Cubic aluminate, typically found in clinkers with low alkali contents and Al_2O_3/Fe_2O_3 weight ratio $\geqslant 1.5$.

[d] Orthorhombic or pseudo-tetragonal aluminate, as found in high-alkali clinkers.

[e] Tentative composition suggested for C_3A aluminate in white cement clinker.

[f] Additionally, 0.7% Mn_2O_3. Composition from normal clinker with $Al_2O_3/Fe_2O_3 \geqslant 1.5$.

[g] Additionally, 0.7% Mn_2O_3. Tentative composition from ferrite in sulfate-resistant Portland clinkers.

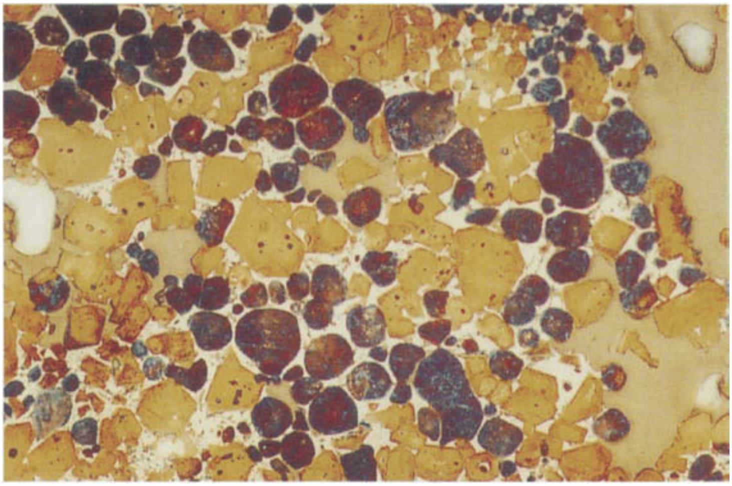

Plate 1 A relatively common texture in Portland clinker. The tan crystals occasionally showing hexagonal or pseudo-hexagonal outlines are alite. The more rounded, dark crystals are belite. At this low magnification, x 500, the bright groundmass is largely undifferentiated. At high temperatures, what is now the interstitial phase was a melt which strongly wets and partially separates the primary alite and belite crystals. It has crystallised during cooling to a mixture of ferrite and dendritic C_3A solid solutions. Occasional irregular tan blobs are mounting resin which has filled pores.

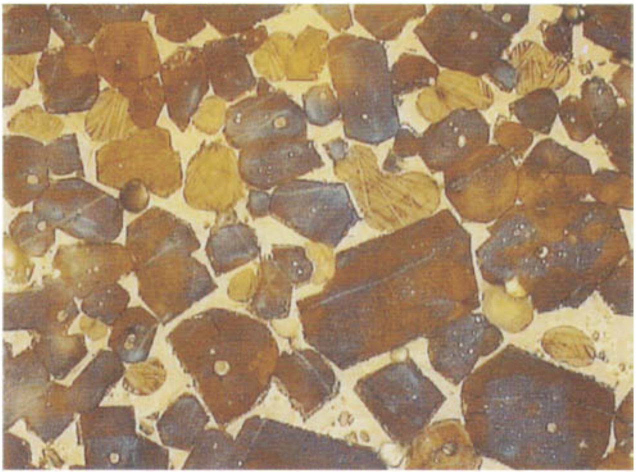

Plate 2 This clinker texture is similar to Plate 1; the matrix contains prismatic alite crystals (dark, with a bluish cast) and more round belite crystals. Most of the belite crystals display complex twinning which arises as a consequence of a complex series of topotactic phase transformations occurring during cooling. Note that the alite contains numerous inclusions of belite. These also occur in Plate 1, but are less conspicuous. The interstitial phase has crystallised to a mixture of phases, although not in a dendritic texture. The bright, pale yellow phase is ferrite; the darker, yellow--tan phase is C_3A (x 500).

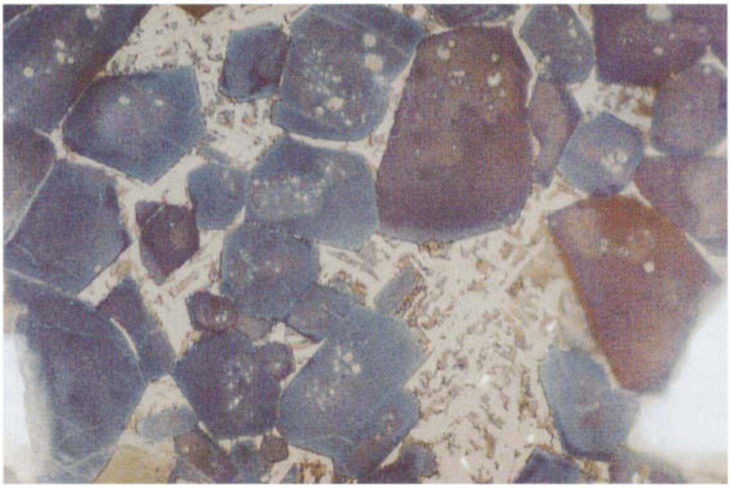

Plate 3 Photomicrograph at x 1000 selected to show crystallisation of the interstitial phase, in this instance in a strongly dendritic texture. The dendrites are probably C_3A, or mixtures of C_3A and belite, while the bright matrix is mainly ferrite.

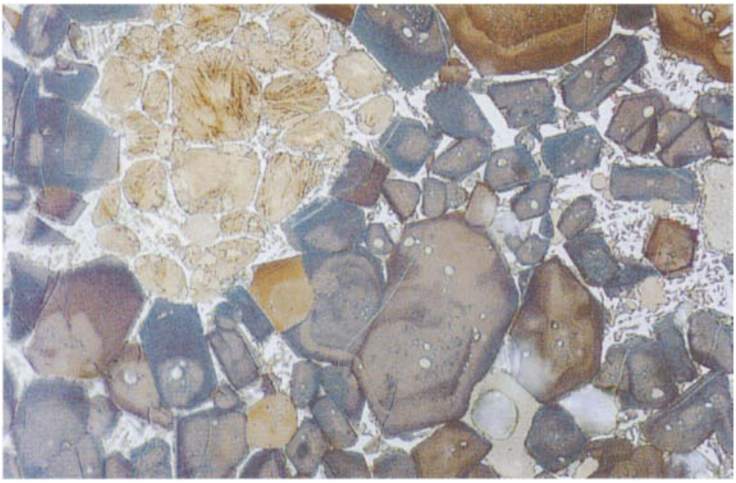

Plate 4 This photomicrograph, at x 1000, shows belite (brown–tan), alite (blue–grey) and interstitial phase. The belite occurs in lumps, or 'nests'. This clustering is probably developed when relatively coarse quartz crystals react with lime and clay forming local belite clusters and a high proportion of interstitial melt. The alite crystals are strongly zoned: note how etching reveals zones of differing composition as shadows. The photomicrograph indicates how a skilled microscopist can infer the behaviour of raw material during clinkering.

5.2.3 OPTICAL MICROSCOPY

For the determination of phase composition, optical light microscopy offers certain advantages: it reveals the crystal form, abundance and spatial distribution of the phases. Furthermore, with the advent of semi-automated image analysis systems, quantitative analyses can be made without a highly skilled operator.

Galehouse[6] has reviewed the problems associated with the microscopic determination of phase abundance. Basically, two methods are available. In the Rosiwal–Shand method, micrometer measurements of distances occupied by individual phases are made along lines of traverse over a thin section or, more usually, a polished section. The second method, the Glagoler–Chayes technique, involves a phase identification and tally at the number of points defined by the intersection of a grid, usually consisting of multiple cross-hairs or sets of dots in the optical path, positioned over the phases. The mass of phases present is calculated by multiplying the volume per cent, as determined by microscopy, by the respective density of that phase. The method for conversion of microscopic point counts to clinker chemistry has been further described by Friedman.[7]

In some applications it may not be possible to prepare coherent polished sections from clinkers. Appropriate methods for examination of isolated particles are described by Fleet.[8]

For dealing with Portland cement clinker, various specialised nomographs, tables of density and other relevant data have been compiled by Hofmänner.[9] This publication also gives many illustrations showing the microstructural features of Portland cement clinkers, interprets these microstructures and relates them to clinker composition, thermal history and processing. Previous editions of Lea's *Chemistry of cement and concrete* have given 'typical' micrographs of clinker, showing principally large calcium silicate crystals. Indeed, many clinkers do contain large faceted alite crystals and more rounded belite crystals embedded in a fine-grained groundmass which, at high magnification, consists partly of intergrowths of C_3A and ferrite. However, the microscopic method has progressed and only detailed monographs, e.g. Ref. 9, can do justice to the full range of microstructures which are observed. These include relatively large-scale features, such as crystal size and morphology, as well as smaller-scale features including zonation and twinning within the individual silicate phases. Plates 1–4 provide selected examples of clinker microstructures and illustrate a few of the many phenomena which can be explained and, if necessary, controlled by optical microscopy. The interpretation of clinker microstructures, particularly for analysis of problems encountered in clinker burning has also made impressive advances. Ono[10] has applied microscopy to the determination of clinker quality, and related the microstructure to strength development. Four quantities should normally be measured to achieve the best statistical correlation, although it may be possible to work with fewer. The quantities are the intercept size of alite crystals (AS) and their birefringence (AB) and the size and colour of belite crystals, BS and BC respectively. Quality factors are assigned to each of these factors according to Table 5.3. Grouping the sizes of crystals and their birefringences into classes speeds the optical measurements: Table 5.3 gives point scores, which can then be used to assess the potential compressive strength achieved from the clinker when hydrated under defined conditions.

The strength of mortar prisms, using cement of equivalent surface areas and constant water contents, can be calculated from the above factors using a series of equations. The choice of equations depends on the amount of information available. For example, at 28 days, three equations for predicting compressive strength, in kg/cm^2, and which have regression coefficients between 0.93 and 0.94 and standard deviations in the range 15–16 per cent are:

Table 5.3 Optical quality factors for cement clinkers

Alite				Belite			
Size (μm)	Quality (points)	Birefringence	Quality (points)	Size (μm)	Quality (points)	Colour	Quality (points)
15–20	4	0.01–0.008	4	25–40	4	Clear	4
20–30	3	0.007–0.006	3	20–25	3	Faint yellow	3
30–40	2	0.006–0.005	2	15–20	2	Yellow	2
40–60	1	0.005–0.002	1	5–10	1	Amber	1

After Ref. 10.

$$\text{strength} = 67 + 109\,\text{HM} - 22\,\text{FL} - 0.005\,\text{BL} + 7.7\,\text{AS} + 22.3\,\text{AB} + 0.6\,\text{BS} + 20.7\,\text{BC} \quad (5.1)$$

$$\text{strength} = 175 + 0.5\,(7\text{d}) + 5.8\,\text{AS} + 13.1\,\text{AB} + 8.9\,\text{BS} + 17.0\,\text{BC} \quad (5.2)$$

$$\text{strength} = 31 + 86\,\text{HM} - 15\,\text{FL} - 0.000\,\text{BL} + 0.4\,(7\text{d}) + 6.6\,\text{AS} + 14.8\,\text{AB} + 5.5\,\text{BS} + 17.6\,\text{BC} \quad (5.3)$$

where (7d) indicates the measured compressive strength at 7 days; also, HM is the hydraulic modulus, FL the per cent free lime and BL the Blaine specific surface in cm^2/g. The BL value in equation 5.3 is apparently zero but, if so, this can only be true over certain ranges of specific surface.

The Ono method and its application has also been described in detail by Campbell.[11] This publication additionally illustrates typical clinker microstructures and their interpretation. Ono's method has found widespread application as a quality control technique although its theoretical justification is, as yet, not well founded.

5.2.4 X-RAY DIFFRACTION

It has long been recognised that quantitative X-ray diffraction (QXRD) offers great potential for the quantitative analysis of cement and clinker phases. Unlike optical methods, which only accept physically small and possibly unrepresentative samples, it is easier to obtain representative bulk samples for X-ray diffraction. However, QXRD does present a number of potential pitfalls. Struble[12] has suggested that the difficulties of achieving quantitative analysis are of two types: those inherent to QXRD itself and those which are peculiar to cement clinker. Progress in addressing the latter difficulties is being made through the American Society for Testing and Materials which publishes an updated but non-critical bibliography of the methodology as applied to cement.[13] Perhaps the most significant recent development has been the availability of reference standards for cement clinkers. These provide a source of authenticated standards, the phase composition of which has been determined in inter-laboratory trials.[14]

Two of the principal problems in developing satisfactory QXRD routines arise from (1) reflection overlap and (2) the minor polymorphic variants of many of the principal phases, e.g. C_3S and C_3A, which result in the splitting of reflections with consequential intensity changes. To these should be added the variability both in peak positions and intensities, notably in the ferrite solid solutions, arising as a consequence of extensive solid solution which changes the unit cell size, symmetry and the mean scattering power of the constituent atoms.

Many attempts have been made to estimate the chemical composition of the ferrite phase by X-ray diffraction, which is often an essential preliminary step in the QXRD process. While it is possible to construct laboratory calibration graphs of the Fe/Al ratio as a function of *d*-spacing, these are non-ideal inasmuch as they depart markedly from Vegard's law, particularly at Fe/Al < 2, beyond which the slopes of the unit cell parameters become relatively insensitive to changes in Fe/Al ratios. Since the ferrite composition in the majority of Portland cements lies below this critical ratio, X-ray methods tend to be rather insensitive to changes in composition. Moreover, the symmetry of the solid solutions changes, which affects X-ray intensities. Coupled to this is the tendency of the ferrite phase selectively to incorporate many of the minor elements (Mn, Ti, etc.) present in raw meal; by concentrating in ferrite, with as yet ill-characterised consequences to the X-ray *d*-spacings, they also affect the unit cell size and true symmetry. Thus the overall conclusion must be that it is not practical to determine the A/F ratio of ferrites in real clinker using powder X-ray diffraction alone.

The present state of the art may be summarised as follows. Satisfactory quantitative procedures presently exist for determining the amounts of MgO (periclase) and C_3A, both cubic and orthorhombic, in clinker. Ferrite determination is satisfactory but perhaps less accurate due to its variable composition and associated complexities. Problems associated with quantitative determination of C_3S and C_2S are, as yet, not fully resolved although some workers claim to have developed satisfactory procedures.[15] Clinker from a particular plant may well present fewer problems of consistent analysis than clinkers made at different plants, from different raw materials and with different processing conditions, the consequences of which are that the suite of clinkers may contain different polymorphic variants of C_3S and C_2S.

Other minor clinker phases which can probably be determined quantitatively include alkali sulfates, calcium langbeinite, free lime (CaO), the calcium sulfates (gypsum, anhydrite) and calcium carbonate (calcite, aragonite).

5.2.5 SCANNING ELECTRON MICROSCOPY

The advent of image analysis, coupled with scanning electron microscopy (SEM), opens new possibilities for the quantitative analysis of clinker. Like the optical microscope, SEM examination of suitably prepared specimens will reveal a wealth of detail on the clinker microstructure. The interaction of the electron beam with the specimen can be used to generate additional information. Three signals are useful: the low-energy secondary electrons, used to image surface topography; high-energy backscattered electrons and X-rays. The backscattered electron images are sensitive to the mean atomic number of the surfaces and give chemical contrast to the image – useful for rapid phase identification and point counting techniques, similar to those described for optical microscopy – while the X-rays can be analysed with a suitable detector system, also giving a chemical image. The X-ray image of the surface may be qualitative or, with suitable calibration of X-ray production, quantitative. The interstitial phases of clinker are often difficult to resolve by optical microscopy, the useful magnification limit of which is 500–1000×. However, even relatively inexpensive scanning electron microscopes give good analytical resolution in the range up to 2000×, which assists greatly in analysing the fine-grained interstitial phases, mainly aluminate and ferrite. Stutzsman[16] has analysed NIST standards, which can be used for calibrations. The limits of substitution vary widely; Figure 5.1 shows the range of values reported. It should be noted, however, that the detector systems of SEM's typically use energy-dispersive analytical systems, the accuracy of which is not as good as the

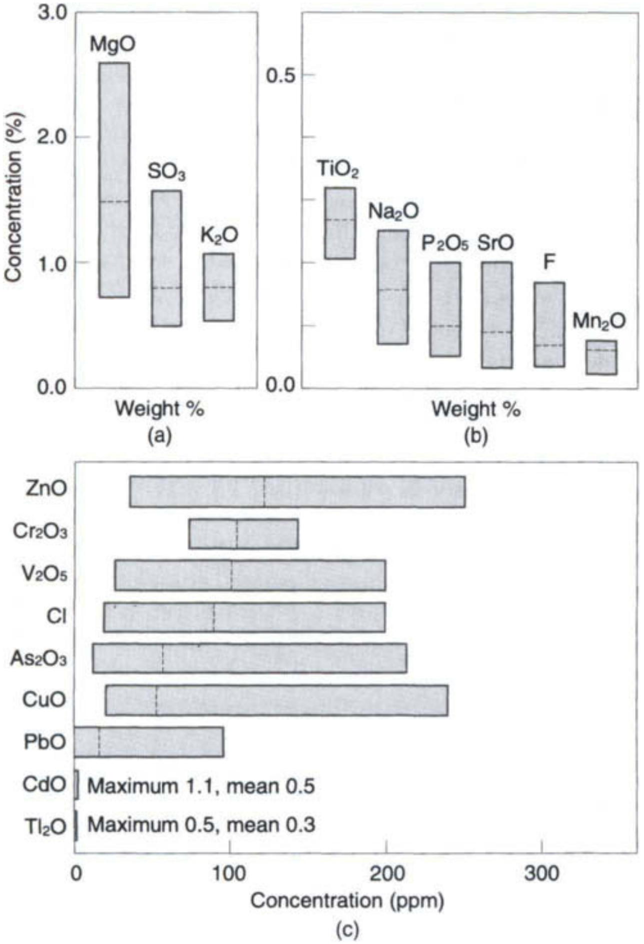

Fig. 5.1 Minor and trace element concentration of some cements in clinker. Note different ranges of concentration. Broken line shows mean values. Data are for 13 Blue Circle (UK) production clinkers (from Ref. 17). Note that the trace element concentration reflects the geochemical provenance of both raw materials and fuel.

wavelength-dispersive systems which are more commonly used with electron microprobes. Wavelength-dispersive systems are slower, requiring longer counting times, and are at a disadvantage in SEM systems. Hence it is usual to specify energy-dispersive systems for SEM work, despite their insensitivity and interchannel overlap for lower atomic numbered elements, e.g. Na and Mg.

5.2.6 *MISCELLANEOUS TECHNIQUES*

The range of techniques available for analysis have been greatly extended and a thorough review with bibliographical citations has been given by Uchikawa.[18] The selection of an analytical technique requires an assessment of what information is required, the nature of the sample and what concentrations of the analyte are being sought.

For bulk analysis, the majority of the world's cement plants probably use XRF (X-ray fluorescence). The equipment is expensive to buy but is rapid and, moreover, accommodates either solid or liquid samples. It can determine quantitatively all major elements likely to be present in cement raw materials and clinkers, with the exception of water and CO_2.

Some plants still use wet chemistry for clinker and raw material analyses although traditional gravimetric and volumetric methods are often partly supplanted by more modern absorbimetric methods, usually using electrical detection or spectrophotometry. Examples include solution ion chromatography and atomic absorption (AA), respectively. The latter requires a liquid sample which is aspirated directly into a flame or, for greater sensitivity, into a heated graphite furnace. The method also requires a source of radiation characteristic of the element sought, e.g. a calcium lamp is required for a calcium determination. AA is also suitable for major element determination but analytes may require high dilutions to come within the working range of the instrument, i.e. the range in which response is a linear function of composition. Interferences are most commonly encountered with the easily ionised elements, for example sodium and potassium and, for this reason, many laboratories continue to determine alkalis by the simple but robust method of flame photometry, using AA for the other elements. Many AA instruments can be operated in the flame photometry mode.

Neither AA nor XRF will distinguish the oxidation state of a species; for example, they will not distinguish between Fe^{2+} and Fe^{3+}. Classical methods are still employed for the determination of oxidation state but, alternatively, polarography or ion chromatography may be used provided the balance of oxidation states remains stable upon dissolution. Both cation and anion-detecting columns are available for ion chromatography; the latter is particularly useful for anions, e.g. Cl^-, CO_3^- and SO_4^{2-}, which are either not detectable or only poorly detected by other techniques.

Emission spectroscopy, with the advent of improved ionisation and detector systems, has had a new lease of life for the determination of trace or ultratrace elements. Basically, the technique accepts solid samples which are vaporised using arc discharge, spark or plasma. Stable plasmas, comprised mainly of argon, are sustained by inductively coupling the hot cloud of ionised gas to an electrically driven radio-frequency coil, hence the further development of ICP (inductively coupled plasma). ICP is best suited to the analysis of liquid samples which are directly injected into the plasma. The concentrations of numerous atoms can be measured directly and simultaneously by atomic emission (ICP-AES) or indirectly by coupled mass spectroscopy (ICP-MS). Both can have high sensitivities; for example, ICP-MS may have detection limits in the part-per-billion (ppb) or sub-ppb (parts per 10^9) range but, since the response curve of the MS detector is linear over many orders of magnitude concentrations, the method is also suitable for major element determinations. A limitation is that the total solids content of solutions aspirated into the plasma needs to be kept low.

If desired, solid samples can be vaporised with a focused laser beam, for example by focusing on a thin or polished section while guiding the laser under a microscope. In this way, analyses can be obtained from solids, including micrometre-sized crystals; the method is sufficiently sensitive that large clinker crystals can be depth-profiled by controlling the laser focus and power. Such refinements are, however, laboratory rather than production tools.

Gas chromatography (GC) and liquid chromatography (LC) have also been increasingly used. The choice of detector systems depends on the nature of the analysis: detector systems based on IR or FTIR (Fourier transform infrared), NMR (nuclear magnetic resonance) and MS (mass spectroscopy) are all commercially available.

The nature and condition of the surfaces or near-surface layers of clinker phases may influence their reactivity. Two closely related techniques, electron spectroscopy for chemical analysis (ESCA) and X-ray photoelectron spectroscopy (XPS), have been developed which are particularly suited to the analysis of solid surfaces. Bombardment of the surface by X-rays releases photoelectrons which are detected and analysed according to kinetic energy. This reveals details of bonding of individual atom species: oxygen, calcium, silicon, etc. Unfortunately, hydrogen cannot be detected. The technique has, however, been useful in distinguishing the oxidation state of elements such as sulfur and iron in the near-surface layers of clinker minerals.

Mössbauer spectroscopy has also been used to investigate the structural state of iron; the harder γ-rays used in this technique have much greater penetrating power than soft X-rays, so Mössbauer tends to be a tool for exploring the bulk, rather than surface chemistry as with ESCA or XPS. Unfortunately, iron is the only chemical species likely to be present in cements which is also Mössbauer active, thus limiting its range of applicability. Although the technique is specialised, it will distinguish between Fe^{2+} and Fe^{3+} directly in solids, without the need for a chemical dissolution stage prior to analysis with attendant risk of changes in oxidation state.

NMR may also be used as a bulk technique. The principal nuclei in cement clinkers which are NMR sensitive include ^{29}Si, ^{27}Al and ^{13}C. The technique senses the bonding of the particular atom: thus monomeric silicon, SiO_4^{4-}, can be distinguished from dimeric and other more highly polymerised states of silicon. For example, the isolated tetrahedra which occur in both Ca_2SiO_4 and Ca_3SiO_5 can be distinguished from more polymerised silicon occurring in rankinite, $Ca_3Si_2O_7$. The selection of experimental conditions for the analysis of solids and interpretation of results are not straightforward and, moreover, the presence of iron degrades the quality of the signal. Much of the work on cements has therefore had to be carried out on pure (or nearly so) single phases or, for clinkers, using white cement clinkers low in iron.

Electron spin resonance (ESR) has also been used. Unfortunately, relatively few components of cement have the necessary unpaired electron spin necessary to apply ESR; Mn, Ni, Cr and Fe are amongst the potentially applicable elements. A useful signal can only be obtained at very low concentrations, typically ppm, of the relevant element.

Clinker components and batches may also be analysed by thermal methods. The development of simultaneous differential thermal analysis (DTA) and thermogravimetric analysers (TGA) have simplified the correlation of results from these two complimentary techniques. Many modern DTA-TGA systems have relatively small gas volumes, so that when gas is evolved in the course of reaction it is also possible to apply evolved gas analysis (EGA): both chromatographic and mass spectroscopic techniques can be used for analysis. Species-specific electrochemical or optical sensors are also available if it is known what gas is being sought. In this way, the chemical nature of the gas species and amount of each component can be determined.

X-ray diffraction methods have also advanced. The advent of position-sensitive detectors has enabled diffraction patterns to be obtained very rapidly, thus enabling time-resolved diffraction patterns to be obtained. These are particularly useful in following the course of relatively rapid reactions. Alternatively, very powerful synchrotron X-ray sources can be used. These produce very intense bursts of X-rays which enable time-resolved diffractometry to be pursued. Neutron diffraction has also enabled more precise location of atoms which scatter X-rays poorly, e.g. hydrogen. Advances in the interpretation of powder patterns, using X-rays or neutrons, have also enabled more structural information to be obtained by the use of Rietveld methods.

5.3 Polymorphism and phase equilibria of pure and doped cement clinker phases

5.3.1 TRICALCIUM SILICATE (ALITE)

The polymorphism and crystal chemistry of alite have been reviewed by Moranville-Regourd and Boikova.[19] Chemical dopants, included in solid solution during clinker burning, markedly influence the polymorphism. However, data for pure Ca_3SiO_5 should be considered first. For Ca_3SiO_5 the sequence of polymorphic transformations upon heating appears to be as follows:

$$T_1 \xrightarrow[620^\circ]{} T_2 \xrightarrow[920^\circ]{} T_3 \xrightarrow[980^\circ]{} M_1 \xrightarrow[990^\circ]{} M_2 \xrightarrow[1060^\circ]{} M_3 \xrightarrow[1070^\circ]{} R$$

where letters indicate the formal crystallographic symmetry: T = triclinic, M = monoclinic and R = rhombohedral; subscript numerals designate variants of a particular symmetry. The sequence presented here is in general agreement with that previously reported except for the recently discovered M_3 polymorph, which is said to be stable only over a 10°C range.[20] This transformation sequence is at least partially reversible on cooling. Reversible heat effects, revealed by high-temperature calorimetry and thermal analysis, disclose that phase transformations occur at 620 and 920°C, and also between 920 and 990°C. On the other hand, optical data support the existence of only two triclinic forms between 620 and 980°C and of only two monoclinic forms, between 980 and 1070°C.[20] Thus the sequence of phase transformation is not completely reversible and, moreover, different techniques lead to minor differences concerning the number of polymorphs. It is of course possible to have phase transformations which would escape detection by thermal methods because ΔH is fortuitously nearly zero. But these differences in interpretation are relatively minor and the general sequence of phase transformations in alite must now be considered to be well established; upon cooling, the high-temperature R phase tends to convert to monoclinic and triclinic phases.

What is of significance to cement making is that at high temperatures, defined as above ~1070°C, Ca_3SiO_5 has rhombohedral symmetry. Moreover, during the peak temperature excursion of the clinkering cycle, the rhombohedral phase incorporates various ions in solid solution – Mg, Al, Fe, etc. Upon cooling, the high-temperature rhombohedral structure is no longer stable and normally undergoes polymorphic changes, although the rhombohedral phase may be at least partially preserved to ambient in some clinkers. The lower-temperature polymorphs may be regarded as distortions of the high-temperature rhombohedral (R) phase: although the various triclinic and monoclinic phases differ in formal crystallographic symmetry, they are nevertheless closely related to the parent rhombohedral structure. The impurity atoms incorporated into the R phase may cause the transformation sequence to differ in detail from that found for pure C_3S. Impurities have a pinning role; not only do they influence the subsequent sequence of minor phase transformations but they also help stabilise Ca_3SiO_5 itself (which is generally unstable against decomposition to Ca_2SiO_4 and CaO at all temperatures below ~1250°C). Thus impurities have a dual role: they are partly responsible for preservation to ambient of Ca_3SiO_5 in clinker and they also exert a strong influence over which of the numerous alite polymorphs are obtained. This directing power is also a complex function of chemistry and pyro-processing history. The close structural similarity of all the variants justifies the use of the collective term 'alite' to describe the family of phases closely related to R Ca_3SiO_5 (M, T and other variants). Reports of the R phase itself being preserved to ambient are common, although it would appear that most clinker alite is in fact a mixture of polymorphs, and that even individual crystals may be zoned. For example, higher levels of doping generally favour preservation of M at the expense of T: crystals which consist of M_1 at the core but M_3 in their outer zones are apparently common in clinkers. Maki[21] and Hahn *et al.*[22] conclude from surveys of commercial clinkers that M_3 or M_1, or mixtures of both M_3 and M_1, are most likely to be encountered in commercial clinkers.

The zonation of individual crystals in works clinker was examined in greater detail by Uchikawa and colleagues.[23] Microscopic examination of zoned crystals with an inner core of M_1, enclosed within an outer envelope of M_3, revealed that the core had lower optical birefringence, 0.006 at the periphery and 0.004 at the core; the boundary between zones was sharp at the optical microscopic scale. The inner core was also more readily etched by 0.01 per cent NH_4Cl, indicating differences in reactivity. The optical and etching zonation corresponded closely to chemical differences; Table 5.4 shows analyses reported from the separate zones of real crystals. Note that, in general, the inner zone tends to concentrate impurity which, in turn, tends to stabilise to ambient temperature the cores of crystallites as M_1.

One aspect of alite behaviour which the cement manufacturer might hope to control is the extent of solid solution in alite. Since cement raw meals are already oversaturated with respect to the total amount of many impurities which can be incorporated in alite, the main controls available to the cement manufacturer are to regulate (1) burning time and temperature and (2) the presence and amount of melt and other crystalline phases which might compete with alite and melt as 'sinks' for the relevant ions. The variable most easily controlled is, of course, burning temperature and it might be supposed that laboratory studies would prove to be a guide to the relationships between solid solution and burning conditions. However, almost all synthetic studies show that the extent of solid solution apparently increases with rising temperatures, whereas experience of clinkers suggests that the relation is more complex. Reasons for this are shown by means of the hypothetical phase diagram in Figure 5.2. In laboratory experiments made by adding the chosen substituent(s) (we assume the maximum extent of solid solution in Ca_3SiO_5 is of the order of 1 per cent), the solidus temperature is high, and entropy considerations suggest that the extent of solid solution will, in general, continue to increase with increasing temperatures. On the other hand, when the same substance is added to a 'real' clinker but in much larger amounts (Al_2O_3 and Fe_2O_3 are examples), the solidus temperature is drastically lowered by the large amount of fluxes present and the potential substituent becomes fractionated between alite and melt; the presence of a liquid phase drastically alters the impurity distributions. The usual situation which obtains once the solidus temperature is exceeded is shown in Figure 5.2; at temperatures above the solidus, the extent of solid solution normally decreases with rising temperature. This affects the evolution of the growing crystals. The zonation pattern shown in Table 5.4 could be achieved if, for example, the

Table 5.4 Analyses of chemically zoned alite (weight per cent)

Polymorph	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
M_1 (inner part)	25.12	0.93	0.82	72.45	1.20	0.10	0.25	0.18
M_3 (outer part)	24.09	0.71	0.58	73.76	1.11	0.07	0.21	–

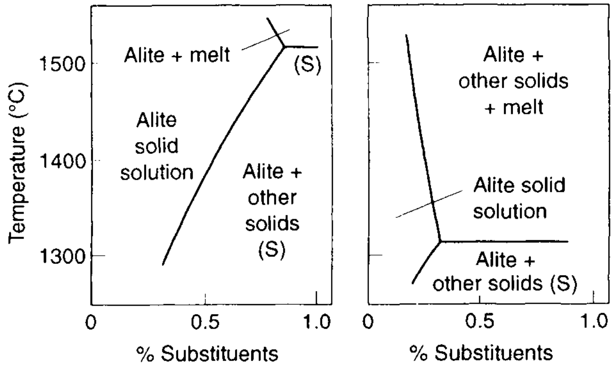

Fig. 5.2 Schematic diagrams showing fractionation of an impurity.

first-formed cores of alite crystals were nucleated and grew close to the solidus temperature, at which solid solution was most extensive, but continued the bulk of their growth – with formation of their outer zones – at progressively higher temperatures well above the solidus, where the extent of equilibrium solid solution was reduced. In response to this changing thermal regime, the rapid growth of alite would lead to production of crystals having impurity-rich centres but with outer zones containing generally lower levels of the same substituents. At clinkering temperatures, the entire crystal would have R symmetry. During clinker burning and cooling, atomic diffusion between zones is slow and the varying concentrations of impurity are not annealed out. This leads to differences in polymorphism developing within individual crystals. For all these reasons, coupled with the inflexibility of the clinkering process, it has not yet proven practicable to produce homogeneous, single-phase alite clinkers in a controlled manner.

The crystal structure of the aristotype R phase of Ca_3SiO_5 is now well established,[24] although the structure reported differs considerably from that reported previously by Jeffery[25] who had to use a heavily doped crystal; the more modern structure was determined from an unstabilised crystal, measured directly at elevated temperature.

The complex polymorphism of C_3S introduces problems of quantitative phase analysis of clinkers by X-ray powder diffraction. The diffracted energy of a single reflection in the R phase becomes split amongst the multiple, closely spaced reflections in the lower-symmetry phases, and the extent to which reflections overlap those of the belite phase tend to increase as the symmetry of the C_3S decreases. Moreover, minor shifts in atomic positions within the lower-symmetry alite phases alter the absolute reflection intensities, making it difficult to secure satisfactory calibration; the usual assumption which is made – that the multiple reflection contains the same total diffracted energy as the associated single R reflection – remains unproven.

The relative reactivity of the alite polymorphs towards hydration has been the subject of controversy. About all that can be concluded is that it is impossible to separate effects which are due to polymorphism from those due to changing levels of chemical dopants. In other words, it is not generally possible to compare the reactivity of different polymorphs with the same chemistry, or to obtain the same polymorph but with substantially different chemistries. These comparisons are especially difficult in respect of the M and T variants.

5.3.2 DICALCIUM SILICATE (BELITE)

Two classification schemes may be distinguished for belite polymorphs, one based on optical characteristics, the other on crystal chemistry. The polymorphism and sequence of phase changes is, however, the key to the internal microstructure and optical properties.

The structures of all the main polymorphs have now been determined from single crystals.[26–29] The amount of structural rearrangement required to transform from one polymorph to another during thermal cycling varies, and this is partly responsible for the kinetics and sequence of phase transformations encountered during heating and cooling. Figure 5.3 shows the commonly encountered transformation sequences; those occurring during cooling are of most relevance to clinkering. Where a particular Greek letter is used, e.g. α, all phases prefixed α are thought to be closely related in structure, e.g. α_L and α_H, the subscripts indicating lower and higher temperature respectively. Corresponding to this structural similarity, comparatively little energy is required to effect phase transformations within a given family, with the result that such transformations are characteristically rapid and reversible in response to changing temperature. However, at low temperatures, such that comparatively little thermal excursion of the constituent atoms occurs, phase transitions tend to become more sluggish, especially if major atomic rearrangement is required. Thus, upon cooling α', the stable phase (γ) is not normally obtained directly; instead, the α'_L phase distorts to the structurally related β phase. The tendency towards subsequent atomic rearrangement of β to γ is difficult and tends to be slow. Since β is considerably more reactive towards water than γ, this state of affairs is fortunate for industrial scale clinkering, where it is difficult to obtain very rapid cooling relative to laboratory practice. Moreover, the kinetics of the low-temperature sequence of transformations, and hence the proportions of β and γ phases obtained at ambient, are affected by a number of other factors: by grain size, mechanical stress introduced by clinker grinding, internal strain and cooling rate. These factors have not been quantified, but chemical purity plays a major role in controlling the reaction sequence occurring during cooling and is of utmost importance in controlling belite transformation in real clinkers. These typically contain relatively coarse, micrometre-sized belite crystals. Under these circumstances, not only do Mg, Al and Fe oxides act as fluxes, but they also enter the structure of α at burning temperatures where they assist its preservation to ambient as β, by inhibiting the structural rearrangement necessary to form the more stable phase (γ) at lower temperature. Thus the β phase is normally sufficiently well stabilised against conversion to γ to persist unchanged even during clinker grinding. Mechanical grinding, it will be recalled, imposes high local pressures and may also result in some heating, both of which factors promote the $\beta \rightarrow \gamma$ transformation.

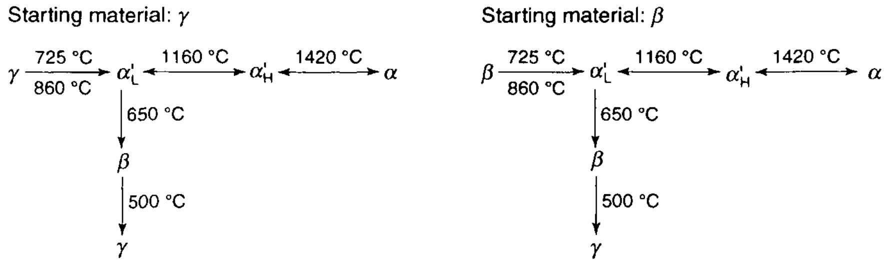

Fig. 5.3 Some transformation sequences encountered during the heating and cooling of γ- and β-Ca_2SiO_4.

It has also been claimed that a distinctive β polymorph, designated β^*, can be obtained. The status of this phase, variously described as β^* or as 'β-belite', still has to be clarified with respect to the other polymorphs. The β-belite phase was first reported by von Lampe and Seydel[30] who obtained it by rapid cooling of an experimental clinker with (in weight per cent) 38.16 CaO, 16.41 SiO_2, 5.02 Al_2O_3, 2.07 Fe_2O_3, 2.86 MgO, 0.25 SO_3, 1.04 K_2O and 0.22 Na_2O; the raw meal had an ignition loss of 33.41. This basic composition was doped with increasing alkali, ranging up to 1.12 Na_2O and 5.6 K_2O. At total alkali contents as low as 1.78 weight per cent, the β^* phase was consistently obtained with fast cooling in the range 20 000–50 000 K/min. It was characterised by having greater hydraulic reactivity than 'ordinary' belite. Preliminary data show that β-belite can be distinguished by characteristic shifts in its X-ray powder diffraction pattern. Thus its fourth strongest reflection (103), lies at 0.263–0.264 nm compared with 0.2612 nm in ordinary belite. The structural significance of this shift is unknown. The possibility of producing 'active belite' clinkers is of great technical importance because of the lower energy requirements for producing belitic clinkers relative to alite-rich clinkers. Therefore continued efforts to synthesise and characterise the internal state of belite can be expected.

In real clinkers, many of the chemical impurities present, including K and trivalent elements such as Al, Fe and Cr, as well as those higher-valent elements capable of forming tetrahedrally coordinated XO_4 groups (the latter including S, V, Cr and P), are observed to be fractionated into clinker belite in preference to alite. Thus the β phase found in ordinary clinker is undoubtedly stabilised against inversion to γ, the stable phase, and may even have sufficient stabiliser to be present as β^*. It is debatable if the crystallochemical stabilisation is purely kinetic, or whether the increased doping relative to pure C_2S provides outright thermodynamic stabilisation for either or both β and β^*, thereby altering the relative order of stability encountered for pure Ca_2SiO_4. It is most likely that the stabilisation is purely kinetic. However, the persistence of β as a metastable phase contributes greatly to the hydraulic reactivity of the belite phase: γ, the stable phase, is almost unreactive towards water at ~20°C.

The original scheme of designation of belite, which derives from its microscopic appearance in thin and polished sections, was developed by Insley.[31] His subdivision is shown in Table 5.5, together with the probable correlation with the polymorphism. The complex history of inversions during cooling, as well as the topotactic nature of the phase transformations, is responsible for the production of twin lamellae. The orientation of lamellae is controlled by preferred nucleation within the host crystal, as well as by the oriented exsolution of other ions which become progressively expelled during cooling. Considerable controversy persists over the complex crystallographic orientation relationships between host and product phases; these aspects have been reviewed by Moranville-Regourd and Boikova.[19]

Table 5.5 Microscopic features of belite and their interpretation[30]

Type designation	Characteristic features
I	At least two sets of striae, resulting from complex history of inversions: normally β polymorph
II	One set of striations. May be α' or mixtures of β and α' phases
III	Free of striations and often clear. Consists of mainly α' polymorph

The stoichiometry of Ca_2SiO_4 has been the subject of controversy. If belite were to depart from stoichiometry, such departures could potentially exert much influence over its reactivity; and would also affect calculations based on compound content. Careful investigation discloses that clinker belite may contain both crystalline intergrowths and exsolutions, as well as glass.[32-35] Although the presence of these materials affects the apparent bulk analysis of the crystal, they do not constitute proof of non-stoichiometry either now or at some point in the clinkering cycle. Indeed the presence of a second phase or phases could suggest the opposite: that belite is essentially stoichiometric. Nevertheless, exsolved or occluded phases may contribute to strain energy within belite crystals and thereby enhance its reactivity. Amongst the crystalline impurities thus far identified as inclusions are gehlenite, ferrite and rankinite, $Ca_3Si_2O_7$. Thus at present there is no compelling evidence to show that belite made by conventional clinkering is non-stoichiometric in the conventional usage of the term: such departures from a Ca/Si ratio of 2.00 are due to well-recognised crystallochemical substitutions occurring on an atomic scale or to the physical presence of microscopic inclusions of another phase or phases, or to both.

In summary, the polymorphism of the belite phase is well understood, as are the kinetics of its phase transformations encountered on cooling. One exception is the nature and role of the supposed β-belite; this and other related developments will undoubtedly be the subject of intensive study as it appears more practicable to control the reactivity of the belite phase than the alite phase.

The limits of solid solubility of other ions in the Ca_2SiO_4 structures are often substantial and exceed those in Ca_3SiO_5; Al_2O_3 and K_2O are examples of species which prefer C_2S to C_3S (Table 5.2). The salt-like, rather open structure of the α-type phases have a high lattice energy which increases their tolerance for crystallochemical substitutions. Nevertheless, the limits of solid solution observed in real clinkers are often less than those recorded in laboratory studies. In real clinkers, impurities can fractionate between melt and belite, as well as into other crystalline phases, e.g. alite. The simple argument which was developed to explain the temperature dependence of fractionation between alite and other phases, shown in Figure 5.2, is also applicable to belite. With MgO a special case operates, because the ordered bredigite-structured phase forms at rather low magnesia contents: this is discussed more fully under MgO (section 5.4.5).

5.3.3 TRICALCIUM ALUMINATE

The structure of the aluminate is now well established and was reviewed together with new data by Moranville-Regourd and Boikova.[19] There is a close relationship between the nature of the particular polymorph obtained in clinker to clinker chemistry and cooling history. Table 5.6 shows the relationship between polymorphism and Na_2O content, the

Table 5.6 Polymorphism of C_3A solid solutions

Range of Na_2O contents (wt%)	Polymorph obtained at ~20°C[a]
0–1.9	CI
1.9–3.7	CII and O
3.7–4.6	O
4.6–5.9	M

[a] CI and CII refer to cubic polymorphs, O and M to orthorhombic and monoclinic polymorphs respectively.

latter component having the greatest influence on polymorphism. For pure C_3A and its low-Na solid solutions, the cubic structure, designated CI, is most stable. In common with the structures of the other polymorphs, the CI structure is built of rings, Al_6O_{18}, linked by Ca ions.[35] The structure exhibits rather open packing of its constituent structural units with the result that Na ions can substitute for Ca while electroneutrality is maintained by inserting extra Na into cavity sites; in pre C_3A, these sites remain unoccupied. Increasing the sodium content in the clinker leads to its concentration in C_3A and a structural rearrangement ensues: the structure of a second cubic modification, designated CII and containing 2.4 weight per cent Na_2O, has been determined.[36-38] The CII modification contains the same aluminate rings as are found in the CI modification, but stacked differently. However, owing to geometric similarities, the powder X-ray patterns of CI and CII are virtually identical. As the sodium content increases further, the cubic structure can no longer be preserved to ambient and becomes distorted to lower symmetry, and both orthorhombic and monoclinic polymorphs are known to occur.

The partial substitution of Al by Fe^{3+} has relatively little effect on the polymorphism of the aluminate; sodium substitution dominates and continues to determine which polymorph is obtained. Figure 5.4 shows the influence of Na and Fe on the limits of solid solution and the stability regions of different polymorphs.[39] The diagram relates to the polymorph(s) obtained at ambient following isothermal annealing at elevated but subsolidus temperatures, such that no melting occurs. It is not strictly a phase equilibrium diagram, because it does not conform to the phase rule; moreover, some of the products obtained at ambient are probably metastable, as a consequence of relatively rapid cooling. The diagram is, however, a useful guide to the relationship between composition and polymorphism of the C_3A phase as it is likely to occur in clinker. Under normal conditions of clinker burning the solid solution of other oxides, notably SiO_2, is small, probably not exceeding 0.5 weight per cent in the Na_2O–Al_2O_3–CaO–SiO_2 system but perhaps extending to a maximum of about 2 per cent in the Na_2O–CaO–Al_2O_3–Fe_2O_3 system.

However, much of the C_3A in clinker arises by crystallisation from undercooled melts, rather than by annealing at subsolidus temperatures or by equilibrium crystallisation from a melt. The clinker melt phase, it will be recalled, contains relatively little SiO_2 and as a

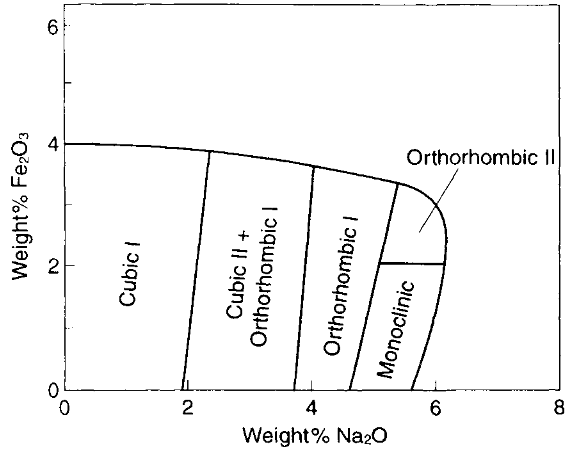

Fig. 5.4 Limits of stable solid solution of Na_2O and Fe_2O_3 in $Ca_3Al_2O_6$ and the effect of solid solution on polymorphism.

consequence crystallises mainly to C_3A and ferrite. The nature of the C_3A product thus obtained was studied by Han and Glasser.[40] When crystallisation occurs with undercooling, solid solution of other oxides, notably SiO_2, is markedly enhanced. Figure 5.5 relates the nature of the products obtained to composition. At low impurity contents, Figures 5.4 and 5.5 are essentially identical; the difference is that Figure 5.5 shows phase changes and compositional boundaries when the limits of solid solution are further prolonged into the metastable region as a consequence of more rapid undercooling. It is further suggested that the CII modification is silica-stabilised, as is the supposed OII modification, although evidence for the existence of the latter is not conclusive.[41]

As the rate of undercooling of the melt increases, the C_3A product formed by its crystallisation becomes less well ordered. The X-ray diffractions characteristic of the ~ 1.6 nm cubic or pseudo-cubic cell are unequally affected: those characteristic of a ~0.4 nm subcell remain, although broadened, while the remainder weaken progressively. This presumably disordered phase, exhibiting only Bragg reflections attributable to a ~0.4 nm cell, was termed 'proto-C_3A'. Evidence for the solid solution of other oxides, notably iron and silicon, much in excess of the stable limits (as depicted in Figure 5.5) is corroborated by the discovery of proto-C_3A in rapidly cooled industrial clinker: SiO_2 content of this 'proto-C_3A' ranged from 4.4 to 5.5 weight per cent. Thus crystallisation of C_3A and ferrite together enables the incorporation of much of the SiO_2 present in the clinker melt phase, thereby limiting its potential to form C_2S and C_3S etc. during its rapid crystallisation with undercooling. These departures of the composition of the interstitial phases from ideal undoubtedly affect the mineralogical balance of the clinker; for example, silica which becomes bound into C_3A is not available for forming silicates, thereby increasing the C_3S/C_2S ratio: see discussion of the Bogue calculation.

5.3.4 *ALUMINOFERRITE PHASE: 'FERRITE'*

This solid solution, based on $C_2A_{1-x}F_x$, has long been known to occur in clinker. At 1 bar pressure, solid solution extends from $x = 1$ to $x \sim 0.3$, although at higher pressures

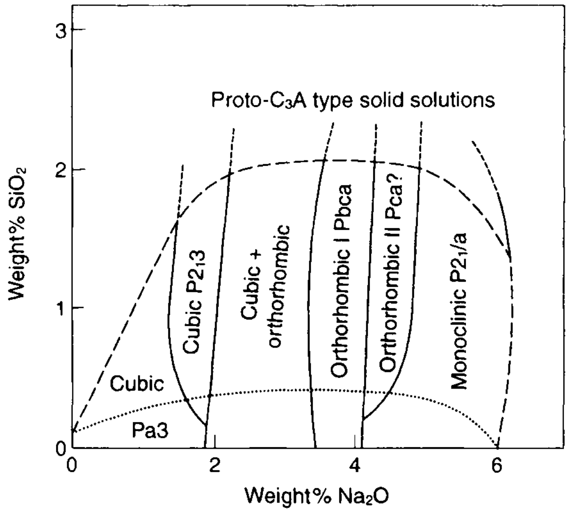

Fig. 5.5 Approximate limits of metastable solid solution of Na_2O and Fe_2O_3 in $Ca_2Al_2O_6$ showing especially the domain of 'proto-C_3A'.

solid solution becomes complete.[42] The mechanism of solid soution is, however, not entirely straightforward. C_2F itself contains iron as Fe^{3+} in both tetrahedral and octahedral sites, the latter being twice as numerous as the former. As Al is added to C_2F (initially, $x = 1.0$) it preferentially enters tetrahedral sites. However, at $x \sim 0.67$, the tetrahedral sites are filled and Al substituted in excess of this ratio must increasingly enter octahedral sites. As the pattern of Al site occupancy changes, the lattice parameters undergo a change in slope at about the ratio C_6AF_2. Moreover, the intensities of the characteristic X-ray reflections undergo changes because at about this composition the symmetry also changes, from Pcmn for the iron-rich solid solutions to Ibm2, encountered at $x \leqslant 0.67$.[43] Thus indirect methods of determining the composition and amount of ferrite based on X-ray diffraction need to take account of these changes, as many of the lattice parameter values and reflection intensities undergo a region of accelerated change at values of x close to 0.67.

The ferrite phase can also accommodate limited Mg in solid solution[44] and much of the clinker Ti becomes concentrated in ferrite. The incorporation of Ti may be accounted for on the basis of a structural similarity, admittedly somewhat distant, between ferrite and perovskite; the latter is an ABO_3-type structure, e.g. $CaTiO_3$. As Ti is progressively incorporated in ferrite, blocks of the structure concentrate Ti, and these regions become increasingly perovskite-like, leading to both random and regular interstratification of ferrite-like and perovskite-like slabs. The *b*-axis periodicity is affected by the stacking of these slabs.[45] Titanium is believed substantially to reduce the reactivity of ferrite towards hydration even when the intercalation density of perovskite-like slabs is low.

5.4 Minor components

5.4.1 INTRODUCTION

Interest in the minor components arises because of their role in the clinkering process, in the possibility of improving the performance of cements by incorporating these components, as well as from environmental and health considerations. Amongst the oxides present in clinker in the range 0.2–2 per cent are MgO, SO_3, K_2O, TiO_2, Na_2O, P_2O_5, SrO, F and Mn_2O_3. Oxides generally present in the range 0.5–200 ppm (all limits are approximate) are ZnO, Cr_2O_3, Rb_2O, Cs_2O, V_2O_5, Cl, As_2O_3, CuO, PbO, CdO, BaO and Tl_2O; also, Cl^-. Of course the geochemical nature of the raw materials, including the normally present additives, such as the mineral content of fuel, as well as other novel and semi-artificial materials, e.g. ash, metallurgical slags, industrial and municipal wastes, will substantially influence the content and nature of minor elements. Supplementary fuels, including waste oil and used tyres, will also influence the trace element concentrations. Since the kiln is an ideal way of combusting many wastes, the coupling of cement clinkering with waste disposal is attractive. The patterns of trace element supplementation from wastes are sometimes predictable: for example, combustion of tyres will result in an increase in clinker ZnO contents. Table 5.7 summarises in general terms the main influences.

It should be noted that the literature on minor components is of very variable quality and numerous unquantifiable claims have often been made of the beneficial effects of incorporating trace elements in clinker. In this presentation we concentrate on effects which are proven to have some basis in physical chemistry.

Table 5.7 Influence of minor components on clinkering*

General action	Examples
Fluxing	Temperature of first liquid formation lowered Melt viscosity altered Melt surface tension affected Crystal growth morphology altered
Mineralising	Relative thermodynamic stabilities of the clinker minerals are changed by solid solution
Phase relations	Phase boundaries and amounts of phases are affected by fluxing/mineralising action and solid solutions new phases created, for example, $C_6Z_2A_2$ in zinc doped clinker a
Hydraulic activity	Reactivities of clinker minerals modified by solid solution and its impact on polymorphism

* Bolio-Arceo H., Glasser F.P. Zinc Oxide in Cement Clinkering: Part I. Systems (a)-ZnO–Al_2O_3 and CaO–ZnO–Fe_2O_3. *Advances in Cem. Res.*; 1995; 25–32.

5.4.2 VISCOSITY AND SURFACE TENSION OF THE MELT

At clinkering temperature, the reactants are partially fused. In the C–A–F–S system, the relevant temperature above which liquid forms is 1338°C but this will be decreased by the fluxing action of minor components, although the extent of the decrease is normally slight.[46] Much more important is the ability of fluxing agents to increase the amount of liquid developed at a fixed temperature and its transporting properties. These factors have been studied by Timashev[47] and by Odler and Abdul-Maula.[48,49] Figures 5.6 and 5.7 show how the viscosity function correlates with the ratio Z/r (formal charge/ionic radius) and the energy of the M–O bond. The two functions show a good correlation with viscosity which, in turn, relates to the mobility of species within the melt. Increasing oxidation state generally lowers viscosity while decreasing the Z/r value weakens both the strength of the M–O bond and also the acidity of the additive. The use of the term 'acid' and 'base' are of course not those employed in aqueous solutions: in the present context, bases are oxygen donors,

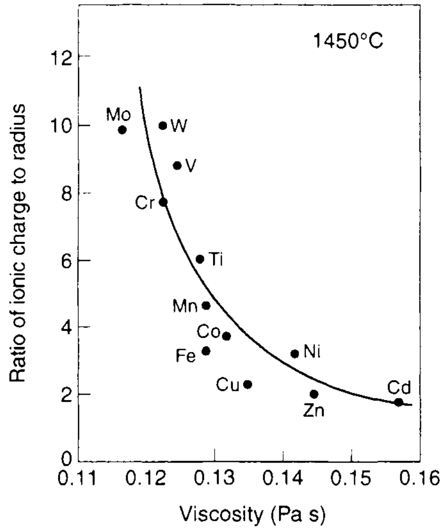

Fig. 5.6 Viscosity of cement clinker melt doped with metal oxides. Viscosity is shown as a function of formal charge/ionic radius (after Ref. 47).

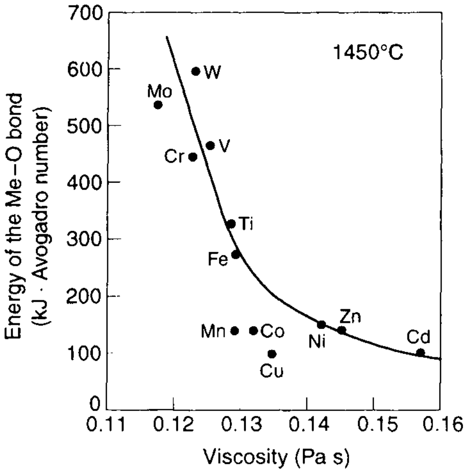

Fig. 5.7 Viscosity of cement clinker melt doped with metal oxides. Viscosity is shown as a function of the energy of the metal–oxygen bond (after Ref. 47).

e.g. Ca, Na and K, while acids, e.g. S and Cr, both in their (VI) oxidation state, are oxygen acceptors. As with aqueous solutions, acids may vary in strength, with Al and Si being typically weak while others, such as P(V) and S(VI), are strong.

5.4.3 INFLUENCE ON SINTERING

At lower temperatures, such that liquid has not yet developed, minor elements influence the rate of combination of raw materials. Odler and Abdul-Maula[48,49] studied the effect of a 1 per cent transition metal additive at 1200 and 1300°C: the raw mix had a lime saturation factor of 85 per cent and a silica ratio of 2.6. The influence of additives on sintering was in the following order.

$$1200°C:\ CuO > Co_2O_3 = V_2O_5 > Cr_2O_3 = ZnO > TiO_2$$

$$1300°C:\ CuO = Co_2O_3 = ZnO > TiO_2 > CdO > MnO > V_2O_5 > Cr_2O_3$$

At 1200°C, CuO was very effective in reducing free lime, from 19 to 8 per cent, while TiO_2, ZnO and Cr_2O_3 had only a marginal effect. At 1300°C, CuO, Co_2O_3 and ZnO were effective in promoting combination. However, addition of a number of these oxides to clinker batches is impractical.

Other substances more likely to be present in the decarbonation zone of the kiln, such as halides, carbonates and sulfates, also interact strongly with clinker components during the earlier stages. Because of the difficulty in obtaining kiln samples from within this zone, the extent of reaction(s) and their overall importance to the clinkering process are largely unknown. What is certain is that some components generally regarded as fugitive; for example, carbonates can interact strongly with lime and silica components in the lower-temperature regions. In this instance the reaction product is spurrite, $2C_2S \cdot CaCO_3$. Spurrite is actually slightly more stable with respect to decomposition than $CaCO_3$ itself.[50] Another important phenomenon is the development of a transient melt phase, conditioned by the presence of as-yet undecomposed but low melting point sulfates and carbonates. Additional data on these reactions will be given under the specific minor components.

5.4.4 DISTRIBUTION OF MINOR CATIONIC COMPONENTS IN CLINKER PHASES

The advent of electron-optical-analytical methods has resulted in a vast increase in knowledge concerning the distribution of minor elements in clinker phases. Many of these studies, however, do not clearly relate the observed distribution to thermal history and other relevant factors. Figure 5.8 shows the various possibilities for the incorporation of trace elements into clinker phases as a function of a somewhat idealised clinkering cycle.

Some clinker minerals, principally C_2S, begin to form as the incoming meal is heated above 1000°C during the initial solid-state sintering; sulfates, carbonates and water vapour appear to assist this process. Upon continued heating, melt appears above ~1338°C; C_3S and C_2S are the principal phases which remain stable in contact with melt. Since C_2S is stable throughout the clinkering process, there is a tendency for early-formed belite crystals to persist and, moreover, to act as nuclei for further growth in the high-temperature zone. The onset of most of the crystal growth of clinker phases, especially of C_3S, occurs at temperatures well above that at which melting commences; under these conditions, the minor elements fractionate between melt, solid and vapour phases. Some clinkers may retain a little C_3A and ferrite at the high temperatures and, if present, these phases will of course also participate in element fractionation. However, C_3A and ferrite are quantitatively not very significant at peak clinkering temperatures because much of the alumina and iron oxide necessary for their formation are instead in the melt phase. During cooling, this melt freezes, often with undercooling. Most of the C_3A and ferrite content of clinker, together with a little C_2S and C_3S, form at this stage at the beginning of clinker cooling. Under these conditions of relatively rapid cooling, at least over the first hundred degrees, metastable solid solutions based on C_3A and ferrite develop. Precipitation of C_3S and C_2S may also occur preferentially on the rims of alite and belite crystals whose cores were developed at higher temperatures; the change in thermal regime and in the composition of the melt phase from which precipitation occurs leads to zoned crystal formation. Finally, during cooling, the solid solutions initially formed at high temperatures become unstable; excess impurity atoms contained in clinker minerals may be partly retained but may also be exsolved. The limited diffusion rates lead to internal precipitation as inclusions, or if coherent precipitation is favourable, to oriented lamellar precipitation. Twin lamellae,

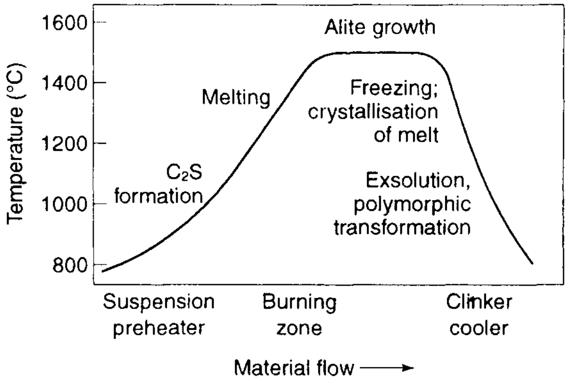

Fig. 5.8 Idealised clinkering cycle, showing reactions of mineral formation favourable to trace element incorporation.

formed during topotactic phase changes, as well as at mosaic boundaries within the host crystals, often serve as preferential sites for precipitation. Not surprisingly, therefore, the sequence of minor element distribution in ferrite and aluminate is much influenced by the primary fractionation occurring between melt and the two solids – alite and belite – present in the burning zone. Those minor elements which are rejected by alite and belite tend to remain in the melt and, during cooling, fractionate between the aluminate and ferrite which develop by crystallisation of the melt. The chemical analyses of the crystalline phases, as well as zonation within crystals, reflect this complex and often somewhat varied history and should be interpreted in this context. As noted earlier, optical microscopic and electron-optical studies have been helpful in determining the complex relations between morphology and pyro-processing. Some data on trends of fractionation are reproduced in Figure 5.9.

The distribution of some normally cationic constituents has been the subject of conflicting claims in the literature. Five elements are especially important in this context: Cr, Co, Ni, V and Mn. One characteristic which Cr, V and Mn have in common is their occurrence in multiple oxidation states. The properties of these elements, including their crystallochemical behaviour, are very dependent on oxidation state which is, in turn, a function of raw materials chemistry and firing conditions. Some examples are developed.

The most probable oxidation states of chromium in clinker are Cr(III), with possibly some higher oxidation states: Cr(IV), Cr(V). At peak clinkering temperatures, and in slightly oxidising atmospheres, thermodynamic balances show that Cr^{3+} is the most stable state. This species resembles Fe^{3+} in ionic size and covalence and therefore concentrates in ferrite. Like iron, lesser amounts of Cr^{3+} concentrate in clinker aluminates. Cr(III) is not known to occur with oxygen in tetrahedral sites, so it is not found in the tetrahedral sites of the silicates. Any chromium present which is believed to substitute for Si must almost certainly occur in its higher oxidation states, IV and V, for which limited Si substitution is feasible. However, as the oxygen pressure increases, and especially at lower temperatures, chromium oxidises and it's tetra- and pentavalent states are increasingly stabilised in a wide range of cement solids. The effective size and ionicity of Cr species decrease as the oxidation state increases, and as this happens, chromium becomes progressively more readily substituted into tetrahedral sites, where it may replace either or both Al and Si. At normal temperature chromium in the IV and V states is sensitive to reoxidation and in aqueous solution, to disproportionation to equivalent amounts of Cr(III) and Cr(VI). For example, much of the Cr found in belite is present as Cr(IV) and Cr(V) but in the presence of moisture, these

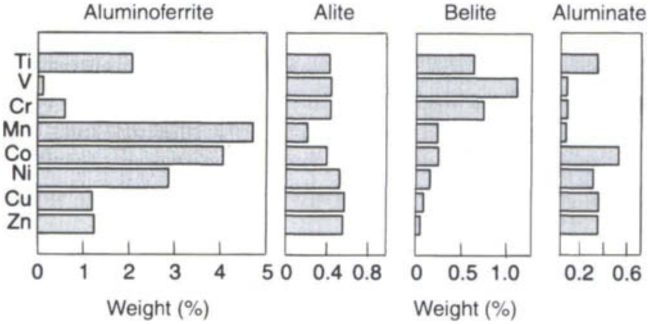

Fig. 5.9 Range of values for the substitution of selected minor element in cement clinkers (from Ref. 17 after Ref. 51).

oxidation states disproportionate to mixtures of Cr(III) and Cr(VI). Thus, wet-chemical analysis indicates mixtures of the III and VI states, leading to the incorrect conclusion that the cement solids must also have contained chromium in these two oxidation states – III and VI.

There is much concern over the chromium content and its oxidation state on account of health problems, which are associated mainly with Cr^{6+}. It should be recalled that any oxidation state likely to be present in cement, other than Cr^{3+}, will, upon reaction with water, disproportionate to yield at least some Cr^{6+}. Oxidation of Cr^{3+} in alkaline cements exposed to air has not been observed.

Cobalt and nickel predominantly occur in clinker as Co^{2+} and Ni^{2+}; whereas V is probably present as a mixture of V^{4+} and V^{5+}. Mn occurs as a mixture of Mn^{2+} and Mn^{3+}. The oxidation states of V and Mn are probably very sensitive to kiln atmosphere and the presence of oxidising or reducing agents in the raw meal; hence the distribution of these elements may, like chromium, differ considerably from one situation to another. Under reducing conditions, manganese tends to follow Ca whereas under more oxidising conditions it follows Fe(III) into ferrite.

5.4.5 *MAGNESIUM OXIDE*

MgO is difficult to combine chemically: not only is periclase not very soluble in clinker melts, but the surfaces of periclase grains are kinetically inert and hence resistant to dissolution. Indeed, the use of well-burned periclase refractories in the kiln relies on this inertness; kiln linings are only slowly eroded by partially fused clinker even though the melt phase of the clinker may be undersaturated with respect to MgO.

Free periclase, MgO, is an undesirable constituent of clinkers. It hydrates rather slowly in hardened products to yield brucite, $Mg(OH)_2$, resulting in large and localised volume increases which may cause hardened cement products to expand and crack. MgO which is distributed uniformly on an atomic scale, as occurs when it is dissolved in other clinker phases, e.g. belite and ferrite, or if it is contained in glassy slag, is innocuous in this respect and does not normally cause problems.

However, many plants must rely on MgO-containing raw materials, and numerous studies of MgO assimilation have been published. The consequences of having higher MgO contents have been explored and the relationships between bredigite and α'-Ca_2SiO_4 have been re-examined.[52] It had previously been assumed that bredigite and α'-Ca_2SiO_4 were essentially identical: the two are very similar in crystallography, optical properties and powder X-ray pattern. But whereas α'-Ca_2SiO_4 is hydraulically active, bredigite is essentially inert. Figure 5.10 shows the phase relations, principally between C_2S and bredigite. Bredigite is believed to be stable up to 1372°C and to have a range of compositions centred about the ratio $Ca_{1.7}Mg_{0.3}SiO_4$. Thus Mg is potentially liable to form bredigite once the limits of its solid solution in α and α'-C_2S are exceeded. The crystallochemical substitutions in bredigite have been reviewed.[53] It was shown that bredigite is not totally inert; it will react with water at ~200°C, although the reaction products have poor strength.

5.4.6 *ALKALIS AND SULFATE*

Clinker raw meal varies in alkali content and in the ratio of the two principal alkalis, sodium and potassium. The alkali sources include fuel – mainly coal – and shale. Limestone itself is generally low in alkali although its clay content may contribute alkali. The clay

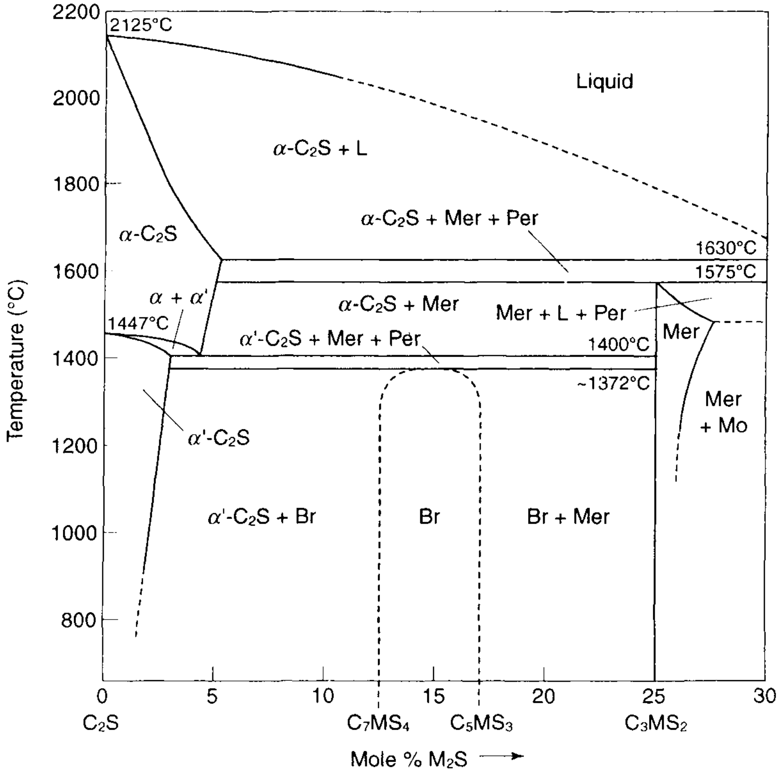

Fig. 5.10 Phase relations between bredigite and Ca_2SiO_4 (after Ref. 17).

components of shales and coals show strong geochemical affinities: both typically have very variable patterns of Na/K ratios.

The circulation of many elements is facilitated by cycles involving the transportation of specific elements or combinations of elements. The flow of solid material through the kiln is opposite in direction to gas flow; this is deliberate, to facilitate thermal economy by using hot gas from the burning zone to heat incoming raw materials. However, it encourages formation of closed-loop cycles. An example of such a cycle, for sulfur, is shown in Figure 5.11, which also shows schematically how the movement of alkali and sulfur are coupled. Sulfur is introduced in fuel, especially when using coal or oil, as well as in raw materials. Recycling of alkali-containing kiln and baghouse dusts tends to increase the amount of alkali in circulation within the kiln. All minor elements introduced into the kiln must inevitably appear in the solid or gaseous discharges, or in both, so that alkali appears partly in clinker; partly in kiln dusts. Some is removed as dust in electrostatic precipitators. Sulfur appears partly in gaseous effluent, mainly as SO_2, and partly in clinker and dust.

There is a unique association within the kiln between alkalis and sulfur. Although 'Na_2O' and 'K_2O' may be present as a very complex mixture of species in kiln gases, the vapour pressures of the relevant alkali- and sulfur-transporting species are comparable in magnitude, with the result that they appear to move together. The impression of a coupled cycle is enhanced by the observation that alkali sulfates may condense at certain points in the kiln. Many of the treatments of this process in the literature are qualitative, but

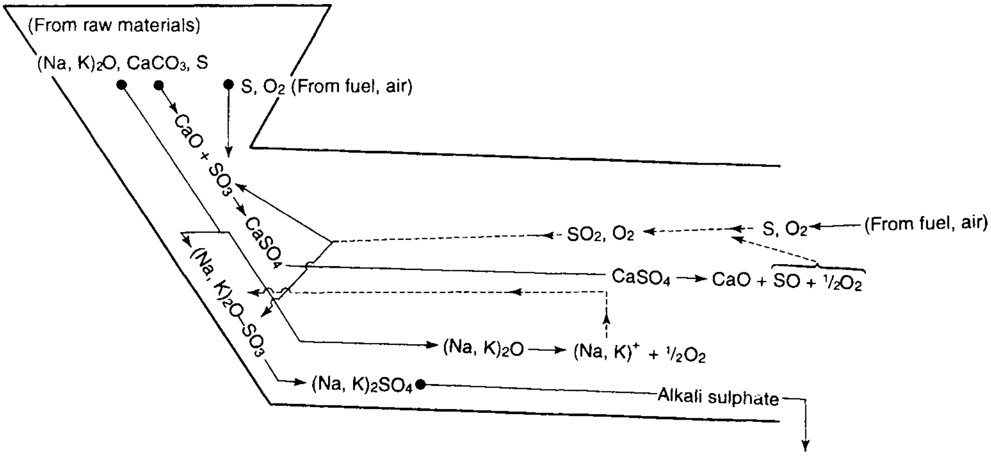

Fig. 5.11 Schematic view of the clinkering process, showing especially the alkali and sulfur cycle.

large quantities of data are also available which would enable the sulfur cycle to be treated more quantitatively. Understanding the role of alkalis is important for two reasons. First, environmental pressures have meant that less alkali can be discharged as dust, in flue gas, etc., which, other factors being equal, implies relatively more in clinker. Second, to avoid alkali–aggregate reaction, cement makers strive to produce low-alkali cements.

The two alkalis – Na_2O and K_2O – are often treated together, although they often show significant differences in behaviour. For example, sodium in clinker preferentially concentrates in the C_3A phase, whereas K is preferentially fractionated, albeit weakly, into belite. However, an important point of similarity between the two alkalis is their preference to combine with sulfate and, moreover, for the alkali sulfates to be somewhat volatile in the kiln. The form in which the alkalis are held in clinker is important for several reasons. First, it controls the rate at which alkali is released during the early stages of cement hydration and second, by combining with sulfate, it affects sulfate availability and release during the early stages of hydration.

Some of the alkali introduced into the kiln participates in a cycle of volatilisation and condensation. Basic to this process is the vapour pressure of the sulfates themselves. Vapour pressure data have been obtained on a self-consistent basis[54] for the relevant sulfate-containing phases; these are shown in Figure 5.12. As would be expected, the magnitude of the sulfate vapour pressure increases rapidly with rising temperature; $\log P$ against $1/T$ for each of the principal solid substances gives a series of virtually straight-line plots, albeit of somewhat differing slopes. Two mechanisms of sulfate decomposition by evaporation occur; the process may be either congruent or incongruent. Some sulfate species, e.g. K_2SO_4 and Na_2SO_4, evaporate congruently; that is, they evaporate totally, leaving no solid residue. Incongruent evaporation, as occurs with $CaSO_4$, leaves a solid residue, in this instance CaO. Since some of the sulfate phases remain stable until well into the burning zone, incongruent decomposition is a potential mechanism whereby free lime can be produced relatively late in the clinkering cycle.

Given the normal dwell time of clinker in the kiln, the kinetics of evaporation only become significant as the vapour pressure, $\log P$, becomes greater than 10^{-2} to 10^{-3} bar. In the higher-temperature regime necessary to achieve these vapour pressures, the steep

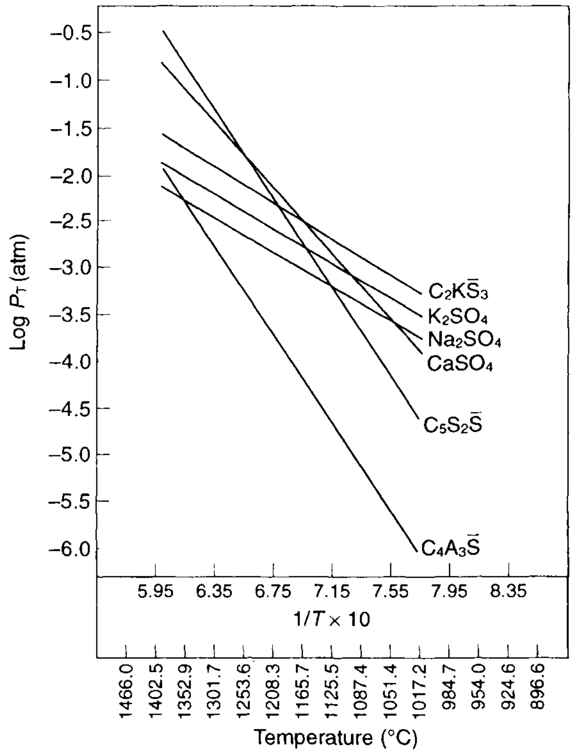

Fig. 5.12 Vapour pressure of some sulfates relevant to cement burning (after Ref. 53).

slope of the vapour pressure curves for calcium sulfoaluminate and sulfosilicates indicates their rapidly decreasing stability. Thus calcium sulfosilicate becomes unstable with respect to $CaSO_4$ and Ca_2SiO_4 in the burning zone and will not normally survive the highest temperatures achieved. It is also noteworthy that at a fixed temperature, the vapour pressure of a K-containing species is always higher than that of the corresponding Na-containing species.

Just as evaporation can occur, so condensation reactions may lead to removal of alkali sulfates from cooling vapour streams. Each species will have a ‘dew point’ (analogous to that of water) which, if exceeded, leads to condensation. The nature of the vapour species in the kiln is, however, complex. Whereas ordinary dew (water) involves an equilibrium between one molecular species in two states (vapour, liquid), the situation in the kiln is more complex. Water vapour, CO_2 and O_2 are likely to interact with alkalis and sulfur oxides: NaOH and KOH are probably important vapour species. Nevertheless, reaction between the complex species present in hot vapour is apparently rapid, with the result that liquid and solid sulfates reform rapidly by condensation at appropriate points of the cooling cycle.

When condensation occurs, the condensate may be either liquid or solid. The initial condensate may also be unstable; for example, molten K_2SO_4 condensing onto a clinker grain may undergo a secondary reaction with lime or calcium silicates to form calcium langbeinite, $CaK_2(SO_4)_2$. Because of the low vapour pressure of CaO, calcium is not transported within the vapour stream, so calcium langbeinite cannot be a primary condensate.

The balance between sulfate transported in the vapour and that which is transported in solid clinker is apparently variable, depending in part on the mechanical structure of the developing clinker. In some cases, solid or molten sulfates become physically entrapped within the clinker and thus are mechanically prevented from evaporating. The behaviour of confined sulfate melts and their interaction with silicate melts at 1350°C was studied using sealed crucibles.[55] In these experiments, a glass having the C–A–F–S eutectic composition, as given by Lea and Parker,[46] was prepared and crushed. Weighed portions of the glass were mixed with $CaK_2(SO_4)_2$, K_2SO_4 and Na_2SO_4, sealed into silica capsules and reacted for 1 h at 1350°C. Extensive liquid miscibility occurred, one liquid containing most of the silicate and the other, most of the sulfate. After quenching, the two liquids were seen to have undergone clean physical separation, with the less-dense sulfate melt floating on the denser silicate, and the two could be hand-picked for analysis. Al_2O_3, Fe_2O_3 and SiO_2 were found to be virtually insoluble in the sulfate melt, as was SO_3 in the silicate melt, while alkali and calcium were fractionated between the two immiscible liquids.

Thus the high vapour pressure of alkali sulfates leads to evaporation of these components, with condensation occurring in cooler zones. Evaporation is not, however, complete; some sulfates may be mechanically enclosed and entrapped by clinker. These will persist in the hot zone, where immiscibility occurs between the normal clinker melt and the molten sulfates. It is noteworthy that where molten sulfates persist at <1250°C in contact with C_3S, this melt serves as a powerful catalyst for the local decomposition of alite. This mechanism of C_3S decomposition may be responsible for the association of free lime with sulfates, a feature which is sometimes observed by clinker microscopy.

At lower temperatures, such that all the phases are solid, the patterns of stable coexistence of silicate, aluminate and sulfate phases are shown in Table 5.8. C_3S is not a stable phase at <1250°C, so it is not shown in the assemblages. The division of phases into two columns

Table 5.8 Compatible phases in the system $CaO–Al_2O_3–SiO_2–CaSO_4–K_2SO_4$ at $\leqslant 1250$°C

	Oxide, silicate and aluminate (ferrite)	Sulphate(s)
Phase assemblages definitely located		
I	C_2S, C_3A	CaL[a], K_2SO_4
II	CaO, C_2S, C_3A	CaL, K_2SO_4
III	CaO, C_2S, C_3A	CaL
IV	CaO, C_3A	CaL, C_5S_2S
V	CaO, C_2S, C_3A	CaL, C_5S_2S
VI	C_2S, C_3A	CaL, C_5S_2S
VII	C_2S, C_3A	CaL, C_5S_2S, C_4A_3S
VIII	C_2S, C_3A	CaL, C_4A_3S
IX	C_2S	CaL, C_5S_2S, C_4A_3S
X	C_3A	CaL, C_5S_2S, C_4A_3S
Phase assemblages believed to be stable		
XI	CaO, C_2S, C_3A, C_4AF	CaL, K_2SO_4
XII	CaO, C_2S, C_3A, C_4AF	CaL, C_5S_2S
XIII	C_2S, C_3A, C_4AF	C_5S_2S, C_4A_3S

Note: for convenience the ferrite phase composition is designated C_4AF although its exact A/F ratio was not determined.
[a] Calcium langbeinite, $CaK_2(SO_4)_2$.

is to facilitate comparison: the sulfates shown in the right-hand portion of the table can coexist with the more familiar clinker minerals shown on the left-hand side.

5.4.7 FLUORINE

The use of fluorine has a long history in cement clinkering. It interacts strongly with both major and minor components of the batch and also influences melt properties. Introduction of F into clinker batches favours preservation of rhombohedral (R) C_3S to ambient temperature. The reasons for this were not initially clear, although F was clearly entering the alite structure. However, in the absence of any charge compensating mechanism, substitution of F^- for O^{2-} is minor as the omission of calcium, necessary to preserve charge balance, occurs to only a limited extent (see below).

Phase relations on the pseudo-binary join $Ca_3Si_{1-x}Al_xO_{5-x}F_x$ show[56] that a double substitution leads to much more extensive solid solution with Al and F for Si and O, respectively, thus enabling charge balance to be maintained without need for vacancy or interstitial mechanisms;[2] Figure 5.13 shows the results. The normal lower stability limit of C_3S, at 1250°C, decreases with increasing (Al + F), eventually reaching a peritectoid at $x = 0.15$ and 1075 ± 15°C. Thus pure, single-phase alite can in theory be obtained at temperatures as low as 1075°C, although in practice temperatures of ~ 1100°C were required

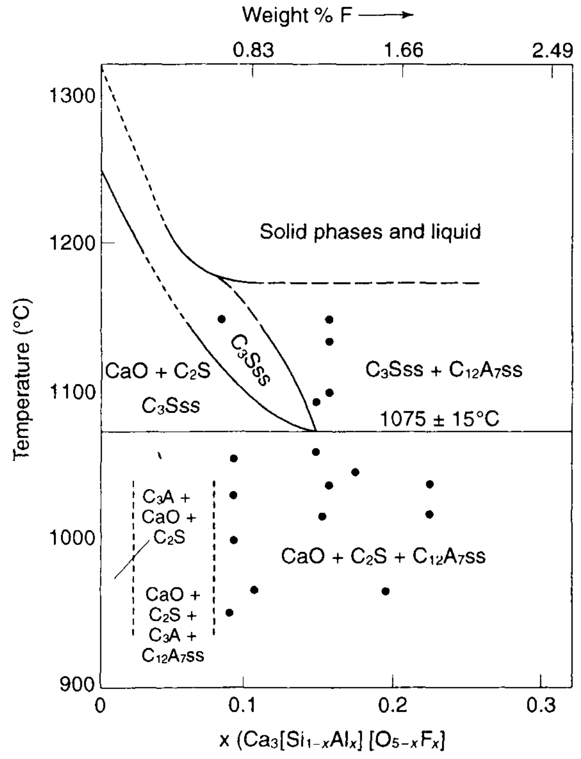

Fig. 5.13 Stabilisation of Ca_3SiO_5-type solid solutions by coupled substitution of Al for Si and of F for O (after Ref. 55).

to drive the reaction to completion. The Al- and F-substituted alite product gave rapid strength gain and excellent compressive strengths.

Other fluorosilicates are reported, the best-characterised of which is the $Ca_{6-0.5x}Si_2O_{10-x}F_x$ phase, first described by Bereczky.[57] It is stable up to liquidus temperatures and has a small primary place field in the system $CaO-SiO_2-CaF_2$. The structure was refined using melt-grown single crystals.[58] A crystal structure determination and analogy with the isostructural germanate suggests that its constitutional formula is represented by: □ $Ca_{11}Si_4O_{18}F_2$ where □ designates a cation vacancy. In the crystal studied, about 9.2 per cent of the Ca sites were vacant. Gutt and Osborne[59] and Tanaka *et al.*[60] appear to have described essentially the same phase, although they arrive at a somewhat different chemical formula; for example, Tanaka gives $Ca_{12}Si_4O_{19}F_2$. The formula derived from the crystal structure is preferred. Its structure is closely related to that of C_3S but, despite the close structural relationship, the fluorosilicate is only feebly active in water and its formation in clinker thus represents an inefficient use of fluorine.

Formation of fluoraluminate, $C_{11}A_7 \cdot CaF_2$, enhances early strength development. Fluorine also reacts strongly with aluminates, notably $C_{12}A_7$, forming solid solutions extending towards $C_{11}A_7 \cdot CaF_2$. The fluorinated phase has a higher melting point than $C_{12}A_7$ and it often appears as the aluminate component in fluorine-mineralised cements to the exclusion of C_3A. The fluoraluminate is very reactive and forms the basis of some rapid-hardening clinkers.

The reactions of fluorine in clinker batches is complex; while it promotes reactions and lowers melting points, thus facilitating burning, fluorine also alters the mineralogy of the clinker and it has not always been possible to develop one or more desirable phases selectively without also incurring disadvantages. Many of the early studies of fluorine utilisation lacked knowledge of the phase equilibrium and attempted to progress by trial and error. Of course the cement system becomes very complex when fluorine, and perhaps sulfate, are added to the basic components – CaO, Al_2O_3, Fe_2O_3 and SiO_2. Nevertheless, progress on understanding phase relations has been made.[61]

Table 5.9 shows subsolidus relations for the iron-free system. The principal difference between the two temperatures shown is that calcium sulfosilicate is stable at 1050°C, but not at 1100°C. Other workers have reported that sulfosilicate decomposes to Ca_2SiO_4 and

Table 5.9 Compatible assemblages in the system $CaO-Al_2O_3-SiO_2-CaSO_4-CaF_2$

1050°C
$CaO-C_3A-C_{11}A_7 \cdot CaF_2-C_5S_2\bar{S}$
$CaO-C_3A-C_{11}A_7 \cdot CaF_2-C_5S_2S-C_4A_3\bar{S}$
$CaO-C_{11}A_7 \cdot CaF_2-C_5S_2\bar{S}-C_2S-3C_2S \cdot 3CaSO_4 \cdot CaF_2$
$CaO-C_{11}A_7 \cdot CaF_2-C_5S_2\bar{S}-C_4A_3\bar{S}-3C_2S \cdot 3CaSO_4 \cdot CaF_2$
$CaO-C_4A_3\bar{S}-C_5S_2\bar{S}-CaSO_4-3C_2S \cdot 3CaSO_4 \cdot CaF_2$
$CaO-C_{11}A_7 \cdot CaF_2-3C_2S \cdot 3CaSO_4 \cdot CaF_2-C_3S_{SS}-C_2S$
$CaO-CaSO_4-C_4A_3\bar{S}-CaF_2-3C_2S \cdot 3CaSO_4 \cdot CaF_2$

1100°C
$CaO-C_4A_3\bar{S}-C_2S-CaSO_4-3C_2S \cdot 3CaSO_4 \cdot CaF_2$
$CaO-C_4A_3\bar{S}-C_2S-3C_2S \cdot 3CaSO_4 \cdot CaF_2-C_{11}A_7 \cdot CaF_2$
$CaO-C_4A_3\bar{S}-C_{11}A_7 \cdot CaF_2-C_3A-C_2S$
$CaO-C_2S-3C_2S \cdot 3CaSO_4 \cdot CaF_2-C_{11}A_7 \cdot CaF_2-C_3S$
$CaO-CaSO_4-3C_2S \cdot 3CaSO_4 \cdot CaF_2-C_4A_3S-CaF_2$

$CaSO_4$, but only at much higher temperatures; for example, see Figure 5.12, from which it is possible to infer the stability from the absolute magnitude of the vapour pressures.

At subsolidus temperatures, much fluorine (together with Ca and Si) can be tied up in phases which are relatively unreactive towards water, for example as fluorellestadite ($3C_2S{\cdot}3CaSO_4{\cdot}CaF_2$). Most workers have implicitly recognised this, and sought to minimise the amount of fluorine thus combined.

The influence of CaF_2 and $CaSO_4$ in conjunction has been determined by a study of the $CaSO_4$–CaF_2–Ca_2SiO_4 system; the results are shown in Figure 5.14. The apatite-structured phase fluorellestadite, $Ca_{10}(SiO_4)_3(SO_4)_3F_2$, is stable to liquidus temperatures, melting incongruently to C_2S and liquid at 1240°C. A low-melting eutectic with Ca_2SiO_4 and CaF_2 occurs at about or just below 1113°C. The study suggests that compositional areas of fluorellestadite formation should be avoided as it ties up F, as well as SO_4 and Ca, in an essentially inert phase. Nevertheless, fluorellestadite probably cannot be avoided completely and is likely to be a minor component of many fluorine-mineralised clinkers.

Two solid solutions which are frequently encountered in cement kilns have the silicocarnotite and apatite structures. Because both structures are very tolerant of crystallochemical substitution, their compositions may vary widely: Figure 5.15 shows the phase relationships.[62] The composition of silicocarnotite solid solutions lies primarily along the join $Ca_5(SiO_4)_2$–$Ca_5(SiO_4)(PO_4)_2$ and its structure contains little halide. The apatite composition is more complex. Basically, there are four apatite end-members: $C_{10}(PO_4)_6F_2$, $Ca_{10}(PO_4)_6Cl_2$ (the apatites most closely resembling in composition the naturally occurring mineral), $Ca_{10}(SiO_4)_3(SO_4)_3F_2$ and $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$, known as fluorellestadite and chlorellestadite, respectively. The four end-member compositions are apparently completely miscible in all proportions. Extensive solid solution also occurs between the ellestadite-type apatite and the sulfate-rich silicocarnotite phase: the limits of solid solution shown are for 1000°C. One aspect is not, however, shown: this relates to the halide deficiency sometimes encountered in the apatite-structured phases. This could be due to OH^- substitution for either or both F^- and Cl^- but, as shown in Figure 5.14, it could also result from extensive

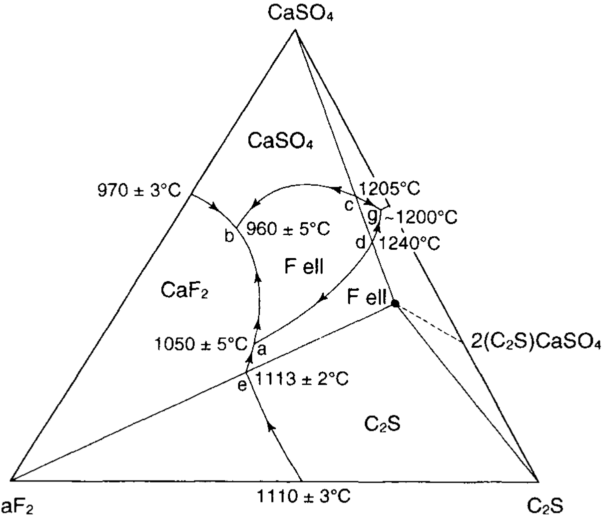

Fig. 5.14 The role of fluorellestadite (apatite) in the system $CaSO_4$–CaF_2–Ca_2SiO_4.

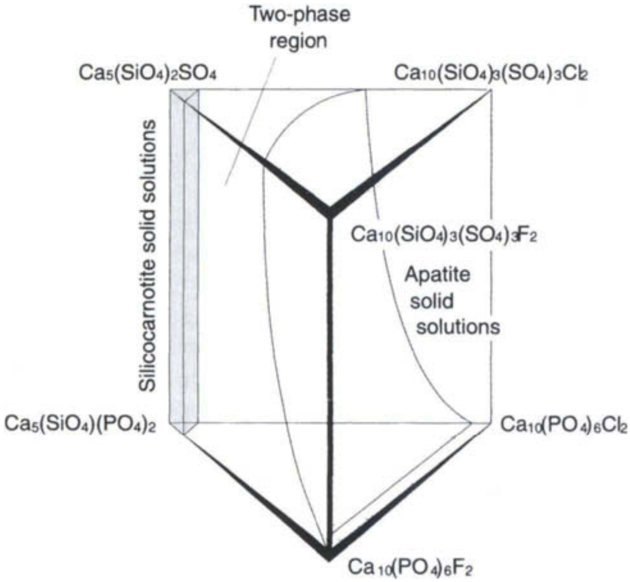

Fig. 5.15 Phase relations between apatite and silicocarnotite-structured phases, showing especially the extent of reciprocal solid solution at ~1200–1100°C. (Cross-hatched lines mark the boundaries of regions of homogeneous solid solutions.)

solid solution of an apatite-structured phase with silicocarnotite, which would also lower the halide/calcium ratio.

In the presence of alkali and sulfate, another phase containing essential fluorine which may form is $KF \cdot 2[Ca_6(SO_4)(SiO_4)_2O]$. It was first found in kiln linings and described by Trivino.[63] Its crystal structure has been determined and is also closely related to that of Ca_3SiO_5.[61] It is, however, also poorly reactive with water.

This discovery adds to the list of phases that have structures which are closely related to those of C_3S. These phases vary greatly in their reactivity towards water and bring into question the extent to which the crystal structure controls reactivity. It has often been suggested that Ca_3SiO_5 contains structural units like those in CaO itself, and that these are responsible for initiating rapid reaction with water. Yet many of the C_3S-related structures are not reactive towards water although, on the basis of this theory, they might be expected to be so. In the author's view, the distinction is that many of the fluoride-containing phases are thermodynamically stable in their anhydrous systems even at ~25°C, whereas Ca_3SiO_5 itself is thermodynamically unstable in the $CaO-SiO_2$ system below ~1250°C. It is this relatively high-energy state of C_3S, arising from its thermodynamic metastability, which decreases the activation barriers towards rapid reaction with water. Both structural and thermodynamic considerations control reactivity, but in the case of Ca_3SiO_5 its thermodynamic metastability dominates its behaviour towards water.

In conclusion, fluorine has three impacts on cement making. It may be used simply as a flux, to promote more rapid burning of the components. It may also be used as a mineraliser, to alter the phase relations; formation of (F, Al)-substituted C_3S and of $C_{11}A_7 \cdot CaF_2$ are examples. Finally, it can be an important volatile element in the kiln linings, forming clinker rings and influencing the early states of reaction.

5.4.8 BORIC OXIDE

Boric oxide has long been used as a flux in oxide technology. However, numerous investigators have been disappointed in its application to cement systems. Boric oxide appears to lower the potential for C_3S formation. The portions of this system relevant to cement making were restudied by Fletcher:^{64} Figure 5.16 shows the liquidus surface of the lime-rich portion of the system. C_3S was not observed to crystallise at liquidus temperatures, even up to 1700°C. When preformed C_3S was used as a reactant, addition of boric oxide led to its rapid decomposition, to $C_2S + CaO$. Stabilisation of this assemblage in preference to C_3S was attributed to two factors: (1) the rather small free energy difference between C_3S and $(CaO + C_2S)$, even at $T > 1250°C$, and (2) the extensive and apparently very stable solid solutions of boric oxide in C_2S, which altered the energetic balance of reaction (1) in favour of C_2S solid solutions and free CaO.

The system was also shown to contain a congruently melting compound, $C_{11}S_4B$; it had little cementitious potential. The C_2S-containing boric oxide was, however, well stabilised as β and reactive towards water, although lacking in the good early-strength characteristics of C_3S.

5.5 Kinetics of cement making

5.5.1 INTRODUCTION

Broadly, two approaches to cement burning have been developed. Various empirical tests designed to measure the 'burnability' of raw meals have been devised but the kinetics of reactions have also been studied in a more fundamental way. Owing to the complexities of reaction(s) and the complex chemistry of the system, neither approach has been completely successful in achieving a quantitative description of the overall process. Nevertheless, considerable progress has been made in understanding how kinetics relate to equilibrium and, in turn, how they affect the processing of raw materials.

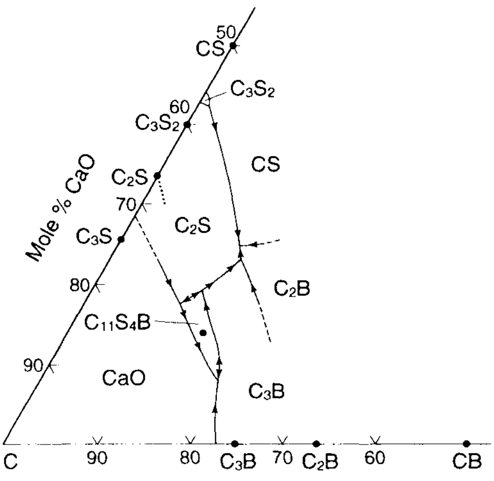

Fig. 5.16 Liquidus of part of the $CaO-B_2O_3-SiO_2$ system showing how formation of boron-containing C_2S solid solutions suppress crystallisation of C_3S (after Ref. 62).

Table 5.10 Reaction kinetics occurring during cement burning

Reaction type	Examples and comment
Decomposition	$CaCO_3 \rightarrow CaO + CO_2$: one or more volatile substances form in the course of reaction. The example given is of incongruent decomposition (see text)
Diffusion	$2CaO + SiO_2 \rightarrow Ca_2SiO_4$: solid-state reactions between components
Melting	Formation of C–A–F–S eutectic at 1338°C between C_3S, C_2S, C_3A and 'C_4AF'
Liquid phase sintering	$3\langle CaO\rangle + \langle SiO_2\rangle \rightarrow Ca_3SiO_5$:[a] precipitation of alite from melt
Nucleation and crystal growth	Liquid $\rightarrow C_3A$ + 'C_4AF': freezing with crystallisation of undercooled melt to yield interstitial phases
Polymorphic transformation	α'-$Ca_2SiO_4 \rightarrow \beta$ and/or γ-Ca_2SiO_4: polymorphic changes occurring during cooling
Evaporation/condensation	$K_2SO_4(l) \Leftrightarrow K_2SO_4(v)$:[b] evaporation and condensation of alkali sulfates

[a] ⟨ ⟩ indicates species dissolved in melt.
[b] l = liquid, v = vapour.

The nature of the reactions occurring, classified according to a kinetic scheme, can be appreciated by reference to Table 5.10. The formalism of chemical kinetics demands such an approach because different kinetic theories have been developed to deal with different types of reaction. Space precludes more than an outline of the state of theoretical development and its application, but the basic ideas and concepts are important because they underlie many of the more empirical approaches so often used in practice.

5.5.2 DECOMPOSITION

Decomposition during the early stages of cement burning is responsible for much of the energy consumption of the cement kiln; the reaction $CaCO_3 \rightarrow CaO + CO_2$ is very endothermic. Figure 5.17 shows a graphical representation of the free energy–temperature relations in the system $CaCO_3$. The standard state, for which $P_{CO_2} = 1$ atmosphere has, by definition, $\Delta G = O$. The position for the equilibrium curve for the decomposition of $CaCO_3$ is marked; it is nearly a straight-line relationship over the range of CO_2 partial pressures shown. Isobaric CO_2 pressures are shown with an interpolated air isobar corresponding to $P_{CO_2} \sim 10^{-3.5}$ atm.[65] Reaction will not proceed spontaneously to the left of the ΔG curve. In regions favourable to reaction, the rate at which reaction proceeds is a complex function of several factors; (1) initiation of reaction, by loss of CO_2: this process is generally termed 'nucleation' because CaO first forms at this stage; (2) the rate-controlling mechanism whereby the main stage of the reaction occurs, (3) the energetics and geometry of the reaction, including the conditions of heat flow and mass balances, as well as surface area and particle size of the reactant; and (4) the impedence or barrier effect of the solid

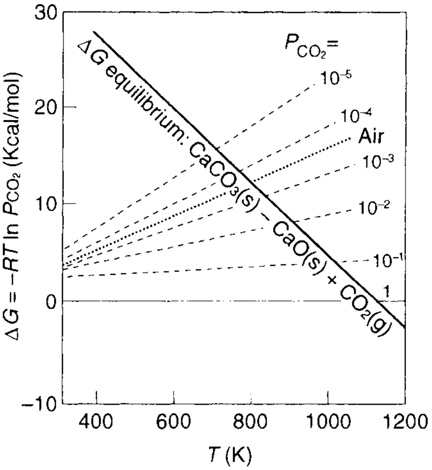

Fig. 5.17 Free energy and vapour pressure as a function of temperature for $CaCO_3$ decomposition.

product to further reaction. This last factor is sometimes included in the previous category, giving rise to a single complex term.

The decomposition rate measured from loose $CaCO_3$ powders is shown in Figure 5.18. The data confirm what might be suspected intuitively, that decomposition rates increase rapidly with increasing temperature. The kinetics obeys, to a remarkable degree, equations of the type:

$$(1 - \alpha)^{1/2} = 1 - kt/r_0 \tag{5.4}$$

where α is the fraction decomposed at some time t for particles having an initial cylindrical radius r_0 (other particle geometries can of course be treated by appropriate modification). The factor k is termed the 'activation energy': a graph of $1 - \alpha$ against t produces a straight-line relationship for constant temperature.

This analysis is satisfactory to account for the initial and intermediate stages of reaction but may fail to account for its final stages. During this stage, the growing skin of reaction product increasingly acts as a barrier layer and, moreover, stress accumulation may cause

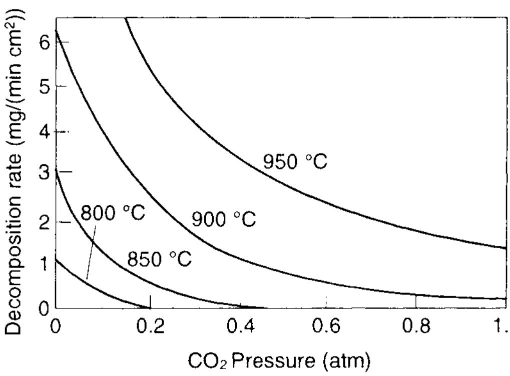

Fig. 5.18 Decomposition rate of $CaCO_3$ powders as a function of CO_2 pressure and temperature.

the remaining reactant to develop cracks and fissures, thereby increasing its apparent surface area.

Jander's original equation,

$$(1 - 3\sqrt{1 - \alpha})^2 = (k/r^2)t \tag{5.5}$$

is generally applicable to the beginning and intermediate stages of the decomposition of loose powders; r is the particle radius, α the fraction reached at some time t at constant temperature and k is a rate constant. However, many workers now use the more sophisticated Ginstling–Brounschtein relationship, which is believed to give a better overall description of the process:

$$F(\alpha) = (1 - \tfrac{2}{3}\alpha) - (1 - \alpha)^{\frac{2}{3}} = (k/r^2)t \tag{5.6}$$

It uses the same quantities and, at earlier stages of reaction, it reduces to the Jander equation. The presence of impurity may also influence the kinetics; further details are given in a review[66] but it is noteworthy that many metal oxides are catalytic towards the thermal decomposition of carbonates and sulfates. Thermochemical calculations show that lowering decomposition temperatures and enhancing reaction kinetics does not significantly reduce the overall energy required for clinkering.

5.5.3 SOLID-STATE REACTIONS

The direct solid-state reaction of constituents is also important, especially in kilns with long burning zones. Historically, the solid-state reaction between CaO and SiO_2 was one of the first to be studied. Nevertheless, there is still a lack of agreement on the nature of the products obtained and the adequacy of various methods of analysing the data. Reaction has typically been studied using loose powders or, in more sophisticated approaches, by making a sandwich of discs composed of the reactants; for example, by using a sandwich of sintered discs of CaO and SiO_2 which are reacted isothermally in close physical contact. After heating, the sandwiches are cooled and sectioned to determine the mineralogical zonation. Markers inserted at the junction between the reactants, e.g. a Pt wire, may be used to assist the location of the position of the original interface, while the thicknesses and mineralogy of the reaction zones and their physical position with respect to the marker indicate the relative diffusability of species. For example, in CaO–SiO_2 couples, Ca is invariably found to diffuse more rapidly than Si.

5.5.4 ROLE OF DEFECTS IN CONTROLLING THE REACTIVITY OF CLINKER PHASES

Many of the properties of single crystals, including strength, plasticity, electrical conduction, ion migration and diffusion rates, as well as reactivity, are controlled in part by the defect type and population. Defects in crystalline solids are of two types: 'point' defects and extended defects. Point defects involve a single atom or small cluster of atoms and are, in turn, subdivided into two types: 'vacancies', where an atom (or in an ionic substance an atom pair, to conserve charge balance) is missing, and 'interstitials', where the extra atom is situated in a normally unoccupied structural site. The latter are almost invariably thermodynamically metastable, whereas the vacancy population can be in a thermodynamic, temperature-dependent equilibrium. In ionic crystals, vacancies and interstitials may also be coupled; for example, an anion displaced from its ideal lattice site, leaving a vacancy, may become interstitial, thus enabling the overall charge balance to be maintained. The free energy of an ideal crystal is actually lowered slightly by the inclusion of point vacancies up to some equilibrium population. While this may seem surprising at first sight, it arises from the extra gain in entropy obtained by distributing a relatively small number of vacancies amongst a numerically much larger number of lattice sites. The theory of defects, their classification and thermodynamics has been developed further by Kröger.[67] Consider CaO as an example. The energy for creation of a pair of vacancies, Ca^{2+} and O^{2-}, is about 6 eV per event (it is desirable to pair cation and anion vacancies to avoid charge compensation problems). Theory enables the equilibrium defect ratio n/N to be calculated where n is the number of defects per N, the total atomic population. Thus for 1 mol (56 g) of CaO, $N = 2 \times 6.02 \times 10^{23}$ and the numerical value of the ratio n/N is $\sim 3 \times 10^{-41}$ at 100°C, 3×10^{-20} at 500°C, 1×10^{-12} at 1000°C and 3×10^{-9} at 1500°C. Comparable values are obtained for calcium in calcium silicates. The significance to cement making is that the equilibrium defect population is very temperature dependent. Although the defect population ratio n/N remains low even at peak clinkering temperatures, it is nervertheless sufficient to assist rapid diffusion in the solid state.

Quenching often preserves the characteristic defect content to ambient temperature: the decay to the equilibrium population, even during normal clinker cooling, may be slow. Nevertheless, the intrinsic ratio n/N is always low, almost insignificant, relative to the density of chemically induced defects normally present in the Portland cement minerals. Such defects, induced by the chemistry, are termed 'extrinsic' defects. For example, even using laboratory reagent grade materials, the chemical level of impurity in C_3S fired at 1500°C, and hence the level of extrinsic defects, is likely to be several orders of magnitude greater than the intrinsic defect population. It is thus concluded that the intrinsic defect population does not significantly affect reactivity in materials of normal commercial purity; the extrinsic defect population induced by solid solution is more important and is inextricably linked with the nature and amount of chemical doping.

Extended defects occurring over rows or blocks of atoms may also occur. These can be of many different types. In practice, the most important are likely to be associated with the complex series of inversions arising as a consequence of polymorphic transformations during clinker cooling. These sequences have been described for C_3S and C_2S. The progressive lowering of symmetry with decreasing temperature leads to twinning with mismatch of the structure across twin boundaries and concomitant displacement of slabs of atoms from their ideal locations. Since the individual twin domains may be very small, perhaps of the order of 10^{-3} to 10^{-1} μm thickness in the case of parallel slabs, the total volume fraction of the crystal within strained regions may be correspondingly large. This undoubtedly raises the mean free energy, and hence the reactivity, of the entire crystal well above that which would be expected of an ideal supercooled but untwinned crystal. Other features such as exsolution also contribute to the strain energy.

In conclusion, therefore, point defects are unlikely to contribute significantly to the overall reactivity of clinker minerals. Crystallochemical substitutions in the clinker phase introduce extrinsic defects, and the contribution made to the reactivity by the two overwhelm the contribution made by the point defects. The sequence of inversions encountered during cooling of silicates tends to complicate their internal structure, and thereby increases the potential for reaction within strained regions which form along twin boundaries and as a consequence of internal chemical zonation.

The instability of C_3SiO_5 at temperatures below 1250°C has long been known. The kinetics of its decomposition, to CaO and Ca_2SiO_4, and the influence of impurities have

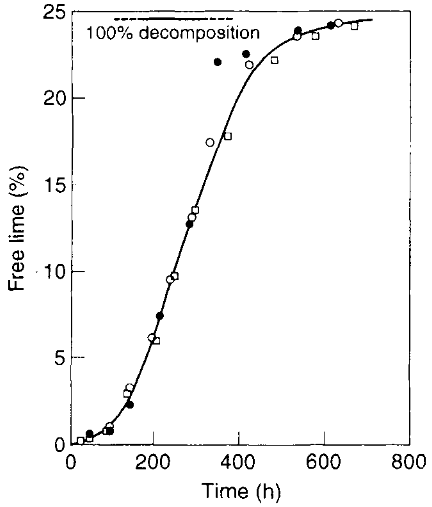

Fig. 5.19 Kinetic decomposition curve for the composition of Ca_3SiO_5 in dry air at 1175°C (after Ref. 66). The extent of decomposition is measured by the increase in free lime.

been studied.[68 70] Figure 5.19 shows an isothermal rate curve for the decomposition at 1175°C: this temperature was chosen as it corresponds closely to the maximum rate velocity. The data were treated according to the Avrami treatment, in which the volume fraction transformed, δ, at some time t is given by the relation:

$$\delta = 1 - \exp(-kt^n) \tag{5.7}$$

where k is a constant; the parameter n is related to the mechanism of nucleation. Avrami suggested that values of n between 2 and 3 indicated two-dimensional nucleation (i.e. surface nucleation and decomposition). Mathematical analysis of data on several isotherms gave a value of n for C_3S equal to 2.59. This value supports an interpretation whereby decomposition is initiated at the surface. It is confirmed by direct microscopic observation of suitably annealed C_3S crystals, showing that surface nucleation was occurring. Impurities in C_3S solid solution, e.g. Mg, Fe, Al and Na, had a relatively minor effect on decomposition kinetics while those which affected the surface, e.g. moisture and molten sulfates, were found to accelerate decomposition drastically. In the presence of water vapour, the kinetics of decomposition were first order: that is, the decomposition rate was a direct function of P_{H_2O}.

It was suggested that much of the data in the literature on the kinetics of C_3S decomposition could not readily be integrated to form a consistent picture; even data on different isotherms were difficult to relate to each other. The time–temperature–transformation (T–T–T) curves were introduced as a useful way to depict and correlate observations. Figure 5.20 shows an example of a T–T–T curve for pure C_3S. The existence of a rate maximum in decomposition at ~1175°C is clearly disclosed and data obtained on one isotherm can be related to others once the shape of the T–T–T curves have been established. It was concluded that C_3S was unlikely to decompose during normal clinker cooling, except in the presence of molten sulfates. However, decomposition could become a problem if more intensive efforts to recover heat were made and if cooling occurred in moist atmospheres.

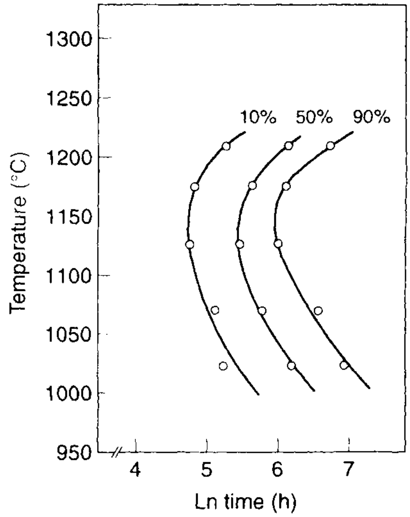

Fig. 5.20 Time–temperature–transformation curve for Ca_3SiO_5 decomposition, from Ref. 66. Percentages refer to the volume % Ca_3SiO_5 decomposed.

5.5.5 *REACTIONS IN THE PRESENCE OF A LIQUID PHASE*

In real clinkers, liquid formation may begin at surprisingly low temperatures. Sulfates and carbonates together have low melting point eutectics, of the order of 800–900°C, and thus liquid formation will be assisted by traces of halides and other fluxes. This low-temperature melt is, however, ephemeral on account of the relatively high vapour pressure of several of its components, notably SO_2, O_2 and CO_2. Nevertheless, this transient melting occurs at an early stage of clinkering and is partly responsible for agglomeration and reaction.

Eventually, clinker reaches the point at which fusion of the silicate components begins. This marks the stage at which rapid C_3S formation occurs. One feature of melting, perhaps unexpected, is that the amount of liquid increases progressively, but not necessarily in a regular manner, with rising temperature. Diagrams based on the phase relations in the CaO–Al_2O_3–Fe_2O_3–SiO_2 system have been presented[71] showing how the quantity of liquid developed at and above 1338°C relates to the chemical Al_2O_3 and Fe_2O_3 contents of the clinker. Figure 5.21 shows an example of a 'clinkering diagram' for ~1400°C. Alumina and iron oxide, it will be recalled, are not essential to the constitution of Portland cement but, being present in raw materials, they constitute a cheap source of fluxes lowering the energy requirement and generally making the process economic. At 1338°C, when melting commences, the quantity of liquid abruptly rises from zero to a significant value, in the range 15–25 per cent. The presence of other minor components, and also of rapid heating under non-equilibrium conditions (the batch will not have fully reacted when more general melting commences) somewhat blurs the precise temperature at which significant melting occurs, but the general principle remains.

The liquid wets all the solid grains, forming an interpenetrating film. It has two functions: its surface tension pulls the solid grains together, helping to form nodules known as 'clinker' and it also facilitates material transport in the liquid phase. Metastable phases (free CaO, SiO_2 as quartz, etc.) dissolve in the melt which becomes supersaturated with respect to the stable phases, which precipitate mainly as alite and belite. Proper mixing and particle size

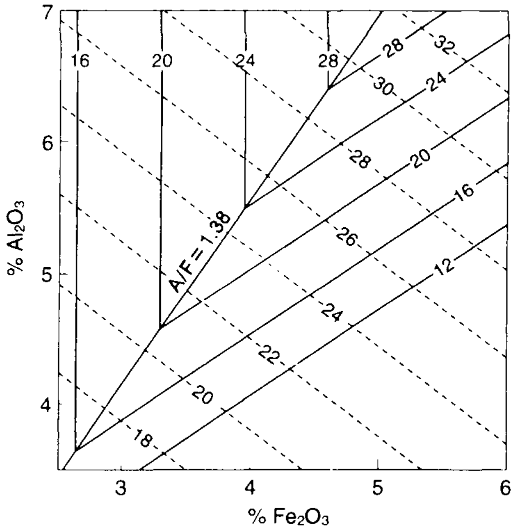

Fig. 5.21 Clinkering diagram showing the % liquid developed at or above the solidus temperature as a function of chemical Al_2O_3 and shown, close to 1338° (solid) and at 1400°C (dashed). The calculated contours assume all the Al_2O_3 and Fe_2O_3 are available for reaction. The position of the contours is independent of the amount of Ca_3SiO_5 and Ca_2SiO_4.

reduction of the reactants enable the melt to work effectively. But it is inevitable that even thoroughly mixed, powdered reactants will exhibit inhomogeneities and the ability of the melt phase rapidly to dissolve, transport and subsequently precipitate phases stable in the high-temperature regime is essential to achieve economic burning.

While the kinetics of dissolution are generally favourable to the cement maker, instances of grains which are relatively inert and resistant to dissolution do occur; for example, MgO (periclase) is slow to dissolve. Partly this is because of its low saturation limit, ~8 per cent, in eutectic clinker liquid at ~1350°C. But the surfaces of periclase grains are also notable for their kinetic inertness. Thus clinkers may often be undersaturated with respect to their chemical MgO content, but nevertheless still contain free MgO after clinkering. Its persistence is mainly due to inertness of the interface between MgO and other solids and with melt.

For the most abundant constituents, CaO and SiO_2, the important rate-limiting stages of the formation of C_3S and C_2S require the attainment of sufficiently high temperatures to ensure that C_3S is thermodynamically stable, >1250°C, and that sufficient liquid is present to wet the reactant grains. Thereafter, the rate of formation of the desired product(s) is limited largely by liquid-phase diffusion.

Christensen and Jepsen studied the effects of fineness of reactants on burnability[72-74] and related reaction kinetics and phase equilibria.[75-77] Diffusion couples composed of 'sandwiches' were constructed. Each slice of a couple was composed of preformed discs of selected reactants. The sandwiches were heated isothermally at temperatures above the solidus, following which the sandwich was quenched and examined. The layer thickness of the intermediate, partially melted zone was found to increase with time, *t*, specifically with $t^{1/2}$. CaO was the main diffusing species: an apparent diffusion coefficient, *D*, for CaO was calculated to be 4.37×10^{-7} cm^2/s at 1500°C. Since the liquid phase composition was not constant across the reaction zone, only a mean or 'apparent' diffusion coefficient could be determined.

Reaction sandwiches, the composition of which was formulated to permit alite to develop, were sectioned after isothermal annealing. The thickness of the alite layer, X, was found to increase with reaction time and a constant, k, characteristic of the system chemistry was defined. Changes in the fluxing power of the system were interpreted in terms of how the numerical value of k changed with chemistry, melt content and temperature. The role of iron oxide has already been discussed; up to certain values, it increases the amount of liquid, enhances its wetting power and decreases its viscosity. These factors all promote reaction in the clinker batch. Small amounts of MgO were also found to be beneficial. This observation that small amounts of MgO promote clinkering receives wide support from empirical studies and kiln practice.

Free CaO particles of known size were included in a laboratory clinker containing (weight per cent) 67 CaO, 6 Al_2O_3 and 27 SiO_2 pressed into pellets and fired at 1500°C for predetermined times. The rate of disappearance of CaO in terms of x, the fraction reacted at time t was given by

$$(1 + \beta_x)^{\frac{2}{3}} - \tfrac{2}{3}\beta x = 1 - [(2\alpha\beta D\Delta C/d_1)](t/r_0^2) \tag{5.8}$$

where D is the effective binary diffusion coefficient of 'CaO' in the melt, ΔC the concentration difference across the reaction interface, d_1 the density of CaO, α the volume fraction of liquid in the interfacial layer, β, which is a complex constant related to the composition and porosity of the material, and r_0 the original radius of the CaO particles. The significance of this relation is that the numerical values of many of the parameters are fixed, or nearly so, by the clinker batch composition and by the known phase equilibrium relations of the $CaO–Al_2O_3–SiO_2$ system. However, the rate of disappearance of CaO was also related to the factor $1/r_0^2$. Hence it is important to reduce particle size, and the value of r_0, by grinding the raw meal, and also to avoid agglomeration of CaO (or $CaCO_3$) particles subsequent to grinding. Calculations made using representative clinkering values of α, β and ΔC gave a value for t/r_0^2 of 2600 mm/mm^2 which, for a burning time of 20 min at ~1500°C, corresponds to a maximum size for total dissolution of CaO to grains equal to 90 μm. This value is frequently quoted in the literature, but out of context, without giving the background assumptions.

Grains of 90 μm would be furnished, after decomposition with sintering, by $CaCO_3$ grains of about 120 μm, so this value in turn sets an upper limit to the size of $CaCO_3$ particles which can be assimilated. The calculations agree well with more empirical studies of burnability, which also disclose an upper size limit to the $CaCO_3$ which can be assimilated. The tendency for clustering or agglomeration of $CaCO_3$ (or CaO) particles has been studied by Chromy.[78,79]

Similar studies of the assimilation of silica (quartz) disclose that, other factors being equal, the particle size reduction of silica required for complete reaction is more severe than for CaO. This is attributed to formation of a layer of silica-rich, high-viscosity melt at and near the surface of dissolving silica: transport through this layer is relatively slow when compared to transport through a low-viscosity, lime-rich melt.

The factor ΔC is derived from the phase diagram, and relates to the width of the C_3S primary phase field. Its width is typically rather narrow in the $CaO–Al_2O_3–Fe_2O_3–SiO_2$ system, hence the rather low driving force for C_3S crystallisation. It is noteworthy that some substances, notably fluorine, increase the width of the C_3S primary phase field and hence the numerical value of ΔC. We have previously explained the mineralising action of fluorine, especially towards C_3S formation. This observation, on the effect of fluorine to increase ΔC, relates directly to its fluxing ability. But one of the interesting aspects of fluorine is its ability to act as both flux and mineraliser.

Many empirical approaches of 'burnability' and 'clinkerisation' have been developed but these often neglect fundamentals. Such studies may be valuable under particular conditions, for example where raw materials and plant practice vary over only narrow limits, but any quantitative conclusions are unlikely to be of general applicability. On the other hand, fundamental studies have greatly assisted the development of empirical studies and enable the practical investigator to gain insight into the mechanisms involved and plan accordingly.

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6

Hydration, Setting and Hardening of Portland Cement

Ivan Odler

6.1 Introduction

6.1.1 GENERAL

In strictly chemical terms hydration is a reaction of an anhydrous compound with water, yielding a new compound, a hydrate. In cement chemistry hydration is understood to be the reaction of a non-hydrated cement or one of its constituents with water, associated with both chemical and physico-mechanical changes of the system, in particular with setting and hardening.

A partial hydration of cement may even take place in humid air, whereas for a complete hydration the cement must be mixed with sufficient amounts of water. The mutual ratio of water and cement in the mix, the water/cement ratio (w/c) [also called the water/solid ratio (w/s)], affects the rheology of the produced suspension, the progress of hydration and not least the properties of the hydrated material. At water–cement ratios between about 0.3 and 0.6 the suspension exhibits a paste consistency and is called 'fresh cement paste'. Such paste sets and hardens as the hydration progresses and converts to a 'hardened cement paste'. The term 'setting' means a rather sudden loss of plasticity of the original paste and its conversion to a solid material with a barely measurable strength. The term 'hardening' means the development of hardness and strength that follows the setting of the paste.

As Portland cement is a multi-component system, its hydration is a rather complex process consisting of a series of individual chemical reactions that take place both in parallel and successively. The process gets under way spontaneously upon contact of the binder with water and is associated with liberation of heat.

The progress of hydration and its kinetics are influenced by a variety of factors, especially

- by the phase composition of the cement and the presence of foreign ions within the crystalline lattices of the individual clinker phases;
- by the fineness of the cement, in particular by its particle size distribution and specific surface;
- by the water–cement ratio used;
- by the curing temperature;
- by the presence of chemical admixtures, i.e. chemical substances added in small amounts to modify the hydration rate and properties of the cement paste;

- by the presence of additives, i.e. materials interground with cement in larger amounts, such as granulated blast furnace slag or pulverised fly ash.

This chapter deals primarily with the paste hydration of Portland cement and its individual clinker phases at ordinary temperature, i.e. 15–25°C. The hydration at higher water–solid ratios and at elevated temperatures, and the effect of chemical admixtures, are discussed only briefly.

6.1.2 EXPERIMENTAL CONSIDERATIONS

The hydration of cement is commonly studied using cement pastes which are allowed to hydrate at room temperature. Precautions have to be taken to prevent a significant loss of mixing water by evaporation and a reaction of the paste with CO_2 from the atmosphere. Typical curing conditions include an initial storage in moist air, followed by underwater curing after setting, or curing for the whole period at 100 per cent relative humidity, or storage in a sealed container. The starting material may be an industrial cement or one produced in the laboratory under controlled conditions. Work performed with cements may be supplemented with experiments on individual clinker minerals; however, one must bear in mind that data obtained here can be applied to cements only with caution, as an interaction between two or more clinker minerals may take place, if they hydrate together.

The progress of hydration may be studied either by measuring continuously one or more selected parameters (e.g. liberation of heat, viscosity, electric conductivity) on a single sample, or by determining one or more parameters in a series of samples in which the hydration is stopped after different periods of time. To stop the hydration process and make the sample suitable for analysis, the 'free water', i.e. that which did not react with cement yet, has to be removed. For this, different procedures may be considered, such as

- equilibration of the sample to constant weight in an atmosphere of low relative humidity at ambient temperature;
- drying the cement paste at elevated temperature, most commonly at 105°C, in an atmosphere of uncontrolled humidity;
- freeze-drying in which the sample, cooled down to a low temperature, is exposed to a high vacuum;
- solvent replacement in which the free water present in the paste is replaced by an organic liquid and the latter is subsequently removed by heating.

In the 'D-drying' procedure the sample is kept, until constant weight is achieved, in a desiccator which is connected to a trap cooled by a mixture of dry ice (solid CO_2) and ethanol to a temperature of -79°C. At these conditions the partial pressure of water vapour over the ice precipitated in the trap is 5×10^{-4} torr. In another widely used procedure the sample is kept in an atmosphere of 11 per cent RH (relative humidity), corresponding to 2.7 torr at 25°C, which may be produced by storing the material over a saturated solution of LiCl in water. In both procedures the sample must be crushed and the system evacuated to attain equilibrium conditions in the sample in a reasonable time.

The liquid most widely employed in the solvent replacement procedure is methanol. It is believed that, due to a lower surface tension of this solvent, the damage to the hydrated cement is less than that produced in heating the water-saturated material directly. The progress of solvent replacement may be monitored by determining the weight of the sample, which declines as water in the pore system is replaced by the organic solvent. In another approach the sample is first soaked or ground with an excess of acetone. In a subsequent step the acetone is replaced with ethyl ether, which is finally removed by drying the sample at ambient or only moderately elevated temperature. It was reported, however, that some organic liquids, including methanol, may react with the hydrated material and thus may affect the outcome of the subsequent tests.[1,2]

It is advisable to express all analytical data on hydrated cements per unit of ignited weight, whereas data on porosity, pore structure and specific surface are most meaningful if reported per unit volume of the material.

6.2 Hydration of pure clinker minerals

Due to the complexity of the hydration reactions in Portland cement, it makes good sense to discuss first the hydration of the individual clinker minerals that constitute the Portland cement clinker. It should be kept in mind, however, that the reactivity of these compounds will depend on the way in which they are prepared and on the presence of foreign ions in their crystalline lattice. Moreover, the progress of hydration will also depend on the experimental conditions employed.

6.2.1 TRICALCIUM SILICATE

Tricalcium silicate ($3CaO{\cdot}SiO_2$, abbreviated to C_3S) is the main and most important constituent of Portland cement, which to a great extent controls its setting and hardening. There exist several modifications of C_3S. Tricalcium silicate produced in the laboratory from pure starting materials is a T_1 modification. Other modifications may be produced by introducing small amounts of foreign ions into the crystalline lattice of C_3S.[3-6] The reactivity of such preparations varies depending on the quality and quantity of foreign ions present.[7-9] The tricalcium silicate present in Portland clinker also exists as an impure material which is doped with other ions present in the original raw mix and exists typically in a monoclinic form, most commonly M_3. Tricalcium silicate found in Portland clinkers is called 'alite'; its exact composition, and together with it its reactivity, may vary in different cements.

The hydration of tricalcium silicate is rather complex, and is still not fully understood. As products of hydration at ambient temperature, there are formed an amorphous calcium silicate hydrate phase with a CaO/SiO_2 molar ratio of less than 3.0, called the 'C-S-H phase' and calcium hydroxide [$Ca(OH)_2$, abbreviated CH].

$$3CaO{\cdot}SiO_2 + (3 + m - n)H_2O = nCaO{\cdot}SiO_2{\cdot}mH_2O + (3 - n)Ca(OH)_2$$

Kinetics of hydration

Due to the amorphous character of the C-S-H phase and its variable stoichiometry, the kinetics of the hydration process can be studied directly only by determining the amount of non-reacted C_3S as a function of hydration time. To do so, quantitative X-ray diffraction appears most suitable and has been most widely employed. Unfortunately, however, the precision of this method is rather low for degrees of hydration below ~0.1. Some indirect methods, such as determination of the development of hydration heat or estimation of non-evaporable water content, have also been employed to study the hydration kinetics. In using such methods a constant nature of the hydrated material thus formed is tacitly presumed, even though there is evidence that it varies with the degree of hydration.

A typical hydration curve expressing the degree of hydration as function of hydration time for tricalcium silicate ground to a specific surface area of ~300–500 m²/kg (Blaine) and hydrated in paste form with a water–solid ratio of ~0.5–0.7 at room temperature is shown in Figure 6.1. Several stages may be distinguished in the hydration of C_3S under these conditions:

Pre-induction period. Immediately after contact with water, an intense, but short-lived hydration of C_3S gets under way. The hydration rate $d\alpha/dt$, where α is the degree of hydration and t the hydration time, reaches ~5/day but decreases rapidly to very low values.[10] An intense liberation of heat may be observed in this stage of hydration. The duration of this period is typically no more than a few minutes.

Induction (dormant) period. The pre-induction period is followed by a period in which the rate of reaction slows down significantly, probably to a few hundredths per day. At the same time the liberation of hydration heat is also significantly reduced. This period lasts typically a few hours.

Acceleration (post-induction) period. After several hours the rate of hydration accelerates suddenly and reaches a maximum within about 5–10 h. At this stage the hydration rate may reach a value of about 1/day. The kinetics of the process follows the Avrami equation:[11-13]

$$-\ln(1-\alpha)^{\frac{1}{3}} = k_N t \tag{6.1}$$

where α is the degree of hydration, t is the time and k_N is the reaction rate constant for a nucleation-controlled process.

The beginning of the acceleratory period coincides roughly with the beginning of the second, main heat evolution peak. The $Ca(OH)_2$ concentration in the liquid phase attains

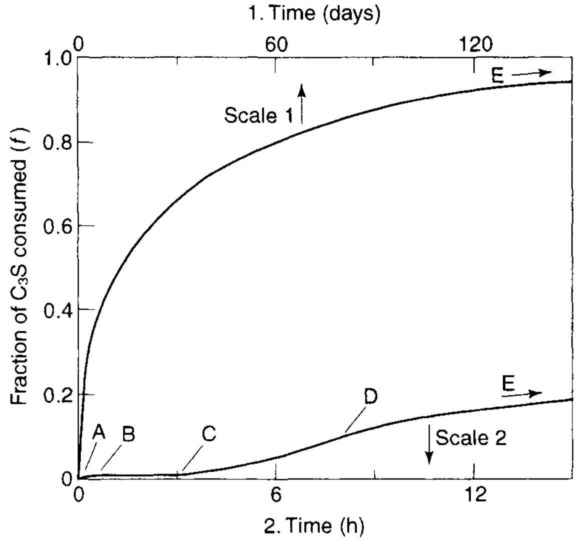

Fig. 6.1 Progress of hydration of tricalcium silicate, in paste form at ambient temperature. (source: Ref. 10) A–B: pre-induction period; B–C: induction period; C–D: acceleration period; D–E: deceleratory period.

a maximum at this time and begins to decline; crystalline calcium hydroxide starts to precipitate.

Deceleration period. After reaching a maximum the rate of hydration starts to slow down gradually; however, a measurable reaction may still persist even after months of curing. The reaction slows down and eventually ceases as the non-reacted C_3S is gradually consumed. In the deceleratory period the kinetics of C_3S hydration follow the Jander equation for diffusion-controlled processes:[13]

$$[1 - (1 - \alpha)^{\frac{1}{3}}]^2 = k_D t \tag{6.2}$$

where k_D is the reaction rate constant for a diffusion-controlled process.

The rate at which C_3S is consumed depends on a variety of factors and may vary in different C_3S preparations, especially at shorter hydration times. In addition to doping with foreign ions, the reactivity of C_3S may be also increased by introducing additional structural defects into the crystalline lattice by rapid cooling in the course of C_3S synthesis.[12,14]

Moderate variations of specific surface area have little effect on the length of the induction period, but mechanical activation of the C_3S surface by prolonged grinding may shorten it.[14] This effect is only temporary and disappears gradually upon extended storage of the material prior to mixing with water.

Chemical substances dissolved in the mixing water may also alter the kinetics of C_3S hydration. Among them, $CaCl_2$ and other chlorides exhibit an acceleratory effect on the process, whereas phosphates, borates and salts of Zn^{2+} and Pb^{2+} cause a retardation. Also, some organic compounds, especially different saccharides (e.g. sucrose), may retard the C_3S hydration rate. Data on the effect of calcium hydroxide dissolved in the mixing water on C_3S hydration are conflicting. Heavy water slows down the rate of C_3S hydration moderately.[15]

The rate of C_3S hydration may also be affected by certain solid substances added to the system: an addition of prehydrated C_3S may shorten the length of the induction period.[16] On the other hand, addition of crystalline calcium hydroxide alone does not exhibit this effect, yet it accelerates the hydration rate in the acceleration period.[16] C_3S hydration may also be accelerated by the addition of anhydrite or gypsum[17,18]. In addition, materials considered to be 'inert', notably calcium carbonate, may increase the C_3S hydration rate, especially if added in finely dispersed form.[18]

The kinetics of C_3S hydration in diluted suspensions differs from that seen in C_3S pastes. The hydration rate accelerates with increasing water/solid ratio.[19,20] The induction period becomes shortened and at very high w/c ratios may be absent altogether.[19] Agitation of the suspension accelerates further the rate of hydration and along with it the rate of Ca^{2+} dissolution.[21]

The hydration of C_3S in humid air is slow and incomplete but still noticeable.[22,23] Finally, the rate of C_3S hydration is also temperature dependent and increases with increasing temperature.[13,24,25]

Composition of the liquid phase

Upon contact with water, both calcium and silicate ions pass rapidly into solution. Initially the Ca^{2+}/SiO_2 molar ratio is 3:1, indicating a congruent dissolution of tricalcium silicate.

The relatively high silicate concentrations observed in paste hydration only seconds after mixing are only transitory and decrease very quickly to very low values, i.e. to $\sim 10\,\mu mol/L$.[21,26,27] Contrary to that the concentration of $Ca(OH)_2$ continues to increase, exceeding the value of 20 mmol/L which would be expected from the solubility product of $Ca(OH)_2$.[10,19,20,26-30] After reaching a maximum within a few hours, the concentration starts to decline and eventually may or may not drop to the saturation level.

In diluted suspensions the $Ca(OH)_2$ concentration in the liquid phase may be lower and at very high water/solid ratios may even not reach the saturation level. Nevertheless, the total amount of $Ca(OH)_2$ in the liquid increases.[19,26] At the same time both the concentration and the total amount of silica in solution increase with increasing w/C_3S ratio.[19,26]

Mechanism of hydration

Upon contact with water a fast reaction between tricalcium silicate and the liquid phase gets under way. The first step of this reaction appears to be a protonolysis of the silicate and oxygen ions at the C_3S surface, followed by a congruent dissolution of the material.[20,21,28,31] The O^{2-} ions originally present in the C_3S crystalline lattice enter the liquid phase as OH^- ions and the SiO_4^{4-} ions as barely dissociated H_4SiO_4:

$$O^{2-} + H^+ \rightarrow OH^- \tag{6.3}$$

$$SiO_4^{4-} + nH^+ \rightarrow HnSiO_4^{(4-n)} \tag{6.4}$$

Thus the positive charge of Ca^{2+} entering the liquid phase simultaneously is outbalanced by the negative charges of OH^- and silicate ions.

Initially, the dissolution rate of C_3S is faster than diffusion can carry the dissolved ions away from the surface, causing a concentration gradient in the vicinity of the surface. Here the liquid phase quickly becomes oversaturated with respect to calcium silicate hydrate and a layer of a C-S-H products starts to precipitate at the C_3S surface.

According to another theory[26,27,32] the initial dissolution of C_3S is incongruent rather than congruent. An SiO_2-rich layer is formed at the surface which subsequently adsorbs Ca^{2+} ions dissolved in the liquid phase. Thus an electric double layer is formed at the C_3S surface.

The reasons for the drastic slowing down of the hydration rate within a few minutes of mixing with water, seen in the paste hydration of C_3S, and a renewed acceleration of the reaction after a dormant period typically lasting several hours, are not obvious. Several theories have been forwarded to explain this phenomenon (Table 6.1).

Impermeable hydrate layer theory. It is postulated that the 'first-stage' product precipitated at the C_3S surface within the first few minutes of hydration acts as a barrier which slows down significantly the migration of water to the non-reacted surface and/or that of Ca^{2+}, OH^- and silicate ions into the liquid phase.[10,19,21,31-34] This way the initial fast hydration is slowed down significantly and is followed by a period in which the reaction barely progresses. Towards the end of this dormant period the initially formed C-S-H layer undergoes changes that make it more permeable, thus making a renewed fast hydration possible. The actual nature of changes taking place in the C-S-H layer is not obvious. They may include a phase transformation, possibly also associated with changes in composition and/or morphology, or they may be better described as an ageing of the material. It has also been suggested that the barrier layer behaves as a membrane, and its breakdown is due to osmotic pressure generated in the liquid located between the layer and

Table 6.1 Theories on the mechanism of C_3S hydration

<table>
<tr><th>Mechanism</th><th colspan="2">Impermeable hydrate layer theory</th><th>Electrical double-layer theory</th><th>Nucleation of CH theory</th><th>Nucleation of C-S-H theory</th></tr>
<tr><td>Pre-induction period</td><td colspan="5">First-stage C-S-H formed</td></tr>
<tr><td>Beginning of induction period</td><td colspan="2">First-stage product acts as diffusion barrier</td><td>Electrical double layer forms and impedes passage of ions</td><td colspan="2">Supersaturation of liquid phase with respect to CH stops further rapid dissolution of C_3S</td></tr>
<tr><td>Changes during induction period</td><td>Phase transformation or ageing of C-S-H layer</td><td>Osmotic pressure phenomena across the first-stage product layer</td><td>Gradual weakening of double layer</td><td>Slow nucleation of CH</td><td>Slow nucleation of second-stage C-S-H</td></tr>
<tr><td>End of induction period</td><td>Increased permeability of C-S-H layer</td><td>Breakdown of C-S-H layer due to osmotic pressure and/or imbibition</td><td>Breakdown of double layer</td><td>CH nuclei reach critical size</td><td>Nuclei of second-stage C-S-H reach critical size</td></tr>
<tr><td>Acceleratory period</td><td colspan="5">Accelerated dissolution of C_3S, growth of second stage C-S-H and CH</td></tr>
</table>

non-reacted C_3S.[35,36] Another mechanism considered is a breakdown of the C-S-H layer due to an imbibition of water[35].

Electrical double-layer theory. It is assumed that a SiO_2-rich surface layer with adsorbed Ca^{2+} ions, which develops as the result of an initial incongruent C_3S dissolution, creates an electric double layer which impedes the passage of further ions into the solution and is responsible for the onset of the dormant period.[26,27,32] The renewed acceleration of the hydration is attributed to a gradual breakdown of this double layer.

Nucleation of $Ca(OH)_2$ theory. As the CaO/SiO_2 ratio of the C-S-H phase thus formed is always lower than that of tricalcium silicate (3:1), hydration of C_3S is always associated with a simultaneous liberation of calcium hydroxide. In the initial stage of C_3S hydration the formed $Ca(OH)_2$ dissolves in the liquid phase; solid calcium hydroxide is not precipitated even after its concentration in the liquid phase had reached and exceeded the saturation level. It is assumed that this is due to a poisoning of the surface of the $Ca(OH)_2$ nuclei by silicate ions.[10,26,30] The C_3S dissolution and C-S-H formation slow down and eventually cease as the Ca^{2+} and OH^- concentrations in the liquid phase increase and the capacity of the latter to accommodate additional amounts of calcium hydroxide becomes exhausted.[16,28,30] Eventually, however, the concentration of $Ca(OH)_2$ in the liquid phase becomes high enough to overcome the poisoning effect of adsorbed silicate ions and solid calcium hydroxide starts to precipitate. At this stage the crystalline calcium hydroxide starts to act as a sink for Ca^{2+} ions, enabling renewed intense C-S-H formation.

Nucleation of C-S-H theory. It is postulated that the end of the induction period and a renewed acceleration of the hydration process is controlled by the nucleation and growth of a 'second-stage' C-S-H which is different from the 'first-stage' product formed initially. The formation rate of the first-stage product is controlled by the $Ca(OH)_2$ concentration in the liquid phase and is slowed down as this concentration reaches its saturation level. The 'second-stage' C-S-H starts to form after the thermodynamic barrier of its nucleation had been overcome and second-stage nuclei begin to form in large numbers and grow, causing renewed fast C-S-H formation.[10,16,37,38] This theory postulates the nucleation of the second-stage C-S-H to be the reason for the end of the dormant period. It assumes that the first-stage product, precipitated at the C_3S surface, does not act as a barrier layer and is not involved in the slowing down of the hydration reaction. It considers the precipitation of portlandite to be a secondary phenomenon resulting from the high degree of $Ca(OH)_2$ oversaturation existing in the liquid phase, brought about by the initial C_3S hydration.

The rate of the renewed fast hydration following the induction period appears to be controlled by the dissolution rate of the non-hydrated C_3S. At this stage the dissolved ions may migrate away from the C_3S surface and precipitate from the bulk solution, even though some preferential C-S-H precipitation on or close to the surface of non-reacted C_3S may still take place. At the same time, solid calcium hydroxide crystallises in the form of relative large portlandite crystals from the bulk liquid phase.

As the hydration progresses, the available space becomes filled with the hydration products and the volume of the liquid phase, which is still present, decreases. Under these conditions the rate of hydration becomes diffusion-controlled. It slows down gradually as the ability of the dissolved ions to migrate decreases and the amount of still non-reacted

C_3S gets smaller. The reaction ends when the C_3S is consumed or – at low water/cement ratios – even before, due to a lack of sufficient space for C-S-H and CH precipitation.

The hydration of C_3S in diluted suspension differs from that in pastes. The overall hydration rate tends to be accelerated and at high water/solid ratios the dormant period may be absent. Two different forms of C-S-H may be formed, depending on the CH concentration in the liquid phase.[39]

C-S-H phase

The term '*C-S-H phase*' is used to denote amorphous or nearly amorphous calcium silicate hydrate products of the general formula $CaO_x \cdot SiO_2 \cdot H_2O_y$ where both x and y may vary over a wide range. Such a phase, together with calcium hydroxide, is produced in the hydration of C_3S at temperatures up to at least 100°C.

Plots of concentration of SiO_2 vs. CaO for solutions in equilibrium with C-S-H, based on the results of studies performed by different investigators, indicate that the values found tend to fall on one or other of two curves. Based on those results the existence of at least two distinct forms of C-S-H has been postulated,[31,34,39,40] of which at least one must be metastable.

The average CaO/SiO_2 ratio of the C-S-H phase in a fully hydrated C_3S paste may be calculated from the content of $Ca(OH)_2$ formed in the reaction. The method may also be extended to incompletely hydrated phases, if the amount of remaining non-reacted C_3S is also known. Unfortunately, however, the accuracy of this procedure becomes low at low degrees of hydration, due to the low precision with which the amount of residual C_3S may be determined. For the same paste the obtained results will depend also on the method used for the determination of free $Ca(OH)_2$. Published data on the CaO/SiO_2 molar ratio of the C-S-H phase present in mature C_3S pastes hydrated at ambient temperature range between about 1.4 and 2.0,[9,11,41 49] the value around about 1.7 being probably most correct. There is also controversy concerning the dependence of the CaO/SiO_2 ratio on the degree of hydration. More recent work, however,[10,11,48] does not support the conclusions of some earlier reports that this ratio changes markedly as the hydration progresses. On the other hand there is evidence that the CaO/SiO_2 ratio declines with increasing water/solid ratio of the starting mix.[44]

The C-S-H phase formed in the pre-induction period differs from that formed later on, in several respects: it has a lower CaO/SiO_2 ratio, a different silicate anion structure and exhibits different DTA and TG patterns.[10,11,39]

To determine the composition of the C-S-H phase formed in C_3S hydration directly, electron probe microanalysis (EPMA) in conjunction with scanning electron microscopy (SEM) has been employed. In this way, regions of only a few cubic micrometres can be analysed. At this resolution the CaO/SiO_2 molar ratio exhibits distinct variations, ranging between about 1.4 and 2.0.[49 53]

Another method, analytical transmission electron microscopy (ATEM), enables the analysis of dispersed particles with diameters of a few tens of micrometres. At this scale the CaO/SiO_2 molar ratio of the C-S-H phase was found to vary between 1.2 and 2.0 with a mean value of 1.5–1.6.[54]

The CaO/SiO_2 ratio of the C-S-H phase formed at the beginning of hydration was studied by X-ray photoelectron spectroscopy (XPS) (also called 'electron spectroscopy for chemical analysis' or ESCA). The method enables the determination of the elemental composition of the surface of the sample to a depth of ~10 nm. Using this method a very rapid decrease was observed in the CaO/SiO_2 molar ratio from its starting value in the non-hydrated material of 3.0 to about 2.0–2.5, followed by a maximum around 2.7–2.8. Subsequently the CaO/SiO_2 ratio declined again, to values <2.0. All of these changes were observed within the first hour of hydration.[55,56] It must be noted, however, that at very short hydration times the thickness of the hydrate layer formed at the surface of C_3S is <10 nm, thus the data obtained by this method at this stage do not reflect the exact composition of the hydrated material, but are also influenced by the underlying non-hydrated C_3S.

Using another method, secondary neutrals mass spectroscopy (SNMS), in which the composition of a surface region only about three atomic layers thick can be analysed. The formation of a hydrate layer with a very low CaO/SiO_2 molar ratio was observed in the initial period of hydration in an excess volume of water.[57]

The water present in a water saturated-hydrated C_3S paste may be divided into several categories, i.e. that bound within the structure of the C-S-H phase, that bound in the form of OH^- ions within the crystalline lattice of calcium hydroxide, that adhering to the solid surface of the hydrated phases that are present by adsorption forces, and finally that which fills the gel and capillary pores of the hardened paste. The distinction between these categories is not sharp as the bonding forces by which the water molecules are bound within the solid structure and within the pores vary in a wide range and may overlap.

The amount of 'bound' water (called also 'combined' or 'non-evaporable' water) present in a hydrated C_3S sample may be determined either indirectly by subtracting the amount of 'free' water from the amount of 'total' water present in the material, or directly as the loss on ignition of a sample in which the free water has first been separated. The free water may be separated either by evaporation or by extraction with a suitable organic liquid or may be estimated by determining the D_2O content of the material after replacing the original pore liquid with D_2O-enriched water.[58] As the fraction of total water removed or replaced by different experimental procedures varies, the amount of bound water gives a value whose magnitude also depends on the method employed by its determination.

The amount of water bound within the C-S-H phase may be determined by subtracting the amount of water bound in the form of calcium hydroxide from the total amount of bound water. This is why the value will depend also on the method used for free calcium hydroxide determination.

There are indications that the H/S ratio of the C-S-H phase formed in the paste hydration of C_3S is independent of the degree of hydration, except in the material formed at the very beginning of hydration.[11,44,48] At a given degree of hydration it increases moderately with increasing initial water/solid ratio. For a C_3S paste with $w/c = 0.59$, in which the free water has been removed by a solvent exchange technique using methanol as solvent and free calcium hydroxide was determined by thermogravimetry, there was found to be an overall bound water content of 0.235 g/g of ignited residue and a H_2O/SiO_2 molar ratio in the C-S-H phase of 1.77.[48]

As the C-S-H phase is a nearly amorphous material, its structure cannot be studied by X-ray diffraction. Most information on the structure of this material may be obtained by ^{29}Si MAS-NMR (magic angle spinning nuclear magnetic resonance). This method makes it possible to distinguish and determine the fractions of SiO_2 present in the form of separated SiO_4 tetrahedra and tetrahedra linked to one, two, three or four neighbouring tetrahedra through Si–O–Si bonds. Such different structural forms of SiO_4 are designated Q_0, Q_1, Q_2, Q_3 and Q_4. Cross-polarisation NMR can distinguish between silicon atoms in SiO_4 tetrahedra that carry one or more hydrogen atoms and those which do not. In the trimethylsililation procedure, the sample is first dissolved in a suitable reagent. Here the silicate anions, converted into corresponding silicic acids, are allowed to react with trimethylsilyl chloride $(CH_3)_3{\equiv}Si{-}Cl$. In this reaction all present $\equiv Si{-}OH$ groups are converted into pertinent $\equiv Si{-}O{-}Si{\equiv}(CH_3)_3$ groups. The resultant trimethylsilylated products may be identified and determined quantitatively by gas–liquid chromatography, thin layer chromatography, gel permeation chromatography, infrared spectroscopy or mass spectroscopy. In a third method the degree of silicate polymerisation may be estimated from the kinetics of the reaction of the dissolved material with molybdate ions.

The published data obtained by ^{29}Si MAS-NMR[59–69] in addition to that by trimethylsililation[61,69–74] and the molybdate[73] methods indicate a gradual chain polymerisation of the SiO_4 tetrahedra that exist in the non-hydrated C_3S in a non-polymerised state.

Unlike the C-S-H phase formed after the induction period, the C-S-H phase formed in the pre-induction period contains, as in the non-hydrated C_3S, only monomeric SiO_4 units, but with attached hydrogen atoms ($\equiv$Si–O–H). In cross-polarisation MAS (CP-MAS) experiments, in which only nuclei that are linked with protons are detected, the formation of protonated units may be observed within a few minutes of mixing. This suggests that a surface hydroxylation may be the first step in the hydration of C_3S.

The C-S-H formed within the first hours of hydration contains predominantly protonated Q_1 species. Thus a dimerisation appears to be the first step in the SiO_4 polymerisation accompanying the hydration process. As the hydration progresses, protonated Q_2 species also become detectable. In the further course of hydration, increasing amounts of Q_2 species become detectable in the hydrated material, in addition to Q_1. At the same time the fraction of Q_1 species reaches a maximum after a few months and subsequently starts to decline. Q_3 and Q_4 species are not formed in the course of hydration. This development indicates a gradual supplementation and later replacement of the initially formed dimers by longer polymeric linear chains. Among them a pentamer unit, $(Si_5O_{16})^{12-}$ is the most abundant one, followed by the octamer $(Si_8O_{25})^{18-}$. With regard to the distribution of the chain length, no differences were found at different stages following the induction period, indicating that short chains may be formed at any stage.[69] It was suggested that in the hydration process, dimers or longer chains are linked together with monomers which originated from the non-hydrated C_3S to form longer units.[69] The average chain length of mature pastes is in the range 2.5–3.0 SiO_4 units.[68]

The fraction of Q_0 species declines steadily as the consequence of the consumption of non-hydrated C_3S. However, in addition to polymerisation, a fraction of monomeric units is only protonated and these $Q_0(H)$ species persist in the C_3S paste to late stages of hydration.[68] The SiO_4 polymerisation continues even after the hydration of C_3S is complete and the fraction of Q_0 has dropped to zero.[63]

In ^1H NMR studies Si–OH groups become detectable immediately after mixing, suggesting again the formation of hydroxylated species at the C_3S surface. Ca–OH groups, in combination with Si–OH groups, corresponding to C-S-H formation, become detectable during the induction period. Later, Ca–OH groups belonging to $Ca(OH)_2$ may also be formed.

In diluted C_3S suspensions, protonated Q_0 species become detectable within minutes after mixing, corresponding to the passage of silicate ions into the solution. After ~1 h Q_1 and Q_2 species, which indicate the formation of the C-S-H phase, also become detectable.[67]

On the nanometre scale the C-S-H phase formed in the hydration of C_3S at ambient temperature seems to be structurally related to the crystalline phases 1.4 nm tobermorite and jennite and to poorly crystalline materials called C-S-H(I) and C-S-H(II).

The idealised constitutional formula of 1.4 nm tobermorite is $[Ca_4(Si_3O_9H)_2]Ca{\cdot}8H_2O$

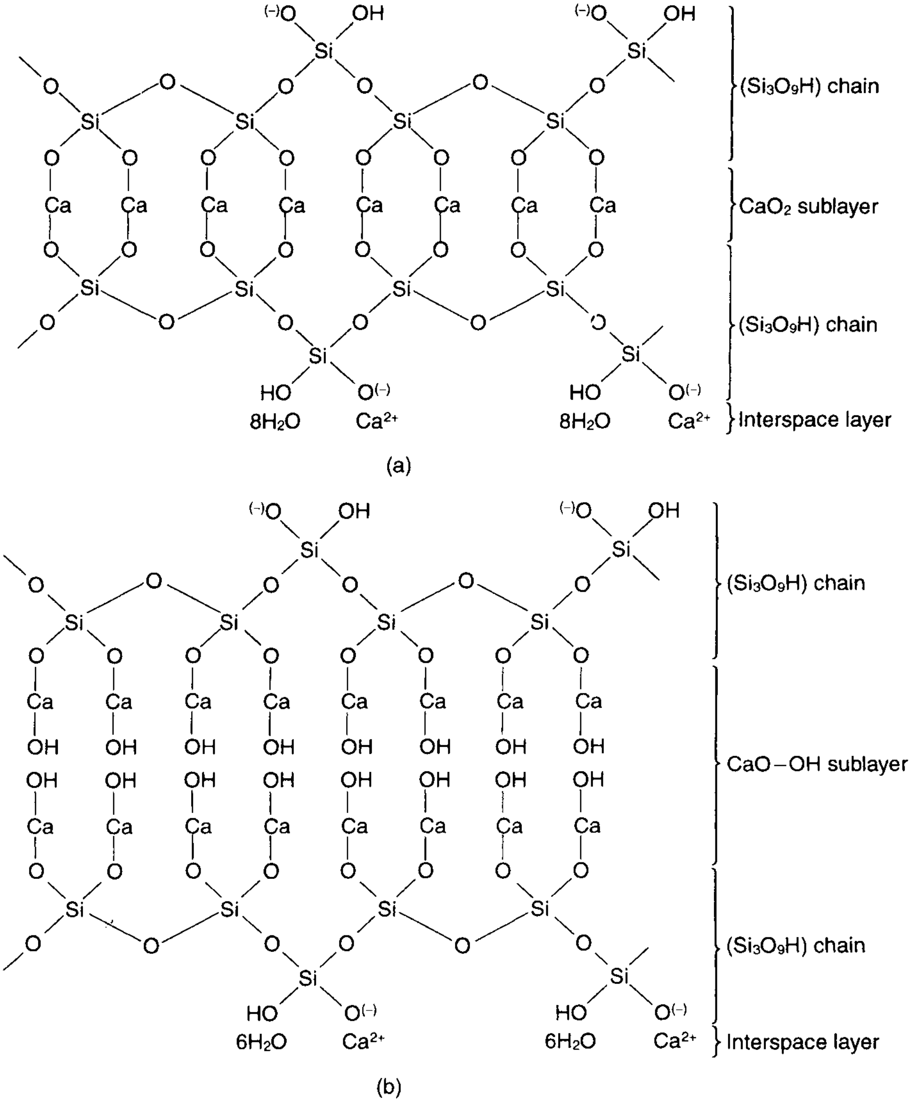

Fig. 6.2 Idealised chemical structure of (a) 1.4 nm tobermorite and (b) jennite.

(Figure 6.2(a)) and that of jennite $[Ca_8(Si_3O_9H)_2(OH)_8]Ca{\cdot}6H_2O$ (Figure 6.2(b)). Both tobermorite and jennite contain their SiO_4 tetrahedra condensed into linear chains that are kinked so that they repeat at intervals of three tetrahedra. Such arrangement is called 'dreierkette' and has an empirical formula Si_3O_9.

Tobermorite has a layer structure. Each layer consists of a central part with an empirical formula CaO_2 in which all the oxygen atoms are shared with those of SiO_4 tetrahedra belonging to SiO_4 chains that envelop the CaO_2 sublayer from both sides. In each SiO_4 triplet only two of the SiO_4 tetrahedra share two of their oxygens with the oxygens of the CaO_2 sublayer. These are called 'paired' tetrahedra. The third tetrahedron is a 'bridging' tetrahedron that is positioned between two pairs of paired tetrahedra to form a continuous SiO_4 chain. The interlayer space between the individual layers is filled with Ca^{2+} ions, to balance out the negative charge of the layers, and with water molecules. The number of water molecules present in the interlayer space determines the distance between the individual layers. The tobermorite form with the highest interlayer water content, i.e. 8 H_2O per layer is 1.4 nm tobermorite. It converts to 1.1 nm tobermorite upon losing half of them. The composition of the natural tobermorite mineral differs from the idealised tobermorite formula inasmuch as its Ca/Si molar ratio is about $Ca_5Si_{5.5}$, rather than Ca_5Si_6, due to the absence of some of the bridging tetrahedra. This corresponds to an average chain length of about 11 tetrahedra.

The structure of jennite has many similarities with that of tobermorite. The main difference lies in the presence of OH groups linked to the calcium atoms present in the central region of the individual layers.

The semi-crystalline phase C-S-H(I), which may be produced by a reaction between calcium hydroxide and hydrous silica, or by mixing solutions of sodium silicate with those of calcium salts, has a structure similar to tobermorite. It consists of tobermorite-like layers in which a significant fraction of the bridging SiO_4 tetrahedra is missing. It may be prepared with Ca/Si molar ratios of ~0.8–1.5. With increasing Ca/Si ratio the degree of crystallinity tends to decline. The phase C-S-H(II), which may be produced by hydration of C_3S or β-C_2S in an excess of water and repeated removal of the liquid, to lower the CaO/SiO_2 ratio in the system, exhibits a similar structure, derived from jennite.

According to a model proposed by Taylor[75 77] the C-S-H phase formed in the paste hydration of C_3S at ambient temperature consists of a combination of highly distorted tobermorite-type and jennite-type layers. In the absence of bridging tetrahedra, the SiO_4 chains characteristic of crystalline tobermorite and jennite are broken down into segments consisting of 2, 5 or 8 $(2 + 3n)$ tetrahedra; however, the distributions of anion size in the two kinds of layers need not be the same. The CaO/SiO_2 ratio in the material is determined by the number of missing SiO_4 tetrahedra and the mutual ratio of tobermorite-like and jennite-like layers in the structure. In a further development of the model it was suggested that regions belonging to tobermorite and jennite may merge into each other within a single layer, with less ordered material in between.[77] It has been also suggested, that monomeric hydrogen silicate ions that persist after the induction period may be present in a distinct phase, formed as an intermediate product.

In a similar model suggested by Richardson and Groves,[78 80] it is assumed that the silicate anion distribution of the T (tobermorite) units mirrors that of the J (jennite) units.

In the hydration of C_3S in diluted suspensions, a C-S-H phase similar to that formed in paste hydration is usually formed. At longer hydration times the material converts into C-S-H(II) if parts of the liquid phase are removed to lower the Ca/Si ratio in the system. In highly diluted suspensions and at prolonged hydration times even C-S-H(I) may be formed.

The C-S-H phase formed prior to the induction period in the paste hydration of C_3S seems to be unrelated to either tobermorite or jennite and contains only single SiO_4 tetrahedra linked to hydrogen atoms.

Under 'ball milling conditions' at ordinary temperatures, C_3S hydrates to yield a crystalline calcium silicate hydrate, afwillite ($C_3S_2H_3$),[64,81] which contains isolated silicate tetrahedra. The same product may be also produced by seeding the C_3S phase with crystals or afwillite.

Calcium hydroxide

The hydration of C_3S is always accompanied by the formation of calcium hydroxide, as the CaO/SiO_2 molar ratio in the calcium silicate hydrate phase thus formed is always lower than that of tricalcium silicate, i.e. 3:1. In highly diluted suspensions, in which the saturation level is not attained, calcium hydroxide remains dissolved completely in the liquid phase. On the other hand, in paste hydration of C_3S most of the calcium hydroxide precipitates in the form of crystals of portlandite, up to several tens of micrometres in diameter, which become evenly distributed within the hardened paste.

The amount of free calcium hydroxide in a C_3S paste may be determined by different methods, such as extraction and determination of extracted $Ca(OH)_2$ by titration, differential thermal analysis (DTA), thermogravimetry (TG) or X-ray diffraction (XRD). Unfortunately, however, different methods yield different results. The highest values are obtained by extraction, in which acetylacetic acid ethyl ester, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}C_2H_5$, in combination with isopropanol, $(CH_3)_2CH{\cdot}OH$, or isobutanol $(CH_3)_2CH{\cdot}CH_2{\cdot}OH$, may be used as a suitable solvent. It is likely that a fraction of the dissolved calcium hydroxide originates from the decomposition of the C-S-H phase under these conditions. Data obtained by DTA and TG may be affected by thermal effects caused by the decomposition of the C-S-H phase present simultaneously in the sample. The determination of calcium hydroxide by XRD usually yields the smallest values, probably due to the imperfection of the crystalline lattice of the portlandite crystals. Moreover, a discrepancy between the intensities of the (0001) and (1011) peaks that depends on the w/s ratio and age of the paste has been reported in the study of portlandite formed in the hydration of C_3S by XRD.[82,83]

Portlandite has a hexagonal structure consisting of octahedrally coordinated calcium ion layers and tetrahedrally coordinated oxygen layers with hydrogen bound to oxygen. There is no convincing evidence of the existence of an amorphous form of calcium hydroxide, which had been postulated in the past.

Microstructure of hydrated C_3S pastes

A hydrated C_3S paste is a porous material that contains a pore system consisting of open pores of variable size. The total pore volume of a water-saturated paste is identical to the volume of 'free' water present and depends on the method by which the fraction of free water is determined. It increases with an increasing initial water/solid ratio and declines with progressing hydration. The porosity of the paste may be also measured by filling the emptied pore space with a suitable medium; however, in most instances a fraction of the pore space remains unfilled under these conditions. Table 6.2 shows the porosity of fully hydrated C_3S pastes as determined by different procedures. It is obvious that both Hg and N_2 are able to fill the pore space only incompletely.[84,85]

The size of pores present in the C_3S paste varies in a wide range with hydraulic radii (defined as pore volume/pore surface area) between < 1 nm and several hundreds of nanometres.

The specific surface area of the hydrated material varies greatly depending on the method employed in its determination and whether methods based on the filling of the emptied pore space are applied, and also on the way in which the sample had been dried. Table 6.2 shows the specific surface area of a series of mature C_3S pastes as determined by different methods on D-dried samples. For determining the specific surface area by adsorption, vapours of H_2O and N_2 have been most widely employed as adsorbates. It is remarkable that significant differences exist between results obtained by these two adsorbates, the values found by nitrogen adsorption being consistently lower. There exist differences of opinion concerning the interpretation of these results.

To study the morphology of the hydrated material formed in the hydration of C_3S, a variety of methods have been employed, such as optical microscopy of thin sections,

Table 6.2 Porosity and specific surface area of fully hydrated C_3S pastes as determined by different methods[84,85]

w/s	P_1	P_2	P_3	P_4	P_5	S_1	S_2	S_3	S_4
0.45	0.347	0.277	0.319	0.197	0.170	128	36.3	38.7	22.6
0.60	0.444	0.340	0.390	0.209	0.185	131	56.0	57.8	31.2
0.70	0.507	0.451	0.419	0.288	0.188	138	57.8	66.8	37.3
1.00	0.620	0.576	0.580	0.457	0.182	142	65.7	67.2	39.9

P_1 = Volume of empty pores after removal of 'free water' by D-drying.
P_2 = Volume of empty pores after removal of 'free water' by extraction with acetone and ethyl ether.
P_3 = Volume of pores determined by H_2O–D_2O exchange.
P_4 = Porosity as determined by Hg porosimetry on D-dried samples (P_{max} = 200 bar).
P_5 = Porosity determined by N_2 adsorption on D-dried samples.
S_1, S_2 = Specific surface area as determined by the BET method using H_2O and N_2 as adsorbates (D-dried samples, in m^2/g).
S_3 = Specific surface area calculated from N_2 adsorption isotherms assuming a cylindrical cross-section of the pores (D-dried samples, in m^2/g).
S_4 = Specific surface area calculated from Hg porosimetry data assuming a cylindrical cross-section of the pores (D-dried samples, in m^2/g).

secondary electron imaging on fractured surfaces, backscatter electron imaging or X-ray imaging on polished surfaces, transmission electron microscopy on ground and redispersed material and high-voltage transmission electron microscopy. The available data may be summarised as follows: The C-S-H phase may exist in a variety of morphologies such as in the form of fibres, flakes, honeycombs, tightly packed grains or of a seemingly featureless dense material. However, at high resolution it becomes apparent that all these C-S-H types have a similar underlying foil morphology and therefore probably contain only one type of C-S-H at the nanometre level.

The very first hydrates become detectable at the C_3S surface within seconds after the initial contact with water in the form of minute particles. In paste hydration the material prominent at early ages is a fibrous or foil-like C-S-H modification. At longer hydration times the material gradually loses its original character, becomes more tightly packed and finally appears compact and featureless. At equal degrees of hydration the prominence of the fibrous morphology increases with increasing initial water/solid ratio.

The C-S-H phase in a mature paste is not evenly distributed. In particular, the product formed *in situ* from anhydrous grains appears dense and without any structure and is called 'inner product'. In contrast, the 'outer product', formed in the space originally filled with water, is less dense with a prevailing fibre-like texture.

The calcium hydroxide precipitates in the form of relatively large crystalline particles, several micrometres in diameter, within the space originally filled with water.

Figure 6.3 shows secondary electron images of a fractured surface of a mature C_3S paste. Figure 6.4 shows backscatter electron and X-ray images of a polished surface of the same material.

6.2.2 DICALCIUM SILICATE

Of the existing modifications of dicalcium silicate $2CaO \cdot SiO_2$ (abbreviation C_2S), the β-C_2S modification is by far the most important since it is a regular constituent of Portland

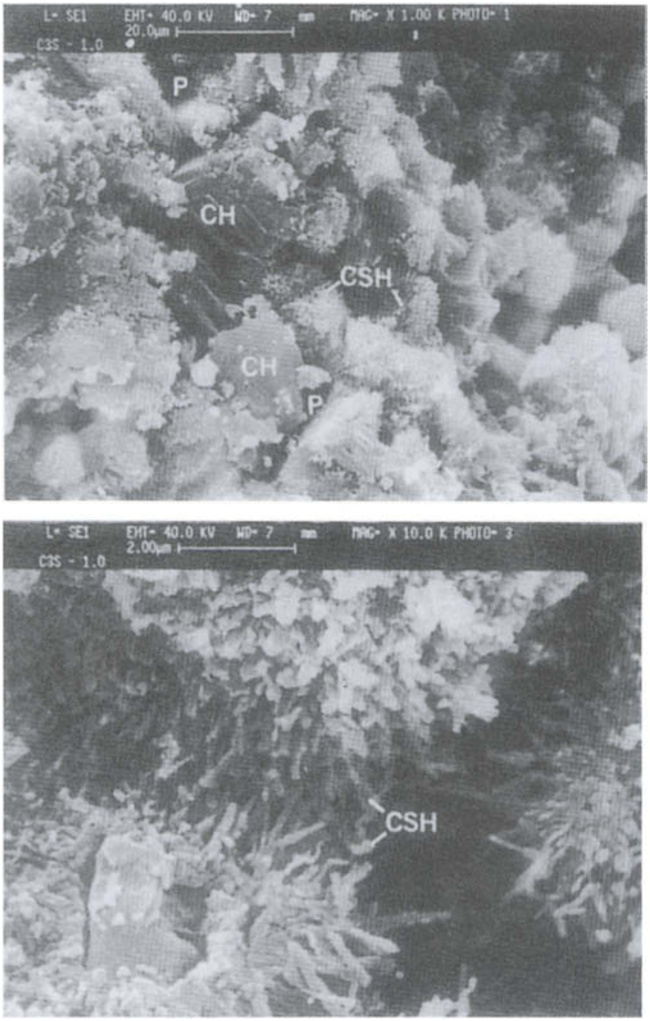

Fig. 6.3 Secondary electron images of a fractured surface of a tricalcium silicate paste obtained at two different magnifications (w/s = 1.0, 20°C).

cement. β-C_2S is a metastable modification at all temperatures, yet it can be stabilised at ambient temperature by incorporating different foreign ions into its crystalline lattice.[86-90] Of these the dopant most commonly used in experimental work is B_2O_3. If produced in non-doped form, β-C_2S is usually contaminated with variable amounts of γ-C_2S. γ-C_2S is the only C_2S modification which is thermodynamically stable at ambient temperature. The modifications α, α'_L and α'_H are high temperature forms, which are stable at ambient temperature only if doped with foreign ions.

Kinetics of hydration

The reactivities of β-dicalcium silicate preparations, produced by heating to high temperatures a blend of CaO and SiO_2 with variable amounts of a suitable doping agent, depend on

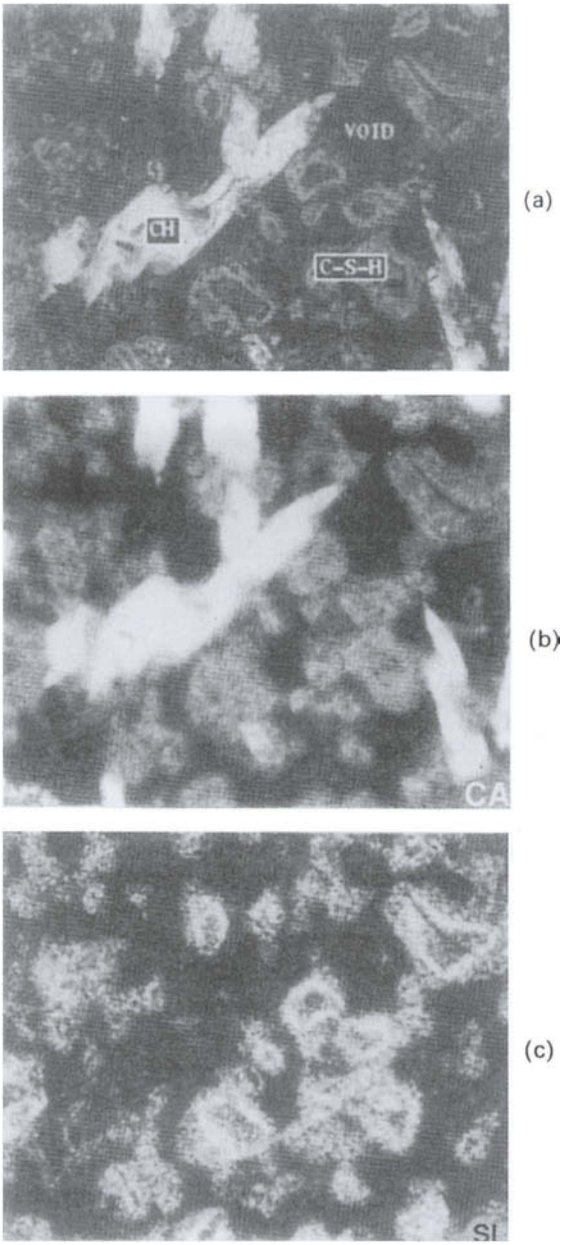

Fig. 6.4 Backscattered electron image (a) and Ca and Si X-ray maps ((b), (c)) of a mature tricalcium silicate paste obtained on a polished surface (w/s = 1.0, 20°C).

the kind and quantity of the employed dopant; however, the differences in reactivity which actually exist are not too great.[86-90] With the same doping agent the rate of hydration will increase with increasing burning temperature[91] and will decline with repeated firing,[86] whereas variable cooling rates have little effect on reactivity.[90] The progress of β-C_2S

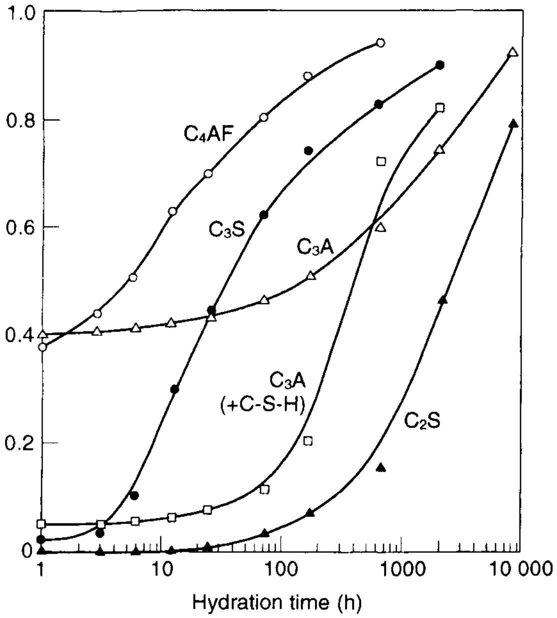

Fig. 6.5 Typical hydration kinetics of pure clinker minerals (C_3A without and with added gypsum) – paste hydration at ambient temperature.

hydration may be also accelerated by increasing the fineness of grinding,[87] by increasing the temperature of hydration,[86] or by increasing the water/solid ratio.[92] Pure, non-doped β-dicalcium silicate, produced from γ-C_2S by heating it to a high temperature and quenching, exhibits a hydraulic reactivity which depends on the thermal history of the material.[93] A product preheated for 24 h at 1500°C was found to be much more reactive than similar preparations preheated at lower temperatures. Generally, however, the reactivity of β-C_2S preparations produced by burning blends of CaO and SiO_2 to high temperatures is rather low and never attains that of C_3S.

Figure 6.5 shows the typical hydration kinetics of β-C_2S hydrated at 20°C compared to that of other clinker minerals. The reaction is characterised by an extended induction period in which the hydration rate is very slow. This period is followed by a gradual increase of the hydration rate and its subsequent slowing down, after reaching a maximum after several days or weeks.[47,86,87,94,95]

Besides the high-temperature sintering of a solid blend of CaO and SiO_2, methods have also been developed which enable the synthesis of β-C_2S forms with a significantly greater reactivity. Roy *et al.*[96] produced β-C_2S with a high specific surface area by spraying a $Ca(NO_3)_2$ solution and colloidal SiO_2 into hot air at 750–1050°C. The product reacted about 10 times faster than β-C_2S produced at high temperatures by solid phase reactions. Yang *et al.*[97] produced a highly reactive β-C_2S form by heating to 850–950°C a hydrothermally pretreated mixture of CaO and SiO_2 (aerosil or silica gel). Ishida and co-workers[98,99] produced a highly reactive β-C_2S by a thermal decomposition at 600°C of hillebrandite, $Ca_2(SiO_3)(OH)_2$, prepared in a hydrothermal process from CaO and quartz. The product hydrated completely within a few days.

Another highly reactive form of dicalcium silicate has been obtained by a thermal decomposition of hydrothermally produced α-C_2SH.[100] α'-C_2S is usually more reactive than β-C_2S; however, the actual reactivity depends on the kind and amount of dopant employed.[101-103] The reactivity of α-C_2S in relation to other polymorphs is not well established, but may lie between those of β-C_2S and α'-C_2S.

γ-C_2S exhibits only an extremely low hydraulic reactivity at ambient temperature.

The hydration rate of dicalcium silicate may be accelerated with accelerating admixtures; however, they seem to be less effective with C_2S than with C_3S.

Just as in the hydration of tricalcium silicate, the hydration of β-dicalcium silicate is associated with the release of calcium and silicate ions into the liquid phase.[86,94,104] The concentration of Ca^{2+} increases until it reaches a maximum within a few hours. At this point the $Ca(OH)_2$ saturation level may or may not be exceeded. The silicate ion concentration in the liquid phase declines from a maximum which is reached within the first minute of hydration and remains very low.

The beginning of hydration is associated with an exothermic maximum whose intensity is similar to that existing in C_3S hydration.[92] A second peak is very weak and barely detectable.

Mechanism of hydration

The available experimental data suggest a mechanism of hydration similar to that of C_3S, even though the whole process progresses more slowly. Thus, different processes occur at different times, although at degrees of hydration not too different from those of C_3S. Available ^{17}O and ^{29}Si NMR results are consistent with a model of hydration which involves the formation of an activated complex with five-coordinated Si, dissolution of Si tetrahedra and precipitation of the C-S-H phase.[105]

Structure of hydrated dicalcium silicate paste

The C-S-H phase formed in the hydration of dicalcium silicate is very similar to that formed in the hydration of C_3S. Data on its stoichiometry calculated from the free lime and combined water content and the degree of hydration vary greatly;[24,87,93,94,95,98 100] however, it appears most likely that it is not too different from that of the material formed in the hydration of C_3S. In direct measurements by analytical electron microscopy, an average Ca/Si ratio of 1.38 with a range from 1.1 to 1.6 was found in pastes hydrated from periods between 7 days and 22 years.[106] NMR studies show that the C-S-H phase consists of a combination of Si_2O_7 dimers and short single-chain polymers. The Q_2/Q_1 ratio in hydrated C_2S pastes is greater than that in similar C_3S pastes, indicating a longer average chain length in the former ones;[107] it increases with progressive hydration. ^{17}O NMR revealed the presence of Si–O–Ca, Si–O–Si, Ca–OH and possibly Si–OH sites in the C-S-H phase thus formed.

Just as in the hydration of C_3S, the C-S-H phase formed during the induction phase differs from that formed later on, inasmuch as it does not contain Q_1 or Q_2 sites. It contains only single SiO_4 tetrahedra with Si–O–Ca bonds.[105]

Besides C-S-H, the hydrated dicalcium silicate paste also contains calcium hydroxide; however, its amount is significantly lower than that existing in C_3S pastes with the same degree of hydration.

6.2.3 TRICALCIUM ALUMINATE

Tricalcium aluminate, $3CaO \cdot Al_2O_3$ (abbreviation C_3A), exists in cubic, orthorhombic and monoclinic modifications, of which the latter two occur only if doped with foreign ions, such as Na^+. All three modifications hydrate in a similar way; however, their reactivity may vary, depending on the quality and quantity of the dopant employed. In the hydration of Portland cement, tricalcium aluminate reacts with the calcium sulfate present. Thus the reactions in the system C_3A $C\bar{S}$ H_2O are of particular importance and must also be discussed.

Hydration of C_3A in the absence of calcium sulfate

At ordinary temperature and in the absence of calcium hydroxide the first hydration product of C_3A is a gel-like material with no detectable XRD lines, which appears to grow at the C_3A surface. Later, this material transforms into hexagonal crystals corresponding to the phases C_2AH_8 and C_4AH_{19}. Additional amounts of C_2AH_8 and C_4AH_{19} precipitate from the liquid phase. Finally the initially formed hexagonal phases C_2AH_8 and C_4AH_{19} convert to cubic C_3AH_6, the only calcium aluminate hydrate which is thermodynamically stable at ambient temperature.[108-116] The conversion to C_3AH_6 is accelerated with increasing temperature and depends also on the water/solid ratio, the grain size of C_3A and presence or absence of CO_2. At temperatures above about 80°C, a direct formation of C_3AH_6 takes place in the hydration of C_3A. The molar ratio CaO/Al_2O_3 in the liquid phase rises at the beginning of hydration to >3.0[111]. This suggests the formation of more C_2AH_8 than C_4AH_{19} at this stage.

In the presence of calcium hydroxide the rate of reaction slows down and only C_4AH_{19} is formed as the primary product. It again converts to C_3AH_6 as the hydration progresses.[111,117]

The kinetics of C_3A hydration is slowed down soon after mixing with water, due to the formation of a layer of hexagonal hydrates (C_2AH_8 and C_4AH_{19}) at the C_3A surface acting as a protective barrier. Upon conversion of these initially formed hydrates to the cubic C_3AH_6, the barrier is disrupted and the hydration proceeds again with a fairly high speed.[106,107,112-114,118] With regard to the effect of dopants on reactivity, the incorporation of Na^+ into the crystalline lattice slows down the reaction rate distinctly.[118,119] Among chemical additives, the progress of C_3A hydration is accelerated by triethanolamine.[120] It is slowed down in the presence of aldonic acids which are regular constituents of commercial lignosulfonates.[121]

C_2AH_8 and C_4AH_{19} belong to the broad group of AFm phases with the general formula $[Ca_2(Al, Fe)(OH)_6]X \cdot xH_2O$ where X denotes one formula unit of a singly charged anion or half a formula unit of a doubly charged anion. C_4AH_{19} and C_2AH_8 consist of $[Ca_2Al(OH)_6]$ sheets with OH^- or $[Al(OH)_4]^-$, together with H_2O, in the interlayer region. In addition, C_4AH_{19} contains a complete additional layer of H_2O between the principal layers. This fraction of bound water is lost at relative humidities below about 80 per cent and C_4AH_{19} converts to C_4AH_{13}.

C_3AH_6 or $Ca_3[Al(OH)_6]_2$ is one of the hydrogarnet phases which may produce solid solutions within a compositional region bounded by C_3AH_6, C_3FH_6, C_3AS_3 and C_3FS_3.

Hydration of C_3A in the presence of calcium sulfate

In the presence of calcium sulfate the amount of C_3A hydrated in the initial stage of hydration is distinctly reduced when compared to that consumed in the absence of $CaSO_4$.

Ettringite (trisulfate) $C_6A\bar{S}_3H_{32}$ is formed as the main product of hydration.[117,122 126]

$$C_3A + 3C\bar{S}H_2 + 26H = C_6A\bar{S}_3H_{32} \qquad (6.5)$$

Minor amounts of monosulfate $C_4A\bar{S}H_{12}$ or even C_4AH_{19} may also be formed if an imbalance exists between the reactivity of C_3A and the dissolution rate of calcium sulfate, resulting in an insufficient supply of SO_4^{2-} ions. The process is accompanied by a significant liberation of heat. After a rapid initial reaction, the hydration rate is slowed down distinctly. The length of this dormant period may vary and increases with increasing amounts of calcium sulfate in the original paste.

A faster hydration, associated with a second heat release maximum, gets under way after all the available amount of calcium sulfate had been consumed.[117,123 126] Under these conditions the ettringite, formed initially, reacts with additional amounts of tricalcium aluminate, yielding calcium aluminate monosulfate hydrate (monosulfate), $C_4A\bar{S}H_{12}$, as the product of reaction:

$$C_6A\bar{S}_3H_{32} + 2C_3A + 4H = 3C_4A\bar{S}H_{12} \qquad (6.6)$$

As ettringite is gradually consumed, hexagonal calcium aluminate hydrate, C_4AH_{19}, also starts to form. It may be present in the form of a solid solution with $C_4A\bar{S}H_{12}$ or as separate crystals.

In a paste hydration at ambient temperature, a nearly complete hydration of C_3A is attained within several months. The actual reaction rate depends on a variety of factors, such as the water/solid ratio and temperature.

The origin of the dormant period, characterised by a distinctly reduced reaction rate, is not obvious and several theories have been forwarded to explain it. The theory most widely accepted assumes the build-up of a layer of ettringite at the surface of C_3A which acts as a barrier responsible for the slowing down of the reaction.[108,117,122,126] Ettringite is formed in a through-solution reaction and precipitates at the surface of C_3A due to the limited solubility of C_3A in the presence of sulfates. The validity of the theory has been questioned by Mehta;[127] it was argued that the deposited ettringite crystal layer is not dense enough to account for the retardation of hydration.

According to another theory,[113,128] the impervious layer consists of a water-deficient hexagonal hydrate stabilised by incorporation of SO_4^{-2}. It is formed at the surface of C_3A and becomes covered with ettringite.

According to Skalny and Tadros,[129] C_3A dissolves incongruently in the liquid phase, leaving an aluminium-rich layer on the surface. Ca^{2+} ions are adsorbed on it, thus reducing the number of active dissolution sites. In this way the dissolution rate of C_3A becomes reduced. A subsequent adsorption of sulfate ions results in a further reduction of the dissolution rate.

According to Feldman and Ramachandran,[130] the dormant period in the hydration of C_3A is due to the adsorption of SO_4^{2-} ions at the surface of C_3A. Contrary to this theory, it has been found, however, that the hydration of C_3A is not slowed down if calcium sulfate is replaced by sodium sulfate.[126]

Finally, Birchall *et al.*[131] assumed the formation of an amorphous layer at the C_3A surface which acts as an osmotic membrane, and thus slows down the hydration of C_3A.

The termination of the dormant period appears to be due to a breakdown of the protective layer, as the added calcium sulfate becomes consumed and ettringite is converted to monosulfate. In this through-solution reaction both C_3A and ettringite dissolve and monosulfate is precipitated from the liquid phase.

Ettringite belongs to the broad group of AFt phases with the general formula $[Ca_3(Al, Fe)(OH)_6]X_3 \cdot xH_2O$, where X represents a formula unit of a doubly charged anion. The structure of ettringite on the nanometre scale is based on columns of the composition $[Ca_3Al(OH)_6 \cdot 12H_2O]_2^{6-}$ running parallel to the *c*-axis, with $3SO_4^{2-}$ and H_2O molecules in the intervening channels. Ettringite is trigonal. In the absence of free calcium hydroxide it crystallises in the form of well-developed prismatic or acicular crystals, whereas it is formed in colloidal form in its presence.[121,127,132] The morphology of the ettringite thus formed also depends on the availability of free space for crystal growth. Slender needles form only if sufficient free space is available, which is usually the case in mixes with a high water/solid ratio.[127]

Monosulfate (calcium monosulfate aluminate hydrate) is an AFm phase. Its nanostructure consists of $[Ca_2Al(OH)_6]_2^{2-}$ layers with one SO_4^{2-} and $6H_2O$ in the interlayer region. It crystallises in the form of thin hexagonal platelets.

6.2.4 *CALCIUM ALUMINOFERRITE*

The composition of calcium aluminoferrite (ferrite phases) may vary between about $C_2(A_{0.7}F_{0.3})$ and $C_2(A_{0.3}, F_{0.7})$. Under comparable conditions the hydration products formed in the hydration of the ferrite phases are similar in many respects to those formed from C_3A, although the rates of reaction differ.

The reactivity of the ferrite phase may vary in a wide range and seems to depend on the Al/Fe ratio. It generally declines with increasing Fe content.[126,133,134] Pure $C_2(A, F)$ exhibits a rather fast initial hydration rate which soon slows down, yet continues steadily until it is completely hydrated. It usually hydrates faster than pure C_3A.[124]

As with C_3A, the progress of hydration is slowed down in the presence of CH, more strongly by gypsum and most effectively by a combination of both.[41,124,133–136] The retardation in the presence of $CaSO_4$ and $Ca(OH)_2$ appears to be due to the formation of an AFt layer at the $C_2(A, F)$ surface.[134] The reaction is accelerated by finer grinding[136] and by elevated temperature.[133]

In the absence of gypsum an AFm phase of the formula $C_2(A, F)H_8$ and/or $C_4(A, F)H_x$ is formed as the initial product of hydration.[41,133–135,137] In the presence of lime, only $C_4(A, F)H_x$ is formed. The hexagonal phases $C_2(A, F)H_8$ and $C_4(A, F)H_x$ are subsequently converted into an iron-containing hydrogarnet phase, $C_3(A, F)H_6$.[41,133,134,137] At elevated temperature the hydrogarnet phase is formed directly.[133]

In mixes with gypsum and lime, or gypsum alone, an AFt phase $C_6(A, F)\bar{S}_3H_{32}$ is the main product of reaction.[41,135–139] Its formation may be preceded by the formation of an iron-rich gel and either alumina gel or C_2AH_8.[135] The early AFt formation occurs by a through-solution mechanism yielding an iron-free product. Only subsequently does an iron-containing AFt phase start to form.[135] Calcium hydroxide slows down the rate of reaction.

In a subsequent reaction step the AFt phase converts to AFm $C_4(A, F)\bar{S}H_{12}$.[41,135,136] This reaction is already initiated prior to the complete consumption of calcium sulfate. The monosulfate phase may also be formed directly at elevated temperatures and/or low water/solid ratios.[138] In addition to monosulfate, $C_2(A, F)H_8$ and $C_4(A, F)H_{13}$ may also be formed.[140] Generally the Al^{3+}/Fe^{3+} ratio in the formed hydrates tends to be below that of the original calcium aluminoferrite,[133,135,139] and increases with increasing iron content in the anhydrous material. The fraction of iron that has not been incorporated in the crystalline lattice of the AFt, AFm or hydrogarnet phases which form remains in the hydrated material in the form of amorphous iron oxide, hydroxide or another unspecified calcium-containing phase.[135,139] The formation of hydrates with a reduced iron content appears to be due to the low mobility of Fe^{3+} ions as compared to Al^{3+}.

6.3 Interactions in the hydration of clinker minerals

In the combined hydration of two or more clinker phases the hydration kinetics of any of them may be altered. The study of these phenomena is of importance as such a situation exists in the hydration of Portland cement.

6.3.1 *β-C_2S–C_3S SYSTEM*

In experiments with pure clinker minerals an acceleration of the dicalcium silicate hydration in the presence of C_3S[43,95] was reported. Data on the kinetics of C_3S hydration in the presence of C_2S are contradictory;[43,47,95] however, it appears likely that, in the proportions common in Portland cement, the effect of C_2S on the hydration of C_3S is negligible. The average H/S and C/S ratios of the C-S-H phase formed in the hydration of pastes made from blends of C_2S and C_3S are similar to those formed in the hydration of these two compounds when they hydrate individually.

6.3.2 *C_3S–C_3A AND C_3S–$C_2(A,F)$ SYSTEMS*

The interaction between C_3S on the one hand and C_3A or $C_2(A,F)$ on the other has been studied by several investigators. The results obtained are contradictory as both an acceleration and a retardation of the hydration of both C_3S and C_3A or $C_4(A,F)$ was reported.[133] [147] C_4AH_x, C-S-H and portlandite are formed as products of a combined hydration of C_3S and C_3A. In the hydration of C_4AF in the presence of C_3S and CH, the resulting hydrogarnet phase contains significant amounts of SiO_2, i.e. up to a composition of $C_6AFS_{1.5}H_9$.

6.4 Hydration of Portland cement

Chemically, the hydration of Portland cement consists of a series of reactions between individual clinker minerals, calcium sulfate and water, which proceed both simultaneously and successively at different rates and influence each other. The participants of the process are

- alite, i.e tricalcium silicate doped with foreign ions;
- belite, i.e. dicalcium silicate doped by foreign ions;
- tricalcium aluminate;
- calcium aluminate ferrite (the ferrite phase);
- free calcium oxide;
- alkali sulfates;
- calcium sulfate in the form of dihydrate, hemihydrate or anhydrite interground with clinker;
- mixing water.

The progress of the process depends on

- the rate of dissolution of the involved phases;
- the rate of nucleation and crystal growth of the hydrates to be formed; and

- the rate of diffusion of water and dissolved ions through the hydrated material already formed.

At the beginning of hydration the process tends to be controlled mainly by the rate of dissolution of the clinker phases and calcium sulfate. As the hydration progresses, the reaction rate becomes controlled more and more by the rate of nucleation and crystal growth of the formed hydrate phases and finally by the diffusion rate of water and dissolved ions.

The following factors determine the kinetics of the hydration process:

- the phase composition of the clinker and the quality and quantity of foreign ions incorporated in the crystalline lattices of the individual clinker minerals;
- the processing history of the clinker, including the heating rate, maximum burning temperature and cooling rate;
- the quantity and form of calcium sulfate present in the cement;
- the fineness of the cement;
- the technology employed for comminution of the cement;
- the water/cement ratio of the mix;
- curing conditions (air or water curing);
- the hydration temperature; and
- the presence of chemical admixtures in the mix.

The structure of the formed hydrated material on the nanometre (nanostructure) and micrometre scale (microstructure) depends on the following factors:

- the composition of the original binder;
- the starting water/cement ratio;
- the temperature of hydration;
- the absence or presence of chemical admixtures and the time of hydration.

6.4.1 EXPERIMENTAL PROCEDURES

The progress of the hydration process may be followed by determining the amount of non-reacted clinker minerals and calcium sulfate and/or by determining the amount of the formed hydrate phases as functions of time.

For determining the amount of unreacted cement constituents, quantitative X-ray diffraction appears to be the most suitable and most widely used method. Unfortunately, however, the accuracy and precision of the method is limited, especially for phases present in clinker in small amounts and/or at short hydration times. The amount of non-reacted gypsum may be determined conveniently by differential thermal analysis (DTA).

Among the hydrate phases, calcium hydroxide can be determined with acceptable accuracy by a variety of methods, such as DTA, thermogravimetry or XRD. The AFt phase may be determined by XRD or by DTA, but only in samples in which a very gentle free-water removal procedure was employed. Moreover, the C-S-H phase which is present may hamper the determination of ettringite at higher degrees of hydration. At present there exists no generally accepted direct method for the determination of the C-S-H phase, mainly due to its limited crystallinity and variable composition. ^{29}Si NMR may be considered as one possible solution, as any Q_1 and Q_2 units are specific for the C-S-H phase. Data on the amount of AFm as determined by DTA or X-ray diffraction may be considered semi-quantitative at best.

The determination of 'combined' (bound, non-evaporable) water, determined as the loss on ignition of samples in which 'free' water has been removed first, is often used as a measure of the fraction of cement that had reacted. It is assumed tacitly that the amount of combined water is directly proportional to the degree of hydration. Such an approach must be considered approximate at best as the individual clinker phases hydrate at different rates and yield hydrates with different combined water contents.

The amount of combined water depends also on the procedure employed for free water removal, since in some procedures a fraction of loosely bound water may be removed together with the bulk water present in the pore system. In commonly employed methods the free water is separated either by evaporation at a defined temperature and relative humidity or by extraction with a suitable solvent.

The overall kinetics of hydration may be also monitored on the basis of the amount of heat released in the course of hydration. Here also, it has to be kept in mind that the individual cement constituents react with water at different rates and their hydration is associated with the release of different amounts of heat.

The composition of the hydrated material and its variations at the micrometre scale may be studied by energy-dispersive electron probe microanalysis (EPMA) on polished sections. Even smaller paste volumes, i.e. of the order of tens of nanometres, may be analysed by analytical electron microscopy (X-ray microanalysis in transmission) on ground and redispersed samples or on ion-thinned sections.

The silicate anion structure may be studied by the trimethylsililation (TMS) and ^{29}Si NMR techniques.

The microstructure of the paste may be studied by secondary electron microscopy (SEM) on fractured surfaces, by backscatter imaging on polished sections, by high-voltage transmission microscopy (HVTEM) and scanning transmission electron microscopy (STEM) on ion-thinned sections and by similar microscopic techniques.

6.4.2 MECHANISM OF HYDRATION

The paste hydration of Portland cement at ambient temperature is characterised by several stages:

Pre-induction period (first minutes)

Immediately upon contact of cement with water, a rapid dissolution of ionic species into the liquid phase and the formation of hydrate phases gets under way. Alkali sulfates present in the cement dissolve completely within seconds, contributing K^+, Na^+ and SO_4^{2-} ions. Calcium sulfate dissolves until saturation, thus contributing Ca^{2+} and additional SO_4^{2-} ions.

Tricalcium silicate dissolves congruently and a layer of a C-S-H phase precipitates at the cement particle surface. As the CaO/SiO_2 ratio of the produced hydrate is lower than that of tricalcium silicate, the hydration of this phase is associated with an increase of the Ca^{2+} and OH^- concentration in the liquid phase. At the same time, silicate ions enter also the liquid phase, although their concentration remains very low. The fraction of C_3S hydrated in the pre-induction period remains low, probably between about 2 and 10 per cent.[147] [151]

Tricalcium aluminate dissolves and reacts with Ca^{2+} and SO_4^{2-} ions present in the liquid phase, yielding ettringite (AFt) that also precipitates at the cement particle surface. The amount of C_3A that hydrates in the pre-induction period varies in different cements between about 5 and 25 per cent.[147-151] The concentration of Al^{3+} in the liquid phase remains very low.

The ferrite phase reacts in a similar way as C_3A and also yields the AFt phase.

Only a minute fraction of β-C_2S reacts in the pre-induction period, yielding a C-S-H phase and contributing to the Ca^{2+} and OH^- concentration in the liquid phase.

The early fast hydration reaction appears to be slowed down due to the deposition of a layer of hydration products at the cement grain surface. In this way a barrier is formed between the non-hydrated material and the bulk solution, causing a rise in the concentration of dissolved ions in the liquid phase in immediate contact with the non-hydrated material to values approaching the theoretical solubilities of the anhydrous compound.

Induction (dormant) period (first few hours)

After the short initial period of fast hydration, the overall hydration rate slows down significantly for a period of a few hours. In this stage the hydration of all the clinker minerals progresses very slowly. The reasons for the slowing down and renewed acceleration of the hydration process is discussed in sections on the hydration of individual clinker phases. The concentration of calcium hydroxide in the liquid phase reaches at this stage its maximum and starts to decline. The concentration of SO_4^{2-} remains constant as the fraction consumed in the formation of the AFt phase is replaced by the dissolution of additional amounts of calcium sulfate. There are indications that the termination of the induction period and the initiation of the main reaction is mainly due to the nucleation of the 'second-stage' C-S-H phase from the bulk liquid.

Acceleration stage (3–12 hours after mixing)

In this period the progress of hydration accelerates again and is controlled by the nucleation and growth of the resultant hydration products. The rate of C_3S hydration accelerates and the 'second-stage C-S-H' starts to be formed. A noticeable hydration of dicalcium silicate gets also under way. Crystalline calcium hydroxide (portlandite) precipitates from the liquid phase and together with it the concentration of Ca^{2+} in the liquid phase gradually declines. The calcium sulfate, interground to the cement becomes completely dissolved and the concentration of SO_4^{2-} in the liquid phase starts to decline, due to the formation of the AFt phase as well as to the adsorption of SO_4^{2-} on the surface of the formed C-S-H phase.

Post-acceleration period

In this period the hydration rate slows down gradually, as the amount of still non-reacted material declines and the rate of the hydration process becomes diffusion-controlled.

The C-S-H phase continues to be formed due to the continuing hydration of both C_3S and β-C_2S. The contribution of β-C_2S to this process increases with time and, as a consequence, the rate at which additional calcium hydroxide is formed declines.

After the supply of calcium sulfate had become exhausted, the SO_4^{2-} concentration in the liquid phase declines. As a consequence, the AFt phase that has been formed in the earlier stages of hydration starts to react in a through-solution reaction with additional C_3A and $C_2(A, F)$, yielding monosulfate.

At sufficiently high initial water/cement ratios the hydration process progresses until all

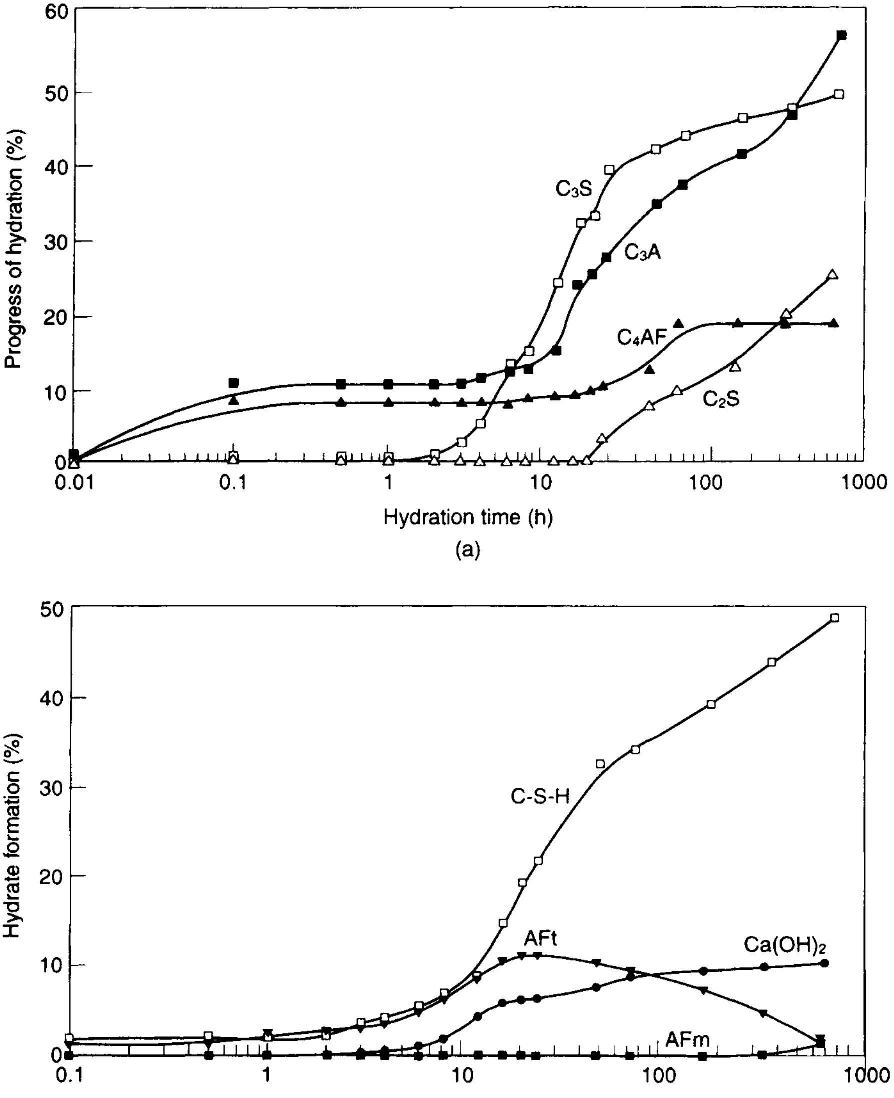

Fig. 6.6 Hydration kinetics of an ordinary Portland cement (paste hydration at ambient temperature). (a) Consumption of clinker phases, (b) formation of hydrate.

of the original cement becomes consumed. However, the residue of larger cement particles may persist even in mature pastes. At low water/cement ratios the reaction may stop in the presence of significant amounts of non-reacted material, due to the lack of sufficient amounts of water needed for the hydration process.

After the hydration process has been completed, an ageing of the hydrated material may take place. It is characterised by a further polycondensation of the SiO_4 tetrahedra which are present and an increase of the average SiO_4 chain length in the C-S-H phase formed.[62]

6.4.3 *KINETICS OF THE HYDRATION PROCESS*

The kinetics of hydration differs in different cement constituents and changes with time.[147-158]

Figure 6.6 shows the progress of hydration of the individual clinker phases as found in the paste hydration of an ordinary cement at ambient temperature. The kinetics of the hydration of individual cement constituents may be summarized as follows.

The hydration of C_3S (alite) is initiated by a fast reaction lasting a few minutes. The amount of C_3S hydrated within this period varies distinctly in different cements between about 2 and 10 per cent. In the subsequent, dormant (induction) period, lasting typically a few hours, the reaction is slowed down significantly. After that the reaction rate increases again and at ambient temperature a significant fraction of C_3S becomes consumed within 28 days. The exact hydration rate depends on the reactivity of alite, which in course depends on the quality and quantity of foreign ions incorporated in its crystalline lattice and on the conditions of clinker burning. It is accelerated with increasing amounts of SO_3 in cement[147] and reduced with an increasing β-C_2S/C_3S ratio in clinker.[154]

The β-C_2S phase (belite) hydrates much more slowly than C_3S. A noticeable reaction gets under way after an induction period lasting many hours or even days. The fraction of C_2S hydrated within 28 days is distinctly lower than that of C_3S.[157]

The initial reaction rate of C_3A is distinctly reduced by the presence of calcium sulfate in cement as compared to that in gypsum-free C_3A or clinker mixes. Nevertheless, between about 5 and 25 per cent of this phase reacts within the first few minutes after mixing. The initial reactivity of C_3A depends greatly on the quality and quantity of alkalis incorporated into the crystalline lattice. K^+ ions tend to increase the reactivity whereas it is reduced by Na^+.[118,119,148] The initial hydration rate is also affected by the rate of dissolution of the sulfates which are present. Most effective in reducing the C_3A reaction rate are mixed-alkali calcium sulfates (calcium langbeinite and syngenite) due to a fast rate at which Ca^{2+} and SO_4^{2-} enter the liquid phase.[155] Interground gypsum is far more effective than interblended calcium sulfate, probably due to a shorter diffusion distance between the sulfate source and C_3A.[155] A faster hydration of C_3A continues after a dormant period lasting several hours. A significant fraction of C_3A becomes hydrated within 28 days.

The reactivity of calcium aluminate ferrite may vary greatly depending on its A/F ratio. Generally, in the hydration of Portland cement it hydrates in a similar way, but more slowly than tricalcium aluminate.

Calcium sulfate is partly used up in the formation of AFt and partly adsorbed by the C-S-H phase.[158,159,160] The latter part of the SO_4^{2-} may be desorbed in the later course of hydration and participates in the formation of additional amounts of AFt.

Figure 6.6(b) shows the formation of the hydrate phases in the paste hydration of an ordinary Portland cement at ambient temperature. The progress of the formation and disappearance of the individual hydrate phases may be summarised as follows.

The formation of the C-S-H phase follows the hydration of alite and belite. After a fast initial formation of small amounts associated with the hydration of C_3S in the pre-induction period, the amount of C-S-H increases only slowly in the inducton period. After a renewed fast reaction rate in the acceleratory stage, the formation of the C-S-H phase slows down gradually in the post-acceleratory stage but may continue for months, especially in cements with high β-C_2S contents.

The formation of calcium hydroxide is associated with the hydration of the C_3S and C_2S phases. Crystalline calcium hydroxide starts to form at the end of the induction period. Its amount increases as the hydration of C_3S and C_2S progresses; however, the amount of calcium hydroxide increases much more slowly in the hydration of C_2S than that of C_3S. The formation of the AFt phase from $C_2(A,F)$ is associated with consumption of the calcium hydroxide that had been formed in the hydration of C_3S and C_2S.

The rate of AFt formation depends both on C_3A and $C_2(A,F)$ reactivity and the form of calcium sulfate present. It proceeds more slowly in the presence of anhydrite than dihydrate or hemihydrate. At normal sulfate contents, all the available calcium sulfate is consumed, and the formation of AFt is terminated within the first 24 h after mixing. After that, additional amounts of C_3A and $C_4(A,F)$ react with AFt to yield the AFm phase. The rate at which AFt is converted to Fm depends on the composition of the original cement and declines as the $C_4(A,F)/C_3A$ ratio increases.[161,162]

The fineness of the cement affects the rate of hydration, especially at shorter hydration times. Generally, the hydration rate increases with increasing specific surface of the cement.

In addition to the specific surface area and particle size distribution, the technology employed in the comminution of cement may also affect its reactivity. In particular, cements ground in high-pressure roller mills hydrate and set faster than those ground in ball mills, even for an equal particle size distribution and fineness. This appears to be due to a higher reactivity of the C_3A and C_3S phases, a reduced rate of decomposition of calcium sulfate dihydrate to hemihydrate and a less favourable distribution of calcium sulfate in cements ground in high-pressure roller mills.[163,164]

The rate of hydration is temperature dependent, especially at shorter hydration times and increases with increasing temperature. At the same time, however, the structure of the hydrated material may also be altered.

For a given cement and curing temperature, the rate of hydration increases with increasing water/cement ratio[165,166] and may also be positively affected by water rather than air curing, especially in small specimens. In air curing the hydration rate increases with increasing relative humidity.[156]

6.4.4 COMPOSITION OF THE LIQUID PHASE

At short hydration times and high enough water/cement ratios the concentration of the liquid phase may be determined after separating it by filtration or centrifugation.[167–169] For longer hydration times a technique may be employed in which the pore liquid is separated from the hardened paste by applying high pressure.[29,170–172]

Data on the composition of the liquid phase for paste hydration of ordinary Portland cement at ambient temperature may be summarised as follows.

Immediately after mixing, K^+ and Na^+ ions present in the form of sulfates, together with pertinent amounts of SO_4^{2-}, enter the liquid phase very quickly, due to the high solubility of alkali sulfates. The concentration of both K^+ and Na^+ attained in the liquid phase may vary over a wide range, i.e. ~5–50 mmol Na^+ and ~20–200 mmol K^+, depending on the alkali sulfate content in the cement and the water/cement ratio of the mix. In the further course of hydration, additional amounts of K^+ and Na^+ ions, bound originally within the clinker minerals, enter the liquid phase.

Ca^{2+} ions are released into the liquid phase in the dissolution of free lime and in the hydration of tricalcium and dicalcium silicate. The liquid phase becomes saturated with respect to $Ca(OH)_2$ within a few minutes and a saturation factor (defined as the activity product divided by its value at saturation) of between 2 and 3 is reached within about 1–3 h. In the later phase of hydration the Ca^{2+} concentration gradually declines due to portlandite precipitation and AFt formation. The final value depends on the alkali content in the liquid phase and declines with increasing K^+ and Na^+ concentrations.

The SO_4^{2-} ions in the liquid phase stem initially from the alkali sulfates present in cement, and their concentration reaches values that depend on the amount of available water-soluble sulfates and the water/cement ratio. The dissolution of calcium sulfate proceeds more slowly; it depends also on the form of calcium sulfate present and increases in the order anhydrite, dihydrate, hemihydrate. As long as solid calcium sulfate is still present, the SO_4^{2-} concentration in the liquid phase changes only slightly, as the SO_4^{2-} consumed in the formation of AFt or adsorbed by the C-S-H phase is replenished by calcium sulfate dissolution. After that, the SO_4^{2-} concentration begins to decline and reaches values closer to zero within a few days.

The OH^- ion concentration in the liquid phase stems from the dissolution of calcium hydroxide in the hydration of C_3S and from the alkalis bound within the clinker minerals. Its concentration increases in the course of hydration and reaches values depending on the K^+ and Na^+ concentration.

The concentration of silicate and aluminate ions in the liquid phase remains very low, i.e. below 0.1 mmol, throughout the course of hydration.

6.4.5 HEAT OF HYDRATION

The hydration of Portland cement is associated with the liberation of hydration heat. Figure 6.7 shows the heat evolution curve for a typical Portland cement.

In cements that contain at least a fraction of the K^+ in the form of potassium sulfate, the hydration process may be marked by a distinct initial endothermic peak immediately after mixing which is due to the dissolution of this cement constituent in the mixing water.

A rather intense liberation of heat with a maximum within a few minutes is due to the initial rapid hydration of C_3S and C_3A in the pre-induction period. Hydration of calcium sulfate hemihydrate to dihydrate may also contribute to this exothermic peak.

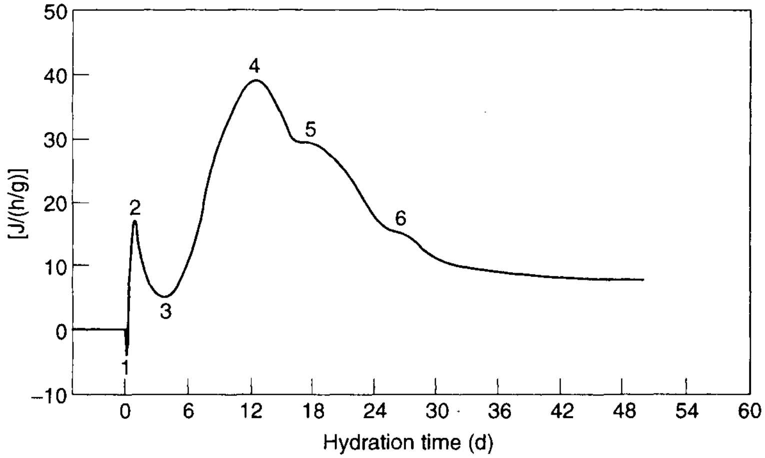

Fig. 6.7 Hydration heat evolution of an ordinary Portland cement. 1: K_2SO_4 dissolution; 2: early stage reaction; 3: dormant period; 4: middle-stage reaction (C-S-H formation); 5: AFt formation; 6: AFt–AFm conversion.

Table 6.3 Enthalpy of hydration of pure clinker minerals

Starting phase		Reaction product	Enthalpy (of complete) hydration	
			kJ/kg	kJ/mol
C_3S	$(+H)$	C-S-H + CH	520	118
β-C_2S	$(+H)$	C-S-H + CH	260	45
C_3A	$(+CH + H)$	C_4AH_{19}	1160	314
C_3A	$(+H)$	C_3AH_6	910	245
C_3A	$(+CSH_2 + H)$	C_4ASH_{12} (AFm)	1140	309
C_3A	$(+CSH_2 + H)$	$C_6AS_3H_{32}$ (AFt)	1670	452
C_4AF	$(+CH + H)$	$C_3(A,F)H_6$	420	203

After a distinct minimum, due to the existence of a dormant period in which the overall rate of hydration is slowed down, a second, main exothermic peak,with a maximum after a few hours, becomes apparent. It is mainly due to the hydration of C_3S and the formation of the C-S-H phase and portlandite. After that, the rate of heat release slows down gradually and reaches very low values within a few days.

In most but not all cements, a shoulder or small peak may be observed at the descending branch of the main peak, which is probably due to renewed AFt formation, there may even be a second shoulder which is attributed to AFt–AFm conversion.

The cumulative heat release roughly follows the overall process of hydration and is affected by the same factors, especially by the composition of the cement and its fineness. Generally, after a given hydration time, the overall release of heat of hydration is smallest in 'low-heat' cements (ASTM Type IV) and highest in 'high early srength' cements (ASTM Type III).

The heat of hydration released in the complete hydration of a cement is approximately an additive function of the heats released in the hydration of individual cement constituents. The pertinent values are summarised in Table 6.3.

6.5 Setting of Portland cement

Setting is a process in which a 'fresh' cement paste of freely flowing or plastic constistency is converted into a set material which has lost its unlimited deformability and crumbles under the effect of a sufficiently great external force. It is followed by the 'hardening' of the paste in which the hardness, strength and modulus of elasticity increase until an ultimate value of these parameters is attained. Setting is a spontaneous process characteristic of all inorganic binders. It is preceded by a 'stiffening' of the paste in which the apparent viscosity of the material increases without losing its plastic character.

After mixing a Portland cement with adequate amounts of water (w/c ~0.3–0.7) the cement grains are initially evenly distributed in the liquid phase. A fresh cement paste is formed whose rheological properties (called also 'consistency') depend on the water/cement ratio, the fineness of the cement and its composition. Within minutes following mixing, a flocculation of the cement particles takes place,[173] [177] associated with an increase in the viscosity of the paste. Discrete aggregates of cement particles are formed which entrap a fraction of the mixing water, thus making it unable to participate in the flow of the paste. This initial flocculation of cement particles is brought about by opposite zeta potentials and by weak van der Waals forces.

Prior to setting, i.e. during the dormant period and at the beginning of the acceleratory stage, the flocculation of the paste is reversible. A remixing or application of ultrasound (sonification) may destroy the structure which is rebuilt again upon renewed standing.

In addition to flocculation, the apparent viscosity of the paste also increases due to a progressive hydration of the cement that results in a gradual increase of the existing solid/liquid ratio and a roughening of the surface of the cement particles caused by precipitation of the hydrates thus formed.[115]

In the acceleratory stage of hydration the amount of hydrated material increases rapidly and along with it the volume of the liquid phase declines. Chemical bonds develop at the points of contact between the individual cement particles covered with the hydrated material. The latter contacts are stronger than the ones due to van der Waals and electrostatic forces which are responsible for flocculation, and are not restored if broken down, e.g. by intensive mixing. As the amount of hydrated material increases, the number of contacts between particles also increases and eventually a continuous, three-dimensional network of solids develops within the paste, associated with the loss of its unlimited deformability; i.e. the paste sets. Shortly after setting the number of contacts between the particles is still low and thus the solid network can be broken down easily by external forces: the strength of the material is still low. However, as the hydration progresses and the amount of hydrated material increases at the expense of the water-filled pore space, the bonds between solid particles strengthen, resulting in a gradual increase of strength of the set paste.

The 'normal' setting of Portland cement appears to be the consequence of both C_3S and C_3A hydration and the formation of the C-S-H and AFt phases. Opinions about the significance of C-S-H and AFt formation in the setting process are not uniform, though most investigators believe that the setting of ordinary Portland cement is mainly due to the formation of the C-S-H phase.[178 183] According to another hypothesis, the setting of Portland cement is due to a recrystallisation of primary microcrystalline ettringite into well-developed crystals.[184,185]

The amount of C_3S and $C_3A + C_2(A.F)$ hydrated by the time of setting varies in different cements and generally increases with increasing water/cement ratio. In pastes with $w/c = 0.30$,[183] values of 1–5.5 g/100 g cement were found for C_3S and 1–2.5 g/100 g cement for $C_3A + C_2(A,F)$.

Figure 6.8 shows an ordinary Portland cement paste at the time of setting. A layer of amorphous or microcrystalline material may be observed precipitated at the cement grain surface. Distinct ettringite crystals cannot usually be detected in pastes made with a 'normal' water/cement ratio as this phase is present in a highly dispersed form.

To produce a cement with acceptable setting characteristics, calcium sulfate acting as 'set regulator' has to be added or interground with the clinker in most instances. In the presence of sufficient amounts of Ca^{2+} and SO_4^{2-} in the liquid phase, the amount of C_3A and C_4AF hydrated in the initial pre-induction period is reduced and AFt is formed during the hydration. The AFt phase precipitates at the cement grain surface in the form of a microcrystalline layer. Under these conditions the flowability and plasticity of the paste is preserved until the formation of more hydrates, in particular C-S-H, causes 'normal set'. Contrary to the situation in the absence of calcium sulfate, plate-like crystals of $C_4(A,F)H_x$ (AFm) are formed which cause a 'quick' (flash) set of the paste, associated with an intensive liberation of heat immediately following mixing with water (Figure 6.9). The subsequent strength developed of such paste is usually reduced, probably due to a weakening of the microstructure by the platelets of AFm. Such a phenomenon may not be seen in cements with very low C_3A contents, in which a 'normal' setting may be observed even in the absence of calcium sulfate.

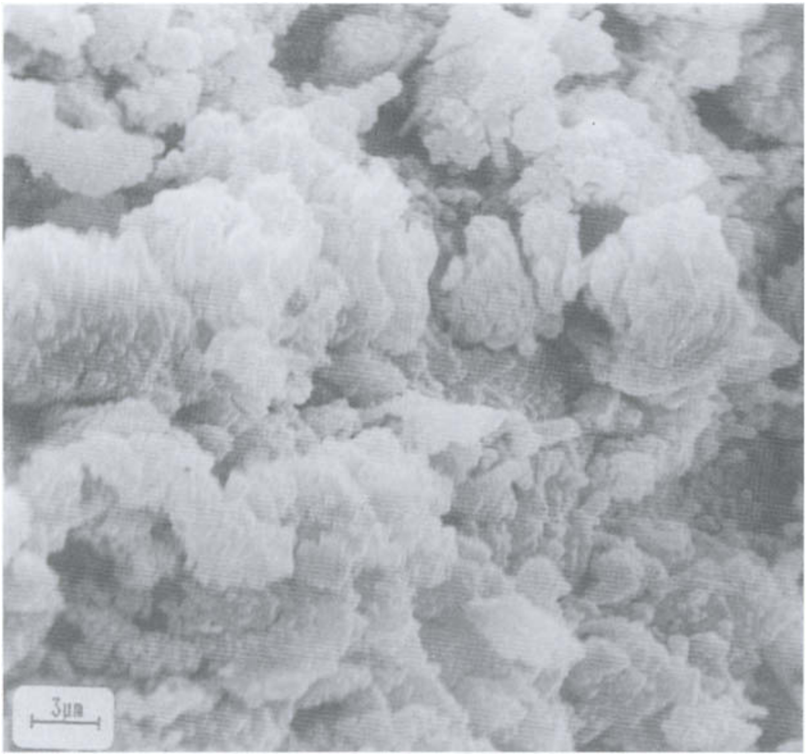

Fig. 6.8 'Normal' set of an ordinary Portland cement. SEM image of a fractured surface of the paste at the end of setting.

As the reactivity of C_3A in different cements may vary, the availability of SO_4^{4-} must be adjusted to the rate at which Al^{3+} ions enter the liquid phase. This may be attained by combining the slowly soluble $CaSO_4$ (anhydrite) with the readily soluble $CaSO_4 \cdot 2H_2O$ (gypsum) as sources of calcium sulfate. Under conditions existing in industrial cement mills (ball mills), the latter compound decomposes partly or completely to $CaSO_4 \cdot \frac{1}{2}H_2O$ (hemihydrate), a form of calcium sulfate that dissolves even faster. If the ratio of anhydrite to dihydrate is not properly adjusted and the dissolution of calcium sulfate is too low, due to an insufficient amount of hemihydrate present, a plate-like calcium aluminate hydrate and/or monosulfate (AFm) is formed instead of ettringite and a flash set of the paste may be observed even if the overall amount of hemihydrate present is adequate.[152]

In cements with C_3A of low reactivity or those with very little or no C_3A at all, part of the hemihydrate may precipitate to yield calcium sulfate dihydrate ('secondary gypsum') crystals which may cause a stiffening or even a 'false set' of the paste.[152] In a false set, unlike the situation in a 'flash set', the plasticity of the mix may be restored by intensive mixing. Moreover, the setting process is not associated with abnormally high heat evolution and the subsequent development of strength is not adversely affected.

An accelerated set may also be observed in cements ground in a high-pressure roller mill rather than in a ball mill, mainly due to the absence of conversion of dihydrate to hemihydrate under these conditions.[163,164] False or even flash setting may also occur in cements high in K_2O due to the precipitation of syngenite, $K_2Ca(SO_4)_2$ (Figure 6.10)[186]

Finally, false set was observed in cements high in C_3A due to excessive formation of AFt.[183]

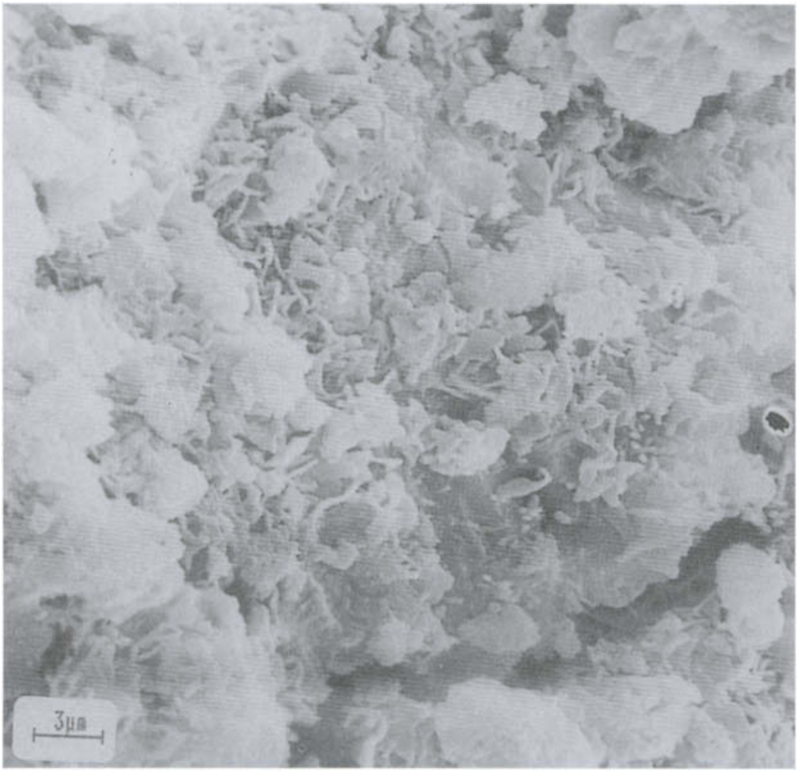

Fig. 6.9 'Quick (flash)' set of a high-C_3A, low-gypsum Portland cement due to AFm formation. SEM image of a fractured surface of the paste at the end of setting.

The overall SO_3 content of Portland cement must not exceed ~3–4 per cent to avoid 'sulfate expansion' in the later course of hydration due to excessive ettringite formation.

6.6 Hydrated Portland cement paste

6.6.1 CONSTITUENTS OF THE PASTE

The following are the constituents of a hydrated Portland cement paste.

The C-S-H phase is the main product of Portland cement hydration. Its structure is similar to that of the C-S-H phase formed in the hydration of pure dicalcium and tricalcium silicate. The material exhibits a very low crystallinity. Its mean CaO/SiO_2 molar ratio may vary depending on the cement composition, water/cement ratio and hydration temperature. Within a single paste the CaO/SiO_2 ratio may vary from one area to another. Typically this ratio may vary between about 1.2 and 2.3 if determined by transmission electron microscopy[187] or electron probe microanalysis[188–191]. Young pastes appear to show a bimodal distribution.[187–190] There is no relationship between the average Ca/Si ratio of the C-S-H phase and the maturity of the paste. This material may also incorporate limited amounts of foreign ions as Mg^{2+}, Al^{3+}, K^+, Na^+ or SO_4^{2-}in its structure.

Portlandite, i.e. crystalline calcium hydroxide, is the second most abundant product in hydrated Portland cement pastes. It is present in the form of relatively large crystalline aggregates and may even be distinguished easily from the rest of the paste by optical microscopy.

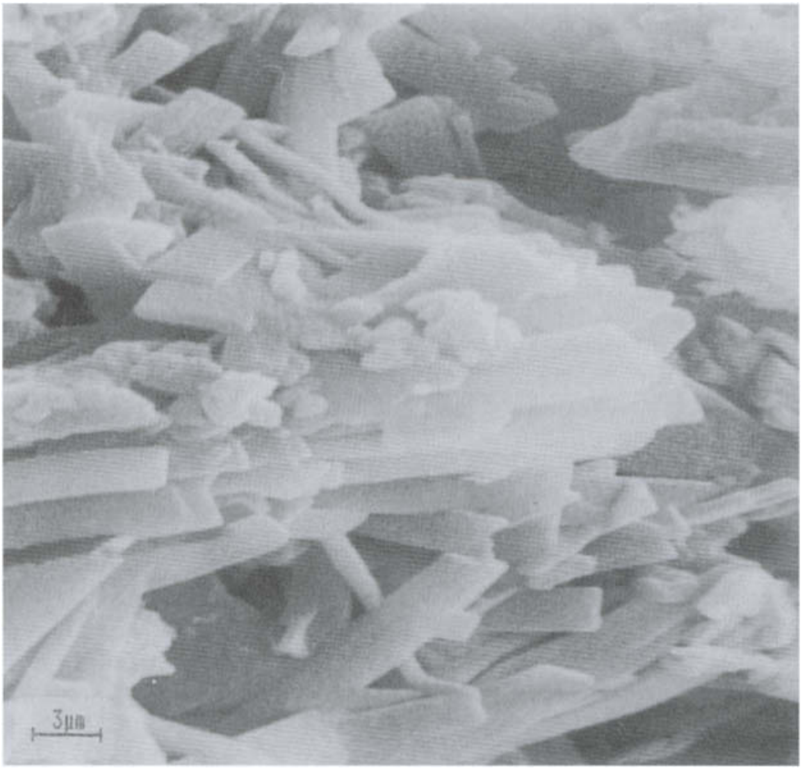

Fig. 6.10 'Quick (flash)' set of a cement with high potassium sulfate content due to syngienite formation. SEM image of a fractured surface of the paste at the end of setting.

The AFt and AFm phases are present in amounts that depend on the amounts of the tricalcium aluminate and ferrite phases in the original cement and the degree of hydration. After reaching a maximum, the amount of AFt in the paste declines and that of AFm increases with progressive hydration. In mature pastes the AFt phase may be completely absent. The Al^{3+}/Fe^{3+} in these phases may vary and depends on the composition of the original cement.

Minor constituents of hydrated Portland cement paste may include a poorly crystalline siliceous hydrogarnet which accommodates a significant fraction of the iron originally present in the ferrite phase,[76,192] a hydrotalcite $[Mg_3Al(OH)_8](CO_3)_{0.5}\cdot 2H_2O$ type phase which accommodates most of the Mg^{2+},[76,187] and brucite $[Mg(OH)_2]$ which is formed when the clinker contains free periclase (MgO).

The amount of 'bound' ('combined') water present in the hardened Portland cement paste depends on the phase composition of the original cement, on the degree of hydration and also on the way in which the term 'bound water' has been defined. Table 6.4 gives bound water values found in pastes made from a Portland cement with different water/cement ratios and hydrated at 20°C for 2 years.

The individual ions are distributed in the hydrated material as follows. The Ca^{2+} of the original cement is present in all hydrated phases as the basic component.

The SiO_4^{4-} originally present in C_3S and C_2S is mainly incorporated into the C-S-H phase. A small amount of silica is also incorporated in the portlandite phase which is formed in the hydration of C_3S and C_2S together with C-S-H. Finally, some of it may be incorporated, together with Fe^{3+}, in a hydrogarnet phase.

Table 6.4 Bound water found in mature Portland cement pastes made from a single cement as determined by different methods[58] (g/g of ignited weight)

w/c	W_{B1}	W_{B2}	W_{B3}
0.30	0.28	0.33	–
0.50	0.33	0.39	0.39
0.70	0.33	0.40	0.41
1.00	0.33	0.41	0.41

W_{B1} = Bound water determined as the loss on ignition of the D-dried paste (also called non-evaporable water).
W_{B2} = Bound water determined as the loss on ignition of the material after extraction with ethyl ether and acetone.
W_{B3} = Bound water defined as the fraction of total water unable to migrate through the pore system under a pressure gradient.

Al^{3+} is present in hydrated Portland cement pastes preferentially in an octahedrally coordinated form. A significant fraction of it is incorporated into the AFt phase which subsequently converts to AFm. The degree of AFt to AFm conversion differs in different cements and is especially low in high-iron cements.[134,153] Limited amounts of Al^{3+} may be also incorporated into the C-S-H phase. Here any substitution of Al^{3+} for Si^{4+} is confined to the bridging tetrahedra. In such cases, Al^{3+} is present in tetrahedrally coordinated form. The resulting charge imbalance is neutralised by the incorporation by alkali cations of additional Ca^{2+} ions into interlayer sites. However, the extent of such substitution is small and is probably limited to an Al/Ca ratio of about 0.2.[76] Some Al^{3+} is also bound, together with Mg^{2+}, in the hydrotalcite-type phase.

Fe^{3+} is present in hydrated Portland cement pastes octahedrally coordinated[193] and may partially replace Al^{3+} in the AFt and AFm phases. A significant part of it, however, appears to enter a poorly crystalline siliceous hydrogarnet phase.[76,192,194] Fe^{3+} does not replace Si^{4+} in the C-S-H phase.

Most of SO_4^{2-} is bound within the AFt and AFm phases. The rest is bound within the C-S-H phase, probably by adsorption.[159,194] In contrast, substitution of Si^{6+} for Si^{4+} in C-S-H appears unlikely.

Most of the Mg^{2+} becomes bound in form of a hydrotalcite phase which also contains Al^{3+}.[194] Some of Mg^{2+} may also be present in the form of brucite $Mg(OH)_2$, if free periclase (MgO) is present in the cement. The substitution of Mg^{2+} for Ca^{2+} in the C-S-H phase is very limited at best.

Alkali ions remain mostly dissolved in the pore liquid. Small amounts of Na^+ and K^+ may be also accommodated in the interlayer sites of the C-S-H phase.[76]

6.6.2 STRUCTURE ON THE NANOMETRE SCALE

At the nanometre scale the mature Portland cement paste consists of a C-S-H phase in which all other constituents are embedded. Of these portlandite, which is present in the form of large crystals, is the most important. According to a model suggested by Taylor[75-77] the C-S-H phase consists of regions structurally related to 1.4 nm tobermorite and jennite. The bulk of Al^{3+}, Fe^{3+} and SO_4^{4-} ions are present in the paste in the form of layers of AFm closely intermixed with C-S-H on a scale ranging from a single layer up to layers a few micrometres thick. The incorporation of Al^{3+}, Fe^{3+} and SO_4^{4-} ions into the tobermorite and jennite chains is very limited; however, distinct amounts of SO_4^{4-} may be sorbed at the C-S-H surface. On the other hand, it has also been suggested[78,79] that Al^{3+} is preferentially incorporated in the C-S-H phase, substituting for Si^{4+}.

The silicate anion structure within the C-S-H phase formed in the hydration of Portland cement has been studied most extensively by the use of ^{29}Si MAS-NMR[61,67,195-203] and by trimethylsililation[74,204-210] techniques. The obtained results may be summarised as follows.

The silicate units originally present in monomeric form undergo polymerisation as the hydration progresses. Monomeric SiO_4 units may be preserved only in the hydration product formed at very short hydration times. In the polymerisation process, first dimeric units (Si_2O_7) and then polymeric silicates are formed. The latter ones contain exclusively linear chains with the predominant species having five or eight silicate tetrahedra linked together. Consequently, with ^{29}Si MAS-NMR only Q_1 and Q_2 units may be found and the ratio Q_1/Q_2 declines as the hydration progresses. Q_3 and Q_4 units are not present in the hydrated material but may be formed in a reaction of the C-S-H phase with CO_2 from the atmosphere.[211]

^{27}Al NMR studies suggest a gradual conversion of tetrahedrally coordinated monomeric AlO_4, present in the original non-hydrated cement, into octahedrally coordinated AlO_6.[211,212] Octahedral coordination of Fe^{3+} was determined by Mössbauer spectroscopy. The octahedral coordinaton of Al^{3+} and Fe^{3+}, as well as the observation that the length of the silicate chains in the C-S-H phase is not altered in the presence of aluminates, ferrites or sulfates, suggest that these ions do not replace Si^{4+} in polysilicate chains, except perhaps to a minor extent.

Spin-grouping NMR has been used to study the state of water in hydrated Portland cement pastes.[213,214,215] This has enabled the identification of protons present in loosely bound water, protons in firmly bound water and those in hydroxyl groups existing in crystalline structures.

6.6.3 STRUCTURE ON THE MICROMETRE SCALE

Electron microscopic methods have been widely used to study the structure of hardened Portland cement pastes on the micrometre scale. Basically, one must distinguish between the 'inner product' formed within the boundaries of the original anhydrous grains and the 'outer product' filling the space originally filled with water. The composition of the C-S-H phase present in the 'inner' and 'outer' products differ, the Ca/Si ratio in the former one being somewhat higher.[187] Crystalline calcium hydroxide is mainly confined to the outer product. The amount and the mutual ratio of AFt and AFm in the paste vary with the degree of hydration and also depend on the composition of the original cement.

Figures 6.11 and 6.12 show the fractured surfaces of mature Portland cement pastes prepared with different initial water/cement ratios as visualised by secondary electron imaging. The material formed in the hydration of a paste with w/c = 0.30 exhibits a very dense structure with no apparent crystallinity even at high magnifications. In contrast, the paste made with w/c = 1.00 exhibits a much less compact structure with easily detectable pores. At high magnifications the acicular character of the C-S-H phase becomes apparent. A few portlandite crystals may be also detectable. Distinct particles that could be attributed to the AFt or AFm phases are not visible. A significant handicap in the observation of fractured surfaces is the fact that the structure of the surface is not necessarily representative of the structure of the whole paste, as the fracturing of the material is not random and occurs preferentially in areas in which the cohesion is weakest.

Figure 6.13 shows the structure of a cement paste as visualised by backscatter electron

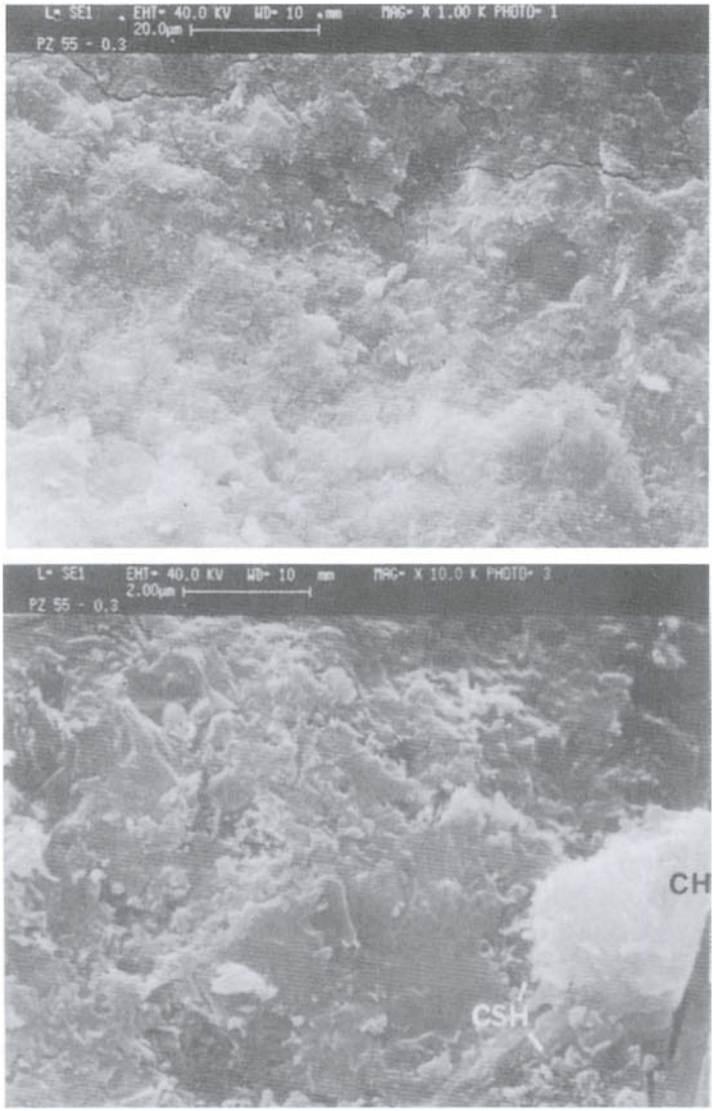

Fig. 6.11 SEM images (at two different magnifications) of a fractured surface of a mature Portland cement paste made with w/c = 0.30, hydrated at 20°C.

imaging of a polished surface. In this technique the brightness of the visualised areas decline in the order non-hydrated cement grain residue > calcium hydroxide > other hydration products, essentially the C-S-H phase > pores.

The chemical composition of the hydrated cement paste and its variation on the micrometre scale has been studied by energy-dispersive electron probe microanalysis (EPMA).[188 191] This method enables us to determine the composition of the paste as it exists in a volume of a few cubic micrometres. Figure 6.14 shows the composition of a mature paste determined along a straight line at intervals of 5 µm, while Figure 6.15 indicates

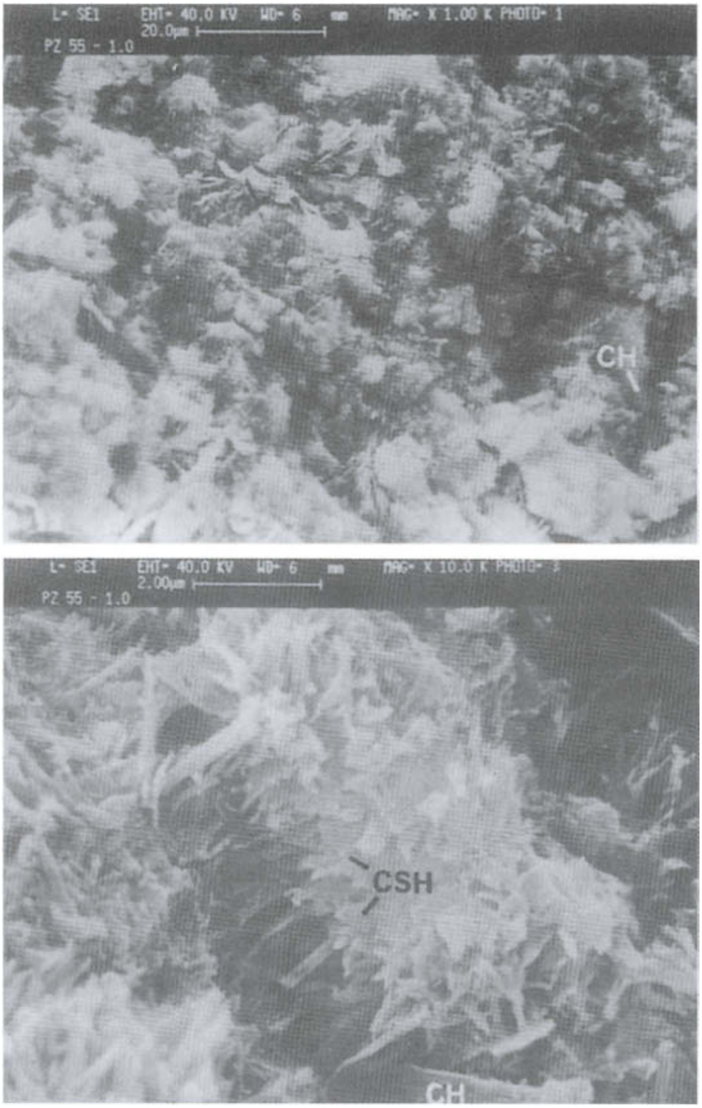

Fig. 6.12 SEM images (at two different magnifications) of a fractured surface of a mature Portland cement paste made with w/c = 1.00, hydrated at 20°C.

the composition of the same paste presented in the system $CaO-SiO_2-(Al_2O_3Fe_2O_3)$. Available data obtained by EPMA may be summarised as follows.

A hydrated Portland cement paste exhibits distinct compositional variatons if studied by EPMA. Except for spots corresponding to the paste formed *in situ* from larger alite and belite grains which contain the C-S-H phase alone, and spots belonging to pure portlandite, most of the analysed spots correspond to a mixture on the micrometre scale of C-S-H with CH and the AFm phase. In particular; spots coresponding to pure AFm are very rare. In the system Ca-Si-(Al + Fe) three main compositional regions may be distinguished:

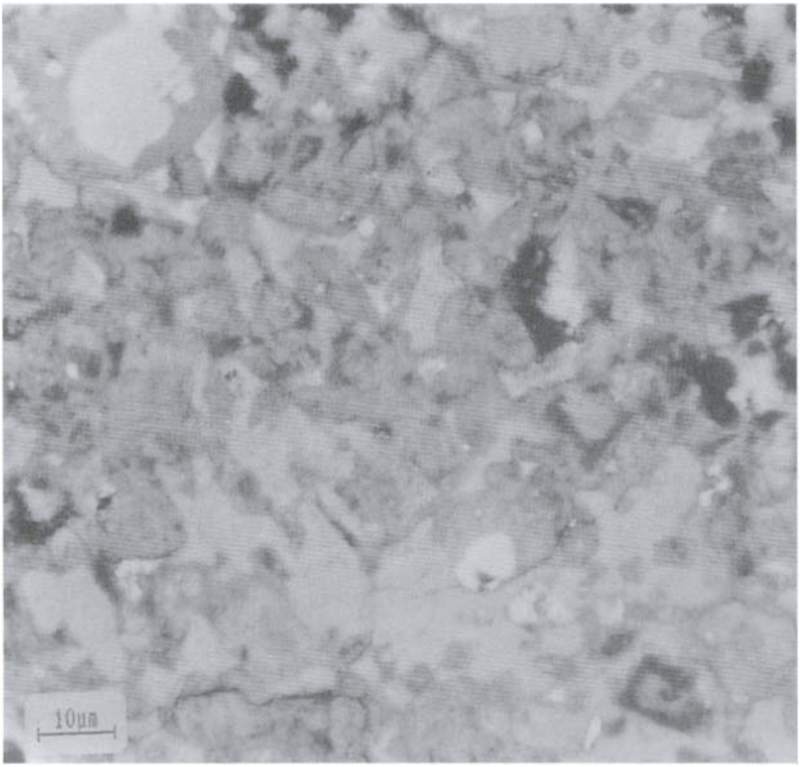

Fig. 6.13 Backscatter electron image of a polished surface of a mature Portland cement paste.

1. high in Ca + Si, low in Al + Fe: spots high in C-S-H;
2. very high in Ca, low in Si and Al + Fe: spots high in CH; and
3. high in Ca and Al + Fe, low in Si: spots high in AFm.

In cements sufficiently high in Fe_2O_3, spots high in Ca, Fe and Si and corresponding to the hydrogarnet phase may be also found. Atomic ratios were estimated for the individual hydrate phases based on analyses of 190 spots of a hydrated cement paste (Table 6.5).[190] In a different study,[187] distinct differences were found in the X/Ca atom ratio for the inner and outer products.

Results obtained from area scans on polished surfaces also reveal an uneven distribution of individual elements with the paste.[190] They may be summarised as follows.

- In the Si image a region relatively high in Si and belonging essentially to the C-S-H phase and low-Si regions corresponding mainly to CH may be distinguished.
- Regions high in Fe are also high in Al but the reverse is not true all the time. The former ones are sharply defined, apparently due to the low solubility of iron in the alkaline pore fluid and thus its low mobility in the paste.
- The sulfur image shows relatively little differentiation.
- Magnesium tends to associate with Al and Fe.

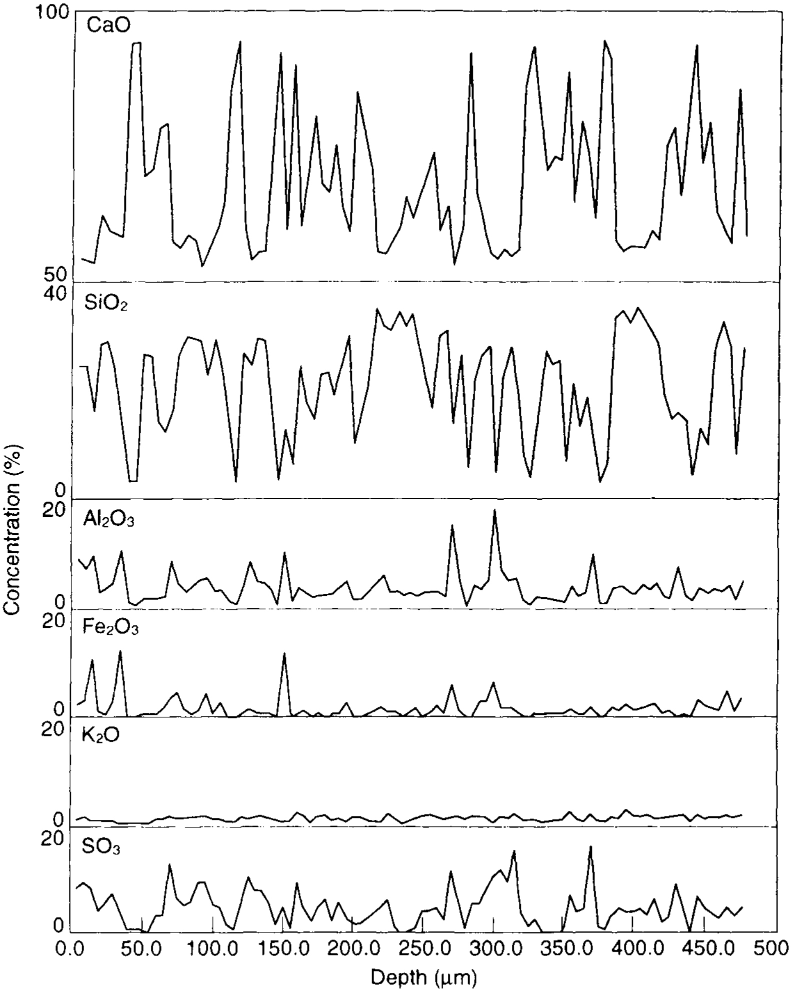

Fig. 6.14 Oxide composition of a mature Portland cement paste as determined along a straight line on a polished surface by energy-dispersive electron probe microanalysis (w/c = 0.6, 20°C).

- The calcium image is also relatively uniform but shows discontinuous regions of higher Ca content corresponding to CH.

Analytical electron microscopy (AEM) studies performed on ground and redispersed material,[216,217] in which the analysed volume is at least two orders of magnitude smaller, revealed a fair agreement with results obtained by EPMA. Here also, all the hydrated phases, other than CH, exhibited marked compositional variations between particles in the same specimen. The mean Ca/Si ratio for the C-S-H phase varied between 1.5 and 2.0. Particles of AFm had a A/F ratio which was distinctly lower than that of the original cement and also contained significant amounts of Si.

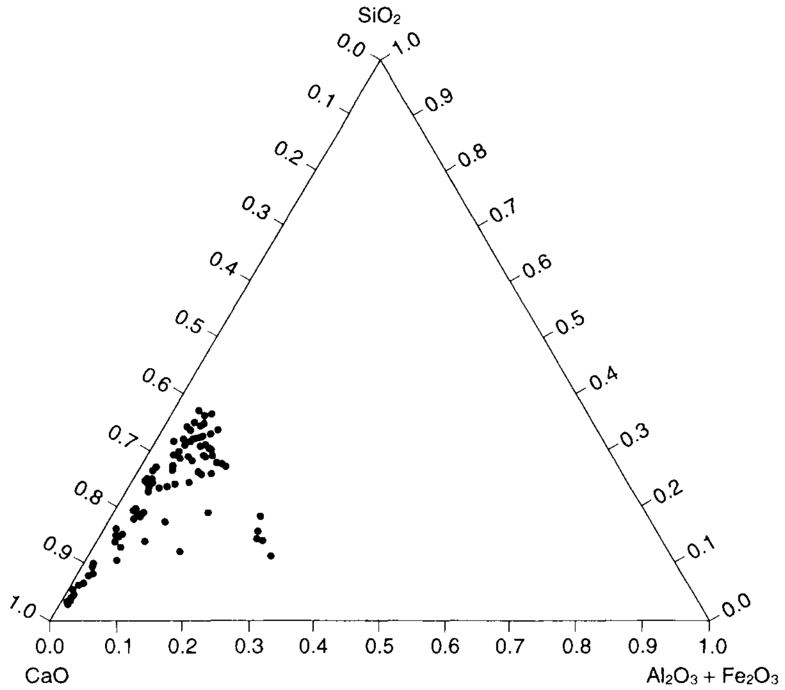

Fig. 6.15 The composition in the system CaO–SiO_2 (Al_2O_3 + Fe_2O_3) of a mature Portland cement paste as determined on a polished surface by energy-dispersive electron probe microanalysis (w/c = 0.6, 20°C).

Table 6.5 Atomic ratios of hydrated phases of a hydrated cement paste[190]

	C-S-H	CH	AFm	Hydrogarnet
Mg/Ca	0.03	0.01	0.00	0.11
Al/Ca	0.08	0.03	0.55	0.36
Si/Ca	0.60	0.04	0.04	0.32
S/Ca	0.03	0.004	0.24	0.04
Fe/Ca	0.02	0.01	0.00	0.26
(Al + Fe)/Ca	0.11	0.04	0.55	0.63
Ca/Si	1.67			

6.6.4 PORE STRUCTURE

A hardened Portland cement paste is a porous material with an open, continuous pore system. In water-saturated pastes the volume of the pores is identical with the volume of 'free' water and depends also on how this term is defined. Generally, the porosity increases with increasing initial water/cement ratio and declines with progressing hydration, as an increasing fraction of the 'total' water becomes 'bound' within the formed phases. Table 6.6 shows the porosities of mature cement pastes made with different water/cement ratios as determined by different procedures. Note that the filling of the pore system with both

Table 6.6 Porosity of Portland cement pastes hydrated for 2 years at 20°C as determined by different methods[84]

w/c	P_1	P_2	P_3	P_4	P_5
0.30	0.142	0.098	–	0.100	0.102
0.50	0.299	0.204	0.195	0.226	0.178
0.70	0.417	0.350	0.341	0.387	0.144
1.00	0.555	0.473	–	0.503	0.140

P_1 = Volume of empty pores after removal of 'free' water by D-drying.
P_2 = Volume of empty pores after removal of 'free' water by extraction with acetone and ethyl ether.
P_3 = Volume of pores determined by H_2O–D_2O exchange.
P_4 = Porosity as determined by Hg porosimetry (P_{max} = 2000 bar).
P_5 = Porosity as determined by N_2 adsorption on D-dried samples.

Hg and N_2 is incomplete and in the case of N_2 adsorption does not increase with increasing water/cement ratio of the paste.

The pore system includes pores with hydraulic radii (defined as the ratio of the volume to the surface area of a pore fraction) between <1 and 1000 nm. The maximum on the pore size distribution curve, as determined by Hg porosimetry, shifts to higher values with increasing water/cement ratio and to lower values with progressing hydration. Pores with smaller radii, amounting in fully hydrated pastes to about 0.2–0.3 ml/g of cement, are believed to be an integral part of the hydrated material and are called 'gel pores'. Pores with greater radii, whose volume increases with increasing water/cement ratio and overall porosity are called 'capillary pores'. Such differentiation is, however, rather arbitrary, since there is no distinct division between the two categories of pore.

Indicators of the fineness of the pore system are the specific surface area of the material and the hydraulic radius of the pore system. Unfortunately, however, values of the specific surface area obtained by different methods vary greatly and depend also on sample preparation (Table 6.7). If the BET method is employed, the results obtained may also

Table 6.7 Specific surface area of Portland cement pastes (m^2/g) as determined by different methods on D-dried samples hardened for 2 years at 20°C[85]

w/c	S_1	S_2	S_3	S_4
0.30	105	4.4	5.8	5.4
0.50	109	9.5	18.9	20.0
0.70	113	18.8	21.7	27.4
1.00	114	–	23.5	33.4

S_1 = Specific surface area as determined by the BET method from water vapour isotherms (293 K).
S_2 = Specific surface area as determined by the BET method from N_2 adsorption isotherms (77 K).
S_3 = Specific surface area calculated from the pore size distribution determined from N_2 adsorption isotherms (77 K), assuming a cylindrical cross-section of the pores.
S_4 = Specific surface area calculated from mercury intrusion porosimetry data assuming a cylindrical cross-section of the pores.

vary for different adsorbates. In particular, data obtained by adsorption of N_2 or other non-polar sorbates are significantly lower than those found if water vapour is employed in the experiment. The origin of these differences is not obvious and has been the subject of discussion.

The BET_{H_2O} surface area seems to be an integral characteristic of the formed C-S-H phase. Its value increases proportionally with increasing degree of hydration and is barely dependent on the water/cement ratio and thus overall porosity. The possibility exists, however, that a fraction of the adsorbed water enters vacant interlayer spaces, thus yielding erroneously high surface area values.

Unlike the values found by water vapour adsorption, the BET specific surface area, as determined by N_2 adsorption, increases tc a certain value and declines subsequently as the hydration progresses. It also increases with increasing water/cement ratio and is distinctly affected by the way in which free water is removed from the sample. These observations may at least in part be explained by the limited accesibility of the pore system to N_2 under the experimental conditions employed.

In the determination of the specific surface area by mercury porosimetry, very fine pores, which represent a small volume fraction but accommodate a significant fraction of surface area, are excluded from the measurement.

6.6.5 CEMENT PASTE STRUCTURE IN THE VICINITY OF THE CEMENT PASTE-AGGREGATE INTERFACE

The structure of the hydrated Portland cement paste in the vicinity of rock surfaces, as it exists in hardened concrete, differs from that of the bulk material. The structure of this 'transitional zone' has been extensively studied.[218 236] Most investigators reported the presence of a thin continuous film, consisting of calcium hydroxide, adhering to the aggregate surface. It was also suggested that a layer of rod-shaped C-S-H gel particles covers the calcium hydroxide layer, producing an assemblage called 'duplex film' with an overall thickness of about 1–2 µm. In contrast, investigations performed by Scrivener and coworkers[232,233] gave no indication of the presence of a duplex film or of a continuous layer of calcium hydroxide at the rock surface. Instead it was reported that the phase which is in immediate contact with the aggregate surface most often is C-S-H.

The region of the hardened cement paste that is in the vicinity of the duplex film is more porous than the bulk material, due to the formation of a water film at the aggregate surface and a less dense packing of cement particles in its vicinity in fresh concrete mixes. This region is also enriched with 'secondary' calcium hydroxide and ettringite. The pertinent ions migrate from more distant regions of the paste towards the interface and precipitate in the transitional zone.

Based on measurements of the peak intensity ratio $I_{(001)}/I_{(101)}$, a preferential calcium hydroxide crystal orientation in the transitional zone, with the *c*-axis normal to the interface, was suggested.

It appears that a chemical reaction between the cement paste and some aggregates may take place in some instances. Thus in concrete mixes made with calcium carbonate-based aggregates a calcium carboaluminate may be formed in a reaction with C_3A.

It was also reported that, within the transitional region, cement particles may dissolve away to leave partly or completely empty hydrate shells that have been termed 'Hadley grains'.[218,219]

The thickness of the interfacial region may vary between about 30 and 60 µm.

6.7 Strength of hydrated cement

6.7.1 FACTORS DETERMINING STRENGTH

Just as in other materials, the strength of a hardened cement paste is defined as the maximum on the stress–strain curve determined by exposing a test specimen to an external, gradually increasing strain. Depending on the direction of the applied stress, one has to distinguish between compressive, tensile, flexural or torsional strengths. Other parameters, which may be determined from the strain–stress curve are the 'modulus of elasticity', defined as the ratio stress/strain, and 'work of fracture' given by the area under the stress–strain curve.

The 'strength of cement' is defined as the strength of mortar test specimens prepared, cured and tested according to a national or international testing standard, to eliminate the effect of factors other than cement quality on the obtained value. It is obvious that a particular cement may yield different 'strength' values if tested according to different testing standards.

The strength of a hardened cement paste is due to the presence of a continuous three-dimensional network of hydrate phases which can resist external stresses without being broken down.

Of the three components of the hardened paste, i.e. hydrated material, non-hydrated residual cement and pores, the first is the constituent which is mainly responsible for the attained strength. The non-hydrated material present acts as a filler and also exhibits the capacity to resist external stresses. However, at a constant porosity of the paste the strength increases with an increasing amount of hydrates being formed and a declining amount of non-hydrated material.[237]

The pores of the paste have an adverse effect on strength and above a certain porosity the strength drops to zero. Pores of different size affect the strength unequally: generally, pores with greater radii are more detrimental than very fine gel pores.[237,238]

For a given cement there is a proportionality between strength on the one hand and modulus of elasticity and hardness on the other. Thus measurements of the two latter parameters may be employed for the non-destructive determination of strength.

The following are the main factors determining the strength of hardened cement pastes.

- The nature of the binder which determines the 'intrinsic bond properties' of the hydrated material.
- The fineness of the binder, which is one of the factors that determines the kinetics of the hydration process and thus the rate of strength development. Generally the initial rate of strength development increases with increasing proportions of fine particles.
- The water/cement ratio, which determines the porosity of the hydrated cement paste. At a given degree of hydration the attained strength increases with declining water/cement ratio.
- The hydration time, as the amount of hydrated material and thus the strength increases with progressing hydration.
- The hydration temperature, which affects both the rate of hydration and the structure and thus the intrinsic bond properties of the hydrated material which is formed.

Of these, the short-term strength is determined mainly by the fineness of cement and increases with increasing amount of fine particles and increasing specific surface area (at constant water/cement ratio). In contrast, the long-term strength is only slightly dependent on the fineness of the binder and for a given water/cement ratio is determined mainly by the composition of the cement.

6.7.2 STRENGTH OF PURE CLINKER MINERALS

Figure 6.16 shows the compressive strength development of pastes made of pure C_3S, β-C_2S, C_3A and C_4AF as reported in two fairly recent papers.[145,239] Similar results were reported also by Mironou and Malining[240] and by But *et al.*[241] The obtained results may be summarised as follows:

> C_3S exhibits fairly rapid short-time strength development and subsequent gradual strength increase for at least 1 year;
> The initial strength development of C_2S is sluggish, yet the strength increases gradually for at least 1 year and reaches reasonably high final values;
> The strength of hydrated C_3A is very low even ater 1 year of hydration;
> C_4AF exhibits a rapid short-term strength development but only a very moderate strength increase, or even a moderate strength decline later on.

For a given degree of hydration the strength increases in the order $C_3A < C_4AF < C_3S < C_2S$, indicating the existing differences in the intrinsic strengths of hydrates formed in the hydration of different clinker minerals.

Finally, Table 6.8 summarises the strength properties of the individual clinker phases after 180 days of hydration. It is remarkable that the ratio of flexural to compressive strength varies greatly in different hydrated materials.

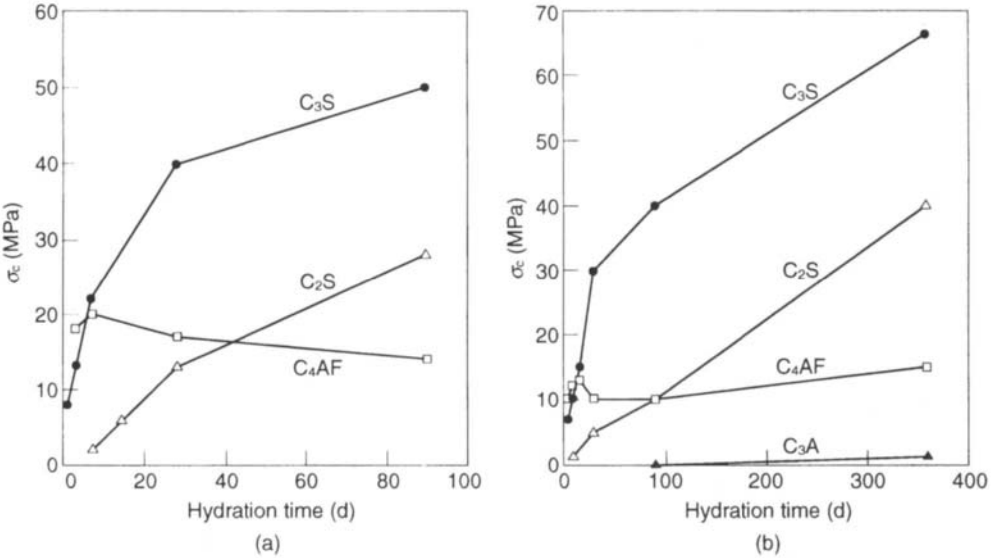

Fig. 6.16 Compressive strength development of C_3S, C_2S, C_3A and C_4AF pastes at 20°C. (a) w/s = 0.40, 3000 cm^2/g (source: Ref. 145), (b) w/s = 0.45 (source: Ref. 239).

Table 6.8 Strength properties of pastes made from pure clinker minerals (w/s = 0.40, t = 180 d)

Binder	Temperature (°C)	σ_c (MPA)[a]	σ_f (MPa)[b]	E (GPa)[c]	Products of hydration
C_3S	20	90	3.3	31	C-S-H + CH
C_3S	95	89	13.5	32	C-S-H + CH
C_2S	20	62	3.0	22	C-S-H + CH
C_3A	20	28	5.8	27	$C_3AH_6 + (C_4AH_{19})$
C_4AF + CH	20	26	6.0	21	$C_3(A,F)H_6$
C_3A (34%) + CSH_2 (66%)	20	36	6.3	2	C_6ASH_{32}(AFt)
CA	5	192	6.4	55	CAH_{10}
CA	30	29	2.1	27	$C_3AH_6 + AH_3$

[a] Compressive strength.
[b] Flexural strength.
[c] Modulus of elasticity.

6.7.3 EFFECT OF CEMENT COMPOSITION

The effect of cement composition on cement strength has been studied extensively.[148,154,161,239 250] It appears that this effect is a rather complex one and depends on a variety of factors such as the mutual ratios of clinker minerals, the amount and form of added calcium sulfate, and the presence of minor oxides. The available experimental data may be summarised as follows.

- The existing relationship between clinker phase composition and cement strength is typically not a linear one and the strength of cement cannot be considered to be just an additive function of the strengths of the participating clinker minerals.
- All clinker phases contribute to strength development; however, the magnitude of this effect differs for different clinker constituents and depends also on the hydration time.
- The effect of C_3S is most pronounced at all ages, whereas the contribution of C_2S to strength becomes significant only at longer hydration times. The strength at any hydration time increases with increasing C_3S content up to ~70 per cent and tends to decline when the content of C_3S in clinker is even higher.
- The contributions of C_3A and C_4AF to strength are relatively small but complex. With increasing content of C_3A or C_4AF the strength increases only to a certain degree and tends to decline at higher contents. There exists an obvious interaction between C_3A and C_4AF with regard to their effect on strength.

For narrow ranges of clinker composition and a constant gypsum content and fineness, the existing composition–strength relationship may be expressed with an acceptable accuracy with an equation of the type

$$\sigma = a_0 + a_1 c_1 + a_2 c_2 + a_3 c_3 + a_4 c_4 \qquad (6.7)$$

where c_1, c_2, etc. are the contents of the phases C_3S, C_2S, etc. in clinker and a_0, a_1, a_2... are constants (regression coefficients) whose magnitude depends also on the hydration time and employed testing method.

Besides the clinker phase composition, the presence of minor oxides may also affect the resultant cement strength. Among these, the effect of alkali oxides K_2O and Na_2O has been studied most extensively.[154,186,239,245,251–255] Unfortunately, even though a significant effect of alkalis on cement strength has been generally recognised, data on the character and magnitude of this effect are not uniform. Alkalis bound within the crystalline lattice of clinker minerals appear to act differently to those present in the form of soluble sulfates.

The effect of MgO on strength was found not to be very significant.[155,256,257] Free-lime CaO affects cement strength by inducing unsoundness and by reducing the amount of C_3S formed.

Calcium sulfate interground with clinker affects cement strength at all hydration times. With increasing SO_3 content the strength tends to increase up to the 'optimum gypsum' value and declines at even higher SO_3 contents. The exact amount of calcium sulfate that produces highest strength depends on the composition of the clinker, cement fineness, the form of added sulfate and hydration time.[155,161,252,258–261]

6.8 Portland cement hydration at elevated temperature

6.8.1 HYDRATION AT 0–100°C

The rate of hydration of Portland cement increases with increasing temperature, especially at lower degrees of hydration, whereas this effect becomes less pronounced as the hydration progresses.[262–264] Among the individual clinker mineral, only the hydration of C_2S was found to be accelerated significantly even months after mixing with water.[263]

With regard to the products of hydration, an amorphous C-S-H phase, together with calcium hydroxide, is formed in the hydration of C_3S and C_2S over the whole temperature range between the freezing and boiling temperatures of water. Up to about 50°C the composition of the C-S-H phase formed differs little from that formed at ambient temperature, whereas at even higher temperature its CaO/SiO ratio increases moderately and the H_2O/SiO_2 ratio declines.[262] At the same time the degree of SiO_4 polymerisation increases distinctly.[65]

With increasing temperature the amount of SO_4^{2-} bound reversibly within the C-S-H phase increases, and less calcium sulfate remains available for a reaction with C_3A and $C_2(A,F)$.[262,263,265] At the same time, the amount of AFm formed at the expense of AFt increases with increasing hydration temperature.[262,265] At temperatures above about 70°C the SO_4^{2-} concentration in the liquid phase declines to a concentration at which AFt is no longer stable and AFm is formed exclusively. At the same time the AFt phase that was formed at lower temperatures also converts to AFm. Finally, at even higher temperatures, i.e. close to 100°C, the amount of AFm, detectable by DTA or XRD declines and may even disappear completely, probably due to increasing amounts of SO_4^{2-} and Al^{3+} bound within the C-S-H phase.[262,265]

Upon subsequent curing at ambient temperature, AFt may again be formed in the hardened cement paste and its formation may or may not be associated with expansion and crack formation in the heat-cured cement paste or concrete. This process, however, progresses very slowly and it may take many months before damage to the material may be observed.[266–268]

At equal degree of hydration and water/cement ratio the porosity of the paste increases, due to a lower bound water content. At the same time the BET specific surface area, as determined both by H_2O and N_2 adsorption, declines, indicating a coarsening of the structure.[269,270] Microstructural observations also revealed the formation of a coarser and more uneven cement paste structure and the presence of 'shells' around the cement grains whose density increases with increasing temperature.[271-273]

At shorter hydration times the strength of the paste increases significantly with increasing temperature, due to the faster rate of hydration. In contrast, at longer hydration times and especially at high curing temperatures, the attained strength may lie below that of a paste hydrated at lower temperature, mainly due to a higher porosity and/or coarser pore structure.

In heat curing of concrete, the concrete mix prepared at ambient temperature is heated to obtain an accelerated hardening. Under these conditions, especially at fast heating rates and short precuring times, macrocracks may be formed within the material due to the differences which exist in the coefficients of thermal expansion of the individual concrete constituents. Especially significant is the fact that the coefficient of expansion of the pore water is about one order of magnitude higher than that of other phases. Due to these differences the thermal expansion of water may cause stresses and cracks in the hardened paste. Such cracks may lower the strength of the hardened concrete even further. Upon subsequent curing at ambient temperature, the formed cracks, especially the gaps between larger aggregate particles and hardened paste, may be filled with secondary ettringite crystals. At low temperatures the ettringite which forms may be intermixed or even replaced with thaumasite, $[Ca_3Si(OH)_6 \cdot 12H_2O]\ (SO_3)]$.

6.8.2 HYDRATION ABOVE 100°C (HIGH-PRESSURE STEAM CURING)

At temperatures above 100°C the hydration of Portland cement may take place only in an autoclave, in a saturated steam atmosphere. The hydration products formed under these conditions differ essentially from those formed at temperatures below 100°C.

In the hydration of C_3S and C_2S, in the absence of an SiO_2 source, crystalline α-dicalcium silicate hydrate, $Ca_2(HSiO_4)(OH)$, is formed instead of an amorphous C-S-H phase. C_3A and $C_2(A,F)$ yield a hydrogarnet phase. The bonding characteristics of both phases are rather unfavourable.

In the presence of finely ground quartz and/or other SiO_2 sources and at temperatures between aout 150 and 200°C, a pozzolanic reaction takes place, yielding crystalline 1.1 nm tobermorite, $[Ca_4(Si_5O_{16}H_2]Ca \cdot 4H_2O\ (C_5S_5H_5)$, as the main product of reaction. At even higher temperature, xonolite (C_6S_6H) may also be formed. Intermediate products formed under these conditions include C-S-H(I), C-S-H(II) and α-C_2SH. The Al^{3+} which is present may substitute for Si^{4+} in the crystalline lattice of tobermorite with a simultaneous increase of Ca^{2+} in the interlayer region. The formation of both 1.1 nm tobermorite and xonolite is associated with a favourable development of strength of the autoclaved material.

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7

Resistance of Concrete to Destructive Agencies

Margi Eglinton

7.1 Introduction

The subject of this chapter is the behaviour of concrete in use and the various conditions that may be encountered in practice which have a deleterious effect on it. Concrete is a material of widespread utility, adaptable to many purposes, but there are situations in which it may be used where precautions must be taken to provide protection against potentially destructive agencies, which may be physical in action, for example frost, or chemical. Damaging chemical substances are numerous, and include those which occur naturally in soils and waters, and those which are of industrial origin. Briefly, it is the weathering of concrete, interpreting weathering in a wide sense to include both natural agencies and artificial conditions, which will be considered here.

The usefulness and versatility of concrete as a construction material are due in great part to the many field and laboratory investigations made over the past century into its performance when exposed to aggressive conditions. The results of the studies have led to the development of cements having increased chemical resistance and have also shown that the quality of the concrete is of primary importance in resisting damaging chemical or physical actions. Quality is not necessarily related to the mechanical strength of the material, and it does not follow that, because a concrete has ample strength to fulfil the purpose for which it was designed, it will resist attack and disintegration in any environment in which it is placed. There are conditions under which a strong concrete will suffer attack, while a weaker one, made from materials which are chemically more resistant to the destructive elements concerned will prove more durable. Nevertheless it is true that when using any given cement, the less permeable the concrete produced, the greater will be its resistance to attack. Since many factors which influence favourably the density and water tightness of a concrete also have a beneficial effect on the strength, it is also generally true that the stronger a concrete made from any one cement, the more durable it will prove. A dense Portland cement concrete, for instance, may be almost immune from attack where one of poorer quality suffers disintegration and failure within the course of a few years. There are exceptions, as in the case of air-entrained concrete. In considering in this chapter the extent to which concrete may be expected to give durable service under any specified conditions, it is emphasised that the standard of reference is a good concrete.

7.2 Action of frost

The resistance of concrete to frost is of considerable importance in northern Europe and in Canada and northern parts of the USA, where much damage has resulted from its action. Though less serious in the more temperate climate of Britain, it has led to severe failures of kerbstones and other exposed features, and is often the final cause of destruction of concrete already weakened from other causes. Water is essential for frost damage to occur; dry concrete is unaffected. Water expands ~9 per cent in volume during freezing, and when it is trapped in cavities the large pressures which develop may exceed the strain tolerance of the concrete. In a wet concrete the water enclosed in the pores of the material tends on freezing to force the particles of mortar apart or to set up severe initial stresses. The effect is intensified by repetitions of the processes of freezing and thawing. Minute cracks first develop and become filled with water which on subsequent freezing produces further cracking and fissuring. The severest conditions for frost action arise when concrete has more than one face exposed to the weather, and is in such a position that it remains wet for long periods. Examples are to be found in road kerbs, parapets and concrete members in hydraulic structures just above water level. The first appearance of frost action is usually a flaking of the surface which works progressively further into the mass, although in cases of very poor concrete deep fissures may also appear. The requirements for normal concrete to be frost resistant are low permeability and absorption. In climates or situations where there is the likelihood that concrete will be exposed to frequent severe frosts, any initial cracks due to frost action may, with repeated attack, extend quite deeply into the concrete and in these situations care should be taken to ensure that any reinforcement is protected from the risk of corrosion by the provision of an adequate depth of cover. It is also necessary that local weaknesses, such as honeycombed patches, segregated layers, bands of laitance and faulty joints should be avoided, since attack usually starts at points where the concrete is weak or porous.

7.2.1 CAUSES OF FROST DAMAGE

There are various explanations of frost damage. In earlier theories the damage was attributed directly to the empty space available being insufficient to accommodate the additional solid volume produced when the water in the concrete freezes. Damage is related to the degree of saturation, as discussed later. The frost heave theory[1] ascribes the production of pressure to the growth of ice lenses parallel to the surface of the concrete due to the migration of water from capillaries where the freezing point is depressed. This is similar to the theory of frost heaving in soils. In another theory[2,3] the action is ascribed to the generation of water pressure within the capillary cavities as ice crystals grow. This hydraulic pressure can only be released by flow of water into other spaces since the ice seals the exterior, and the pressure required to force water through the fine capillaries rises as the length of the flow path increases. In these theories the permeability, rate of absorption and degree of saturation of the concrete are important and interrelated factors. For example, a high permeability would allow easier flow of water and, since it will arise from larger capillaries, more room for ice growth, but such a concrete would readily become highly saturated. In practice, frost resistance is high for dense impermeable concretes and for open-textured or very porous concretes, such as no-fines and some lightweight concretes, and is lower for the more permeable 'dense' concretes. In air-entrained concrete the function of the voids, according to Powers,[2,3] is to limit the hydraulic pressure by providing release spaces, and to limit the time during which capillary ice can grow by diffusion of water, for this in turn is dependent on the existence of differential pressure.

7.2.2 FACTORS AFFECTING FROST RESISTANCE

The resistance of concrete to frost depends on the quality of the cement mortar and, to some extent, of the aggregate. Fairly wide variations in the quality of the coarse aggregate can be tolerated, for there is no close correlation between the durability of aggregates and the concrete made from them, but argillaceous or soft, porous limestones, gravels containing too much weak material, such as particles of porous chert, shales and friable sandstones are susceptible to breakdown by frost action.

There is no close relation between the total porosity or absorption of aggregates and their frost resistance, for it is the character of the pores which is of predominant importance. The larger pores are not necessarily detrimental, and it is the finer pores, for example, $<5\,\mu m$ in diameter which, if present in abundance, have most influence in reducing the frost resistance of concrete, since they tend to remain full of water. This leads to an expectation that aggregates with a large internal, but accessible surface area should tend to be less frost resistant, and there is some evidence to support this.[4]

7.2.3 ASSESSMENT OF FROST RESISTANCE

The frost resistance of aggregates may be assessed from freezing and thawing tests on concrete made from them, but a sodium or magnesium sulfate crystallisation test[5] has also been used as a simulated frost test, although it has not proved a reliable index of behaviour of aggregates in concrete. It has been suggested that it should be used only as an acceptance test and that failures under it should be taken as no more than an indication that further investigations by freezing tests on concrete or a study of performance in actual use is needed. Unfortunately, the test has not proved reliable even for this limited purpose, since some aggregates that pass it can fail under frost. A comparable test method is given in BS 1438.[6] This stipulates the use of sodium sulfate and 20 cycles of immersion and drying instead of the five cycles adopted in the ASTM method. A direct test[7] for frost susceptibility of aggregates has been developed in which measurements are made of the heave of cylindrical specimens of graded and compacted aggregates. The cylinders are placed in a self-refrigerated unit so that the bases of the specimen are in contact through a porous plate with water at 4°C, while the air temperature above is maintained at -17°C.

The effect of the type of cement on frost resistance is a matter of controversy. Conflicting claims have been made of the higher resistance of Portland blastfurnace cements compared to ordinary Portland cement, and of the influence of various constituents of Portland cements, for example tricalcium aluminate or alkalis. It can only be concluded, that, apart from air-entrainment, the cement itself is a minor factor in determining the frost resistance of concrete. With sound aggregates, failure under frost occurs by the weakening and breakdown of the cement mortar which binds the coarse aggregate together. It is the quality of the mortar, therefore, which determines the resistance of the concrete, and since the type of cement used has little effect, the resistance depends on the cement content, water content, air content and the grading of the mix.

Much effort has been directed to predicting the behaviour of concrete placed in situations where it will be exposed to freezing conditions. Actual freezing and thawing of specimens would appear to offer a direct answer, while an empirical approach to frost resistance in relation to the absorption of the concrete has attracted attention. There are, however, disadvantages in both methods.

In principle, freezing and thawing tests are simple; specimens are prepared and cured under some specified conditions, then subjected to cycles of freezing and thawing, and the effect produced evaluated by visual inspection or some physical measurement. In practice, minor variations in test procedures have such a disproportionate effect that it is not possible to attach an absolute meaning to the results, and the most that can be achieved is generally no more than a broad indication of the relative frost resistance of different materials when tested under identical conditions. Even so, no direct relationship can be expected between any test results and durability in service since the severity of exposure to frost can vary widely.

In tests, freezing is carried out in air or in water, the latter resulting in more rapid deterioration. The faster the rate of freezing, that is, the rate of temperature drop of the specimens below 0°C, the more rapid is the rate of deterioration, but the degree of discrimination between concretes of differing frost resistance also decreases. In actual practice, the temperature of exposed materials under freezing conditions does not normally drop at a rate greater than about 1.5°C/h in England at low altitudes and 5°C/h at high altitudes in colder climates. Thawing is generally carried out in water at temperatures varying from 5 to 25°C. The degree of saturation of the concrete at the commencement of the freezing and thawing cycles greatly influences the rate of failure, and even the best concretes fail rapidly if fully saturated by immersion in water under vacuum. With increasing times of curing in water before commencement of the tests, the frost resistance usually rises to a maximum at between 1 and many months and then decreases again. The rise is attributed to the development of strength, and the subsequent fall to the increasing extent of saturation of the concrete. Concretes which are allowed to dry before commencing the frost resistance tests show an enhanced resistance because of the slowness with which the pores refill with water, but the onset of damage is only postponed, not prevented.

Two ASTM methods[8] have been developed to standardise test procedures. The C 290-67 method involves freezing and thawing in water, and the C 291-67 method freezing in air and thawing in water. The kind of deterioration observed in frost tests varies somewhat with the type of concrete and the method of freezing. Specimens frozen in water tend to show much more surface crumbling and crazing than those frozen in air, while the latter exhibit more general cracking and disintegration. Pitting or spalling may occur in either case from unsound particles of aggregate near the surface. Estimation of the progress of deterioration is most commonly made by non-destructive tests on replicate specimens, for example, loss in weight, expansion, change in modulus of elasticity (static or more usually dynamic) and ultrasonic wave velocity. Loss in weight is not a good criterion for specimens frozen in air, but is used in conjunction with water freezing, although in the earlier stages of deterioration it may show little relation to expansion or changes in the value of E. The dynamic modulus of elasticity, measured from the resonant vibration frequency, is the most common method and is the one adopted in the ASTM tests. The reduction in E is fairly well related to the fall in transverse strength; the latter is more sensitive to the deterioration occurring in frost tests than is compressive strength. Since no single method of non-destructive testing is an entirely reliable index to the progress of deterioration, it is advantageous to use more than one and at the end of the programme to carry out a strength test.

7.2.4 *MEASUREMENT OF ABSORPTION*

The assessment of frost resistance by measurement of the absorption of the concrete offers the advantages of quick results without the need for elaborate equipment. It is based on the premise that since water expands by about one-tenth of its volume in freezing, damage by frost should not occur until ~90 per cent of the pore space in a material is filled with water. Difficulties arise, however, in the determination of absorption. The ratio of water absorbed by a material to its total pore space, as determined from measurements of true and apparent density, has often been regarded as an index of resistance and called the saturation coefficient. A different ratio, that of the absorption after 48 h total immersion is that obtained after 48 h immersion followed by 5 h boiling, has also been used. However, tests on different concretes have failed to show any definite correlation between frost resistance and either of these ratios, but some relation has been found with the capillary absorption of air-dry concretes placed on wet sand. In tests on concrete kerbs, the amount of water taken up in 10 min immersion in water, after drying at 100°C, has been found to be a more reliable guide than the 24 h absorption.

One of the main difficulties in attempting to relate frost resistance to the absorption, or the degree of saturation, lies in the definition of these terms. Porosity arises from the following.

1. Voids in the aggregate particles.
2. Spaces between the aggregate particles and the cement paste.
3. Capillaries in the set cement gel. These are the spaces originally occupied by water and which are too fine to have allowed hydration products to form and fill them. The gel capillaries vary in size from several tens of nanometres up to 1 μm.
4. Gel pores, which are ultrafine slits, less than 2μm, and smaller than the solid particles.
5. Air bubbles entrapped in the concrete during making.

These are not all of equal significance. Thus spaces under aggregate particles may not, once the water originally filling them has dried out, be easily filled again by simple contact with water, although if subjected to one-sided water pressure they may fill readily and are regarded as one cause of low frost resistance of concrete in hydraulic structures. Very small bubbles, accidentally or deliberately entrained in the concrete, are very difficult to fill with water. The porosity of the cement paste itself arises from the excess water present in the mix and the contraction of the system cement–water during hydration, the capillaries becoming partially emptied during hydration unless water can flow in to fill them. This self-dessication of the paste is probably an important factor in contributing to frost resistance. The water in the capillaries can, however, come and go in response to changes in external conditions, and the amount that can do so is an index of the porosity of the hardened paste.

7.2.5 *EVAPORABLE AND NON-EVAPORABLE WATER*

The water present in set cement has been classed[9] as non-evaporable and evaporable. The former is considered to represent the chemically combined water and is proportional to the extent of hydration of the cement, while the latter includes not only water in pores which freezes at 0°C and water in capillaries which freezes at lower temperatures, depending on the diameter of the capillaries, but also water held by surface forces in the gel, as in (4) above, and which for practical purposes can be regarded as non-freezable. The amount of this water in the gel is related by a roughly constant factor to the extent of hydration of the cement and thus to the non-evaporable water.

For practical purposes, freezable water in the set cement paste can be identified with the capillary water and most of this is frozen by −12°C, although supercooling to at least this temperature can occur if there is no seeding from external ice crystals. Powers and Bromyard[10] obtained an equation:

$$W_f = W_t - aW_n \tag{7.1}$$

relating the weight of water (W_f) in a saturated cement paste freezable at a given temperature to the total water content (W_t) and the non-evaporable water (W_n). The constant a varies with the temperature of freezing.

Since the capillary pores represent spaces originally filled by water added to the mix, it follows that a reduction in the amount of freezing water will result in fewer capillaries and less freezable water can be held in the set cement paste. It is inherent in the equation, therefore, that below a certain initial water/cement ratio there will be no water freezable at any given temperature in a set cement paste unless additional water is subsequently gained from external sources. For an average set cement at an age of 90 days and at a freezing temperature of −15°C, this water/cement ratio was found to be ~0.30–0.35. Water in excess of this ratio, whether introduced initially or gaining access later, will be freezable at −15°C. In practice it is found that the frost resistance of non-air-entrained concrete with a water/cement ratio of 0.50–0.55 is usually high, but it decreases progressively with further increases in this ratio. Higher values are acceptable for many conditions of exposure, while for severe conditions lower values may be required.

7.2.6 AIR ENTRAINMENT

Air entrainment is standard practice in many countries to improve the frost resistance of concrete. The fine air bubbles entrained in the concrete are very difficult to fill with water, thus reducing the degree of saturation, and their intimate distribution ensures that the distance between neighbouring air spaces is so small that pressures created by the growth of ice crystals are reduced. It is usual to aim at an air content of 5–6 per cent by volume in the concrete. For good frost resistance the distance between individual air bubbles should not exceed about 0.25 mm. Occasional large air voids do not have the same beneficial effect of small, closely spaced bubbles, even when the total void space is the same.

Air entrainment has proved of particular benefit in giving protection against the deterioration of concrete road surfaces arising from the use of calcium chloride or sodium chloride to remove ice in winter. Trouble may still be experienced on general road surfaces under very severe climatic conditions and on concrete bridge decks, where deterioration may be accentuated by corrosion of the reinforcement owing to the penetration of chlorides into the steel. The problem has been less widespread in Britain than in northern America where more severe winters are experienced, but some serious trouble has occurred.

7.2.7 ACTION OF DE-ICING SALTS

The action of de-icing salts on concrete surfaces is not fully understood. It is known that concrete frozen in solutions of calcium chloride suffers more rapid deterioration than when frozen in water, and that a 3.5 per cent solution is more destructive than weaker or stronger solutions. Other solutions which depress the freezing point of water, for example sodium chloride, ethyl alcohol and urea, are active in the same way. This indicates that the action is primarily a physical, not a chemical one, and it has been suggested[11] that the damage to concrete is caused by the absorption of heat during the melting process, with consequent rapid cooling of the surface layers of the concrete. The resulting sharp change in temperature is thought to produce stresses in the frozen surface layers of the fine mortar and that this causes deterioration. Unfrozen water in a deeper zone parallel to the surface will also, as a result of the abstraction of heat, be caused to freeze quickly, increasing the risk of spalling of the overlying concrete.

In an alternative theory[12] the damage is attributed to osmotic pressure effects caused by the build-up of the de-icing agent in the capillaries of the cement paste to a greater concentration than in the gel pores, resulting in water being drawn from the gel pores into the capillary spaces. The de-icing agent is considered to have two opposite effects. By reducing the amount of ice that can form in the capillaries of the cement paste at a given temperature, it tends to reduce the pressure, either hydraulic or osmotic, generated on freezing. On the other hand, it increases the osmotic pressure arising from the differences in salt concentration between capillaries and gel pores. These opposite effects are used to explain the observation that the maximum destructive effect occurs at an intermediate salt concentration.

7.3 Thermal expansion and the durability of concrete

Differential thermal movements in concrete, either between the aggregate and the cement paste, or between different aggregates, has been suggested as one factor which might contribute to deterioration. The coefficient of thermal expansion of natural aggregates varies considerably. The normal range is $1\text{–}4 \times 10^{-6}$/°C, although individual aggregates may fall outside, and extreme values are 0.3×10^{-6} and 5×10^{-6}/°C. The thermal expansion of cement pastes is about $5\text{–}6 \times 10^{-6}$/°C and it is rare for aggregates to have expansions greater than this. Some aggregates, however, have expansions as low as $0.5\text{–}1 \times 10^{-6}$/°C and these may have more influence on the durability of a concrete. Crystals of orthoclase and microcline felspars, for example, have a very low, unidirectional thermal expansion. Coarse calcite crystals, of ~8–10 mm size, show anisotropic properties and have thermal expansions seven times greater in one direction than at right angles to it, and this differential expansion is a source of internal stress. Coarse-grained limestones have been found to show a non-linear behaviour, expanding with rise in temperature at a very low rate below 20°C and at a much higher rate above. In contrast, fine- and medium-grain limestones show intermediate rates of expansion, almost linear with temperature rise.

The effect of combining coarse and fine aggregates differing in thermal expansion in a concrete, thus setting up a differential movement between mortar and coarse aggregate, has been suggested as a possible cause of expansion, and while there is evidence that this contributes to deterioration, most failures of concrete arise from a combination of causes and it is questionable whether this individual factor is normally significant.

7.4 Resistance to fire

Concrete, although not a refractory material, is non-combustible and has good fire-resistant properties. The term fire-resistant should not, by standard definition, be applied to a material, but only to structural elements of which it forms a part. Accordingly, it is incorrect to apply the term to concrete alone, and it should be used to refer specifically to, for instance, a concrete wall, a reinforced concrete column, or a steel joist encased in concrete.

The contribution of the components to the fire resistance of a structure are detailed in BS 476.[13] It is nevertheless convenient to refer to fire resistance in describing the relative value of different types of concrete in producing structural units of good resistant properties, and that approach is adopted here.

The fire resistance of structural elements is measured by the length of time for which they continue to perform their normal functions as partition walls, load-bearing units, etc., when exposed to fire. The fire resistance of a concrete structure is determined by three main factors: (1) the capacity of the concrete itself to withstand heat and the subsequent action of water without losing strength unduly and without cracking or spalling; (2) the conductivity of the concrete to heat and (3) the heat capacity of the concrete. These factors together determine the extent to which the effects of high temperatures, persisting only for a limited time, will be restricted to the surface of the concrete, or be transmitted to the interior of the mass and to embedded reinforcement or encased steelwork. When the steel becomes exposed to high temperatures, excessive expansion and loss of strength occur, and the steel tends to become warped and twisted out of shape. The fire resistance of a reinforced concrete structure is thus dependent not only on the type of concrete, but also on the depth of cover to the reinforcement and on the presence of surface coatings, such as plaster.

On heating, a neat Portland cement paste first expands owing to the normal thermal expansion; this expansion is opposed, however, by a contradiction due to the shrinkage of the material as water is driven off from it. The contraction due to drying eventually becomes much larger than the normal thermal expansion and the material then begins to shrink. The temperature at which the maximum expansion is reached varies with the size of the specimen and the conditions of heating. It may be as high as 300°C for air-dry specimens under conditions of fairly rapid heating. At higher temperatures the neat cement steadily shrinks, the contraction from the original dimensions amounting ultimately to 0.5 per cent or more. During this process severe cracking occurs.

Hydrated Portland cement contains a considerable proportion of free calcium hydroxide which loses its water above 400–500°C, leaving calcium oxide (quick lime). If this calcium oxide becomes wetted after cooling, or is exposed to moist air, it rehydrates to calcium hydroxide accompanied by an expansion in volume which may disrupt a concrete which has withstood a fire without disintegration. Portland blastfurnace cement has been found to be more resistant to an action of this type. This may probably be attributed to the lower proportion of free calcium hydroxide present in such cements after setting, and also to combination of free lime with granulated slag during exposure to high temperature.

In mortars and concretes the aggregates undergo progressive expansion on heating while the set cement, beyond the point of maximum expansion, shrinks. The two opposing actions progressively weaken and crack the concrete. The various aggregates used in concrete differ considerably in their behaviour on heating. Quartz, the principal mineral constituent of sands and most gravels and a major constituent of the acid igneous rocks, expands steadily up to 573°C. At this temperature it undergoes a sudden expansion of 0.85 per cent, caused by the transformation of 'low' or α-quartz to 'high' or β-quartz. This expansion has a disruptive action on any concrete in which quartz forms an aggregate. Concretes with aggregates of siliceous gravels, flint and granite spall when exposed to fire and are among the least resistant concrete materials. Sandstones, although containing quartz, do not cause a concrete to spall so badly. The intergranular natural cementing material in sandstones shrinks on heating, and so to some extent tends to counteract the expansion of the quartz grains. The loss in strength of sandstone concretes on exposure to fire is, however, often high and sandstones do not form good fire-resistant aggregates.

The best fire-resistant aggregates among the igneous rocks are the very finely crystalline, or non-crystalline, basic rocks such as dolerites and basalts. Limestones expand steadily until a temperature of about 900°C is reached and then begin to contract owing to decomposition with liberation of carbon dioxide. It has often been considered, on account of this decomposition, that limestones are of little value for making concrete resistant to fire. Actually, however, this decomposition does not occur until a temperature is reached considerably above that at which quartz aggregates spall. In fire tests it has been found that dense limestones form good fire-resistant aggregates, and that, except under prolonged exposure to high temperatures, only the surface material becomes decomposed. The most resistant of all concretes to fire are probably those made with a blastfurnace slag aggregate. This has been shown by both small-scale laboratory experiments and large-scale tests on structures. Broken brick also forms a good aggregate in respect of fire resistance provided it is free from quartz. Lightweight aggregates, such as pumice, foamed slag and expanded clay products, have in themselves a high resistance to fire, and concretes made from them have a low heat conductivity. Their heat capacity, on the other hand, is less than that of heavier concretes.

Long series of tests on the fire resistance of structures have been carried out in Britain and USA. Even concretes which are considered the most fire resistant have been found in the tests to fail if exposed for a considerable time to a temperature exceeding 900°C, while serious reductions in strength occur when a temperature above 600°C is attained. If held continuously exposed to heat, any cement product will suffer considerable loss in strength and undergo gradual breakdown at temperatures lower than 600°C. Up to 300°C the loss in strength is small, but at 500°C it can be 50 per cent or more.

7.5 Electrolysis of concrete

Deterioration arising from the electrolysis of concrete[14,15] caused by stray leakage currents is comparatively rare. It is only in reinforced concrete that damage may occur and then only with direct, not alternating current. When the reinforcement acts as the anode it can be oxidised and the corrosion products cause expansion and cracking. As a cathode, there is no action on the steel, but the alkalis from the cement tend to concentrate there and under severe conditions the concentration of alkali hydroxides can become high enough to attack the set cement and soften it to such a degree that the bond between concrete and steel is almost destroyed. Little or no action occurs in dry concrete and in wet concrete potential gradients as high as 200 V/m are needed to cause appreciable anode corrosion, but softening of the concrete at the cathode can occur at lower gradients. The resistivity of moist concrete is of the order of $10^4\,\Omega$cm and that of oven-dry concrete $10^{11}\,\Omega$cm.[16] The risk of corrosion is much more serious if the concrete contains soluble salts, particularly chlorides, as in concrete exposed to sea water. The resistance of the concrete is reduced and the efficiency of the corrosion process at the anode greatly increased. This is the reason why reinforced concrete jetties in sea water have been the most susceptible to damage by electrolysis.

7.6 Action of sulfates

Sulfates of various bases occur naturally and are also extensively used in industry. Their solutions enter into chemical reactions with compounds present in set cements, causing expansion, cracking or spalling of the concrete or softening and disintegration. Ordinary

Portland cement is the most vulnerable to attack, but while sulfate-resisting Portland, pozzolanic and Portland blastfurnace cements have greater resistance, they are not immune to attack in all situations and at all concentrations of sulfate solutions. The action of sulfates and the protection of concrete against their damaging effects are therefore matters of considerable concern, and have been the subject of extensive investigation.

Calcium, magnesium, sodium and potassium sulfates are found throughout the world in clays and other soils, frequently in considerable quantities. In the UK they occur in parts of the London, Gault, Weald, Lias, Oxford and Kimmeridge formations[17] and in parts of the Keuper Marl, where gypsum is the predominant sulfate. The alkali soils which extend across large areas in North America often contain several per cent of these sulphates and attracted attention early in the twentieth century when trouble was experienced with concrete in sewers, drainage pipes, culverts and foundations. During the nineteenth century, work had begun in France into the cause of the deterioration of concrete placed in gypsiferous soils. The investigations gained impetus as a result of a number of failures of concrete in railway and other works and resulted in the development of high-alumina cement. Similarly, the development of sulfate-resisting Portland cement was due in some part to work on the causes of deterioration of concrete in the sulfate-bearing soils and ground waters of America.

The distribution of sulfates in clays is often very irregular, and concentrations may vary between points only a few metres apart. In clay soils gypsum frequently occurs as discrete crystals or clusters of crystals. It may also occur massively in bands, as in the Keuper Marl. There can also be a considerable variation in sulfate concentration with depth, depending on climatic conditions. In temperate zones, where rainfall exceeds evaporation, sulfates are mainly absent from the top 1 m of soil as a consequence of gradual leaching by rain water. In drier regions, where rates of evaporation are high, as in the prairies of Canada, there may be a greater concentration of sulfates near the surface. In hot, arid regions, where the excess of evaporation over rainfall leads to continual upward movement, salts carried in solution crystallise at the surface in deposits, which can be of considerable thickness. This is very marked where there is a high and saline water table, as in coastal areas.

The concentration of sulfates in ground water also varies widely. The sulfate content of the soil and the movement of the water are important, but the chief factor that determines how much sulfate may be present is the solubility of the sulfate salt. Calcium sulfate is of limited solubility in water (2 g/L) and this sets a limit of 1.2 g/L SO_3 to which it can give rise in ground water. A value in excess of this figure indicates the presence of the more soluble sulfates of magnesium, sodium or potassium. In Britain the amount of sulfate in ground water rarely exceeds 5 g/L, but high concentrations of 10 g/L or more are not uncommon in other parts of the world, as in the alkali soils of North America and in arid areas elsewhere.

7.6.1 ACTION OF CALCIUM SULFATE

All soluble sulfates have a deleterious action on Portland cement concrete, but the mechanism and severity of attack vary according to the base present. Thus while calcium sulfate reacts only with the hydrated calcium aluminates to form calcium sulfoaluminate, sodium sulfate reacts with the free calcium hydroxide in the set cement to form calcium sulfate, which then reacts with the aluminates. The reactions can be formulated as:

$$Ca(OH)_2 + Na_2SO_4{\cdot}10H_2O = CaSO_4{\cdot}2H_2O + 2NaOH + 8H_2O \qquad (7.2)$$

$$\begin{aligned}4CaO{\cdot}Al_2O_3{\cdot}19H_2O &+ 3(CaSO_4{\cdot}2H_2O) + 16H_2O\\ &= 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O + Ca(OH)_2 \qquad (7.3)\end{aligned}$$

With calcium sulfate only reaction (7.3) takes place.

The extent to which reaction (7.2) proceeds depends on the conditions. In flowing waters, with a constant supply of sodium sulfate and removal of the sodium hydroxide, it will eventually proceed to completion. If, however, the sodium hydroxide accumulates, an equilibrium is reached depending on the sodium sulfate concentration. With 5 per cent of sodium sulfate only about one-third of the sulfur trioxide content is deposited as calcium sulfate when equilibrium is reached, and with 2 per cent sodium sulfate only about one-fifth. The calcum hydroxide required in reaction (7.2) is liberated in the setting of the tri- and dicalcium silicates of the cement, but sodium sulfate does not attack the hydrated silicates themselves to any appreciable extent, since these are more insoluble than the calcium sulfate and alkali silicates which would result. This is demonstrated when sodium sulfate solution reacts with the pure minerals. Crystals of gypsum are soon formed from tricalcium silicate, but with dicalcium silicate the reaction proceeds much more slowly, corresponding to the very slow rate at which this compound splits off calcium hydroxide in water.

7.6.2 ACTION OF MAGNESIUM SULFATE

Magnesium sulfate has a more far-reaching action than other sulfates and decomposes the hydrated calcium silicates in addition to reacting with the aluminates and calcium hydroxide. If tri- or dicalcium silicate is placed in magnesium sulfate solution, formation of gypsum crystals occurs rapidly. The hydrated calcium silicates react in the following general manner:

$$3CaO{\cdot}2SiO_{2\,aq} + MgSO_4{\cdot}7H_2O = 3CaSO_4{\cdot}2H_2O + 3Mg(OH)_2 + 2SiO_{2\,aq} \qquad (7.4)$$

The reason why this reaction proceeds to completion, while with sodium sulfate it does not occur, is to be found in the low solubility of magnesium hydroxide and the resulting low pH value of its saturated solution. It is soluble only to the extent of ~0.01 g/L and its saturated solution has a pH value of about 10.5. This is lower than the pH required to stabilise the hydrated calcium silicates. The silicates liberate lime to the solution to establish their equilibrium pH, but when magnesium sulfate is present the lime reacts with it, forming magnesium hydroxide and reducing the pH value to 10.5 again; more lime passes into solution to re-establish the pH, and so the reaction proceeds. The calcium sulfate accumulates in solution until it becomes saturated and crystals of gypsum separate out.

Equation (7.4) is not the end of the reaction since the magnesium hydroxide and the silica gel can react very slowly to form a hydrated magnesium silicate. This was confirmed[18,19] by the finding in a deteriorated sea wall of a white material which gave an X-ray pattern not unlike that of $4CaO{\cdot}Al_2O_3{\cdot}12H_2O$, but which proved to have a composition approximating to $4MgO{\cdot}SiO_2{\cdot}8.5H_2O$. This hydrated magnesium silicate appears to have no binding power, in contrast to silica gel, and its formation therefore represents a final stage in the deterioration of concrete attacked by magnesium sulfate solutions, although in practice it may only be reached after long periods.

The action of magnesium sulfate on the hydrated calcium aluminates is initially similar to that of the other sulfates, and calcium sulfoaluminate is first formed together with magnesium hydroxide. Calcium sulfoaluminate is itself, however, unstable in the presence of magnesium sulfate solution, and by the continued action of this salt is ultimately decomposed again to form gypsum, hydrated alumina and magnesium hydroxide. The action must also be attributed to the pH value of the saturated magnesium hydroxide solution being below that required to stabilise calcium sulfoaluminate. This can be demonstrated if calcium sulfoaluminate is placed in a magnesium sulfate solution, when crystals of gypsum gradually form. The external skin of cement mortars which have been exposed for a fairly long period to the action of magnesium sulfate sometimes appears to be quite free from calcium sulfoaluminate crystals, while gypsum is present in large amounts. In the interior of the mortar, where access of the solution has been much slower, both calcium sulfoaluminate and gypsum are found. Attack by magnesium sulfate also results in a hard, dense skin forming on the concrete owing to the deposition of magnesium hydroxide in the pores, and this tends to hinder penetration of the solution. A mortar attacked by calcium or sodium sulfate ultimately becomes soft and incoherent, but with magnesium sulfate the disrupted mass more often consists of hard, granular particles.

7.6.3 VOLUME CHANGE

The conversion of calcium hydroxide to gypsum more than doubles the solid volume, the respective molecular volumes being 33.2 and 74.2 mL. The combination of hydrated calcium aluminate and gypsum to form calcium sulfoaluminate also rather more than doubles the solid volume. The changes in solid volume for other reactions with sulfates can be calculated from the densities and molecular volumes given in Table 7.1. Although it is clear that sulfate attack leads to an increase in solid volume, there is uncertainty as to the precise mechanism. One difficulty in ascribing expansion directly to the increased volume of the solids produced is that there is little correlation between the amount of calcium sulfoaluminate or gypsum formed and the degree of expansion observed. The distinction between solid- and liquid-phase reactions is important. It is generally accepted that the combination of sulfate in a solid-state reaction results in expansion, whereas there is no expansion when the reaction takes place in solution and the products can be distributed throughout the mass. There are, however, differences of opinion as to which cement compounds are involved in the reactions. It has been suggested, for example, that it is the solid-state conversion of $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ to $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$ that is responsible[20,21] but evidence[22] points to the presence of the $19H_2O$ and not the $13H_2O$ hydrate of tetracalcium aluminate in set cement. As can be seen from Table 7.1, this conversion for the $19H_2O$ hydrate would lead to a decrease, not an increase, in solid volume.

Table 7.1 Molecular volumes of concrete compounds

Compound	Molecular weight	Density	Molecular volume (mL)
$Ca(OH)_2$	74.1	2.23	33.2
$Mg(OH)_2$	58.3	2.38	24.5
$CaSO_4{\cdot}2H_2O$	272.2	2.32	74.2
$3CaO{\cdot}Al_2O_3{\cdot}6H_2O$	378.2	2.52	150.1
$4CaO{\cdot}Al_2O_3{\cdot}19H_2O$	668.3	1.81	369.2
$3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$	622.3	1.99	312.7
$3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$	1236.6	1.73	714.9

An earlier theory[23] based on the influence of electrolytes and other factors on sulfate expansion suggested that the volume changes are controlled by osmotic forces concerned with the shrinkage and swelling of the gel system. The chemical reactions condition the gel system and destroy the cementing substances. The formation of new crystalline substances as a result of these reactions is considered incidental to them and not the prime cause of expansion. An extension of this theory suggests that, provided water can diffuse freely out of capillaries or cavities in the cement paste, it is not possible by a solid–liquid reaction for the volume of growing crystals to exceed the space available to accommodate them. The swelling pressure arises from the diffusion of the sulfate salts into the gel pores. This disturbs the equilibrium between the gel and its surrounding liquid phase resulting in the movement of more water from the outside into the gel pores causing them to expand.

7.6.4 RATE OF ATTACK

The rate of attack on mortar and concrete by sulfate solutions depends on the strength of the solution. It increases rapidly up to a concentration of ~0.5 per cent for magnesium sulfate and ~1 per cent for sodium sulfate, but beyond these limits only at a diminishing rate. Thus the loss of strength in a 5 per cent solution may be only about two or three times that in a 0.5 per cent solution. At a concentration of 5 per cent, magnesium and sodium sulfates have roughly the same effect, but at 0.5 per cent, sodium sulfate has the less rapid action. This is illustrated in Figure 7.1 where data are reproduced for the strength

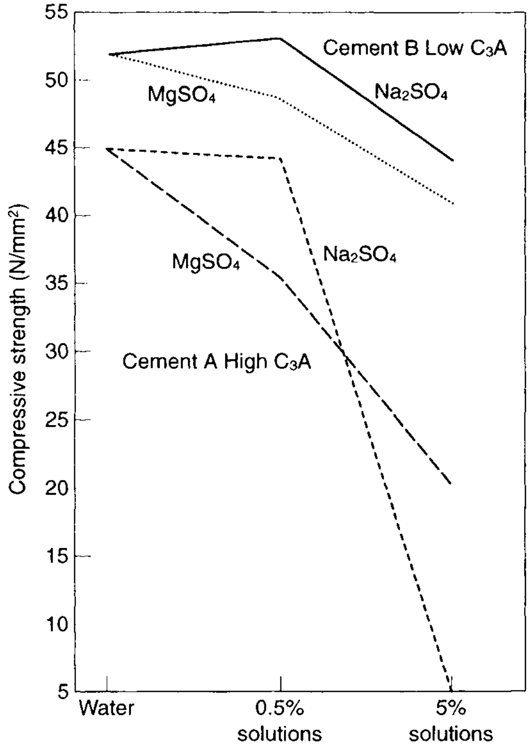


Fig. 7.1 Strength of concrete after one year's storage in water, sodium and magnesium sulfate solutions.

Table 7.2 Relative rate of expansion of cement minerals in 1:10 mortars

Aggressive solution	$1.8\%\ MgSO_4$	Saturated $CaSO_4$	$2.1\%\ Na_2SO_4$
	Equivalent SO_3 content 1.2%		
Compound	Time to expand 0.5%		
$2CaO \cdot SiO_2$	28 days	Negligible expansion in 18 years	
$3CaO \cdot SiO_2$	35 days	0.22% in 9 years	12 years
$80\%\ 2CaO \cdot SiO_2 + 20\%\ 3CaO \cdot Al_2O_3$	6 days	10 days	4 days
$80\%\ 3CaO \cdot SiO_2 + 20\%\ 3CaO \cdot Al_2O_3$	4 days	11 days	7 days
$80\%\ 3CaO \cdot SiO_2 + 20\%\ 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	16 days	0.15% in 3 years	400 days
$40\%\ 3CaO \cdot SiO_2 + 40\%\ 2CaO \cdot SiO_2 + 20\%\ 4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	43 days	~0.06–0.07% in 3 years	
$50\%\ 3CaO \cdot SiO_2 + 50\%\ 2CaO \cdot SiO_2$	65 days	0.19% in 18 years then rapid expansion	0.04% in 12 years
Mean of eight Portland cements	11 days	–	13 days

Rectangular mortar bars 16 mm thick aged in water for 8 weeks before immersion in the solution.

of concrete cubes made using 320 kg/m^3 cement and stored for 1 year in water and in 0.5 and 5 per cent sodium and magnesium sulfate solutions. Results are shown for two Portland cements of differing sulfate resistance. The relative action of magnesium and sodium sulfate is also affected by the composition of the cement; the former tends to have the more severe action on cements of lower C_3A content and sodium sulfate on those of higher content. Calcium sulfate, because of its low solubility, has a much slower action on dense mortars and concretes than the stronger solutions which can be obtained with the more soluble sulfates, but its eventual effect is comparable with that of a sodium sulfate solution of greater strength. On porous mortars and concretes its action can be rapid. The relative resistance of cements and cement compounds to calcium, magnesium and sodium sulfate solutions as measured by the time required to expand 0.5 per cent is shown in Table 7.2.

7.6.5 *IMPROVEMENT OF SULFATE RESISTANCE*

Early efforts to improve the sulfate resistance of Portland cement concretes were concentrated on the effects of physical factors, such as steam curing, the duration of water curing or allowing the concrete to dry in air to give an impermeable carbonate skin before exposure to sulfate solutions. While having some beneficial effects, these measures were limited in their practical application to precast units. Significant improvements in sulfate resistance came with a change in the composition of the cement, whereby the compound tetracalcium aluminoferrite largely replaced tricalcium aluminate. The substitution of ferric oxide for alumina was suggested by le Chatelier before the end of the nineteenth century and was adopted in Germany, where it led to the manufacture of Erz cement, a material in which iron ore replaced the clay fraction of the raw charge to the kiln. This cement originally had a very low alumina/iron oxide ratio, about 0.25, later increased to about 0.7. Erz cement was replaced by Ferrari cement, produced in Italy, in about 1920. This originally had a low alumina/iron oxide ratio of ~0.25, later increased to nearer 1.0. Ferrari cement falls in the class of sulfate-resisting Portland cements, which have a ratio of 1.0. In ordinary Portland cements the ratio is, on average, 1.8.

The value of a reduced tricalcium aluminate content in increasing the sulfate resistance of Portland cements was demonstrated by a number of field and laboratory trials of concretes made with different cements and exposed to sulfate solutions for lengthy periods. Of the many investigations carried out, mainly in North America, possibly the most significant results came from the work of D.G. Miller for the US Department of Agriculture.[24,25] In his investigation Miller immersed small concrete cylinders made using over 100 cements in sodium and magnesium sulfate solutions in the laboratory and in the waters of Medicine Lake, South Dakota, for periods up to 25 years. The lake contains salts varying in concentration from about 2.3 to 7.4 per cent over the years, averaging ~5 per cent. The salts consist mainly of magnesium sulfate (3.3 per cent) and sodium sulfate (1.2 per cent) with a small amount of calcium sulfate (0.3 per cent) and minor amounts of carbonate, hydrogen carbonate, etc.

The general findings of the work confirmed the results obtained in other investigations. They showed that little benefit was derived from the use of air-entraining agents or of other additives, and that thin surface coatings, while giving some early protection to the concrete, retained little protective effect after about 5 years. High-temperature steam curing, at 175°C for 6 h, increased the resistance to sulfate attack to such a degree that almost complete immunity for 17 years was obtained. Lower temperatures or shorter times of curing gave only limited improvement in durability. The importance of high-quality concrete with low permeability and freedom from honeycombing in giving maximum resistance was clearly demonstrated.

The most notable feature of the results obtained was the difference in performance of the Portland cements used. Concretes made from cements giving the greatest resistance to sulfate attack retained more than half their strength after immersion for 10 years in the lake water, whereas the strength of concretes made with the least resistant cements dropped to a similar proportion after 1 year, and the specimens then completely disintegrated. The difference in performance was found to correlate broadly with the calculated content of tricalcium aluminate in the cement. Miller divided the cements into 12 groups, of which the most resistant averaged 4.4 per cent C_3A and the least resistant 11.9 per cent. The maximum C_3A content of the cements forming the most resistant group was 5.4 per cent, and Miller proposed that for use in concrete exposed to sulfate solutions, Portland cements should not contain more than 5.5 per cent C_3A.

The US Bureau of Reclamation[26,27] also concluded from trials and field experience that the C_3A content is the greatest single factor influencing the resistance of Portland cement concretes to sulfate attack, with cement content second. Increasing the cement content improves resistance but some 415 kg/m^3 was reported to be required with a cement containing a maximum C_3A content of 8.0 per cent (ASTM Type II) to give as good a resistance as the use of 250 kg/m^3 with a cement containing a maximum of 5.0 per cent C_3A (ASTM Type V).[28]

Both the cement content of the concrete and the C_3A content of the cement were considered to influence durability in trials conducted at Sacramento, California, as part of the American Long-time Study of Cement Performance.[29] Large concrete prisms were partially buried in two soils, each containing about 10 per cent soluble salts, but in one these were composed of 85 per cent sodium sulfate with 10 per cent sodium carbonate and little magnesium sulfate, and in the other about one-third of the sodium sulfate was replaced by magnesium sulfate. The beds were flooded periodically during the summer, resulting in crystallisation of salts by evaporation over the exposed surfaces. After about 5 years under these conditions the factor of major importance was the cement content of the concrete, while the type of Portland cement was secondary to this. Lean concretes of about 224 kg/m^3 deteriorated badly and many disintegrated completely in a shorter period. With medium concretes of about 310 kg/m^3 the deterioration after 5 years varied from slight to severe, while most of the rich mixes with about 390 kg/m^3 cement content showed only slight deterioration. In the concretes of low and medium cement content there was a general relation between degree of deterioration and the calculated C_3A content of the cement. After 20 years' exposure of the rich concrete specimens it was concluded that a limit of 5.5 per cent should be placed on the C_3A content, corrected for minor components, or about 3.5 per cent as determined by X-ray diffraction. These values correspond roughly to $\sim$6.5 per cent calculated by the Bogue method.

The limiting values for C_3A suggested as the result of the various trials can be compared with the 5 per cent maximum of the ASTM specification for Type V cement and the 3.5 per cent maximum of the British Standard specification for sulfate-resisting Portland cement.[30] The difference between these values is due to a difference in the methods used to arrive at the C_3A content. This is customarily calculated from the determined contents of aluminium and iron oxides in the cement using the Bogue formula. The value obtained from the calculation depends on the analytical method used to determine the aluminium oxide. In the British Standard method[31] this is determined directly, whereas the ASTM method gives a value which includes some minor constituents of the cement. Irrespective of the analytical methods, there are inherent uncertainties in applying the results to the calculation of compound composition. Methods which measure the compounds directly may be expected to offer a more accurate assessment, and X-ray diffraction analysis is a technique which has received much attention. In general, the results obtained by X-ray diffraction and by the Bogue method have shown that while there is little significant difference between the two values at higher C_3A contents, at low C_3A contents there is considerable variation.

Although the connection between the sulfate resistance of Portland cements and C_3A content has been established, the connection with other compounds in the cement is less clear. It is known that too high a content of C_4AF decreases the resistance of cements of low C_3A content, and that it should not exceed about 15 per cent. The ASTM specification limits its content by placing a maximum of 20 per cent on the sum of the C_4AF plus twice the C_3S content. However, it is not clear why C_4AF is more resistant to sulfate attack than C_3A, since it should be capable of forming calcium sulfoaluminate and the corresponding sulfoferrite, producing expansion. The reason may lie in work by Cirilli,[32,33] who found that when cements containing C_3A and C_4AF were hydrated in the presence of lime and calcium sulfate, the amount of calcium sulfate taken up corresponded to the complete formation of $3CaO \cdot Al_2O_3 \cdot 3CaSO_{4_{aq}}$ and $3CaO \cdot Fe_2O_3 \cdot 3CaSO_{4_{aq}}$ whatever the Al_2O_3/Fe_2O_3 ratio of the cement. If, however, the cement was hydrated before being exposed to the calcium sulfate solution, the amount of sulfate taken up steadily decreased with decreasing Al_2O_3/Fe_2O_3 ratio. In this case a solid solution can first be formed between tetracalcium aluminate and ferrite, and this is attacked by calcium sulfate at a rate which decreases with decreasing Al_2O_3/Fe_2O_3 ratio. The tetracalcium ferrite is more resistant than the solid solution, and if any free calcium aluminate is formed it may be protected by films of the ferrite over it.

Another cause contributing to increased sulfate resistance is suggested by the observation[34] that, whereas the high-sulfate calcium sulfoaluminate formed in the setting of ordinary

Portland cements later converts into the monosulfate sulfoaluminate, this appears not to occur with cements of low C_3A content. If the low-sulfate sulfoaluminate later comes into contact with additional sulfate, it is converted back into the high-sulfate compound with an accompanying increase in volume. Some other evidence[35] bearing on this suggestion comes from an observation that the severity of attack on a cement mortar was greater at a temperature of 5°C than at higher temperatures. This was attributed to the formation of the monosulfate sulfoaluminate instead of the trisulfate compound at low temperatures and its subsequent destructive conversion to the trisulfate sulfoaluminate under sulfate attack.

The effect of the relative proportions of tri- and dicalcium silicates on sulfate resistance is also rather uncertain. The rate of attack by sulfates such as sodium sulfate which react with calcium hydroxide is influenced by the rate of hydration of the silicates and hence the rate at which calcium hydroxide is released. Concrete made with a cement having a high proportion of dicalcium silicate may therefore be expected to suffer attack more slowly, but if adequate aggressive sulfate is available, the concrete will eventually disintegrate.

The field and laboratory studies have provided information on the types of cement best able to resist sulfate attack and the quality of the concrete necessary for durability. These, however, can only be taken as a general indication of the behaviour to be expected, for local conditions will modify them in varying degrees. Water is necessary for the chemical reactions to take place, hence a soil which is relatively high in sulfates but which is dry for long periods of the year, or one which is so drained that the solutions formed by leaching of the soil are removed from the vicinity of the concrete, will be much less destructive than one which may have a lower sulfate content but where physical conditions are more unfavourable. Regions in which alternate wetting and drying occur fairly frequently are likely to be particularly subject to destruction. The sulfate content of the soil is only important insofar as it represents the reserve supplies available for maintaining or increasing the sulfate content of the waters contained in it or draining from it.

The least severe condition of exposure to sulfate action is where concrete is completely buried above the water table and where the excavation for the structure does not form a channel along which water is likely to flow. The most severe condition is when concrete is exposed on one side to water pressure and on the other side to air, promoting evaporation and so tending to increase the volume of sulfate-bearing waters drawn through it. The use of precast concrete products is advantageous, where practicable, since the quality of the concrete can be controlled more easily than with *in situ* work and it can be well matured before exposure. Lean concretes, often used for bedding or haunching pipes, are very vulnerable to attack, irrespective of the type of cement used. The use of sulfate-resisting Portland cement, pozzolanic cements or slag cements will help give durable structures in conditions of moderate severity, but none of these cements is immune from attack in low-quality concrete.

7.6.6 ROLE OF WATER

The classifications of soil aggressiveness in some European countries have placed much importance on the role of water in sulfate attack, and have taken account of such factors as soil permeability, whether the water is static or moving and the ratio of the head of water to the dimensions of the concrete. Elsewhere, assessments of risk have generally been based on the sulfate content of the soil or ground water at the time of sampling, and as a consequence recommendations for the protection of concrete have tended to be conservative. This is prudent under conditions, as in the UK, where there are large local and seasonal variations in the concentration of sulfates in the ground water and samples taken at any one time may not represent the worst conditions. The classification of severity of exposure and recommendations for concrete to be used in each class currently in use in the UK[36] are outlined in Table 7.3.

An investigation of the long-term (25 years) resistance of concrete exposed to aggressive ground conditions has been carried out at Northwick Park, London, UK, but at the time of writing the final results have not been reported. The soil is a gypsum-bearing clay, with numerous sandy fissures. There is a high water table, at an average depth of 1.4 m below ground level, and a flow rate across the site of 100 mm/year. The sulfate content of the ground water averages 2.6 g/L SO_3, of which 1.3 g/L is due to magnesium sulfate and 1.0 g/L to calcium sulfate. The average sulfate contents of samples taken from six boreholes over a period of 5 years ranged from 1.6 to 3.8 g/L, corresponding to the 'severe' to 'very severe' classifications of BS 8110. Five cements – ordinary Portland, sulfate-resisting Portland, supersulfated, high-alumina and sulfate-resisting Portland blended at the mixer with a 40 per cent replacement of ground granulated blastfurnace slag – were used to prepare small concrete cylinders for burial below the water table, for small-diameter piles cast *in situ* and for panels cast *in situ* to form the walls and floor of a basement. Cubes were made from each concrete mix for accelerated testing in sulfate solutions in the laboratory. In addition, a number of materials, mainly precast concrete products, were submitted by manufacturers for burial on the site. A bulk sample of pulverised fuel ash was included in this category and was used as a 20 per cent replacement of ordinary Portland cement in two mixes selected by the supplier. Cylinders for burial and cubes for laboratory tests were prepared from these concretes.

Table 7.3 Recommendations of BS 8110 for concrete exposed to sulfates

	Sulfate content (SO_3)				
	Soils		Water		
Severity of exposure conditions	Total SO_3 (%)	SO_3 in 1:2 soil/water extract (g/L)	g/L	Type of cement recommended[a]	Cement content (kg/m^3)
Moderate	0.2–0.5	1.0–1.9	0.3–1.2	Any[b] plus OPC with pfa or GGBFS	330
				OPC plus 25–40% pfa OPC plus 70–90% GGBFS	310
				SRPC or SSC	280
Severe	0.5–1.0	1.9–3.1	1.2–2.5	OPC plus 25–40% pfa OPC plus 70–90% GGBFS	380
				SRPC or SSC	330
Very severe	1.0–2.0	3.1–5.6	2.5–5.0	SRPC or SSC	370
Extreme	>2.0	>5.6	>5.0	SRPC or SSC with protective coatings	370

[a] OPC = ordinary Portland cement (BS 812); SRPC = sulfate-resisting Portland cement (BS 4027); SSC = supersulfated cement (BS 4248); pfa = pulverised-fuel ash (BS 3892); GGBFS = ground granulated blastfurnace slag.
[b] Including Portland blastfurnace cements (BS 146 and BS 4246) and pulverised-fuel ash cement (BS 6588).

The programme was started some years before BS 8110 was published and there are a number of discrepancies between the materials used and the recommendations of the specification. For example, when the work was begun, high-alumina cement had not been excluded from use in structural concrete, and the use of ground granulated blastfurnace slag and pulverised fuel ash as cement replacements was at an experimental stage in Britain. As a result the proportions of these materials used at Northwick Park are less than those now recommended. Two departures from practices adopted in earlier investigations were introduced into the programme. One was to use the workability of the concrete, as determined by either the compacting factor or the slump, as the standard for producing consistent mixes with each cement rather than, as in past work, by using the same proportions of cement and aggregate and the same water/cement ratio for each cement. The new approach entailed some adjustment of the water/cement ratios and of the aggregate gradings according to the type of cement. The investigation also included a study of the performance of porous concrete. This had formed part of previous investigations, but the means used to produce specimens, for example, very lean or over-wet mixes, oversanding with fine sand or omission of the finer fractions of the sand, were considered not to approach the problem of inadequate compaction of a mix designed to produce good-quality concrete. In this study cylindrical specimens were prepared by means of the compacting factor apparatus described in BS 1881,[37] a method which was found to be satisfactory for producing uniform partially compacted concrete. Details of all the concrete mixes and their site installation were given in an early report.[38]

The results of tests on the concretes after exposure for 5 and 15 years have also been published.[39,40] The overall conclusion was that the sulfate resistance of concrete does not depend solely on the type of cement used, the cement content and the water/cement ratio, but in many cases is largely dependent on the method of manufacture, the curing and the conditions of exposure or, as in the case of ordinary Portland cement concrete, on both sets of factors. Any lowering of the quality or the workmanship, such as a low cement content, a high water/cement ratio or poor compaction, was found to increase the amount of sulfate entering the concrete and the amount of ettringite, $C_3A \cdot 3CaSO_4 \cdot 31H_2O$, in the surface layers. In the partially compacted cylinders made with ordinary Portland cement, sulfate penetration averaged 20 mm after 5 years, while the average depth into the same concrete fully compacted was <2 mm. Similarly, after 5 years the small-diameter piles which were poured into holes without any compaction had high concentrations of sulfates in the surface layers of concretes at all cement contents made with ordinary Portland cement. The method of casting resulted in poor surfaces of parts of the piles and these areas were preferentially attacked. After 15 years, high-workability concrete showed a large increase of sulfate content in the outer layers, the increase being greatest where the concrete showed a lack of compaction.

7.6.7 *EFFECT OF SURFACE CONDITION OF CONCRETE*

The effect of the surface condition of the concrete was also demonstrated in the basement. For one wall the panels were cast against steel sheet piling and compacted against the clay face of the excavation. For the opposite wall the panels were cast in steel shuttering and backfilled. The penetration of sulfates into the smooth surface of this wall was negligible but, in the majority of the panels cast against the clay, sulfates had entered to depths of up to 8 mm. Significant amounts of ettringite had also formed in the surface layers of the panels made with ordinary Portland cement. The basement is subjected to hydrostatic pressure and the importance of the permeability of concrete in such conditions was clearly shown. Well-compacted, medium-workability concrete made with ordinary Portland cement at 285 kg/m^3 contained high levels of sulfate after 15 years, but concretes containing 335 kg/m^3 or more had reduced levels.

7.6.8 RESISTANCE OF DIFFERENT TYPES OF CEMENT

The degree of resistance of the cements to three sulfate solutions after storage for 5 years is broadly summarised below and in Table 7.4. This simplified presentation does not distinguish between the concrete mixes, full details of which are given in Ref. 39.

Minimum resistance to sulfate action was shown by ordinary Portland cement. Deterioration was especially marked in the 1.5 per cent SO_3 sodium sulfate solution, but even in the dilute 0.35 per cent SO_3 magnesium sulfate solution the degree of attack was greater than that suffered by the other cements.

Sulfate-resisting Portland cement showed a high degree of resistance to the dilute magnesium sulfate and the sodium sulfate solutions. The 1.5 per cent SO_3 magnesium sulfate solution had some effect on a small number of cubes.

The resistance of supersulfated cement to dilute magnesium sulfate and to sodium sulfate was similar to that of sulfate-resisting Portland cement, but its resistance to the strong magnesium sulfate solution was less.

The two mixes made with ordinary Portland cement and pulverised fuel ash showed good resistance to the dilute magnesium sulfate and the sodium sulfate solutions. Cubes stored in the strong magnesium sulfate solution showed similar resistance to that of the supersulfated cement concretes. The performance of the blend of sulfate-resisting Portland cement and ground granulated blastfurnace slag was very variable and, particularly in the degree of attack observed in the 1.5 per cent SO_3 magnesium sulfate solution, was poorer than that of supersulfated cement. The lack of resistance was attributed to the low slag content of the mixture and to the fact that the slag used had a higher aluminium oxide content than is desirable to give increased sulfate resistance.[41]

Table 7.4 Resistance of concrete to sulfate solutions after 5 years' storage

Solution	$MgSO_4$ (0.35% SO_3)	$MgSO_4$ (1.5% SO_3)	Na_2SO_4 (1.5% SO_3)
Cement used		Degree of resistance	
Ordinary Portland	Poor	Poor	Very poor
Sulfate-resisting Portland	High	Slight effect	High
Supersulfated	High	Reduced	High
Sulfate-resisting Portland 60% and slag 40%	Variable	Poor	Variable
Ordinary Portland 80% and pfa 20%	High	Similar to supersulfated cement	High

7.7 Action of sea water

Concrete is widely used in the construction of harbours, docks, breakwaters and other structures exposed to the action of sea water, and its durability in maritime works is a matter of considerable importance. Concrete in sea water may suffer attack through the chemical action of dissolved salts, the crystallisation of salts within the concrete under conditions of alternate wetting and drying, frost action, mechanical attrition and impact by waves, and through the corrosion of embedded reinforcement. Attack in any one of these ways renders the material more susceptible to the action of the remaining potential agents of destruction.

The average amounts of the major constituents present in sea water are given in Table 7.5. The proportions in which the constituents occur are fairly constant throughout the world, but the total amount of dissolved salts present can vary considerably, depending on the geographical location of the water. Land-locked seas which receive little influx from rivers have higher contents of salts than open seas, while those receiving large inflows of river waters have lower concentrations of salts, and in parts of the Baltic, for example, the water is nearly fresh.

7.7.1 CHEMICAL ACTION

The chemical action of sea water on concrete is mainly due to the magnesium sulfate present. As was seen in section 7.6, magnesium sulfate reacts with the free calcium hydroxide in set Portland cements to form calcium sulfate while at the same time precipitating magnesium hydroxide. These have often been assumed to be the reactions primarily responsible for the chemical attack by sea water and, although they do occur, the picture they give is too simple to account for all the facts. It is, for example, a common observation that deterioration of concrete in sea water is often not characterised by the expansion found in concrete exposed to non-saline sulfate solutions, but takes more the form of an erosion or loss of constituents from the mass. Although laboratory data are conflicting, it seems that the presence of chloride retards the swelling of concrete in sulfate solutions. It is also found that concretes that have suffered deterioration have lost part of their lime content. Both calcium hydroxide and calcium sulfate are much more soluble in sea water than in fresh water, and this, when combined with the conditions produced by wave motion, must lead to an increased leaching action. Again, calcium sulfoaluminate, although one of the initial products of the reactions of set cement with magnesium sulfate, is unstable in the resulting solution and eventually decomposes again to form hydrated alumina, gypsum

Table 7.5 Composition of sea water (g/L)

Constituent		Mediterranean	Atlantic	Mean sea water
Sodium	Na	11.56	9.95	11.00
Potassium	K	0.42	0.33	0.40
Magnesium	Mg	1.78	1.50	1.33
Calcium	Ca	0.47	0.41	0.43
Chloride	Cl	21.38	17.83	19.80
Bromide	Br	0.07	0.06	–
Sulfate	SO_4	3.06	2.54	2.76

and magnesium hydroxide. The hydrated calcium silicates in set cement are also decomposed by the magnesium sulfate in sea water, as in fresh water, to give gypsum, hydrated silica and magnesium hydroxide. The last two may combine, very slowly, to give a hydrated magnesium silicate, but this, unlike silica gel, has little binding power. Indeed, one of the theories of the beneficial action of pozzolanas in resisting sea water is that an increased amount of silica gel is formed by the action of magnesium sulfate on the hydrated silicates arising from the reaction of lime with the pozzolana as well as on those present in the cement.

Analyses of concrete progressively attacked by sea water show a continuing rise in the magnesium hydroxide content and a fall in that of calcium hydroxide, while the sulfate content tends first to increase and then to decrease again. This is illustrated in Table 7.6 by the analyses of Portland cement concretes taken from a structure exposed to sea water for 10 years. Part of the aggregate was separated before the anlayses were made, but the extent of attack is shown by the ratios of MgO/CaO and of SO_3/CaO compared with those of Portland cement. Sample A showed no signs of deterioration while samples B, C and D had been progressively more attacked.

The chemical action of sea water should therefore be pictured as one of several reactions proceeding concurrently. Leaching actions remove lime and calcium sulfate, while reaction with magnesium sulfate leads to the formation of calcium sulfoaluminate which may cause expansion, rendering the concrete more open to further attack and leaching. The deposition of magnesium hydroxide in the pores of the concrete probably tends to slow down the action on dense concretes, although on more permeable materials it may be without much effect. The relative contributions to deterioration by expansion and leaching will depend upon conditions. Concrete of not too massive dimensions exposed to the open sea is more likely to show the effects of leaching than of expansion. Structures such as dock walls, on the other hand, into which the water may percolate but without causing any considerable degree of leaching, may show the effects of expansion. The rate of chemical attack increases with temperature and both the rate and the effect are influenced by the type of cement used. With the appropriate choice of cement and high-quality concrete, deterioration from chemical action can be kept very slow; conversely, poor concrete can suffer severely.

The most severe attack of sea water on concrete occurs just above the level of high water; the part between high and low water marks is less affected and the parts below low water level which are continuously immersed are rarely damaged. Concrete is not attacked unless the sea water can penetrate into it. Although no concrete strictly is impermeable, a good concrete is so dense that the rate of penetration of water into it is negligible when it is completely immersed and not subject to a one-sided water pressure. Above water level, the water tends to rise in the concrete by capillary action and to evaporate at the surface, allowing more water to be drawn continuously through the mass. Under these conditions

Table 7.6 Analysis of concrete exposed to sea water for 10 years (weight per cent)

Sample		A	B	C	D	OPC
Calcium oxide	CaO	20.3	16.2	16.4	12.6	
Magnesium oxide	MgO	0.36	2.9	5.9	5.5	
Sulfate	SO_3	0.60	1.78	2.17	0.93	
Ratio MgO/CaO		0.02	0.18	0.36	0.44	0.02
Ratio SO_3/CaO		0.03	0.10	0.44	0.07	0.03

the sea water may slowly attack the concrete chemically, while crystallisation of salts in the concrete may have a disruptive action. Alternate wetting and drying of the surfaces accentuates the disintegration. It is also the concrete above water level which is most exposed to wave action and attrition.

7.7.2 FROST ACTION

Concrete in sea water can also suffer deterioration caused by frost action and, in the case of reinforced concrete, from corrosion of the steel. In the severe climates of northern regions, frost action is the main cause of damage. Concrete in the tidal zone may undergo up to 200–300 cycles of freezing and thawing in a year, as it is alternately immersed in the sea or exposed to air at low temperatures. Freezing in sea water is also much more detrimental than in fresh water. Although reinforced concrete is more liable to serious deterioration if damage due to frost action allows sea water to penetrate to the steel, plain concrete may also suffer if frost action is severe. Slag cements with a high slag content have a good record of durability under very cold conditions. Portland cement concrete suffers severely unless air entrainment is used, but up to 10–12 per cent of entrained air, about twice the amount used to protect concrete in fresh water, may be required. The use of about 30 per cent pozzolana by weight of Portland cement offers advantages in severe winter climates provided that the pozzolana is used as an addition to, and not a replacement for, the cement. In warm climates, where chemical attack is a dominant factor, slag cements, sulfate-resisting Portland cement or pozzolanic cements have proved to give good service. The mildest conditions of exposure are those found in temperate waters, such as around the British Isles, where much well-made ordinary Portland cement concrete has shown a good record, but advantage is still to be gained from the use of more resistant cements.

7.7.3 CORROSION OF REINFORCEMENT

Corrosion of reinforcement, which is a major cause of deterioration of concrete in sea water anywhere, becomes a progressively more serious risk as the temperature rises, as does chemical attack on the concrete. Air entrainment has been found to increase the resistance of concrete to damage due to corrosion, but to have no effect in reducing chemical attack. The prime essential for all seawater concrete is that a dense product of low porosity should be obtained and that there should be adequate cover to reinforcement, especially above low tide level. A minimum cover of 50 mm is generally considered sufficient for most situations, but in tropical or subtropical waters an even greater depth of cover is desirable. It is not only concrete placed in the sea that is at risk, and corrosion has been found with particular frequency on the underside of deck slabs, which are subject to deflection from live loads and cracking which allows access of chlorides to the steel. Deterioration of reinforced concrete from the effects of sea water salts can also occur in structures up to several kilometres inland from the coast. This happens most frequently in tropical or semi-tropical countries and has been reported from South Africa, Italy, California and the South Pacific. The damage arises not by chemical attack on the concrete itself, but from corrosion of the reinforcement caused by sea spray carried inland by prevailing winds. The salts accumulate in the concrete, and by wetting and drying gradually migrate inward to the steel.

The depth and rate of chloride penetration into concrete in sea water and the corrosion of embedded steel formed part of a research programme Concrete in the Oceans,[42] which was initiated as the result of increased oil production in the North Sea and designed to give information on the behaviour of large concrete gravity platforms in deep waters. The full programme comprised a number of projects covering, among others, such aspects as fatigue, loading stresses and fundamental studies of the mechanisms of corrosion, and the report should be consulted for details.[42]

7.7.4 INVESTIGATION OF CORROSION

The work on chloride penetration and corrosion was conducted at Portland Harbour on the south coast of England and at Loch Linnhe on the west coast of Scotland. Concrete specimens were exposed to five different conditions, or zones, of marine environment. At Portland the zones were (1) atmospheric, where the specimens were in a humid, saline atmosphere but not in contact with sea water; (2) the splash zone, just above mean high water level, where the specimens were subject to wave action but not immersed in sea water; and (3) the tidal zone at mean water level, where the specimens were frequently submerged in tidal water. Owing to a small tidal range and to calm water at times, it was not possible to maintain the required degree of wetting in the splash zone, and the specimens were therefore sprayed with sea water on a regular daily basis in addition to being subjected to natural splash conditions during rough weather. At Loch Linnhe the concrete was fully submerged in sea water at depths of 10 and 140 m. For measurement of the depth of penetration of chloride, plain concrete prisms, in which all faces except the ends were sealed, were placed in the five exposure zones. Sets of specimens were also prepared with simulated longitudinal cracks formed by splitting prisms lengthwise and reassembling the halves. For the study of corrosion, concrete beams stressed back to back to induce cracking in the outer surfaces were exposed in the splash zone at Portland Harbour and at 140 m in Loch Linnhe. The reinforcement was so placed that cracking could be induced either longitudinally along the main bar or transverse to it.

Two grades of concrete made with ordinary Portland cement were used – a standard grade with a 28-day strength of 65 N/mm^2 and a low grade of 30 N/mm^2. Concrete made with a 20 per cent replacement of cement by pulverised fuel ash was used for some specimens. The prisms for chloride penetration measurements were tested after exposure periods of 6 months, 1 year, 2.5 years and 5 years. Longitudinally cracked beams were tested at 1 and 5 years, and transversely cracked beams at 1, 2.5 and 5 years. Specimens incorporating pulverised fuel ash were tested after exposure for 2.5 years. The depths to which chloride penetrated and the amounts absorbed in the concrete were found to depend more on the grade of concrete and the exposure conditions than on the time of exposure. The depth of penetration into low-grade concrete was up to twice as much as into standard grade concrete in the same exposure zones. In the pre-cracked specimens, chloride penetrated up to 180 mm, a distance six times greater than into uncracked specimens made with standard-grade concrete, and 3–3.5 times greater than into those made with low-grade concrete. The amounts of chloride present showed similar variations between the grades of concrete and the conditions of exposure. At Portland Harbour the average maximum chloride content of the low-grade specimens was three times that of the standard grade specimens. At Loch Linnhe, where the highest chloride levels were found in the specimens in the deep-water zone, there was less difference between the amounts present in the two grades of concrete. Specimens in all zones showed a significant decrease in both the rate and depth of penetration and an increase in chloride content after the initial 6-month period of exposure, although there was a continuous increase throughout the 5 years' duration of the test, but at a much slower rate.

The importance of good design and workmanship in achieving durable concrete was demonstrated in a number of the projects studied in the programme. Proper curing was found to be one of the most important factors in providing protection against corrosion of reinforcing steel. The effects of curing in air, by fog or by immersion in sea water were investigated and it was found that curing in conditions of high humidity or by immersion produced concrete of greater impermeability than air curing. The use of sea water, however, should be avoided unless the concrete is to be submerged quickly and permanently. It can result in high initial levels of chloride which will increase when the concrete is exposed to sea water, and is likely to result in depassivation of the steel. Where the concrete remains submerged, the lack of readily available oxygen and its slow rate of diffusion into saturated concrete will prevent active corrosion of the steel, irrespective of the presence of cracks, crack width or depth of cover. This was demonstrated at Loch Linnhe, where there was no corrosion in the beams after immersion at 140 m for 5 years, despite a level of chloride at the reinforcement high enough to result in depassivation. However, when the beams were brought to the surface and exposed to the atmsophere, corrosion occurred very rapidly at cracks in the concrete cover and was attributed to oxygen being freely available to promote the corrosion of steel which had lost its passivity during immersion.

Reinforcement steel was found to be most vulnerable to corrosion in the splash zone, where the concrete is alternately subjected to wetting and drying and oxygen is freely available. At Portland Harbour, chlorides penetrated rapidly down all cracks in the concrete, even those as narrow as 0.1 mm, initiating corrosion at the reinforcement. Chloride also penetrated into uncracked concrete specimens, although no corrosion of the reinforcement occurred during the 5 years of exposure. It was estimated, however, that levels of chloride sufficient to cause depassivation of steel could reach reinforcement depths within 10 years.

In all cases corrosion was more severe where cracks were longitudinal to the reinforcement and the steel was exposed for the full length of the crack than where cracks of similar width were transverse to the bars. At some transverse cracks, however, corrosion extended along the bar on either side of the crack for a distance of ~40–50 mm. In general, no corrosion was found in sound concrete away from cracks. Voids in the concrete at the bottom of the cracks, if adjacent to the surface of the reinforcement, resulted in pitting corrosion in the steel which, it was considered, could lead in the long term to total loss of sections of the bar.

Studies of various properties of concrete made with a 20 per cent replacement of cement by pulverised-fuel ash produced results similar to those of Portland cement concrete. The permeability was not significantly different while the porosity was about the same, and although there was some difference in pore size distribution, it was found that curing conditions had a greater influence on pore size than the inclusion of pulverised-fuel ash. The depth of chloride penetration into concrete made with pulverised-fuel ash was less than into Portland cement concrete, although the difference was marginal when high-quality mixes were compared. Oxygen diffusion rates measured on standard-grade Portland cement concrete cured in air or with sea water were substantially lower for the concretes containing pulverised-fuel ash. The resistivity of concrete made with the blended cement was as much as three times higher than that of unblended Portland cement concrete, a factor which might be expected to have a beneficial influence on the degree of corrosion of embedded steel. However, in the short term of 2.5 years there was no significant difference in the corrosion found in cracked specimens made with or without pulverised-fuel ash. Examination of a number of structures over 10 years old in which pulverised-fuel ash had been used similarly found that the incidence and severity of corrosion were no different from Portland cement concrete. The structures examined had not been exposed to the action of sea water but were in coastal locations.

7.8 Action of acids

It can be accepted as a general rule that acids are damaging to concrete. They do not enter into complex chemical reactions such as those that take place during sulfate attack, resulting in expansion and cracking of the concrete, but simply dissolve the more soluble constituents of the set cement, destroying its crystalline structure and leaving only an incoherent residue. Different acids act preferentially and at different rates on the cement compounds, but the ultimate result of sustained attack is destruction of the concrete.

The extent to which attack may occur is influenced by a number of factors, the most important of which are the permeability of the concrete, the conditions to which it is exposed and the type of cement used. A further factor is the solubility of the salts, in particular the calcium salts, formed by the reaction of the acid with compounds present in the cement. Portland cements are the most vulnerable to attack, since they contain a high proportion of calcium hydroxide released during hydration of the calcium silicates. Cements such as pozzolanic cements and those based on blastfurnace slag, in which calcium oxide is combined in a less soluble form, have a greater degree of resistance. The quality of the concrete influences the severity of any attack and, whereas the action on an impermeable set cement mass may be so low and limited in depth as to have only a negligible effect, serious damage may result to permeable concrete which allows acid solutions to penetrate more deeply. When concrete is used where it will be subjected to pressure from acidic water on one side and exposed to air on the other side, so that the aggressive solution may be drawn through it, a high degree of impermeability is required.

The degree of acidity of a solution is conveniently assessed from its pH value, which is a logarithmic function of hydrogen ion concentration measured on a scale from 0 to 14. The neutral point is at pH 7; a value below 7 represents acid conditions and a pH above 7 alkaline conditions. Since it is a measure of the number of hydrogen ions in a solution, or the extent to which substances in solution are dissociated into their constituent ions, there is a limiting pH value for a particular concentration of a substance. The pH values of some common solutions are shown in Table 7.7. Although easily measured, the pH value alone is of limited value in assessing the risk to concrete since, by its definition, it can give little information on which acids are present in a soil or water. A very low value will indicate an inorganic acid, which can be identified by chemical tests, if required, but above a value of ~ 4.5 much more difficult problems arise.

7.8.1 INORGANIC ACIDS

Inorganic, or mineral, acids are manufactured products and are mainly solutions of gases in water. Some have limited use and are prepared only in small quantities. The concrete employed where they are manufactured, stored or used requires protection against attack, but the acids are unlikely to enter soils and ground waters in deleterious amounts. Hydrochloric, sulfuric, nitric and phosphoric acids, which are produced and used in large amounts, present a more serious risk of contamination of soils and waters. This generally occurs accidentally as the result of spillages or leakages, but unauthorised dumping of acid wastes is also a source of contamination.

Table 7.7 Concentrations and pH values of some common solutions

Substance		Strength of solution		pH values
		Molarity	(g/L)	
Sodium hydroxide	NaOH	1.0 M	40	14.0
		0.1 M	4	12.9
Calcium hydroxide	$Ca(OH)_2$	Saturated	1.2	12.4
Magnesium hydroxide	$Mg(OH)_2$	Saturated	0.01	10.5
Calcium carbonate	$CaCO_3$	Saturated	0.02	9.4
Ammonia	NH_3	0.1 M	1.7	11.3
Acetic acid	CH_3COOH	1.0 M	60	2.4
		0.1 M	6	2.9
Humic acid		Saturated	0.19	3.5–4.0
Sulfuric acid	H_2SO_4	1.0 M	98	0.3
		0.1 M	9.8	1.2

Of the inorganic acids, only sulfuric acid may occur naturally in soils and ground waters. It results from the oxidative weathering of certain sulfide minerals, chiefly the iron disulfides pyrite and marcasite, FeS_2, which are abundant, pyrite more so than marcasite. In the presence of air and moisture, pyrite is oxidised to ferrous sulfate and sulfuric acid. This is a chemical reaction and, unless biochemical reactions are introduced, the oxidation proceeds no further. If, however, certain strains of aerobic bacteria are present, two further stages are introduced and breakdown of the pyrite is greatly accelerated. The bacteria belong to the species *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*, which are autotrophic, that is they are able to obtain the energy for their growth and proliferation by the oxidation of inorganic compounds in the presence of atmospheric oxygen. These particular autotrophs require an acid environment, in the pH range of 2.0–4.5; at higher values they become inactive. They bring about the oxidation of the ferrous sulfate to ferric sulfate, a reaction that does not take place chemically in the presence of sulfuric acid. Ferric sulfate is an oxidising agent and acts on unaltered pyrite to give ferrous sulfate and sulfuric acid, the products of the first stage of the oxidation processes. The cycle of oxidation can thus continue for as long as pyrite is available according to the following reactions:

$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4 \tag{7.5}$$

$$4FeSO_4 + O_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + 2H_2O \tag{7.6}$$

$$7Fe_2(SO_4)_3 + FeS_2 + 8H_2O = 15FeSO_4 + 8H_2SO_4 \tag{7.7}$$

Both oxygen and moisture are necessary for the reactions, and in undisturbed soils the position of the water table is of predominant importance in determining the degree to which they can occur. If the pyrite remains permanently below water level, no oxidation takes place, while in areas of fluctuating water levels which allow replenishment of oxygen to the soil, the reaction proceeds readily. If there are sufficient calcium salts in the soil, the sulfuric acid is neutralised, but in some cases its production may be so marked that it is present in the free state in the ground water. An example is the marsh, or lowland moor, around Osnabruck in Germany, where the peat soil contains up to 17 per cent of pyrite and free sulfuric acid has been found in the ground water in amounts as great as 80 mg/L.

Disturbance of natural ground conditions by excavation or drainage is a frequent cause of oxidation of pyrite by providing access for air. Rapid oxidation resulting in large increases in the acidity and in the sulfate content of ground waters has been reported when compressed air has been used to keep back water during underground work, as in the construction of tunnels. One case[43] occurred in southeast England when a tunnel was driven in compressed air through water-bearing alluvial clays, sands and gravels containing pyrite. After the use of air was discontinued the ground water, originally neutral, which returned into contact with the concrete lining of the tunnel, showed pH values down to 1.8, sulfate contents up to 28 g/L SO_3, iron equivalent to 36 g/L of $FeSO_4$ and up to 9.5 g/L H_2SO_4. The reaction slowed after the source of oxygen had been removed and within a few weeks the pH value of the most acid water rose from 1.8 to 3.5. A secondary lining made with supersulfated cement was installed and was found to be in good condition after 3 years. It was not possible, however, to examine the original segments which had been made with sulfate-resisting Portland cement.

The oxidation of pyrite may be followed by other reactions which cause expansion, and a number of cases have been recorded of uplift of floors and displacement of walls when buildings have been founded on pyritic shales or placed over fill material containing pyrite. The free sulfuric acid produced in the oxidation reactions acts on any calcite present to give gypsum, and on clay minerals such as illite to give jarosite, a hydrated potassium iron sulfate having the formula $KFe_3(SO_4)_2(OH)_6$. The molecular volumes of these reaction products are greater than those of the unaltered minerals, and hence expansive forces are created. The formation of gypsum from calcite results in an increase in molecular volume of 103 per cent, while jarosite occupies a volume 115 per cent greater than that of pyrite. In fissile rocks the reaction products often form in the bedding planes, and it is not uncommon to find in shales that the laminae have been forced apart by crystal growths.

Heaving is often not apparent for some time after completion of a building, but can then proceed rapidly and very quickly become a serious problem. First, the pyrite is oxidised by the reaction (7.5). This is fairly slow. Once sufficient sulfuric acid has been produced to lower the pH, however locally, to a level favourable for the bacteria to become active, reactions (7.6) and (7.7) follow rapidly. The bacterial activity is also encouraged by warm conditions. The optimum temperature for the growth of *T. ferrooxidans* is 15–20°C and that for *T. thiooxidans* 28–30°C, but these figures apply more to the efficient isolation and culture of the organisms in the laboratory than to their essential requirements. A certain amount of heat is given off in the chemical oxidation of pyrite, reaction (7.5), but overall warmth from external sources increases the rate at which the organisms proliferate and hence the rate at which expansion occurs in affected ground.

An account has been given by Penner *et al.*[44] of heaving of the basement floor in a building in Ottawa. The basement was in an extension added in 1961 to a building constructed in 1929. The ground on which both buildings were placed was a black, pyritic, calcareous shale about 6 m deep. A small amount of heave had occurred in the basement of the original building, but not to a serious extent. In the new basement, however, heaving was seen about 4 years after construction and 2 years later had progressed to the stage where it seriously affected the alignment and operation of machinery located there. The maximum heave recorded over 32 months of observation was 56 mm, or nearly half of the total movement over 9 years, calculated from the elevation of the floor immediately after construction.

Below the heaved area the shale had been altered to a depth of about 1 m. This zone had a high sulfate content, a low carbonate content and was acidic, with pH values ranging from 2.8 to 4.4. Gypsum and jarosite were present between horizontal laminae and in vertical cracks and fissures in the rock. The sound shale below contained twice as much carbonate as the weathered material, but only trace amounts of sulfate. Pyrite was present in both zones. Bacteria of the *Thiobacillus–Ferrobacillus* group were isolated from the affected shale. The severity of the heaving and the rapidity of its onset were attributed to the ready access of air to the shale and to exceptional warmth (30°C) in the basement. Air was able to enter the shale through an empty tile drainage system installed in a levelling course of crushed limestone below the floor slab and to spread rapidly through cracks and fissures in the shale.

Unusually high summer temperatures in two consecutive years with a fairly mild winter between were thought responsible for increased bacterial activity leading to expansion of the underfloor fill and damage to a number of houses in northeast England.[45] The fill used was a locally quarried calcitic ironstone shale, containing ~ 1–2 per cent by volume of pyrite and with a significant content of clay minerals, mainly illite. Shale from three sources within the quarry had been used extensively in the region as bulk fill, but only material from one source developed disruptive swelling. During the first hot summer, damage to two houses had been reported, but by the end of the second summer over 150 houses were affected.

Attack on concrete in sewers

Sulfuric acid produced by the activities of other types of microorganisms has been the cause of severe attack to concrete in sewerage systems. Normal sewage is usually without any action on concrete, but under some conditions considerable evolution of hydrogen sulfide may occur and give rise indirectly to acid attack. This occurs when oxygen in the sewage becomes depleted, causing the aerobic, purifying bacteria normally present to become inactive. Anaerobic bacteria of the species *Desulfovibrio desulfuricans*, which obtain the oxygen required for their growth by reducing organic sulfur compounds and inorganic sulfates and other sulfur compounds, then proliferate. This action appears to have its seat primarily in the slime deposits on the sewer walls and perhaps also in silt deposits. Certainly, an effluent which on its own may generate little hydrogen sulfide in 24 h will commence doing so within a few hours if mixed with slime. Temperature has a very important influence, the anaerobic bacteria becoming almost inactive below ~ 10°C. The generation of hydrogen sulfide is also affected by the pH, being at a maximum at a slightly alkaline value and falling to almost zero below pH 5 and above pH 10. No definite relationship is to be found between the content of sulfur compounds in the sewage and the incidence of problems, but there is some indication that thiosulfates and partially reduced sulfur compounds may be reduced more readily.

Hydrogen sulfide itself has no marked action on concrete, but when evolved into the air space of a sewer it dissolves in moisture films on the exposed concrete surfaces and there undergoes oxidation by aerobic bacteria to sulfuric acid. The attack takes place only on the roof and upper part of the sewer; the part below liquid level is not affected. Sewers running full are not attacked. The sulfur-oxidising bacteria can remain active at high acid concentrations, and solutions as acid as pH 1 have been observed on the surfaces of affected sewers. In the early stages of corrosion, a whitish surface deposit appears, followed later by gradual softening of the cement paste. In concrete made with siliceous aggregates the fine material drops away, leaving a rough surface with particles of coarse aggregate projecting, and later these fall away as the acid eats deeper into the concrete. Rates of attack of up to 6–12 mm depth per year have been recorded.

Evolution of hydrogen sulfide tends to increase with the age of the sewage, and thus with the time it remains in the system. Shallow falls to the sewers, long pipe runs, low flow rates and lengthy intervals between pumping cycles contribute to the problem. Since the bacteria grow more rapidly at raised temperatures, it is not surprising that there has been a much greater prevalence of trouble in countries with hot climates. Serious problems have been experienced at Cairo, Cape Town, Melbourne, Los Angeles and other cities in USA, and in India and the Middle East. Isolated cases have also occurred in more temperate climates, as in the UK and Germany. In the UK the number of cases has increased in recent years and this is attributed to the trend towards fewer and larger treatment works, resulting in longer retention times in the collecting system.[46]

Measures adopted to deal with sulfuric acid generation are generally directed towards the prevention of hydrogen sulfide evolution or prevention of its condensation. Normal sewage will commonly contain enough sulfur compounds to give rise to sulfide production if the other necessary conditions are also present, but in special cases a reduction in sulfur content by elimination of particular industrial effluents may be beneficial. The use of bactericides is impractical, since not only would it be extremely costly at the dosages required, but it would also have the unwanted effect of killing the purifying bacteria present in the sewage. Chlorination, which at practicable doses appears to act primarily by oxidation of sulfides rather than by killing the bacteria, has been used successfully to prevent sulfide production, and the injection of compressed air into rising mains has also achieved some success. The addition of lime to raise the pH of the sewage to above ~ 10 may also be of benefit. Other measures which have been found to be useful include the removal of slimes and silt, the reduction in retention times by increasing velocities, and avoidance of points of turbulence. Forced ventilation of sewers has been found to be effective in that it dries the exposed surfaces of the concrete preventing the absorption of the hydrogen sulfide and the proliferation of the sulfide-oxidising bacteria.

Concrete has a long history of satisfactory service in sewerage systems. However, no hydraulic cement can withstand the degree of acidity that anaerobic conditions in the sewage can cause. The use of limestone aggregate has been found to reduce the rate of attack by sulfuric acid on Portland cement concrete, because the aggregate itself is dissolved and thus assists in the neutralisation of the acid and also prevents the entire action being concentrated on the cement binder. It has been found that the life of a sewer under acid attack could be expected, with a limestone aggregate, to be 3–5 times that of concrete made with siliceous aggregate.[47] A further advantage is that the uniform attack to both cement and aggregate leaves an even surface, whereas where siliceous aggregates are used, attack on the cement alone results in particles of coarse aggregate protruding from the walls or being dislodged to add to the debris on the floor of the sewers, thus contributing to turbulent flow in the pipes.[48]

7.8.2 ORGANIC ACIDS

Organic acids are those which have their origins in nature. They are far more numerous than the inorganic acids and their effects on concrete are much more difficult to predict. Simple guidelines based on pH values or concentrations of solutions, which may reasonably be applied to inorganic acids as a whole, are of little value where organic acids are concerned, and virtually each acid must be considered individually with regard to properties such as its solubility in water and, most importantly, the solubility of its calcium salt. Organic acids are widely distributed in nature, occurring in living plants and as decomposition products of vegetable and animal matter. Generally the amounts present in soils and waters are small, but under certain conditions acids can accumulate to a significant degree. The organic acid most commonly present is a complex material called humic acid, which results from plant decay. Acids of this type are produced in temperate climates, but in tropical places much more aggressive acids may be produced under partially anaerobic conditions. Lactic acid has been found in swamp waters in concentrations of >1 per cent or more and has been the cause of severe deterioration of concrete.[49]

In mountain or high moorland regions where peat covers large areas, the drainage waters are often acidic owing to the presence of humic acid and also carbon dioxide, which is a product of plant decay. In these regions the rock formations are often igneous or siliceous or dense limestones into which water cannot penetrate, and there is an almost complete absence of bases and soluble salts in the surface soils. The waters in such areas are therefore almost free of dissolved salts. Where rocks are composed of less dense limestones, neutralisation of the acid constituents in the water can occur. Moorland waters, which are practically free of dissolved salts, show pH values between 4 and 7. The acidity fluctuates with the seasons and weather conditions and is usually greatest after heavy rain following a warm, dry period. This may be due to the increased production of acids in the peat under warm conditions.

A saturated solution of humic acid in water has a pH value of 3.6–4.1. Owing to its low solubility, ~ 0.19 g/L, the amount which can be carried in water is small and, although it has some action on concrete, this is much less serious than that of very pure waters or of those containing carbon dioxide. Calcium humate, which is formed by the reaction of humic acid with calcium salts, is practically insoluble in water. It has been shown in laboratory tests[50] that under static conditions there is a clear relationship between the degree of deterioration of concrete specimens and the solubility of the calcium salts of the acids in which they are stored. Insoluble calcium salts tend to block the pores of the concrete surface and prevent further loss of lime from the cement. Flowing aggressive solutions are more damaging. The reaction products are carried away from the concrete surface, thus preventing the formation of a protective skin. In the studies, pure solutions of individual acids were used. The position is more complicated under natural conditions, as in the case of peaty water, which contains two main acid fractions, each of highly complex composition. More important, however, is the action of free carbon dioxide in the water. Carbon dioxide is classified as an inorganic compound, but as it is a product of the decay of organic matter and is often associated in natural waters with organic acids arising also from plant decay, its action on concrete may conveniently be discussed in this section.

Action of carbon dioxide

Carbon dioxide is present in air to the extent of 0.03 per cent by volume, and at atmospheric pressure is soluble in water to the extent of 0.00054 g/L, giving a solution of carbonic acid which has a pH value of 5.7. Waters from deep underground sources in which carbon dioxide has dissolved under pressure may have a higher content and be more acidic, and pH values as low as 3.8 have been recorded. In river waters dissolved carbon dioxide rarely gives rise to pH values below about 5.5, and lower values are often due to the presence of organic acids. The solubility of carbon dioxide under various partial pressures and the pH values of the solutions are shown in Table 7.8.

Pure water alone has a solvent action on concrete. It dissolves calcium hydroxide to the extent of 1.2 g/L and can leach lime from set cement. This causes gradual deterioration of

Table 7.8 Solubility of carbon dioxide at various partial pressures

				Solution saturated with $CaCO_3$	
CO_2 content of atmosphere (% vol)		CO_2 dissolved at 18°C (g/L)	pH value	$CaCO_3$ dissolved (g/L)	pH value
0		–	–	0.0131	10.23
0.03	Normal air	0.00054	5.72	0.0627	8.48
0.30		0.0054	5.22	0.1380	7.81
1.00		0.19	4.95	0.2106	7.47
10.00		0.18	4.45	0.4689	6.80
100.00	CO_2 at atmospheric pressure	1.8	3.95	1.0577	6.13

Portland cement concretes which are subject to water passing through them for lengthy periods. As calcium hydroxide is removed from the cement, the silicates release more to maintain saturation in the pore water, a process which in extreme cases of leaching can result in a breakdown of the structure of the cement and a loss of strength of the concrete. Alkali metal hydroxides are also readily leached but without adverse effects on the concrete. The alkali metals are adventitious constituents of cement and play no part in its hydration or strength development. They are present in the clinker as sulfates, silicates and aluminates, which dissolve in the mixing water to form alkali hydroxides. The sulfates dissolve rapidly, within a few minutes of mixing, and others more slowly, but all the alkalis are in solution within about 28 days. The alkali hydroxides give the pore water a high pH value, which helps to protect steel reinforcement against corrosion. The content of alkali metals is small, rarely exceeding 1.3 per cent of total alkalis, expressed as equivalent Na_2O. This represents a total alkali hydroxide content of 1.7 per cent, expressed as equivalent NaOH. Portland cements, on the other hand, contain an average of 64.5 per cent calcium oxide, of which the greater part is combined in the di- and tricalcium silicates.

The aggressive action of water is increased if it contains carbon dioxide in a free state. The action ceases to be one of solution only but becomes a series of chemical reactions. Initially the carbon dioxide reacts with calcium hydroxide to form insoluble calcium carbonate, but on further action the much more soluble calcium hydrogencarbonate is formed. This will not dissolve calcium carbonate and will form more if it reacts with calcium hydroxide, according to the following reactions:

$$CO_2 + H_2O = H_2CO_3 \tag{7.8}$$

$$H_2CO_3 + Ca(OH)_2 = CaCO_3 + H_2O \tag{7.9}$$

$$H_2CO_3 + CaCO_3 \rightleftharpoons Ca(HCO_3)_2 \tag{7.10}$$

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O \tag{7.11}$$

It will be seen that equation (7.10) is reversible, and can proceed to the right or left depending on conditions. The direction will be to the right for as long as the calcium hydrogencarbonate can remain in solution, and for this some free carbon dioxide is required. If any of this is lost, the reaction will reverse to the left and calcium carbonate will be precipitated until sufficient carbon dioxide has been released to stabilise the calcium hydrogencarbonate remaining in solution.

In considering the carbon dioxide equilibria in water, it is necessary to distinguish between 'free' and 'aggressive' carbon dioxide. The free carbon dioxide is that present over and above the amount which is required to form calcium hydrogencarbonate. Some free carbon dioxide is necessary, however, to stabilise the calcium hydrogencarbonate; this amount is incapable of effecting solution of more calcium carbonate and is therefore not aggressive. Furthermore, the amount thus required will increase with the amount of hydrogencarbonate in solution. The aggressive carbon dioxide, capable of dissolving more calcium carbonate, is therefore not the free carbon dioxide present in excess of that required to stabilise the existing hydrogencarbonate equilibrium, but this quantity less that proportion of it which will be required to stabilise additional calcium hydrogencarbonate in the solution. The amount of free carbon dioxide required to maintain the equilibrium for various amounts of calcium hydrogencarbonate in solution and the pH values of the equilibrium solutions are shown in Table 7.9.

If the total amounts of free carbon dioxide and calcium hydrogencarbonate in water are determined analytically, then the amount of aggressive carbon dioxide can be derived from the CO_2–$Ca(HCO_3)_2$ curve (2) shown in Figure 7.2. It will be seen from the equation

$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2 \tag{7.12}$$

that for each molecule of free CO_2 consumed, two molecules appear in the hydrogencarbonate. Hence the solution composition must change in this reaction along a line such that the decrease in free CO_2 is half the increase in hydrogencarbonate CO_2. If the free CO_2 is plotted on twice the scale of the hydrogencarbonate CO_2, as in Figure 7.2, then the path representing the change falls on a line at 45° to the axis. Thus if the original composition of a solution of CO_2 and $Ca(HCO_3)_2$ is represented by the point A and it reacts with solid $CaCO_3$, it will change along the line AB. Reaction ceases at B since this point is on the equilibrium curve. The amount of free CO_2 consumed, i.e. the aggressive CO_2, is represented by AC. Thus, of the 100 mg/L of free CO_2 at point A only 22 mg is aggressive. At lower,

Table 7.9 Calcium carbonate–carbon dioxide equilibria data

Free CO_2 (mg/L)	CO_2 combined in $Ca(HCO_3)_2$ (mg/L)	Aggressive CO_2 (mg/L)	pH value
1	0	1	5.6
	4.4	1	7.2
5	0	5	5.2
	4.4	5	6.5
	8.8	4.9	6.8
	22	4.7	7.2
10	0	9.9	5.1
	4.4	9.9	6.2
	8.8	9.8	6.5
	22	9.5	6.9
30	0	29	4.8
	8.8	29	6.0
	22	28	6.4
	44	27	6.7

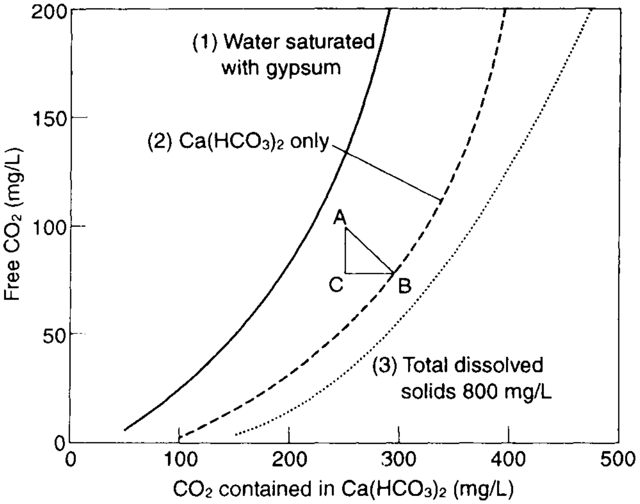


Fig. 7.2 Equilibrium between free carbon dioxide and calcium hydrogencarbonate.

and more usual, free CO_2 concentrations, or at lower HCO_3 contents in the solution, the proportion of the free CO_2 which is aggressive is higher because of the shape of the equilibrium curve. For such conditions the values can be interpolated from the data in Table 7.9. It must be emphasised that these values are only applicable to $CaCO_3$-CO_2 equilibria and will be altered if magnesium hydrogencarbonate or other salts are present. The latter is illustrated by curves (1) and (3) of Figure 7.2. Curve (3) refers to a solution containing no calcium salts other than the hydrogencarbonate, but with a total solids content, of sodium chloride, for example, of 800 mg/L, including the hydrogencarbonate. It will be seen that for a given content of free CO_2 and $Ca(HCO_3)_2$, the amount of aggressive CO_2 is higher in the saline solution and less in the gypsum solution than for water containing only the hydrogencarbonate. The reason is that the amount of free CO_2 required to stabilise a given amount of $Ca(HCO_3)_2$ increases in the presence of other calcium salts and decreases in the presence of salts of other bases. The curves given should be taken only as an illustration of the effect of salts on the equilibrium and not as a precise measure of it. In practice the pH values of natural waters of low hardness may differ by 0.5 units from those calculated from the carbon dioxide equilibria. If humic or other organic acids or mineral acids are present, these will determine the pH value, which is then not an index to the carbon dioxide content.

The structures which are most at risk from the action of acid waters are thin-walled units such as concrete pipes, and concrete subjected on one side to a pressure of water and on the other side exposed to air, so that the water tends to be drawn through it.

Considerable problems with large concrete dams exposed to pure or acid mountain waters were at one time experienced in Scandinavian countries. The dams were mainly constructed in the first quarter of the twentieth century using rather lean concrete mixes. In one survey[51] of a number of dams in Sweden, the cement contents of the concretes were reported to be between 150 and 200 kg/m^3, and the water/cement ratios to be between 0.8 and 1.0. Not surprisingly, these porous concretes all suffered leaching to some extent, as evidenced by seepages and lime deposits on the downstream faces of the dams. The leaching was generally confined to narrow bands on either side of cracks and at joints, and in these areas 50 per cent of the original lime content of the cement had been lost, although at a distance of 30 mm from the affected areas the loss was less than 1 per cent. Similar results were reported from Norway[52] where measurements of the rate of leakage and analysis of concrete of a 45 year old dam indicated that 1.8 per cent of the original lime content would be leached out after 50 years. In contrast, leaching from a dam in Scotland[53] was estimated to represent 0.2 per cent of the cement after 24 years in service. The dam was constructed with a core of 1:5 mass concrete and a facing of 1:4 concrete. The seepage observed was through thermal shrinkage cracks which had developed shortly after the dam was completed.

Few problems due to leaching have been experienced with dams in the UK, mainly owing to the general use of richer mixes than those used where problems have occurred, although differences in the composition of the waters may have a part to play, and the harsh winter conditions in the northern Scandinavian countries no doubt contribute to the degree of deterioration observed there. In the UK, etching of the surface of the upstream faces of dams impounding soft or acid waters is common, but the action usually results in no more than a rough sanded appearance where the cement paste has been leached, leaving fine aggregate exposed. Seepage has been observed through some mortar construction joints and where the water has penetrated through weak areas in the concrete, such as honeycombed patches, or through cracks. The conclusions of a study of a number of concrete dams in Scotland[54] were that the action of acid waters in the deterioration of upstream faces was of less importance than frost action, shrinkage cracking or thermal movements, and that weathering of the surfaces was most pronounced above the water line where the concrete was exposed to wind and wave action. Various degrees of deterioration of concrete have been found in ancillary works such as tunnels, conduits and pipes, where this is a fairly constant flow of water and erosive action can be a contributory factor, even where water velocities are not high.

Carbon dioxide in sea water has also been a cause of damage to concrete. In normal sea water, only small amounts of carbonate and hydrogen carbonate are present, about 10 and 80 mg/L respectively, and a small amount of free dissolved carbon dioxide. The pH value varies between about 7.5 and 8.4, an average value for sea water in equilibrium with the carbon dioxide in the atmosphere being 8.2. In normal sea water some gradual carbonation of set cement occurs, and this may be beneficial by the formation of a protective surface skin, but it is doubtful if the free carbon dioxide plays more than a minor part in the leaching of lime from a concrete. Under exceptional conditions, however, sea water can contain abnormal amounts of dissolved carbon dioxide and become very aggressive, since carbonic acid behaves as a much stronger acid in sea water than in fresh water. These conditions can arise in sheltered bays and estuaries if the sea bed is covered by organic matter, which in its decay produces carbon dioxide. Unless there is a corresponding increase in the calcium hydrogencarbonate content of the water, aggressive carbon dioxide will be available to attack concrete. Such a case was found in a dock at Newport News, USA, where concrete in the floor of a submerged slipway and in piers in the gate structure deteriorated rapidly as a result of expansion of the concrete by sulfate attack and weakening by leaching. Within 3 years after construction, the concrete below water level had lost as much as 27 per cent of its compressive strength. Analyses of water samples showed pH values ranging from 6.9 to 7.8, free carbon dioxide contents up to 100 mg/L and aggressive carbon dioxide contents up to 60 mg/L. The conclusion reached was that when the pH value of a sea water is above 7.5 there is little likelihood of leaching by carbon dioxide, that at a pH of 7.0 the content of aggressive carbon dioxide may be near the tolerable limit, and that below this pH value the content is almost certain to be excessive and cause damage to Portland cement concretes.[55]

The potential aggressiveness of a natural water is difficult to assess since it is dependent on a number of interrelated factors. Some European Standards give limits for particular constituents which are considered to be responsible for different actions, such as leaching of the concrete, acid attack and attack due to aggressive carbon dioxide, but these cannot be considered independently of one another. For any given degree of temporary hardness, the risk to concrete increases as either the free carbon dioxide content increases or the pH value decreases. As the temporary hardness decreases, so does the concentration of carbon dioxide required for the water to be aggressive. As a guide, a water with a temporary hardness, expressed as $CaCO_3$, of not more than 50 mg/L and a pH value not lower than 6.0 is unlikely to cause damage unless its content of free carbon dioxide exceeds 50 mg/L. Soft waters, with a low dissolved solids content and a temporary hardness of <3 mg/L of $CaCO_3$, can have a marked solvent action even if the free carbon dioxide content is negligible and the pH value is 7.0 or higher.

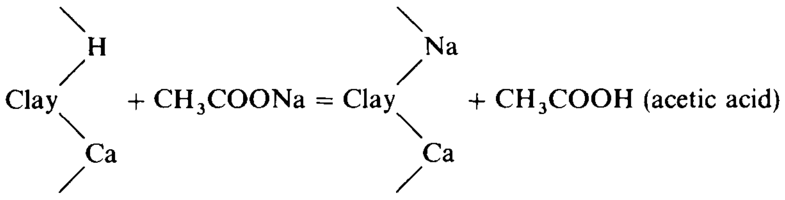
Much work has been done in Europe and USA on damage to concrete pipes by aggressive waters. Particular attention has been paid in Sweden to attack by acid waters containing carbon dioxide but which are free of sulfates and other damaging agents. It was found that pipes laid in sandy soils through which water could percolate fairly readily were at the greatest risk of attack, which was most severe at sockets and on the tops of the pipes. In the cases where damage had occurred, the average content of free carbon dioxide in the waters was 50 mg/L. These investigations and other field and laboratory work led to the classification of the aggressiveness of natural waters shown in Table 7.10.[56] The results, after 10 years, of the performance of a test pipeline carrying water with a low temporary hardness, an aggressive carbon dioxide content varying from 20 to 70 mg/L and a pH value ranging from 4.5 to 6.5 were that porous and permeable pipes had suffered severely, whereas spun and dense machine-pressed pipes had suffered only slightly. It was concluded that high-quality, dense precast concrete pipes made with ordinary Portland cement should withstand the effects of waters of the most aggressive class of Table 7.10 for a considerable time. The conclusions of a survey made in New Zealand of the performance of spun concrete pipes in contact with acid ground waters containing aggressive carbon dioxide were that the classifications given in the table were applicable where freely moving ground water was in continuous contact with the pipes, but where the contact was seasonal and the movement of the water slow, the attack was less severe than indicated by Table 7.10.[57]

Table 7.10 Swedish classification of natural waters containing carbon dioxide

Class of water	Temporary hardness $CaCO_3$ (mg/L)	Aggressive carbon dioxide (mg/L)	Degree of aggressiveness to concrete
I	>35	<15	Very slight
II	>35	15–40	Slight
	3.5–35	<15	Slight
III	>35	40–90	Severe
	3.5–35	15–40	Severe
	<3.5	<15	Severe
IV	>35	>90	Very severe
	3.5–35	>40	Very severe
	<3.5	>15	Very severe

Effect of acid soils

The risk to concrete in acid soils is very difficult to assess. The pH value alone does not give much information, although it is useful in indicating the possible presence of mineral acids. However, because of the complex nature of soil organic acids and the lack of readily performed tests for their determination, the pH value remains the criterion most commonly adopted. The amount of exchangeable acids present in the soil is used in some standard specifications. The measurement is based on the fact that certain soils which are not acidic in reaction when in contact with pure water only are capable of exchanging hydrogen ions on the lattices of clay minerals for base ions when in contact with salt solutions, thus forming an acid. The reaction may be represented in equation (7.13) where sodium acetate, the salt specified in the test procedure, is shown as the reactant.



$$\mathrm{Clay}\begin{matrix}\diagdown \\ \diagup \mathrm{H} \\ \diagdown \\ \diagup \mathrm{Ca}\end{matrix} + \mathrm{CH_3COONa} = \mathrm{Clay}\begin{matrix}\diagdown \\ \diagup \mathrm{Na} \\ \diagdown \\ \diagup \mathrm{Ca}\end{matrix} + \mathrm{CH_3COOH}\ \text{(acetic acid)} \qquad (7.13)$$

The test has a use in agricultural soil chemistry and in various aspects of the behaviour of clays, but it is doubtful if it is of value in assessing the risk of attack to concrete by organic acids.

Acids in industrial processes

There are many industrial processes in which naturally occurring acids take part. They may be present in the raw materials, be formed as by-products or be discharged in effluents. These acids can have a deleterious action on concrete, and conversely, bare concrete surfaces in tanks, for example, may have an adverse effect on materials or products. It is not possible here to give more than a brief account of the action of a few of these organic acids and of the processes in which they mainly occur. Others have been described by Biczok[58] and Barry.[59]

The commonly encountered acids can be divided roughly into two groups. The first group includes water-soluble acids of relatively low molecular weight, such as lactic, butyric, acetic, citric, malic and other acids occurring in fruits, and acids such as oxalic and tartaric acids. The second group includes acids of high molecular weight, such as oleic, stearic and palmitic acids, which are insoluble in water.

Lactic and butyric acids have a most destructive action on set cements. They occur in sour milk and butter and can give rise to pH values as low as 4.0 in the effluents from dairies and cheese factories. Unlined concrete tanks are not used in dairies, because of the need for surfaces which can easily be cleaned and sterilised, but problems have been experienced with concrete floors. Neither pozzolanic nor blastfurnace slag cements offer any advantage over ordinary Portland cement against attack by lactic acid. Thin surface treatments are not of significant value in providing protection against attack. Clay tile floors are frequently used, but the jointing must be of acid-resistant materials. Cement mortars are readily attacked.

Lactic and butyric acids, together with acetic and other acids, also arise during the production of silage from green plant material. If the material is closely packed with little access of air, the fermentation produces ‘acid’ silage. With loose packing, more rapid oxidation occurs, giving ‘sweet’ silage. In either case, organic acids are formed and the temperature of the material rises. Acetic, lactic and butyric acids are present in sour silage to the extent of 0.5–1 per cent, but sweet silage has a lower level of acidity and is therefore less aggressive. Precast concrete staves made with ordinary Portland cement are used in the construction of silos and, although there is some attack if the pH value of the silage is < 5, the degree of attack which may occur depends on the quality of the concrete, and in particular on its permeability and water absorption.

Acetic acid is the principal constituent of vinegars, which contain 3–5 per cent of the acid by volume. A 5 per cent solution has a pH value of 3.5 and rapidly attacks Portland cement concrete. Pozzolanic and Portland blastfurnace slag cements are rather more resistant than Portland cement to low concentrations of acetic acid, but are equally attacked by strong solutions. In pickling and other food preparation processes in which vinegar is used, the aggressive action of acetic acid may be aggravated by acids present in any fruits used, by the action of sugar and by the high temperatures required in the processes.

The same problems occur in jam making and fruit bottling and canning plants. Fruits contain a variety of organic acids and in general have pH values between 2.6 and 3.6. Ripe fruits also contain sugars and the amount present determines whether a particular fruit will taste sweet or sour. Thus while strawberries and raspberries have pH values between 3.0 and 3.5, the pH values of fruits such as gooseberries and rhubarb, which taste considerably more acidic, lie between 2.8 and 3.2. Although a number of organic acids are found in various parts of plants, either as free acids or as salts, those most commonly occurring in fruits are malic acid, which is widely distributed in many fruits, including apples and grapes, and citric acid, which is present in gooseberries as well as in the citrus fruits. Both acids have an action similar to acetic acid and in 1 per cent solutions seriously attack Portland cement concretes within 1 year or so.

Tartaric acid is similar in its action on concrete to lactic and acetic acids. Although it may be found in certain plants in the free state, it occurs chiefly as the acid salt, potassium hydrogentartrate, in various fruits, especially grapes. The salt crystallises from the grape juice during fermentation and is recovered for use in baking and for other purposes under the name of cream of tartar. The salt is less acidic than tartaric acid and as a rule does not have much effect on concrete, but the use of concrete tanks in wine making may have an adverse effect on the juice and hence the wine.

Oxalic acid occurs in many plants as the free acid or as salts. The acid has some initial action on Portland cement concretes, but the calcium oxalate formed as a result is insoluble and is precipitated as a protective surface deposit, preventing further attack. Oxalic acid and its salts have a number of industrial uses, but are poisonous and are not encountered in food-processing plants.

Sugars were mentioned above as being damaging to concrete in plants processing fruits. The sugars involved are glucose (grape sugar) and fructose (fruit sugar), which are present in the juice of sweet fruits and in honey, and sucrose, obtained from sugar cane or beet. Refined glucose and the mixture of glucose and fructose called invert sugar and produced by the hydrolysis of starch are also used, particularly in confectionery. Other sugars and the industries in which they occur are maltose (malt sugar) in brewing, lactose (milk sugar) in dairying activities and xylose (wood sugar), present with other sugars in wood pulping plants.

When sugars act on hardened Portland cement concretes, they react with the calcium hydroxide of the cement to form calcium saccharate. With severe or continued action, depletion of the calcium hydroxide destroys the normal structure of the hardened cement paste, resulting in softening of the mortar and loss of strength of the concrete. This is particularly troublesome on concrete floors, where surface wear adds to the damage.

Sugars are also powerful retarders of the setting of Portland cements, and are present in varying amounts in the lignosulfonate-based retarding admixtures. In the very small amounts entering the mix at dosages of the admixtures recommended by their manufacturers, the sugars do no more than delay the processes of solution, reaction and crystallisation of normal setting, without affecting the properties of the hardened concrete. Used in greater amounts, excessive retardation may occur, and 0.05 per cent of sugar by weight of cement may result in zero strength development of the concrete at 1 day, and only half the normal strength at 3 days. An addition of 1.0 per cent almost completely inhibits setting and hardening.

It is not proposed here to discuss the various theories propounded to explain the delay in setting that sugars cause to fresh concrete. However, to resolve any confusion that may occur because of the conflicting effects of sugars on fresh and hardened concrete, their actions may be likened to those of sulfates. The sulfate present in Portland cements has an important influence on the setting reactions, whereas sulfates entering hardened concrete have a damaging and disrupting effect.

The high molecular weight acids of the second group occur in animal and vegetable fats and oils as glycerides, or esters, and to a lesser extent as free acids. Oils of vegetable origin, even when fresh, usually contain appreciable quantities of free acids, but freshly rendered animal fats contain only very small amounts. Glycerol is the chief alcohol present in the esters, and the acids are most commonly stearic, palmitic and oleic acid. The corresponding esters are glyceryl stearate (stearin), which is present in tallow and suet, glyceryl palmitate (palmitin), which occurs in palm oil, and glyceryl oleate (olein), present in olive and other vegetable oils. Mixed glycerides, in which more than one type of fatty acid is present in the same molecule, also occur. Examples are lard, beef fat and butter, which contain both palmitic and stearic acids.

The glycerides, in common with all esters, are broken down by hydrolysis into their constituent acid and alcohol components. This is mainly brought about by the action of aqueous solutions of mineral acids or of hydroxides. In hydrolysis by acids, the acid acts purely as a catalyst for the reaction, but in alkaline hydrolysis the metal of the hydroxide forms a salt with the fatty acid. This is the principle of soap making in which solutions of sodium or potassium hydroxide act on fats and oils to produce salts, or soaps. By reason of its association with soap making, the process of alkaline hydrolysis became known as 'saponification', a term which is still frequently used.

When fats and oils come into contact with Portland cement concrete, they are hydrolysed by the calcium, sodium and potassium hydroxides present in the set cement to form soaps and liberate glycerol, which can itself react with the cement. Soaps of the alkali metals are soluble in water, whereas calcium soaps are insoluble. Any free acids present in the fats or oils attack the concrete directly. Glycerol is produced on a commercial scale during soap manufacture. It is miscible in water in all proportions and attacks concrete by slowly combining with, and dissolving, calcium hydroxide in the cement, forming calcium glycolate. A solution of glycerol in water as weak as 2 per cent has a destructive action on fresh Portland cement concrete, although there is less effect on matured concrete with a well-carbonated surface. Synthetic resin paints have been used as a protection to concrete against weak solutions of glycerol, but with strong solutions, $\geqslant 10$ per cent, thicker protective linings are required.

The extent to which an oil can attack concrete is dependent on the ease with which it can penetrate, and hence on its viscosity; the more viscous the oil the less serious is its action. Oils which have been exposed to the atmosphere and have accumulated moisture and undergone oxidation (become rancid) are more active in their attack than when fresh.

Oils which can be stored successfully in closed concrete tanks may often be very destructive to concrete floors where there is free access of air and moisture and where any protective films of insoluble soaps which form can be rapidly worn away. The problem of providing suitable floors arises in many industries concerned with the manufacture of soap, margarine and other foods and in oilseed crushing and similar processes. The problem becomes greater if the floors are subjected to heavy wear. It has been found in these industries that Portland cement concrete floors are generally not satisfactory for use. Even the best granolithic floors or floors with a floated finish soften and eventually disintegrate. The higher the content of free fatty acid in the oil, the more rapid is the action. Relatively few test data are available to show the comparative resistance of different cements to attack by oils, but it appears that there is no clear distinction, and a cement with a high degree of resistance to one oil may be rapidly attacked by another. Pozzolanic and blastfurnace slag cements have been considered somewhat less vulnerable than Portland cements, but it is doubtful whether the differences in performance are enough to be of practical significance.

Linseed oil is sometimes used as a protective surface coating for concrete, a use which may appear contradictory to its chemical composition and behaviour. It is a glyceride and in contact with concrete is hydrolysed to give calcium and alkali-metal soaps and free fatty acids. However, the similarity in behaviour with other oils ceases there. Linseed oil is what is called a 'drying' oil, whereas the oils discussed so far are 'non-drying'. The acids present in linseed oil are highly unsaturated in molecular structure, and when exposed to the atmosphere take up oxygen and moisture to form fully saturated hydroxy acids. This causes the oil to harden and to provide an impervious skin on a substrate to which it is applied, whereas the non-drying oils remain soft and become rancid on exposure.

Oils of vegetable origin, such as oil of turpentine and eucalyptus oil, are not glycerides and have no chemical action on concrete, although they may readily penetrate it.

7.9 Action of mineral oils

Mineral oils such as petrol, fuel oils, and petroleum distillates in general, do not attack matured concrete, although they seriously affect the hardening of fresh concrete. Such straight petroleum oils do not contain any constituents which react chemically with cement compounds, and their action on fresh concrete is a physical one by which their immiscibility with water impedes hydration of the cement. Creosotes which contain phenols, cresols and similar acidic compounds may have some effect on concrete. Lubricating oils which are entirely of mineral origin do not attack concrete, but those containing vegetable oils have a definite action and damage has been caused to workshop and garage floors.

Although mineral oils have no chemical action on concrete, it is difficult to make concrete impermeable to them, and in the case of the lighter oils, virtually impossible. Concrete tanks may be used for storage of oils of specific gravity not lower than 0.875, but a rich mix is required. With oils of specific gravity between 0.875 and 0.850, several carefully applied coats of a surface treatment may provide protection against penetration, but oils of specific gravity <0.850 cannot be contained by such means, and resistant linings of materials such as polysulfide rubber are required.

7.10 Action of gases on concrete

Air consists principally of four gases: nitrogen, oxygen, argon and carbon dioxide. Representative values for the proportions (per cent by volume) of these gases in pure dry air are nitrogen 78.0, oxygen 21.0, argon 0.9 and carbon dioxide 0.03–0.04. In addition there are minute amounts of the other inert gases associated with argon. The atmosphere generally contains variable quantities of water vapour and gases which may be emitted locally by certain natural processes, of which the production of methane is an example. Sulfur dioxide is commonly present in the gases emitted from volcanic vents, and is also present in certain sulfur springs. Hydrogen sulfide is also present in some mineral springs, as at Harrogate, UK. Of more widespread occurrence are the gases introduced to the atmosphere by human activities.

Of the four main gases naturally present in air, nitrogen and argon are completely without effect on concrete. Oxygen does not have a direct chemical effect and does not damage plain concrete. Where reinforced concrete is concerned, oxygen may contribute to corrosion of the reinforcing steel if the concrete is porous or contains cracks through which air can penetrate to the metal. The risk of corrosion is increased by the action of the carbon dioxide, which reacts with the calcium of the cement paste to form calcium carbonate, thereby reducing the pH of the cement paste and the protection its normal high alkalinity gives to the steel. Conversely, the same chemical reaction affords protection to the surface of dense concrete by forming an insoluble skin of calcium carbonate.

The gases chiefly responsible for chemical attack are carbon dioxide when present in excess of its normal concentration in air, sulfur dioxide and a mixture of oxides of nitrogen, all of which are products of the combustion of coal or petroleum fuels. Carbon dioxide is always a product of the complete combustion of carbonaceous fuels. The amount of sulfur dioxide which may be emitted in waste gases is dependent on the content of sulfur compounds in the fuel burned and is therefore a variable quantity. The chief source of oxides of nitrogen is exhaust gases from motor vehicles, although the combustion of coal containing nitrogenous compounds may make a small contribution.

The gases dissolve in water to give acid solutions, but are generally quickly dispersed by air movements and so when dissolved in atmospheric moisture form very dilute solutions which are not a source of serious damage to concrete. Limestone or marble stonework may suffer some attack, particularly in urban areas where the combustion products from domestic premises are emitted at low levels. In tall chimneys, as at power stations and other industrial works, the waste gases may cool sufficiently for condensation to occur in the upper part of the chimney, and this can result in attack to concrete and brickwork mortar. The same problem may occur in domestic premises where boilers of high thermal efficiency are used and the flue gases are at a low temperature. In railway tunnels trafficked by coal-burning engines, carbon dioxide and sulfur dioxide may be present in fairly large amounts. Dry tunnels are relatively unaffected, but in damp tunnels quite rapid attack on concrete linings and mortar in brickwork has been experienced.

Sulfur dioxide is more aggressive than carbon dioxide because it is much more soluble in water and so can form more concentrated solutions. Its solubility allows it to be readily removed from flue gases by water scrubbing, and although this is not practicable where only small amounts of coal or oil are burned, it is standard practice in industries using large amounts of fuel, as in power stations. Concrete in washing towers and elsewhere in the treatment plant must be protected against acid attack.

In the UK, levels of sulfur dioxide in the atmosphere have decreased by an average of 97 per cent during the past 40 years. This has been brought about by legislation to control emissions from domestic as well as industrial premises. The replacement of coal gas by natural gas has also had a beneficial effect. In contrast to these improved emissions, levels of oxides of nitrogen have risen as a result of increased road traffic, and have almost doubled in the last 10 years. It is, however, too early to know what damage these oxides may cause, and although very high concentrations in the air are common in some parts of the world, it is doubtful whether serious attack to concrete would be caused by the amounts currently emitted in the UK.

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8

Physicochemical and Mechanical Properties of Portland Cements

C. David Lawrence

8.1 Introduction

The microstructural nature of Portland cement-based products is complex and gives rise to time-dependent physical and mechanical properties, with significant changes taking place over periods of many months or even years. These effects are more fundamental than the continuing hydration reaction of the initial unhydrated cement, and involve slow ageing processes in the colloidal hydration products. In addition, the chemical binding of water in the hydrates takes on a series of energies which result in ready loss of moisture over a wide range of humidities, and a readjustment of water molecules between different sites within the microstructure in response to small changes in environmental temperature and humidity. All such changes, some of which are irreversible, are reflected in changes in physical and mechanical properties. Conventional physical and mechanical attributes suitable for describing the behaviour of solids are allotted to hardened cement pastes and concretes, for example thermal expansivity or elasticity, but it should be realised that these functions have only approximate validity for these systems and are dependent on the length of time for which the external stimulus is applied.

At the present time, the material properties of hardened cement pastes and concretes may be summarised in empirical relationships between formulation parameters and physical or mechanical tests in the laboratory; modifying factors are applied for different environmental conditions (for example, the CEB–FIP international recommendations for the design and construction of concrete structures, 1970). The fundamental relationships between practical performance and chemical or physical microstructure are not at present reliable, but these may become more important as knowledge improves and as new demands on concretes justify a more basic approach. Probable relationships between the properties of hardened cement pastes, the paste microstructure and the conditions of formation may be envisaged. From a preliminary analysis, it appears that strength is controlled by relatively few basic parameters and may be the subject for an initial extension of the current empirical approach.

8.2 Heat of hydration

The chemical reactions between unhydrated cement and water during setting and hardening release heat which results in a rise in the temperature of the fresh concrete.

Eventual cooling of the newly set concrete results in thermal contraction and cracking, and a method of predicting temperature rise, with a means of control, is necessary to limit permeability and improve durability. The temperature rise can be related to the cement content of the concrete (per unit volume of fresh concrete) and to other chemical composition factors of the concrete and the cement.

8.2.1 HEAT OF SOLUTION

The heat of solution method for measuring the isothermal heat of hydration of Portland cements was developed by Woods *et al.*[1] and has become the traditional method specified in National Standards (BS 4550, Part 3, Section 3.8; ASTM C 186-82). Isothermal conduction calorimetry[2,3] has now largely replaced the heat of solution method in the laboratory; however, European Standards have retained the traditional approach.

The heat of solution method consists of measuring, at a particular age of hydration, the difference between the heats of dissolution of partly hydrated and of unhydrated cement in a mixture of nitric and hydrofluoric acid. The difference is equivalent to the heat of hydration at that particular age. The cement/hydrate dissolution is carried out in a glass vacuum flask calorimeter, after forming an acid-resisting lining (i.e. a wax coating on its inner surface), and fitted with a Beckmann thermometer (also protected with a wax coating), thus enabling temperature rises to be measured to a small fraction of a degree Celsius.

8.2.2 CONDUCTION CALORIMETRY

A number of studies of cement hydration using isothermal conduction calorimetry have been reported in the literature.[3–8] One conduction calorimeter which is commercially available has the capability of measuring heat evolution rates from 10 μW to 200 mW for cement samples of mass 0.1–50 g over periods from a few hours up to several weeks, whilst maintaining temperature constant to within 1°C. Rates and total heat evolved (1–10 J) can be measured with an error of less than 1 per cent. Comparisons with the conventional heat of solution method have been reported.[3] The procedure used conforms to that recommended by Cembureau.[9] The isothermal calorimeters used are capable of measuring heat evolution rises over periods up to 28 days at controlled temperatures between 5 and 60°C.

Examples of heat evolution curves for Portland cements are given in Figures 8.1–8.9, carried out on a JAF calorimeter by D.C. Killoh, working at the laboratories of the Cement and Concrete Association. The calorimeter used in these tests was originally reported in 1970;[10] its precision is evaluated by means of electrical power input.[11] There are two heat evolution peaks in these examples; an additional initial peak is also present but occurs in the first few minutes and requires special techniques in order to be revealed on the trace. Comparisons have been made between the data generated from the different methods of measuring heat hydration[3] and excellent agreement has been obtained between the conduction calorimeter results and the traditional heat of solution results, with the former giving data having a much lower standard deviation.

Isothermal calorimetry gives a good separation of the hydration reactions for the different cement minerals present;[7] X-ray diffraction data on the hydrating pastes allow an assignment of chemical reactions to the different peaks in heat evolution over periods of hydration approaching 250 h. If optimum performance is to be achieved from the cement, it is thought that the peak hydration rate associated with C_3A should be delayed by SO_3 additions until the silicate hydration rate has passed its peak. For example, see Figures 8.4–8.6 for cement 3984, where the second C_3A hydration peak is gradually delayed and attenuated by the added $CaSO_4$, leaving the initial C_3S hydration peak to develop fully.

Special developments of isothermal calorimeters have been made in order to allow the measurement of heat evolution at temperatures up to 300°C. These instruments are of value in developing Portland cements that need to set and harden at high temperatures and pressures, for example oil well cements.

8.2.3 *ADIABATIC CALORIMETRY*

A third method, adiabatic calorimetry, is used to estimate temperature rises in mass concrete. Since the total heat evolved for any cement in an adiabatic test is partly dependent on the temperature reached, the measured heat of hydration (i.e. the temperature rise) using this method will depend on the heat capacity of the mix components as well as on the heat generated.

In order to calculate the rise in temperature of a mass of concrete under adiabatic conditions, allowing for the differing heat evolution rates as both time and temperature increase, isothermal heat of hydration data for the cement are required for at least two temperatures. The specific heats of the cement and aggregate together with the mix proportions of the concrete, must also be known.

The method of analysis makes use of the Arrhenius equation:

$$K = A\exp\left(\frac{-E}{RT}\right) \tag{8.1}$$

where K is the specific hydration rate constant, E is the activation energy for hydration, R is the gas constant, T is the absolute temperature and A is a constant.

The hydration reaction cannot be assumed to be a single chemical reaction, so a separate activation energy is calculated for each increment in heat evolved (10 kJ/kg) as the hydration progresses. Thus the rate of temperature increase for a given concrete is modified both by the temperature at which the cement is hydrating and the activation energy associated with this hydration temperature.

8.2.4 *EFFECT OF PROPORTION AND COMPOSITION OF MAIN CLINKER MINERALS*

The use of calculated compound contents as a method of control for the properties of cements originated in the specifications for low-heat cement drawn up in the USA during the years 1932–34.[12] Later chemical specifications for 'modified' (ASTM Type II) and sulfate-resisting cement have since been adopted in other countries for such special types of Portland cement. For the control of heat hydration, the use of compound content limitations is to be regarded as an expedient, to be justified on grounds of convenience or speed, and not as the infallible result of well-established laws. Calculated compound contents are of limited value; they may afford a somewhat better descriptive picture of the nature of a cement than does the analytical composition expressed in terms of oxides.

Whereas the rates of hydration of the different modifications of C_3S, stabilised by various impurities, are not radically different, the same is not true of C_2S. γ-C_2S is the

Table 8.1 Comparisons of rate constants for some calcium silicate hydration reactions[13]

		$K_N \times 10^3$/h	$K_I \times 10^3$(μm/h)	$K_D \times 10^3$(μm^2/h)	
Modification	Amount of stabiliser	Nucleation and crystal growth	Phase boundary	Initial diffusion	Subsequent diffusion
α′	11% BaO	–	31	5.4	1.4
α′	3% B_2O_3	9.1	5.5	5.0	1.1
β	1% B_2O_3	7.3	1.4	3.5	1.8
Alite	–	11.0	67	26	14

stable form at room temperature, but it is usually regarded as being practically non-hydraulic. The other polymorphs are metastable and must be stabilised with impurity oxides, the actual degree of hydraulic reactivity depending on the stabilising oxide. Some kinetic data[13] are given in Table 8.1.

In some cases the compound content requirement is used to supplement direct physical tests, in others as a substitute for them. The earlier US specifications for low-heat cements required that the heat of hydration should be measured as well as imposing calculated compound content requirements, but later the direct physical test was dropped and reliance was placed solely on the latter. Limitations based on the composition of a cement, or the compound contents derived from them, are attractive since direct physical tests need to be carried out over extended periods of time. However, the heats of hydration calculated from the compound content can vary up to 50 kJ/kg from the measured values.[14–16]

8.2.5 *EFFECT OF SULFATE CONTENT*

Measurement of heats of hydration and rates of heat evolution of cements have been made by isothermal conduction calorimetry according to the British Cement Association procedure TP/E/304/1 on a selection of Portland cements (Tables 8.2 and 8.3). The method covers the measurement of the rate of heat evolution of a cement sample under isothermal conditions using a JAF-type conduction calorimeter.[2] Processing of the data

Table 8.2 Chemical analysis of the cements examined in the heat of hydration experiments (main components, per cent)

Cement code	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	LOI[a]	Na_2O	K_2O
3982	20.9	2.80	4.32	62.8	2.14	4.19	0.90	0.32	1.02
3984	21.3	2.82	4.36	63.3	2.15	3.30	0.75	0.31	0.99
4037	20.0	2.19	4.82	62.7	2.61	4.14	1.31	0.41	0.83
3992	20.3	2.28	5.08	63.3	2.70	3.23	0.96	0.44	0.86

[a] Loss on ignition at 1000°C.

Table 8.3 Chemical analysis of the cements examined (minor components, per cent) and specific surface (cement fineness) m^2/kg

Cement	TiO_2	P_2O_5	Mn_2O_3	CaO, free	Na_2O sol	K_2O sol	SO_3 sol	Fineness (m^2/kg)
3982	0.19	0.15	0.03	0.35	0.07	0.58	0.398	552
3984	0.19	0.15	0.03	0.50	0.07	0.68	0.377	537
4037	0.25	0.21	0.03	0.67	0.08	0.47	0.377	583
3992	0.27	0.22	0.03	1.06	0.09	0.46	0.406	529

Na_2O sol, K_2O sol and SO_3 sol represent the percentages of the appropriate chemical components that are readily soluble.

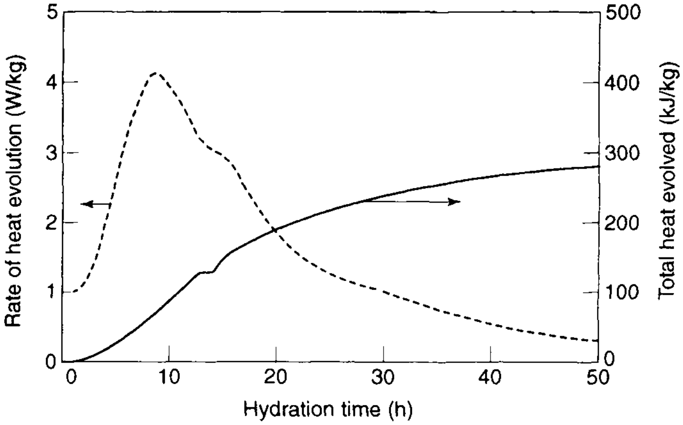

Fig. 8.1 Heat of hydration of cement paste determined by isothermal calorimetry, Cement 3982 (20°C and w/c = 0.375; maximum rate 4.14 W/kg at 8.7 hours).

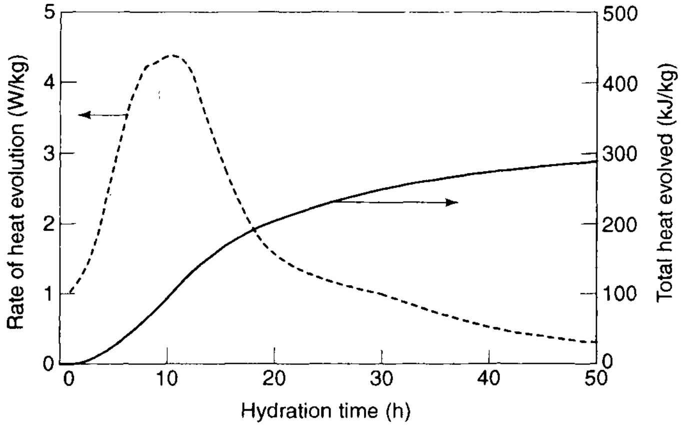

Fig. 8.2 Heat of hydration of cement paste determined by isothermal calorimetry, Cement 3984 (20°C and w/c = 0.375; maximum rate 4.39 W/kg at 10.6 hours).

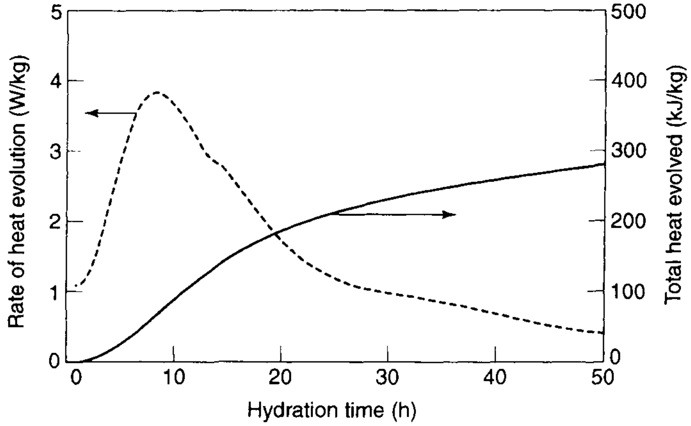

Fig. 8.3 Heat of hydration of cement paste determined by isothermal calorimetry, Cement 4037 (20°C and w/c = 0.375; maximum rate 3.86 W/kg at 8.2 hours).

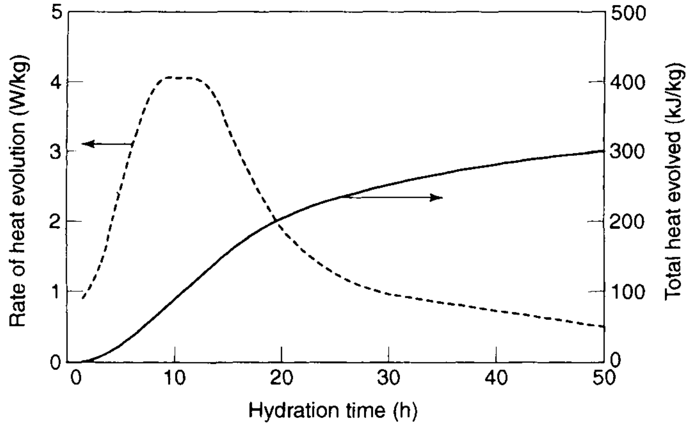

Fig. 8.4 Heat of hydration of cement paste determined by isothermal calorimetry, Cement 3984 (20°C and w/c = 0.440; maximum rate 4.09 W/kg at 11.7 hours).

gives graphs of the rate of heat evolution and of the total integrated heat evolved versus time; examples are shown in Figures 8.1–8.9.

The maximum overall early hydration rate for a cement may be reduced as the sulfate level is increased. Odler[17] has reported the effect of gypsum content on laboratory-made cements with variable C_3A/C_4AF ratios: the optimum SO_3 level was determined by maximising the strength after 28 days, and was increased as the C_3A/C_4AF ratio was increased.

Both total SO_3 and the rate of solution of the added calcium sulfate are important in determining the optimum calcium sulfate level required by a given cement clinker. Gypsum added to the clinker is largely dehydrated by the cement-grinding process, to

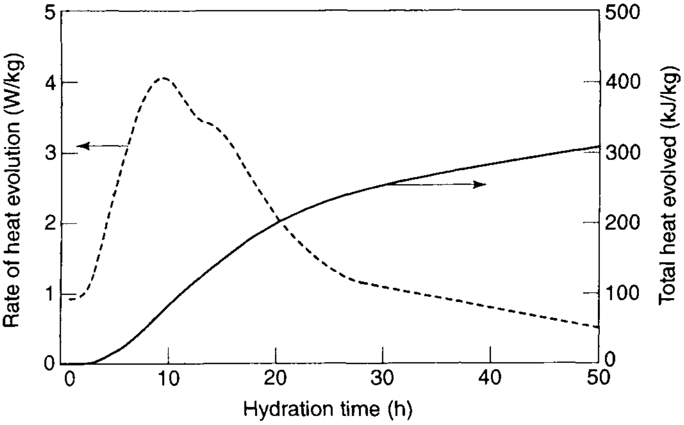

Fig. 8.5 Heat of hydration of cement paste determined by isothermal calorimetry, Cement 3984 + 0.5% SO_3 (20°C and w/c = 0.440; maximum rate 4.07 W/kg at 9.4 hours).

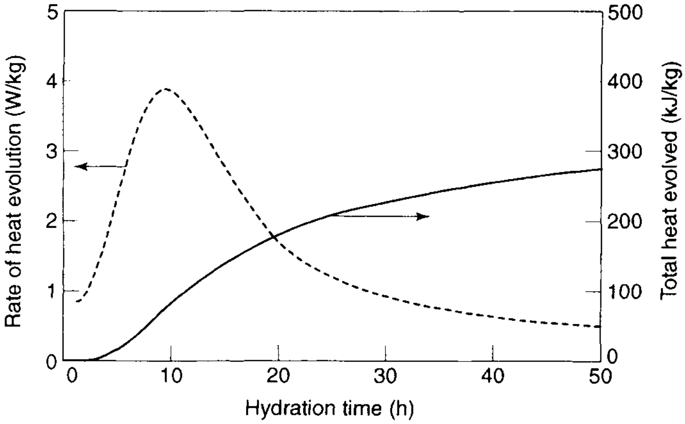

Fig. 8.6 Heat of hydration of cement paste determined by isothermal calorimetry, Cement 3984 + 2.5% SO_3 (20°C and w/c = 0.440; maximum rate 3.91 W/kg at 9.5 hours).

form the rapidly soluble hemihydrate. The strength performance of a cement is a function of the degree of gypsum dehydration; the greater the dehydration, the higher the strength.[18] Rapid rehydration of the hemihydrate when the cement is mixed with water in the concrete mixer can give rise to false set, but this becomes a problem only when the degree of dehydration in the grinding mill reaches 85–90 per cent. The extent to which calcium sulfate dihydrate is dehydrated in a cement mill depends on the temperature and relative humidity in the mill. The hemihydrate formed does not have the precise composition implied by its name because the same crystal structure, with small variations only in the unit cell size, covers the range $CaSO_4 \cdot 0.01$–$0.63\ H_2O$. The name ‘soluble anhydrite’ is used for the low end of this range. These compositions can be interconverted

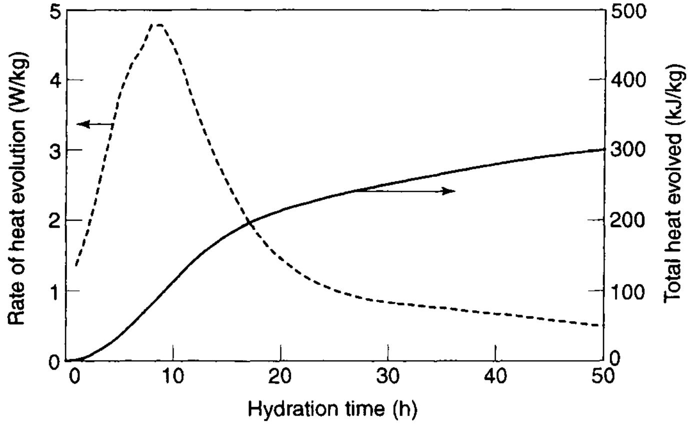

Fig. 8.7 Heat of hydration of cement paste determined by isothermal calorimetry, Cement 3992 (20°C and w/c = 0.440; maximum rate 4.82 W/kg at 8.3 hours).

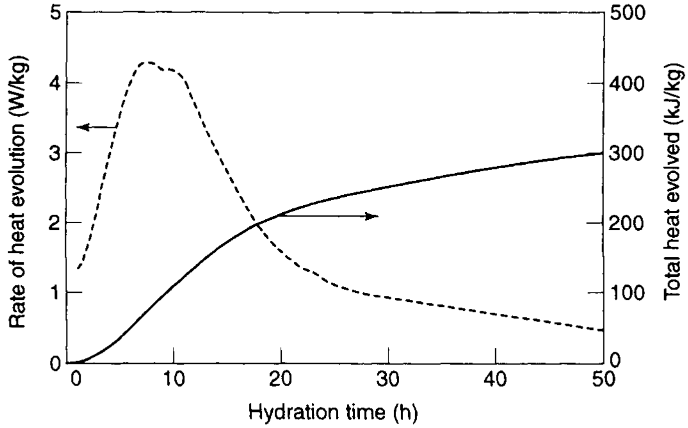

Fig. 8.8 Heat of hydration of cement paste determined by isothermal calorimetry, Cement 3992 + 0.5% SO_3 (20°C and w/c = 0.440; maximum rate 4.30 W/kg at 7.7 hours).

simply by a change in relative humidity since water molecules can enter or leave the structure, as in zeolites. In contrast, conversion of this structure to the dihydrate is believed to occur only by its dissolution in water, from which the dihydrate crystallises as the stable phase at temperatures below 43°C.

Heats of hydration were examined at water/cement = 0.375 and 0.44, at 20°C, for cements 3982, 3984, 4037 and 3992, with SO_3 additions (gypsum) in certain cases (Figures 8.1–8.9). As extra sulfate was added to cement 3984 or cement 3992, a peak in heat evolution (the aluminate peak) that was originally superimposed on the main silicate hydration peak was retarded and weakened, and eventually was suppressed at 2.5 per cent SO_3 addition. Both the maximum rate of heat evolution and the total heat evolved were

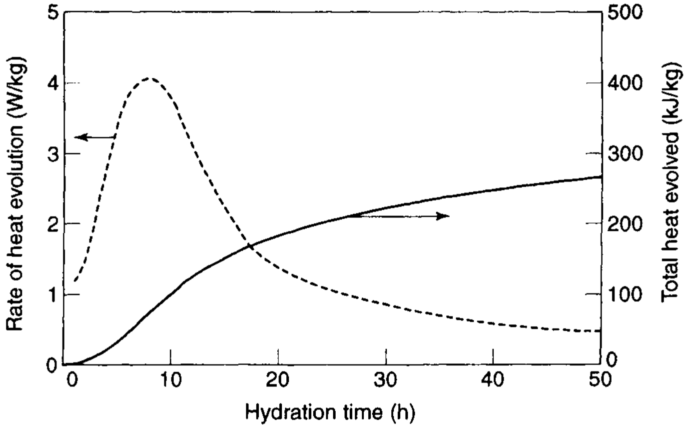

Fig. 8.9 Heat of hydration of cement paste determined by isothermal calorimetry, Cement 3992 + 2.5% SO_3 (20°C and w/c = 0.440; maximum rate 4.09 W/kg at 7.7 hours).

reduced somewhat as sulfate levels were increased. Total heat of hydration after 28 days was not much affected by sulfate levels.[19] The sensitivity of the procedure to changes in cement composition and cement paste water/cement ratio is well illustrated by these results.

8.2.6 EFFECT OF ALKALI CONTENT

Present-day cement processing technology has resulted in an increasing amount of alkali sulfates in Portland cements. Alkali sulfates, in general, accelerate the rate of hydration and give high early strengths.

A detailed study of the effect of alkalis in clinkers on the rate of hydration of Portland cement has been reported.[8] Acceleration occurred when alkalis were present in the clinker and the gypsum requirement for proper retardation was affected, those with higher alkalis requiring more gypsum. As more gypsum is added, the hydration rate was increased.[20]

The degree of hydration of C_3A was decreased as the quantity of Na_2O in solid solution was increased.[20] The degree of hydration of NC_8A_3 is less than that of C_3A after 1 day of hydration, whereas the degree of hydration of $KC_{23}S_{12}$ and β-C_2S were almost the same.

8.2.7 EFFECT OF PARTICLE SIZE DISTRIBUTION

Frigione has published data on the effect of particle size distribution on the heat of hydration of cement.[21] The heat of hydration and the amount of hydration product increase when the particle size distribution becomes narrower.

8.2.8 DISCUSSION

The traditional indirect method of determining the heat of hydration of cements consists of separate experiments to dissolve the cement and the partly hydrated cement paste in strong acid (mixed nitric and hydrofluoric acids), and equates the differences in heat released to the heat released during hydration, using the laws of thermochemistry. In this way the heat released after a single particular curing time can be assessed. The more modern direct method consists of measuring the heat release over an extended period of time from a cement paste that is allowed to hydrate in a closely controlled thermostat, allowing the heat generated to flow through an aluminium block on which are attached heat-flow sensors. This procedure gives data which are sensitive to small changes in cement composition and provides a ready and convenient insight into the chemistry of cement hydration.

8.3 Setting time

It is a necessary property of cements that they exhibit setting when mixed with a limited quantity of water (for example, paste with a water/cement mass ratio in the range 0.2–0.7). The European Standard BS EN 196-3: 1995 (*Determination of setting time and soundness*) contains the relevant standard procedures for use in the UK. Two setting times are described in the Standard for a cement paste of standard consistence, an initial and a final set. There is no well-defined physical meaning to these terms, rather they arbitrarily describe the gradual rheological changes taking place during hydration. Similar standards are incorporated into the American Standard ASTM C 150 and the German Standard DIN 1164. The amount of water used in making the standard cement paste is that giving standard consistence which is achieved when a 10 mm diameter plunger can be forced under its own weight to penetrate the surface of a fresh paste to a standard amount. Trial and error methods determine the correct amount of water to form this paste consistence.

For the determination of initial setting time, a rod of 1 mm^2 cross-section with a flat end is forced into the surface of the fresh cement paste cast in a standard container 40 mm in depth by added weights (total mass 300 g). When the rod is no longer able to penetrate to within 4 ± 1 mm of the bottom of the standard container, initial set is said to have been reached.

The end of the rod is modified with a cylindrical knife edge attachment for the final set determination: final set is reached when the knife edge makes only a shallow impression in the setting paste surface.

8.3.1 EFFECT OF PROPORTION OF MAIN CLINKER MINERALS

The chemical composition of Portland cement clinker may be recorded as a number of parameters derived from the chemical analysis:

$$\text{alumina ratio} = \frac{\%\ \mathrm{Al_2O_3}}{\%\ \mathrm{Fe_2O_3}} \tag{8.2}$$

$$\text{silica ratio} = \frac{\%\ \mathrm{SiO_2}}{(\%\ \mathrm{Al_2O_3} + \%\ \mathrm{Fe_2O_3})} \tag{8.3}$$

In the alkali-free samples, setting time is reduced slightly with increasing silica ratio and with increasing alumina ratio. The setting times of cements made from alkali and sulfate free clinkers were reduced with increasing lime saturation factor.

$$\text{lime saturation factor \%} = \frac{\%\ \text{CaO}}{2.80 \times \%\ \text{SiO}_2 + 1.18 \times \%\ \text{Al}_2\text{O}_3 + 0.65 \times \%\ \text{Fe}_2\text{O}_3} \times 100 \tag{8.4}$$

This formula represents fairly well the maximum amount of lime that can be combined in Portland cement clinker. A refinement for the maximum combined lime content to allow for the small amount of MgO combined in $3\text{CaO}\cdot\text{SiO}_2$, has been suggested:[22]

$$\text{lime saturation factor \%} = \frac{\%\ \text{CaO} + 0.75 \times \%\ \text{MgO}}{2.80 \times \%\ \text{SiO}_2 + 1.18 \times \%\ \text{Al}_2\text{O}_3 + 0.65 \times \%\ \text{Fe}_2\text{O}_3} \times 100 \tag{8.5}$$

The maximum value for % MgO that can be inserted in this formula is ~2 per cent, since any excess tends to be present as free MgO (as the mineral periclase) after firing, thus rendering the formula inappropriate.

8.3.2 EFFECT OF SULFATE CONTENT

Different types of false set have been identified,[19] associated with the dehydration of added gypsum during grinding to give hemihydrate or soluble anhydrite. On hydration this precipitates secondary gypsum and results in premature stiffening of the paste. The setting time of a Portland cement is increased as the quantity of gypsum added is increased, up to a certain level where a plateau is obtained and the setting time becomes insensitive to further additions of gypsum.[19]

The setting of cements was accelerated with increasing SO_3 content of the clinker. Cements made from clinkers which were rich in SO_3 (>2 per cent SO_3) and low in alkali, did not set in a normal manner, even with the addition of calcium sulfate. If SO_3-rich clinkers were also high in alkali (>1 per cent), then setting was normal, even without the addition of calcium sulfate. Sulfur combined in clinker phases apparently has an accelerating effect on the setting while sulfur present as alkali sulfate retards setting.

8.3.3 EFFECT OF ALKALI CONTENT

The effect of alkali additions (in the form of carbonates) to the raw meal before burning was investigated by Odler and Wonnemann[23] on laboratory-prepared clinkers containing (per cent) 70 C_3S, 10 C_2S, 10 C_3A and 10 C_4AF. The clinkers were ground with gypsum (3 per cent SO_3) to form cements with specific surface areas of 300 m^2/kg. The amounts of alkali oxides found in the burned clinker were well below those added to the original raw meal, the volatilisation of K_2O being greater than that of Na_2O. The alkalis were distributed among the clinker phases unevenly, the highest concentrations of both oxides being formed in the calcium aluminate phase. The early hydration rates for the C_3S component of the cement were not significantly affected by the presence of alkali. However, the initial hydration rate of the C_3A was slowed down appreciably by the presence of Na_2O in the crystal lattice and accelerated by the presence of K_2O in the lattice. Alkali oxides affected the setting times in the same way as they affected the hydration rates of the C_3A (Table 8.4).

Additions of alkali sulfate to laboratory-prepared clinker did not cause changes to the degree of hydration of the C_3A or the C_3S components,[24] but the setting times were significantly reduced (Table 8.5), the potassium sulfate being more effective than the

Table 8.4 Setting times of cement pastes made from laboratory-made cement with added alkali in the clinker[23]

Cement + sodium or potassium oxide in clinker	Setting time (min)		
	H_2O (%)	Initial	Final
Control	25	180	215
0.72% Na_2O in clinker	25	185	290
1.26% Na_2O in clinker	25	295	360
0.88% K_2O in clinker	25	150	205
1.48% K_2O in clinker	25	50	135

Table 8.5 Setting times of cement pastes made from laboratory-made cement with added alkali sulfates[24]

Cement + sodium or potassium sulfate	Setting time (min)		
	H_2O (%)	Initial	Final
Control	25	180	210
0.72% Na_2O as sulfate	25	85	160
1.26% Na_2O as sulfate	25	85	140
0.88% K_2O as sulfate	25	60	145
1.48% K_2O as sulfate	25	15	20

sodium sulfate. The cements were ground to a specific surface area of $300\,m^2/kg$, and made into pastes with water/cement = 0.5, and hydrated for various periods at 20°C. The pastes containing potassium sulfate contained well-crystallised syngenite ($CaSO_4 \cdot K_2SO_4 \cdot H_2O$), but no new hydration products were detected when using sodium sulfate additions, and the reason for the accelerating effect of this salt was not obvious. False set has been attributed to the formation of syngenite.[19]

The percentage sulfatisation (SD) of the alkali in a cement is defined by the expression

$$SD = \frac{\%\ SO_3}{1.292 \times \%\ Na_2O + 0.850 \times \%\ K_2O} \times 100 \tag{8.6}$$

In general the setting times of cements were reduced to an increasing extent as the Na_2O content was increased. The most favourable setting behaviour was found at a degree of sulfatisation of 100 per cent. Supersulfatisation accelerated the setting. The setting times of cements containing K_2O tended to be increased at low degrees of sulfatisation (60 per cent), but were shortened at higher degrees of sulfatisation.

K_2O had a slight accelerating effect, but only at high alumina ratios, regardless of the degree of sulfatisation; however, increasing Na_2O content always had an increasingly accelerating effect. An increase in the degree of sulfatisation reinforced this tendency.

At a fairly low lime saturation factor and a high degree of sulfatisation, K_2O had an accelerating effect, but at a high lime saturation factor it always had a retarding effect. Na_2O always had an accelerating effect, especially at a high lime saturation factor and high degrees of sulfatisation.

All cements containing up to 2.0 per cent K_2O showed normal setting regardless of the composition ratios and lime saturation factor. Setting time was reduced by absorption of Na_2O, regardless of the composition ratios. Supersulfatisation reinforced this behaviour.

8.3.4 DISCUSSION

It is a fundamental property of cements that they exhibit setting when mixed with a limited quantity of water. Two setting times are described in the Standard for a cement paste of standard consistence, an initial and a final set. There is no well-defined physical meaning to these terms, rather they arbitrarily describe the gradual rheological changes taking place during hydration. Setting time is greatly reduced by the presence of alkali sulfate. Setting time can be a limiting factor for Portland cement if the geology of the source materials contains minor components, such as fluoride, which results in a low early hydration reactivity.

8.4 Strength

Strength is the most important material parameter used to characterise cement-based products. Usually, the term strength implies a crushing strength of concrete cubes cast in steel moulds, either 100 or 150 mm in length. Much effort has been put into ensuring reproducibility, including specification of cube mould wall tolerances, and specification of rigidity and stiffness for hydraulic testing machines that can generate sufficient force to crush these specimens. An additional factor that has been investigated is the effect of slight inhomogeneity of cubes due to settlement of concrete aggregate during setting and early curing.

Although concrete is usually classified as a brittle material, concrete specimens under uniaxial compression have been found to fail progressively.[25] Hardened cement pastes exhibit gross failure under triaxial compression provided that confining pressures exceed a low limit, near 2.5 MPa,[26] with cracks only rarely visible on external surfaces. The ease with which brittle fracture is suppressed indicates that a process of microscopic flow is the primary cause of failure for these materials. Contrasting macroscopic modes of failure for confined and unconfined test conditions are observed in other non-metallic materials, for example in natural rocks, cast iron and glasses, provided much larger confining pressures are employed.[27,28]

Failure modes can be formally represented by the Mohr theory of strength,[29,31] which states that a material may rupture either by shearing or by fracture. In the former case the shearing stress in the slip plane exceeds a limiting value (which in general is a function of the stress normal to the slip plane; this function is a characteristic of the material under test), while in the latter case the largest tensile stress normal to the fracture plane is exceeded. The effect of confining pressure on axial strength has been presented for hardened cement pastes and concretes.[26]

The testing of concrete in tension or flexure is regarded as being of doubtful significance, largely because of the poor reproducibility that can be obtained for the results, although tensile strength is of interest to the engineer, in anchorage regions for steel stressing cable in prestressed beams, for example. In the early days, compressive testing was not possible because hydraulic testing machines that could generate the high forces required were not available. Much of the early strength data for Portland cement involved the tensile testing of dumbbell-shaped mortar specimens.

8.4.1 STRENGTH OF CONCRETE

The fracture of concrete consists of three stages: crack initiation, slow crack growth, and rapid crack propagation,[32] leading to final rupture. Acoustic emission results show that a process of stable crack formation and growth starts at low loads and continues with increasing intensity as the load is raised (acoustic emissions during controlled crack growth in polycrystalline alumina have also been related to increments in macrocrack length and to the formation of microcracks around the macrocrack tip[33,34]). The resistance to crack propagation, or fracture toughness, can be expressed as the critical stress intensity factor for the region near the crack tip at the onset of rapid crack propagation. Rapid crack propagation occurs when the energy released by a virtual crack extension is sufficient to supply energy requirement for the surfaces created by the virtual crack extension. There are two sources of energy available for crack extension: the energy supplied by the work of external forces, and the change in stored strain energy. The energy release rate takes on a critical value at the instant of instability.

The situation appears to be different in the case of hardened cement pastes: stress–strain plots for this material are more nearly linear, possibly implying that little microcracking is taking place before failure; the absence of acoustic emissions also indicates that cracking is not pronounced at low loads. Some cracking does occur, however, on first loading, which is reflected in a reduction in subsequent elastic modulus; large cracks have been detected by a fluorescent dye technique in specimens loaded to below unstable fracture.[35] In contrast to concretes which can continue to deform plastically after the maximum load is exceeded,[25] hardened cement pastes fail suddenly in a brittle manner at the maximum applied stress (except in the case of very porous pastes[35]); the fracture pattern is one of few vertical cracks with the fragments apparently undamaged.

The energy requirement for crack propagation in cement paste is an order of magnitude greater than the surface energy of the new crack surfaces being formed, implying that the fracture does not propagate as a single crack. It has been suggested that the increased energy requirement for crack propagation is caused by the formation of a microcracked region near the macrocrack tip. The fracturing of concrete is more complex than that of cement pastes; the aggregate particles increase the fracture toughness by arresting the propagation of macrocracks within the mortar fraction of the concrete.

Reloading concrete specimens that have already been stressed below fracture produces negligible extra cracking until the previous highest strains are approached.[25] On restressing concretes, Young's moduli are smaller than for virgin specimens; the capacity to resist loading is thus reduced by stress, indicating that damage is occurring during first-time loading.

8.4.2 STRENGTH–POROSITY RELATIONSHIP FOR CEMENT PASTES

$$\sigma_t = \theta\sqrt{\frac{EG_c}{a}} \tag{8.7}$$

In the 'Griffith analysis' of the failure of brittle materials, as quoted by McLean[30] the above relationship was developed between the critical tensile stress, σ_t, and the dimension of the limiting flaw, a, the Young's modulus, E, and G_c, the surface energy per unit area (θ is a constant).

Hardened cement pastes are porous solids and simple empirical relationships between strength and porosity have been found to represent data for a wide range of materials, including hardened cement pastes.[36] From these results it seems that finely dispersed small pores are able to interact with each other, or with the external surfaces of specimens, resulting in failure at stresses below those indicated when the sizes of individual pores are inserted (for the flaw size) into the Griffith equation. Stereoscan examinations of the fracture surfaces of alumina specimens covering a wide range of porosities have shown that a flaw (or pore) linking process occurs prior to catastrophic failure.

When a concentrated suspension of cement in water is allowed to hydrate, the reaction products are formed as a coherent matrix enclosing remnants of anhydrous cement grains. Densification of the matrix can take place over a long period of time, as the unhydrated cement remnants hydrated, but the matrix retains some of its porosity. Powers and Brownyard[37] measured compressive strengths of mortars and were able to relate strengths to functions of the initial water contents. Their data can be represented adequately by the expression

$$S = S_o \exp(-bP) \tag{8.8}$$

with $S_o = 391$ MPa and $b = 4.3$, where S is the compressive strength and P the porosity. S_o is the theoretical strength for the flaw-free system having zero porosity. Wischers[38] studied the properties of a wider range of pastes, mortars and compacts. His data can also be represented by the above expression, with $S_o = 393$ MPa and $b = 4.3$. A number of other studies have found similar results.

Work at the Cement and Concrete Association in the 1970s produced data (Tables 8.6–8.9) which could be fitted to similar expressions, the exact form of the expression depending on the method adopted to determine the porosity.[36] A carbon tetrachloride adsorption procedure resulted in the expression $S = 530\exp(-13.0\,P)$. This investigation extended the composition of Portland cement pastes by forming them under high pressure,[39,40] thereby reducing the porosity to low levels and simultaneously increasing the strength after hydration (up to ~360 MPa after 28 days; Tables 8.6 and 8.7). There was no evidence of a plateau in the strength–porosity relationship in spite of the reduced level of hydration achieved in these low-porosity pastes.

Kingery[41] quotes a similar exponential expression as being capable of representing the bending strength of cast iron, alumina and gypsum plaster, with $b = 7$. A slightly larger experimental value for $b = 8$ is found to represent the compressive strength of pressed alumina.[42] Hasselman[43] quotes the relationship $S = S_o(1 - bP)$, with b between 3.7 and 6.8 for strength and $E = E_o(1 - kP)$, for Young's modulus with k about half the value of b in the expression for strength. Other relationships between strength and porosity have been reviewed by Schiller.[44] The strength of autoclaved calcium silicates have been studied by Mindess[45] and by Satava.[46]

Practically all porosity measurements on cement products in the literature which have been related to strength have been based on the measurement of loss of water from a saturated paste, under controlled drying: the two methods most frequently adopted are heating to 100°C, and drying to low vapour pressure at room temperature.[47] Under these drying conditions it can be assumed that all free water is lost from the paste. The difficulty is that some structural water, which may be recorded as either that sorbed onto the large internal surface or that situated between lattice layers of the hydrates, depending on the interpretation of water sorption data adopted, is lost: this water is classified as gel pore water by Powers, who presented a method of allowing for sorbed water based on the

Table 8.6 Physical and mechanical properties of cement pastes made with Portland cement D5

No.	Curing temperature (°C)	Age at test (days)	Density (kg/m^3)	Standard deviation	Ignition loss at 1000°C	Standard deviation	Initial porosity	Compressive strength (MPa)	Standard deviation
1	190	28	2448	2.4	0.1642	0.0040	0.3724	208	8
2	25	1	2456	2.5	0.1648	0.0003	0.3708	88	1
3	25	5	2473	2.5	0.1709	0.0008	0.3704	199	2
4	25	28	2482	14.8	0.1726	0.0003	0.3701	237	3
5	25	28	2501	7.5	0.1649	0.0003	0.3593	246	6
6	25	5	2524	15.1	0.1530	0.0017	0.3442	224	5
7	25	28	2531	7.5	0.1551	0.0062	0.3441	258	6
8	25	28	2530		0.1538	0.0003	0.3433	265	4
9	25	102	2536	2.5	0.1546	0.0006	0.3424	298	2
10	25	1	2526	2.5	0.1500	0.0006	0.3414	142	6
11	25	5	2590	15.1	0.1329	0.0015	0.3111	257	8
12	25	28	2600		0.1344	0.0005	0.3097	290	9
13	25	1	2591	5.2	0.1308	0.0005	0.3092	168	2
14	25	20	2600		0.1328	0.0009	0.3083	284	4
15	25	1	2627	18.4	0.1203	0.0006	0.2911	203	2
16	25	28	2639	0.2	0.1237	0.0009	0.2906	308	4
17	25	5	2639	2.6	0.1223	0.0007	0.2895	272	8
18	25	28	2669	2.7	0.1196	0.0002	0.2792	314	9
19	25	1	2670	5.4	0.1142	0.0006	0.2745	220	9
20	25	28	2686	2.7	0.1161	0.0003	0.2709	316	8
21	25	5	2675		0.1174	0.0005	0.2669	274	8
22	190	28	2737	5.4	0.1128	0.0040	0.2551	372	18
23	25	28	2743	2.7	0.1020	0.0032	0.2444	343	7
24	25	5	2740	5.4	0.0984	0.0007	0.2422	311	7
25	25	1	2742	5.4	0.0964	0.0008	0.2400	246	4
26	25	28	2777	2.7	0.0903	0.0005	0.2251	374	2

measurement of specific surface area by BET procedures and water vapour as the adsorbate. A simplified approach has been adopted by Helmuth[48] who equates the gel pore water to a constant fraction of the chemically combined water in the paste; a capillary porosity is derived by subtracting the gel pore porosity from the total porosity.

The porosity of dried pastes can be measured by filling the pores with a second fluid. The drying process causes shrinkage of the paste,[49] but this is generally small and is ignored in the methods presented. Mikhail and Selim[50] measured the volumes of liquid nitrogen, methanol, isopropanol and cyclohexane sorbed by the dried pastes at vapour pressures near their saturation values, and found that the pore volume calculated from the density of the bulk adsorbate liquid depends on the size of the molecules in the adsorbate. They presented evidence for the presence of 'ink-bottle' pores, having very narrow entrances which can exclude larger molecules, thus making the validities of these porosity measurements open to doubt. However, the use of a second fluid seems to be a more definite technique for obtaining capillary porosity than one which relies on drying loss alone. The control of relative vapour pressure of the organic fluid may be achieved by dissolving a proportion of non-volatile compound in the volatile solvent: a solution of *n*-hexadecane in carbon tetrachloride has been used.[51]

Table 8.7 Physical and mechanical properties of cement pastes made with Portland cement D10

No.	Curing temperature (°C)	Age at test (days)	Density (kg/m^3)	Standard deviation	Ignition loss at 1000°C (mass fraction)	Standard deviation	Initial porosity	Compressive strength (MPa)	Standard deviation
1	190	32	1886.6	3.1	0.3426	0.0008	0.6166	10	1
2	25	11	1912.0	4.0	0.3339	0.0009	0.6063	34	2
3	25	25	2048.0	2.1	0.3034	0.0005	0.5590	65	3
4	190	49	2109.7	4.7	0.2679	0.0007	0.5226	39	2
5	25	26	2146.2	3.0	0.2666	0.0002	0.5135	77	4
6	25	14	2261.4	7.7	0.2205	0.0001	0.4551	104	9
7	190	20	2268.7	4.6	0.2118	0.0012	0.4472	65	4
8	25	1	2270.0	5.6	0.2066	0.0003	0.4433	64	2
9	25	27	2447.8	9.4	0.1780	0.0007	0.3780	197	5
10	25	1	2438.9	1.6	0.1633	0.0002	0.3692	98	2
11	25	1	2566.4	2.6	0.1307	0.0010	0.3104	169	4
12	25	16	2634.6	2.9	0.1259	0.0018	0.2881	286	6
13	190	33	2623.6	5.1	0.1217	0.0015	0.2877	259	27
14	25	83	2709.8	1.6	0.1093	0.0015	0.2539	340	7
15	25	31	2767.8	2.2	0.0919	0.0008	0.2230	356	10
16	190	32	2781.0	1.3	0.0897	0.0010	0.2174	407	24
17	25	1	2786.0	1.7	0.0858	0.0013	0.2127	291	4

Table 8.8 Determination of porosity from drying mass loss for cement pastes made with Portland cement D10

	Drying at 100°C, 1.8 mm particles			D-Drying, 1.8 mm particles			D-Drying, 0.9 mm particles		
No.	Mass loss	Standard deviation	Porosity	Mass loss	Standard deviation	Porosity	Mass loss	Standard deviation	Porosity
1	0.2462	0.0007	0.4645	0.2422	0.0003	0.4569	0.2482	0.0024	0.4683
2	0.2254	0.0007	0.4310	0.2391	0.0010	0.4572	0.2526	0.0062	0.4830
3	0.2063	0.0005	0.4225	0.1857	0.0032	0.3804	0.1864	0.0009	0.3818
4	0.1692	0.0004	0.3570	0.1639	0.0004	0.3458	0.1736	0.0013	0.3662
5	0.1614	0.0002	0.3464	0.1538	0.0010	0.3301	0.1447	0.0007	0.3106
6	0.1255	0.0002	0.2838	0.1235	0.0001	0.2793	0.1249	0.0002	0.2824
7	0.1110	0.0004	0.2518	0.1128	0.0003	0.2559	0.1139	0.0001	0.2584
8	0.1369	0.0001	0.3108	0.1355	0.0003	0.3076	0.1393	0.0020	0.3162
9	0.0908	0.0004	0.2222	0.0882	0.0010	0.2159	0.0876	0.0001	0.2143
10	0.1039	0.0002	0.2534	0.1032	0.0004	0.2517	0.1074	0.0011	0.2620
11	0.0823	0.0003	0.2112	0.0808	0.0004	0.2074	0.0824	0.0001	0.2115
12	0.0629	0.0001	0.1657	0.0601	0.0001	0.1583	0.0623	0.0001	0.1640
13	0.0292	0.0004	0.0767	0.0363	0.0004	0.0952	0.0369	0.0005	0.0967
14	0.0538	0.0003	0.1458	0.0370	0.0003	0.1003	0.0438	0.0002	0.1187
15	0.0421	0.0002	0.1165	0.0367	0.0003	0.1016	0.0423	0.0001	0.1171
16	0.0157	0.0001	0.0438	0.0191	0.0001	0.0530	0.0214	0.0001	0.0595
17	0.0442	0.0002	0.1232	0.0401	0.0004	0.1117	0.0428	0.0001	0.1193

Table 8.9 Porosity determinations for cement pastes made with Portland cement D10

	1.8 mm diameter particles					0.90 mm diameter particles				
No.	Dry density	CCl_4 sorbed	Standard deviation	CCl_4 porosity	Capillary porosity	Dry density	CCl_4 sorbed	Standard deviation	CCl_4 porosity	Capillary porosity
1	1429.7	0.2505	0.0060	0.2247	Negative	1418.3	0.2331	0.0123	0.2075	Negative
2	1454.8	0.2333	0.0071	0.2130	0.3231	1429.0	0.2435	0.0083	0.2183	0.3680
3	1667.7	0.2001	0.0084	0.2094	0.2021	1666.3	0.1932	0.0047	0.2020	0.2045
4	1763.9	0.1861	0.0076	0.2060	Negative	1743.5				Negative
5	1816.1	0.1506	0.0040	0.1716	0.1510	1835.6	0.1366	0.0049	0.1574	0.1170
6	1982.1	0.1038	0.0044	0.1291	0.1169	1978.9	0.1075	0.0027	0.1335	0.1224
7	2012.8	0.1412	0.0087	0.1784	Negative	2010.3	0.1559	0.0030	0.1967	Negative
8	1962.4	0.1255	0.0066	0.1546	0.1882	1953.8	0.1201	0.0041	0.1473	0.2032
9	2231.9	0.0534	0.0018	0.0748	0.0523	2233.4	0.0489	0.0017	0.0685	0.0505
10	2187.2	0.0772	0.0041	0.1060	0.1433	2176.9	0.0722	0.0033	0.0986	0.1612
11	2359.0	0.0612	0.0015	0.0906	0.1127	2354.9	0.0663	0.0028	0.0980	0.1198
12	2476.3	0.0313	0.0024	0.0486	0.0299	2470.5	0.0281	0.0012	0.0436	0.0399
13	2528.4	0.0425	0.0007	0.0674	Negative	2526.8	0.0421	0.0007	0.0668	Negative
14	2609.5	0.0162	0.0035	0.0265	Negative	2591.1				Negative
15	2666.2	0.0175	0.0018	0.0293	Negative	2650.7	0.0211	0.0009	0.0351	0.0156
16	2727.9	0.0113	0.0005	0.0193	Negative	2721.5	0.0133	0.0003	0.0227	Negative
17	2674.0	0.0280	0.0011	0.0470	0.0175	2666.8	0.0316	0.0009	0.0529	0.0307

8.4.3 CONCRETE CUBE STRENGTHS

The concrete cube crushing test has been employed as a standard method of determining compressive strength in the construction industry, and until recently was the standard method of classifying the strength properties of cements in the UK. The 100 mm concrete cube (water/cement = 0.65, aggregate/cement = 6) is the usual specimen size adopted in the UK. Curing for up to 5 years under water has been carried out over a number of years, and Figures 8.10 and 8.11 show how strengths develop for plain Portland cements. The

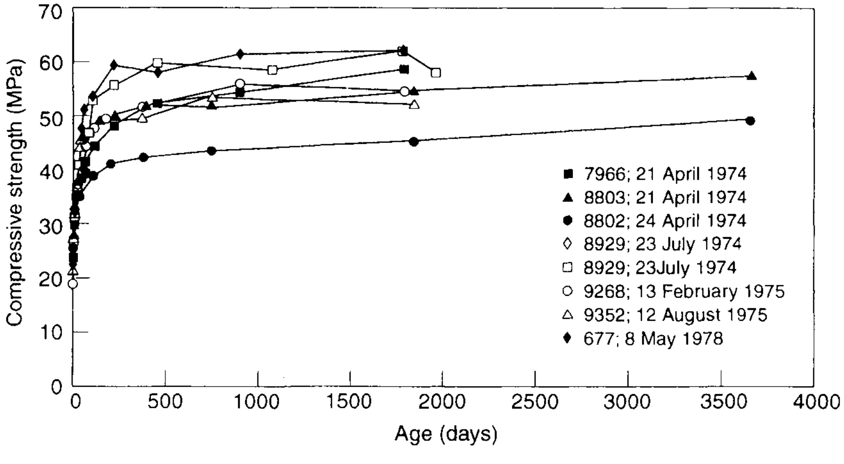

Fig. 8.10 Development of concrete cube strength for Portland cement concretes made between 1974 and 1978.

Table 8.10 Analyses of selected UK Portland cements made between 1965 and 1990

No.	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	Free lime (%)	Fineness (m^2/kg)
D1	21.70	1.86	4.95	64.75	1.32	1.92	0.15	0.64	4.07	372
D2	22.54	1.84	4.33	65.06	1.10	2.56	0.17	0.52	1.69	349
D3	23.59	1.66	4.14	63.86	1.26	2.69	0.17	0.54	0.90	367
D4	20.84	1.94	5.45	65.40	1.20	2.30	0.17	0.55	2.62	337
D5	20.60	2.31	4.79	64.86	1.60	2.62	0.26	0.64	1.70	320
D6	22.39	2.37	3.90	64.22	1.09	2.42	0.15	0.80	2.65	373
D7	22.63	2.09	3.91	64.67	2.33	2.09	0.15	0.80	0.50	311
D8	19.72	2.21	5.71	65.20	0.98	2.85	0.20	0.85	1.75	369
D9	22.60	1.72	4.04	65.46	1.06	2.16	0.18	0.54	2.48	426
D10	19.37	3.98	5.74	63.33	1.43	2.76	0.39	0.90	0.64	356
D11	21.04	2.36	5.48	64.37	1.20	2.35	0.26	0.67	2.24	291
D12	20.49	2.55	5.40	65.02	1.32	2.40	0.33	0.52	0.94	289
D13	21.73	2.32	4.84	64.59	1.32	2.55	0.23	0.65	2.02	326
D14	19.64	2.41	5.53	64.43	1.88	2.81	0.21	1.45	2.64	372
D15	21.42	2.39	5.11	65.14	0.71	2.82	0.26	0.49	1.15	295
D16	21.28	1.78	4.88	65.06	0.93	2.74	0.20	0.69	2.21	330
D17	19.83	2.21	6.89	63.98	1.98	2.65	0.19	0.68	1.58	352
D18	19.65	2.72	5.32	64.32	1.04	2.98	0.27	0.66	2.34	395
D19	20.80	2.30	5.54	63.89	1.22	2.71	0.29	0.56	2.21	365
D20	21.02	2.34	5.77	64.25	1.23	2.67	0.27	0.50	2.34	350
D21	20.96	1.84	4.85	63.80	1.06	3.00	0.22	0.94	3.19	438
D22	23.04	1.96	4.65	63.82	1.49	2.42	0.18	0.62	2.03	345
D23	21.31	2.27	5.30	64.99	1.09	2.42	0.22	0.73	1.72	340
D24	21.60	2.49	4.37	65.21	1.05	2.46	0.15	0.54	1.47	410
D25	21.86	2.47	4.48	65.77	1.08	2.13	0.15	0.66	0.78	348
D26	20.76	3.51	5.64	63.66	1.43	2.92	0.14	0.75	1.11	335
D27	20.93	2.00	5.53	65.21	0.86	2.31	0.34	0.68	0.45	295
D28	20.12	1.87	5.72	65.50	0.93	2.45	0.25	0.72	1.46	345
D29	20.13	1.80	5.30	65.40	1.06	2.70	0.17	0.67	2.60	370
D30	23.37	1.45	4.04	64.23	1.23	2.76	0.14	0.68	1.10	425
D31	21.58	1.69	4.60	65.72	1.00	2.50	0.19	0.38	1.28	330
D32	21.41	2.74	4.09	65.53	1.08	2.99	0.12	0.60	1.64	345
D33	20.33	1.77	5.42	65.74	1.01	2.63	0.15	0.50	1.12	365
D34	24.10	1.43	3.92	64.60	1.34	2.46	0.12	0.54	0.05	370
D35	20.86	2.46	5.53	63.74	1.50	3.04	0.35	0.91	1.40	385
D36	21.19	2.47	3.85	65.50	1.20	2.50	0.15	0.37	3.68	420
D37	19.64	2.09	5.83	66.06	1.05	2.47	0.14	0.65	2.41	380
D38	22.16	1.74	4.20	65.98	1.19	2.01	0.13	0.74	2.11	350
D39	19.90	3.41	5.83	64.02	1.60	2.77	0.34	1.01	1.38	390
D40	20.78	2.10	5.59	64.86	1.00	2.36	0.11	0.75	2.21	385
D41	21.60	1.70	4.88	65.48	1.02	2.75	0.13	0.71	0.54	400
D42	19.85	3.37	5.83	63.78	1.43	2.88	0.30	0.95	1.08	440
D43	22.44	2.58	3.65	65.95	1.16	2.17	0.10	0.38	1.67	395
D44	21.52	1.96	4.76	64.60	1.89	2.74	0.20	0.67	1.11	400
D45	19.63	3.30	5.46	64.36	1.45	2.83	0.33	0.96	1.64	400
D46	22.16	2.59	3.81	66.20	1.08	2.32	0.14	0.51	1.61	320
D47	21.03	1.85	4.92	65.16	1.92	2.77	0.13	1.25	0.90	360
D48	20.56	3.30	5.16	65.07	1.25	2.73	0.07	0.74	1.13	360
D49	20.30	3.23	5.02	64.80	1.35	2.56	0.08	0.71	1.58	405
D50	22.10	2.22	3.80	65.30	1.14	2.66	0.13	0.63	1.99	364

Table 8.11 Strength of 100 mm concrete cubes (MPa) for Portland cements, made with Thames Valley aggregate, water/cement = 0.52, stored under water at 20°C

No.	3 days	7 days	14 days	28 days	56 days	112 days	224 days	448 (365) days	896 (730) days	1792 (1825) days
D1						Unsound				
D2	18.2	26.9		37.5	42.2			(46.2)	(48.7)	
D3	17.3	23.9		36.3	41.6			(49.0)	(50.4)	
D4	19.4	26.6		36.1	39.9			(44.9)	(46.5)	
D5	19.8	28.9		41.0	45.7			(56.9)		(65.4)
D6	16.2	23.4		37.0	43.8			(54.3)		(65.1)
D7	17.6	27.2		44.7	50.2			(56.1)		(63.9)
D8	27.3	34.9		47.5	50.7					(65.2)
D9	23.1	33.5		47.4	52.9			(56.5)		
D10	17.8	27.9		39.6	45.1			(48.9)		(53.7)
D11	17.7	25.4		37.7	43.1					
D12	19.7	29.6		42.1	48.7			(54.0)		(63.7)
D13	19.4	27.8		41.2	46.0			(56.1)		(61.5)
D14	23.9	34.4	38.0	42.4	46.1	47.9	48.8	50.8	55.0	(59.7)
D15	21.4	31.0	39.2	41.0	51.2	51.6	55.0	56.6	61.2	62.2
D16	25.4	33.8	43.0	44.4	53.9	54.0	58.2	57.3	61.3	69.2
D17	20.8	29.8	36.8	41.4	44.3	47.9	49.0	50.1	52.3	53.6
D18	24.3	33.7	39.6	45.5	48.6	51.3	54.4	55.6	61.3	63.0
D19	21.6	30.2	37.9	42.9	46.9	50.7	52.7	53.5	60.2	58.3
D20	18.9	27.2	35.2	40.3	45.5	48.3	50.9	52.4	56.2	54.8
D21	21.6	30.7	36.0	40.2	44.5	49.8	53.2	54.0	58.0	59.4
D22		23.2	30.6	39.6	45.4	53.2	55.9	60.2		62.3
D23	27.1	34.0	41.0	44.7	49.4	53.0	54.0	55.7	58.8	58.3
D25	21.7	32.7	41.6	47.6	53.4	55.4	60.5	59.5	61.7	63.8
D26	19.5	28.2	35.3	42.0	48.5	51.1	54.8	57.2	58.0	66.3
D27	20.7	30.0	35.7	42.6	44.7	52.0	50.7	57.6	59.1	68.5
D28	24.0	33.5	39.5	44.9	50.2	51.3	53.2	52.0	54.8	56.6
D29	23.1	31.4	37.4	40.6	43.5	48.2	50.9	51.7	56.2	54.7
D30	21.3	32.1	40.7	46.2	51.4	54.5	59.6	58.3	61.5	62.0
D31	20.8	34.0	41.1	50.0		57.2	60.5	57.2	59.4	61.1
D32	19.5	27.5	35.4	39.6	46.7	51.5	53.5	52.8	53.9	58.3
D33	19.3	33.4	40.6	45.4	49.1	52.3	54.6	58.0	61.5	
D34	19.0	24.6	33.2	41.2	47.2	54.0	57.8	60.7	60.2	
D35	23.6	32.2	38.5	43.2	48.8	50.6	54.8	56.7	51.9	
D36	21.8	30.3	37.9	42.4	46.1	47.2	54.2	57.8	58.6	
D37	25.7	35.7	42.1	47.6	52.5	54.2		59.0	57.9	58.7
D38	22.9	33.1	39.9	45.6	48.8	54.3	56.3	58.8	58.1	61.3
D39	24.5	33.1	38.2	44.0	47.1	52.3	53.3	51.8	55.5	58.8
D40	25.7	34.4	38.8	45.1	49.0	55.7	58.0	55.4	58.6	57.2
D41	30.5	41.0	47.0	56.5	57.3	61.3	59.0	62.5	63.2	63.3
D42	17.6	27.2		44.7	50.2					
D43	27.3	34.9		47.5	50.7					
D44	28.8	40.2	43.9	49.0	55.2	53.3	58.4	62.3	63.4	65.1
D45	29.1	35.2	42.8	46.3	49.7	48.5	50.8	53.1	58.6	58.6
D47	28.8	43.6	50.6	50.6	56.3	58.8	59.2	63.8	64.7	64.0
D48	23.5	32.9	42.4	48.0	52.8	53.2	56.4	59.0	57.8	62.6
D52	24.3	33.7	41.9	47.3	50.4	54.8	57.9	58.6	58.3	64.3
D53	25.0			47.4	52.7	51.4	52.9		54.6	
D54	25.7	38.2	44.9	52.3	53.0	54.0	54.3	59.1	62.1	66.1

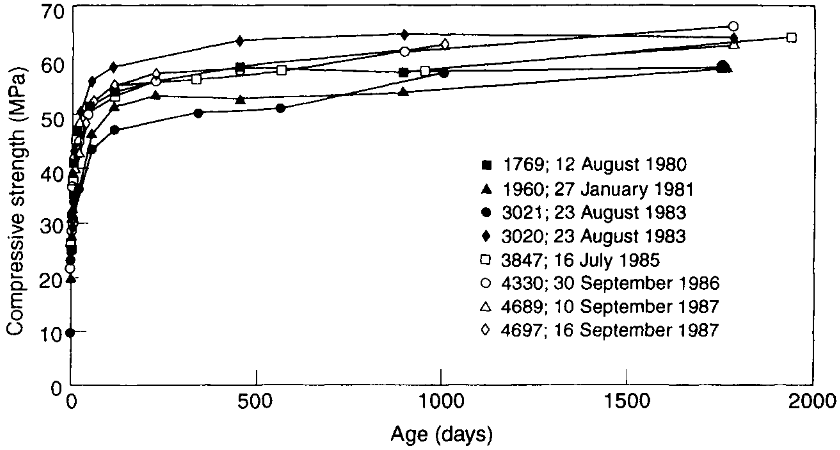

Fig. 8.11 Development of concrete cube strength for concretes made between 1980 and 1987.

dates in the legend are the times of making of the concrete, and also the approximate dates of manufacture of the cements.

Tables 8.10 and 8.11 present information on long-term compressive strengths for a number of Portland cement concretes when stored under water for up to about 5 years at 20°C, with the appropriate chemical analyses of the cements. The data are assembled for UK cements in the manufacturing period 1970–90. Little experimental evidence exists for large changes in performance for Portland cements, in this period, although much is made of the so-called poorer performance of modern Portland cements in the construction industry.

8.4.4 MORTAR PRISM STRENGTHS

The current British Standards BS 12: 1996 and BS 4027: 1996 refer to the European Standard method for cement strength testing, BS EN 196-1: 1995 (*Methods of testing cement; Determination of strength*) which employs RILEM Cembureau mortar prisms (40 x 40 x 160 mm) cast and fully compacted from mortars consisting of one part of cement and three parts of standard sand and 0.5 parts of water. The sand is a natural, quartz sand, the source of the sand being important, and especially prepared material is available ready-batched. Its particle size distribution is given in Table 8.12.

Table 8.12 Grain size distribution for standard sand

Square mesh size (mm)	Cumulative sieve residue (%)
2	0
1.6	7
1.0	33
0.5	67
0.16	87
0.08	99

At the required age, the specimens are taken from their water storage at 20°C, broken in flexure into two halves, and each half tested for strength in compression, using steel platens of area 40 × 40 mm. Typically, a 45 MPa concrete cube strength (100 mm concrete cubes) is equivalent to a 55 MPa mortar prism strength.

8.4.5 INFLUENCE OF CEMENT PASTE–AGGREGATE INTERFACES

The nature of the bond between cement paste and aggregate in concrete has been reviewed;[52] it has been proposed that the bond is composed of both chemical interactions and mechanical interlocking, possibly provided by epitaxial growth of certain cement hydrates onto the surfaces of the aggregate particles. Scans of microhardness across the boundary between aggregate and cement paste provide evidence for the existence of epitaxial growth of calcium silicate hydrate, calcium hydroxide and possibly ettringite. The effects of interfacial microstructure on durability were also reviewed, studies of sulfate attack and freeze–thaw performance being examined. The permeability of the interfacial region is claimed to be many times that of the body of the aggregate or the cement paste.[53] Many investigations of the microstructural features and mechanical properties associated with interfaces between cement paste and aggregates have been published.[54–56] In one investigation, three rock types were included, andesite, dolomite and granite: 42 mm cement paste cylinders, 168 mm long, were cast against previously broken rock cores and then loaded in flexure to failure, first curing under water for 3 weeks,[55,57] then making a diamond wheel saw-cut notch half-way along the cylinder. The influence of additions of microsilica to the cement paste was also included in the research programme. Extended curing resulted in a steady increase in fracture toughness and elastic modulus. The results showed that the fracture surfaces of both rock and cement paste were not planar at the micro level and were dominated by local crystal cleavages. The plain Portland cement paste fracture surface was very tortuous while the cement paste containing microsilica was relatively smooth.

The interfacial zone has been investigated by both mechanical (using the push-out test with specially ground cylindrical aggregates) and chemical procedures.[58] Mechanical simulation was devised in two dimensions using slab specimens that incorporated up to three white granite cylinders of 20 mm diameter, or three porous sandstone cylinders, in order to simulate aggregate particles. Microstructural investigations (SEM and an image analysis system) resulted in porosity gradient plots as the distance from the interface increased. The effect of incorporating microsilica was to improve the microstructure and mechanical properties of the bond. The initiation of cracks at the interfacial zone between the aggregate and cement paste has been investigated by long-distance optical microscopy.[59]

Fracturing could occur either at the interface or within the cement paste, and both types showed extensive branching of crack growth. The andesite rock specimens showed a variety of failure modes, some at the interface between the paste and the rock and some entirely within the paste. All the andesite rock specimens with microsilica in the paste failed entirely through the paste. The dolomite plain Portland cement paste specimens all showed fracture at the interface, but some of the specimens with microsilica in the paste failed within the paste. An influence of surface roughness of the aggregate on the measured values was indicated.

The andesite and dolomite rock cores were by far the strongest specimens tested, being 2.5–5 times those for the composite beams cast against broken rock cores (41 mm diameter); the composite specimens containing andesite rock were marginally stronger than the corresponding dolomite specimens.[60] The same conclusion was reached for measurements of fracture toughness and fracture energy. Microsilica had a minor influence for the mixes employed (15 per cent microsilica replacement). The fracture energy for pastes containing microsilica was about 30 per cent lower than for the neat Portland cement pastes. The fracture toughness for composite specimens was up to 1.5 times those for neat cement pastes; andesite rock has the ability to enhance the interface fracture toughness in the paste zone adjacent to the interface.

The transition zone is often considered to be the weakest part of the composite and microcracks may first start in this region under the influence of external stress; it is claimed to be the preferential route for the penetration of aggressive species from the environment and thus is important for determining the durability of the structure. Computer modelling has been used to simulate both mechanical and durability parameters.[61] The packing of particles at surfaces which act as relatively smooth walls, the wall effect, results in relatively imperfect packing and increased porosity.[62] Bleeding, if present, further intensifies this effect. A second effect which tends to increase the porosity in the interfacial region is the one-sided hydration product which is possible where aggregate closes off the possibilities of hydration from all directions at the interface. Differential diffusion of ionic species results in the formation of relatively large crystals of ettringite and portlandite in this zone.[63] Experimental investigations have confirmed the increased rate of transport of molecular and ionic species at the interfacial region. Where cement clinker has been used as aggregate, the interfacial region showed a denser microstructure and a lower permeability.

Measurements of fracture toughness, work of fracture and elastic modulus have been made on notched cylindrical specimens tested in flexure composed of simple rock (andesite, dolomite and granite) or cement paste (water/cement = 0.3 and 0.4), and composite interface specimens.[64] In contrast to the above theoretical considerations, fracture toughnesses were found to be higher for the composite specimens than for the simple cement paste specimens, raising questions of the validity of considering these interfaces in concrete as weak links in the structure. The different rocks show only moderately different interface fracture toughnesses. The bond strengths of various types of rock (granite, gneiss, quartzite, diabase, gabbro and limestone) were examined with six mortars, using splitting tests, compressive strength and flexural testing of 60 mm diameter cores, 120–320 mm in length.[65] The interface bond strengths are mostly weaker than the mortar or rock strengths.

Some investigators question the degree to which the strength of the interfacial zone affects the strength of concrete.[66] The use of organic coatings on aggregate particles was adopted to reduce the bond strength to mortar (by up to 75 per cent), but the consequent reduction in compressive strength of concrete incorporating this coated aggregate was only of the order of 10 per cent. It has been concluded that the role of the interfacial zone, although having a measurable effect, may be overshadowed by the properties of the cement paste and the aggregate, and the heterogeneous nature of the concrete.

8.4.6 EFFECT OF PROPORTION OF MAIN CLINKER MINERALS

The relation between the chemical characteristics of laboratory clinkers, burning at 1450°C for 2 h, and their strength-generating properties has been investigated[67–70] by modifying the three parameters: lime saturation factor, alumina ratio and silica ratio.

One of these factors was changed while keeping the other two constant. Cements were prepared by grinding the clinkers to 320 m^2/kg with 6 per cent gypsum. Compressive strength testing was carried out on small mortar prisms, 15 × 15 × 60 mm in dimension, using a mix with sand/cement = 3 and water/cement = 0.5.[71]

Investigations have been carried out on laboratory clinker made from cement raw meals with a lime saturation factor of 93 per cent, and an alumina ratio of 2.0. The silica ratio (1.6–3.2), the alkali contents and the degree of sulfatisation were varied. Strength tests showed the following results.

- With increasing silica ratio strength was generally increased, and reduced with increasing SO_3 content.
- Strength at 2 days was increased by K_2O additions of up to 1.5 per cent, and Na_2O additions of up to 1.5 per cent when the degree of sulfatisation was 100 per cent.
- The strengths at 28 and 90 days were reduced by additions of Na_2O and K_2O; for equal additions, Na_2O had a greater influence than K_2O.
- For K_2O, the optimum degree of sulfatisation was 60–70 per cent and for Na_2O it was 90–100 per cent.
- Supersulfatisation of the alkalis results in strength reduction.
- The reduction in strength at 28 and 90 days in cements containing K_2O can be offset by increasing the silica ratio, regardless of whether there was an optimum degree of sulfatisation. This action is only successful in cements containing Na_2O.

Investigations have been carried out on laboratory clinker made from cement raw meals with a uniform lime saturation factor of 93 per cent and a silica ratio of 2.4. The alumina ratio (1.3–2.7), alkali contents (Na_2O and K_2O each ~0–2 per cent) and the degree of sulfatisation were varied. Strength tests showed the following results.

- Strengths always increased with falling alumina ratio.
- Strengths after 2 and 7 days were increased by K_2O and Na_2O contents up to about 1.5 per cent. Higher alkali contents and supersulfatisation reduced strengths.
- The strengths after 28 and 90 days were increasingly reduced by increasing K_2O and Na_2O contents.
- For equally high contents of alkali oxides, the strengths after 28 and 90 days were reduced to a greater extent by Na_2O than by K_2O. Equal molar proportions of the two alkali oxides lowered the strengths by equal amounts where the degree of sulfatisation was below 100 per cent.
- For alumina ratios between 1.3 and 2.7, the optimum degree of sulfatisation was about 60 per cent for K_2O and about 100 per cent for Na_2O.
- Supersulfatisation of the alkalis reduced the strengths considerably; this was especially true of cements containing Na_2O.
- The reduction in strength after 28 and 90 days by K_2O contents up to ~1.5 per cent can be offset by lowering the alumina ratio where there is an optimum degree of sulfatisation, but the reduction in strength caused by Na_2O contents up to 1.5 per cent is only partly compensated.

Investigations have been carried out on laboratory clinkers made from cement raw meals with a silica ratio of 2.4 and an alumina ratio of 2.0. The lime saturation factor, the alkali contents and the degree of sulfatisation were varied. Strength tests showed the following results.

- Strengths were increased with increasing lime saturation factor.
- Strengths after 2 and 7 days were increased by K_2O and Na_2O contents up to ~1.5 per cent. Higher alkali contents and supersulfatisation reduced strengths.
- The strengths after 28 and 90 days were increasingly reduced by increasing K_2O and Na_2O contents.
- For equally high contents of alkali oxides, the strengths after 28 and 90 days were reduced to a greater extent by Na_2O than by K_2O. Equal molar proportions of the two alkali oxides lowered the strengths by equal amounts.
- The optimum degree of sulfatisation of the alkalis was dependent on the lime saturation factor:
    - Lime saturation factor 86%, 90–100% for Na_2O and K_2O;
    - Lime saturation factor 93%, 50–70% for K_2O and 90–100% for Na_2O;
    - Lime saturation factor 98%, 50–70% for K_2O and Na_2O.

  These data are valid for alumina ratios between 1.3 and 2.7, and for silica ratios between 1.6 and 3.2, where the lime saturation factor is 93 per cent. Supersulfatisation reduced the strength, especially at a high lime saturation factor and in cements containing Na_2O.
- The reduction in the strengths at 28 and 90 days by K_2O levels up to 1.5 per cent can be offset by a significant increase in the lime saturation factor where there is an optimum degree of sulfatisation. Lowering the alumina ratio, or raising the silica ratio, improved the strength of alkali-rich cements more effectively than raising the lime saturation factor.
- Cements with lime saturation factors of 93 and 86 per cent, with alkali oxide contents of 1.0–1.5 per cent lead to virtually identical strengths after 28 days and 90 days where there was an optimum degree of sulfatisation. However, strengths after 2 and 7 days were significantly lower with cements with lime saturation factors of 86 per cent.

As expected, the compressive strength of the alkali- and sulfate-free cements increased at all test dates with increasing silica ratio and lime saturation factor. With increasing alumina ratio, the strengths were virtually constant.

A comparison[72,73] of the strengths developed in a series of laboratory-made cements, composed of CaO, SiO_2, Al_2O_3, Fe_2O_3 and MgO, all ground to the same fineness and with the same amount of gypsum added, indicated that strength is primarily a function of the contents of $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$. The strengths at ages up to 28 days were found to be a function of the content of $3CaO \cdot SiO_2$, while the increases in strength between 28 days and 6 months were roughly linearly related to the content of $2CaO \cdot SiO_2$. With more finely ground cements, the dicalcium silicate probably began to produce its effect somewhat earlier.

Cements rich in tricalcium silicate showed high strength at early ages, while those which were low in this compound showed much lower strengths at early ages, but a

Table 8.13 Clinker phase proportions for lime saturation factor = 95%, alumina ratio = 2.0 and a range of silica ratios[71]

Silica ratio	Alite	Belite	C_3A	C_4AF
1.5	50	19	21	10
1.7	54	17	20	9
2.0	58	16	17	9
2.3	61	15	16	8
2.5	63	14	16	7
2.8	65	14	15	6

Table 8.14 Clinker phase proportions for laboratory clinkers with lime saturation factor = 95%, silica ratio = 2.0 and a range of alumina ratios[71]

Alumina ratio	Alite	Belite	C_3A	C_4AF
0.5	68	14	0	18
1.0	65	14	6	15
1.5	63	15	10	12
2.0	58	16	17	9
2.5	56	16	20	8

Table 8.15 Clinker phase proportions in laboratory clinkers with silica ratio = 2.0 and alumina ratio = 2.0, and a range of lime saturation factors[71]

Lime standard	Alite	Belite	C_3A	C_4AF
85	39	37	15	9
90	50	26	15	9
95	58	16	17	9
100	69	4	17	10
105	71	6	17	CaO*

progressive increase with age, so that at 6 months the differences in the strengths were relatively small. At 12 months the strengths of the two groups of cements were about equal.

The interrelationships between the proportions of clinker phases and compressive strength have been studied[71] for laboratory cements made from chemically pure substances ($CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3) fired at 1450°C for 2 h. The free lime in

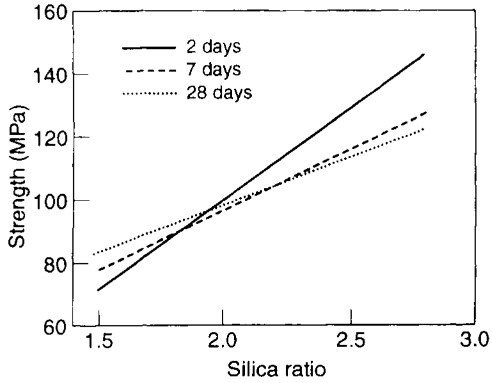

Fig. 8.12 Influence of silica ratio on compressive strength.[71]

the clinker was very low (<0.1 per cent); the cement was ground to a specific surface area of $320 \pm 4\,m^2/kg$ with 6 per cent gypsum. The compressive strength was determined on small prisms ($15 \times 15 \times 60$ mm) made from mortar (sand/cement = 3, water/binder = 0.5).

Attempts have been made, by analysing data from a series of cements, to derive factors representing the contribution of each of the four major cement compounds to a particular property at a given age, and under given conditions. In this analysis the assumption is made that the contributions made by the different compounds are additive, i.e. that a property of a cement may be expressed quantitatively by an equation:

$$P = aA + bB + cC + dD \tag{8.9}$$

where P represents the numerical value of the property, e.g. strength, at a given age and under given conditions; A, B, C and D are the percentage contents of $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ present in the cement, and a, b, c and d are coefficients representing the contribution of 1 per cent of the corresponding compound to the property considered. The use of such an equation also assumes that the contribution of a unit mass of any given compound to a particular property under the conditions postulated remains unchanged, i.e. that the coefficients a, b, c and d are constants. Errors in the calculated amount of the compounds present do not invalidate this method of analysis, but they will be reflected in the degree of uncertainty attached to the coefficients deduced.

The above approach has been more successful when applied to the heat of hydration than when applied to strength or shrinkage data. The relative contributions to strength of the four cement compounds derived from different sets of data are very variable, and it cannot be claimed that they do more than confirm the conclusion that $3CaO \cdot SiO_2$ makes the major part of its contribution to strength in the first 28 days, and that $2CaO \cdot SiO_2$ contributes from 28 days onwards. The results for $3CaO \cdot Al_2O_3$ and $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ are very erratic; this may not be surprising since the content of these compounds calculated by the Bogue formula can be wide of the truth. All that can be said is that the available data indicated that these two compounds contributed positively to early strength, but under moist storage caused regression in strength after longer periods.

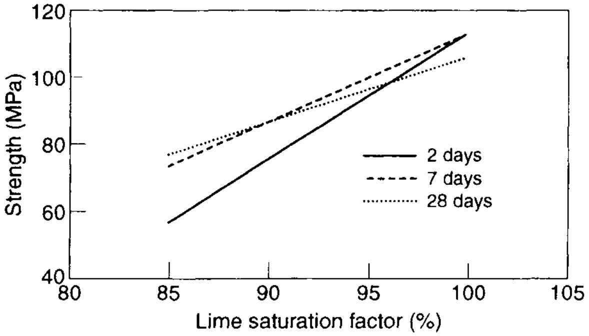

Fig. 8.13 Variation of compressive strength with lime saturation factor.[71]

In an experimental investigation to study the early rate of strength gain, a series of 53 laboratory clinkers was prepared from the system CaO–SiO_2–Al_2O_3–Fe_2O_3 and were formed into cements by intergrinding with 3 per cent $CaSO_4$.[74] Compressive strengths on compacts (pressed minicylinders allowed to hydrate by flooding with distilled water), 11 mm diameter and 11 mm in height were obtained after hydration for 24 h at 20°C. The best relationship between this crushing strength and Bogue composition was given by

$$\text{Strength} = 1.66 \times \%\ C_3S - 1.52 \times \%\ C_4AF - 0.72 \times \%\ C_3A + 0.12 \times \text{fineness} - 3.2 \tag{8.10}$$

where fineness (m^2/kg) is the specific surface area of the cement. The coefficient of determination for this regression, adjusted for degrees of freedom, was 89.6 per cent. The effects of firing time and firing temperature were found to be negligible under the conditions of this laboratory test. The overriding importance of C_3S content to cement reactivity and early strength development was confirmed by these results. Some clinkers showed anomalous expansions after 24 h and low strengths; most of these clinkers were fired at relatively low temperatures and free CaO was present in at least one. All contained substantial quantities of C_3A.

The relationship between clinker phase composition and strength has been much investigated.[75,76] Data from 30 cements containing 46–62 per cent C_3S and 1–11 per cent C_3A have been analysed and the most significant association between strength and compound composition lay in an expression involving the percentage of C_3A alone.[77,78] The percentage of C_4AF was found to have little effect on strength. The contribution of C_2S matched that of C_3S only after 90 days' hydration. The correlation between strength and the percentage of C_3S passed through a maximum at 7 days' hydration, while the correlation with the percentage of C_3A was most significant after 28 days' hydration.

It may be assumed that each of the phases of Portland cement clinker contributes either directly or indirectly to the development of strength and the ultimate strength of the resultant cement. It is conceivable that this effect may be an additive one, in which each of the phases present acts individually, or a cumulative one, in which an interaction between the individual phase takes place, enhancing or weakening their influence.

Several investigators studying the relationship between clinker phase composition and strength have used multiple linear regression analysis, and have assumed that the action of the phases involved is additive, i.e. that the relationship between strength and cement composition may be expressed by an equation of the type

$$\sigma_t = a_0 + a_1c_1 + a_2c_2 + a_3c_3 + \ldots \tag{8.11}$$

where σ_t is the cement strength after hydration time t, a_0, a_1, a_2, a_3 are regression coefficients and c_1, c_2, c_3 are the contents of phases 1, 2 and 3 in a cement.

A series of equations has been obtained by evaluating cement strength against a number of clinker parameters (phase composition, ignition loss, insoluble fraction, air content, alkali content).[79] A multiple correlation analysis[80] has been published between mortar compressive strength after up to 10 years' water curing and chemical composition parameters for setting of up to 199 commercial US cements.

The relationship between strength and cement composition has been studied for 30 Australian cements (containing 46–62 per cent C_3S and 1–11 per cent C_3A).[77] It was concluded that the most significant association between strength and compound composition lay in the regression involving C_3A alone. In contrast, C_4AF was found to have little or no effect on strength. The contribution of C_2S matched that of C_3S only after hydrating for 90 days. In a subsequent work[78] it was found that the significance of the correlation of strength with C_3S passed through a maximum at 7 days, and the correlation with C_3A was most significant at 28 days.

Schrämli,[81] in analysing his own data and data from the literature, concluded that C_3A affected initial strengths positively but the ultimate strengths were affected negatively. C_3A had a negative effect on strengths at 7 and 28 days (31 cements), while the effect of C_3S is positive.[76] The correlation coefficient between strength and C_3S and C_3A content was not significant at 1 and 3 days.

The relationship between strength and phase composition has been studied on 114 cements from New Zealand.[75] It was concluded that an equation of the type

$$\sigma_t = a_0 + a_1 \cdot C_3S + a_2 \cdot (C_3S + C_2S) + a_3 \cdot C_3A + a_4 \cdot SA \tag{8.12}$$

yielded better fits than the simple equation

$$\sigma_t = a_0 + a_1 \cdot C_3S + a_2 \cdot C_3A + a_3 \cdot SA \tag{8.13}$$

C_4AF was found to be influential on strength development.

Alexander and Ivanusec[82] established that the association between strength and C_3S content did vary greatly with the SO_3 content of the cement. However, the effect of C_3A on strength was insensitive to the SO_3 content.

As expected, the regression coefficient associated with C_3S was consistently positive, confirming the positive effect of C_3S on strength. The coefficient associated with C_3A was also positive, its magnitude always being greater in the equation expressing 28-day strengths than that for 3-day strengths. The coefficient for the effect of C_2S after 28 days was either positive, negative or equal to zero. Finally, the coefficient associated with C_4AF was positive, however, its magnitude was significantly lower than that of the coefficient associated with C_3A.

Even though multiple linear analysis has yielded reasonably good fits to data for the relationship between strength and clinker composition, doubts have arisen whether the effect of single clinker phases is linear, independent and additive.

C_3A may enhance the contribution of C_3S to strength either by modifying the hydration products or by accelerating the progress of C_3S hydration.[77,78] The best fit for the data at 3, 7 and 28 days was obtained by an equation of the type

$$\sigma = a_0 + a_1(1 + bC_3A)C_3S + a_2 \tag{8.14}$$

where a_0, a_1, a_2 are empirical constants.

It was also found[78] that the cement strength increased with increasing C_3A content (linearly) only up to an amount of 14 per cent, and decreases as the C_3A content becomes even higher.

A large number of experimentally made clinkers were investigated,[83] varying widely in phase composition. These clinkers were ground with constant amounts of gypsum (SO_3= 2.5 per cent) to identical finenesses (300 m^2/kg). The following conclusions were reached.

- The overall correlation of strength properties with phase quantities was never linear.
- The positive effect of silicates and particularly of C_3S was the most important one at all ages. Nevertheless, the strength started to decline when the C_3S content exceeded 70 per cent.
- The contribution of C_3A and C_4AF to strength development was relatively small. The strength increased with increasing C_3A content only to some limiting value, and decreased with higher C_3A contents. The optimum proportion of C_3A was not constant and changed with the amount of C_3S and C_4AF present.

A catalytic action of C_3A on C_3S hydration has been proposed and the following equation for calculating the compressive strength was presented:[84]

$$\sigma_t = \frac{1 - p\mathrm{e}^{-bt} - (1-p)\mathrm{e}^{-b_2}}{1 - p\mathrm{e}^{90^{b}}t - (1-p)\mathrm{e}^{-90^{b}{}_{2}}} \tag{8.15}$$

where σ = strength after t days, σ_{90} = strength after 90 days, p = C_3S content of the cement and b, b_2 = rate parameters which are functions of temperature, C_3A content and fineness.

A series of laboratory-made cements showed a non-linear effect of the individual clinker phases on cement strength and evidence of an interaction between the phases present.[85] The resultant strength increased at all ages if C_3S was replaced with C_3A, up to an amount of 10 per cent, and declined at higher degrees of substitution. Substitution of C_3S by C_4AF up to 30 per cent had little effect on 1-day strength, but at longer hydration times the resultant strength increased significantly with increasing amount of C_4AF in the clinker. At constant $C_3S + C_2S$ content, the strength in the presence of both C_3A and C_4AF was higher than in the presence of each phase alone.

It may be concluded that the available data on the effect of clinker phase composition on strength are rather contradictory. Even though equations which express the relationship between strength and phase composition of the clinker can be derived from the experimental data using multiple regression analysis, a model that assumes independent and additive contribution of the individual clinker constituents to strength without the existence of any interactions, appears highly unlikely. These relationships are of little practical importance.

8.4.7 EFFECT OF INITIAL TEMPERATURE RISE

The object of heat curing (or steam curing) of concrete is to increase the rate of strength gain and so to increase the rate of utilisation of production equipment by ensuring that concrete rapidly reaches a sufficient strength to allow early demoulding or, in the case of

Table 8.16 Compressive strengths after 28 days (MPa) of mortar prisms (water/cement = 0.375) cured at 20 or 85°C for 6 h, then stored under water at 20°C

Cement	28 days, 20°C	28 days, 85°C
3982	72.4	73.8[a]
3984	69.0	63.3
4037	73.8	69.2
4031	63.7	48.9
4036	69.1	61.4
4044	68.7	58.4
3753	57.3	51.3

[a] This mortar mix was accidentally made without air entrainment, thus possibly accounting for its unusually high strength.

Table 8.17 Compressive strengths after 28 days (MPa) for concrete cubes (water/cement = 0.375) cured at 20 or 95°C for 5 h, then stored under water at 20°C

		Compressive strength (MPa)	
Cement	Aggregate type	20°C	95°C
3982	UK granite/quartz, fine	82.4	71.6
3982	UK flint, coarse/fine	78.3	71.1
3982	US granite, coarse/fine	81.6	68.9
3982	UK limestone, coarse/fine	80.7	66.7
3984[a]	UK granite/quartz, fine	79.1	71.5
4037	UK granite/quartz, fine	79.9	67.1
4031	UK granite/quartz, fine	71.3	52.1
4036	UK granite/quartz, fine	81.1	62.3
4044	UK granite/quartz, fine	72.4	62.9
3753	UK granite/quartz, fine	68.4	58.9

[a] Plus 0.19% of SO_3 added as calcium sulfate.

concrete members to be prestressed, to enable the concrete to be stressed as soon as possible after casting. Several studies of the influence of steam curing of concrete components on strength levels achieved have been published over the years,[86–88] and rules and standards have been developed in order to maximise the efficient use of heat during accelerated curing.

Allowing the temperature during the setting period to rise above about 55°C generally reduces the ultimate strength of the mortar or concrete. A historical review of the factors that have been shown to be important is included in Ref. 89; great emphasis and importance is placed on the time for which the concrete is allowed to develop strength at room temperature before the application of heat. Data for heat cured mortars is shown in Table 8.16, and for concretes is illustrated in Tables 8.17 and 8.18. A delay period of 2–4 h

Table 8.18 Compressive strengths after 28 days (MPa) for concrete cubes (water/cement = 0.375), UK granite aggregate/quartz sand, cured at 75°C for 7 h or 85°C for 6 h, then stored under water at 20°C

Cement	75°C/7 h cure	85°C/6 h cure
3982	81.1	76.9
3984[a]	77.2	77.4
4037	76.5	74.2
4031	61.2	55.9
4036	69.5	–
4036	71.4	68.3
4044	67.7	65.7
3753	66.2	60.4

[a] Plus 0.19% SO_3 added as calcium sulfate.

Table 8.19 Compressive strengths after 28 days (MPa) of mortar prisms (water/cement = 0.5), cured at 20 or 100°C for 3 h, then stored under water at 20°C

Cement	28 days, 20°C	28 days, 100°C
3982	64.3	55.4
3984	62.8	55.1
4037	62.8	51.5
3986	62.1	60.4
3988	63.8	53.7
3990	64.4	49.0
3990 + gypsum[a]	63.7	50.8
3992	60.6	53.4
3994	61.0	54.6
3996	63.7	53.0
3996 + gypsum[a]	63.0	50.9
4167	61.1	52.5
4144	67.6	57.7
4031	59.1	43.3
4036	61.0	46.5
4044	58.2	50.6
3753	53.1	47.9
4176	58.0	52.7

[a] Plus 0.55% SO_3 added as calcium sulfate.

was allowed before applying heat, and a rate of temperature gain of 12.5°C/h was applied generally for mortars and concretes, but 40°C/h for the mortars cured at 100°C (Table 8.19).

The view taken by most commentators for this failure to achieve room temperature cured strength levels is that microcracking and flaws are introduced by differential thermal expansion and contraction of the components of the fresh concrete in the mould as the heat cycle is imposed. One way these defects can be avoided is to heat the fresh concrete in the mixer prior to casting. Alternatively, a sufficiently long precure period at room temperature can allow enough strength to develop to resist microcrack formation. The delay period required is approximately equal to the time for the initial set.

Microstructural changes have been observed to take place during heat cure,[90–93] leading to a densification of the C-S-H microstructure immediately surrounding the cement grains as the rate of hydration is accelerated by the application of higher room temperatures and a heterogeneous microstructure and a coarsening of the hydration product occurs; these factors present an additional parameter possibly able to account for a reduction in ultimate strength and an increase in permeability.[94] At a hydration temperature of 41°C, as much as 30–40 per cent of the cement may be hydrated in a 2 h period,[94] and at steam curing temperatures as much as 50 per cent of the cement may be hydrated in 1 h or less. The low solubility and low diffusibility of cement hydration products encourages a build-up of hydrates in the immediate vicinity of the hydrating cement grain which may prevent further hydration at later ages and so reduce the ultimate strength development.

There is a general decline in 28-day compressive strength as the curing temperature is raised from 20 through 75, 85 to 95°C for the concretes illustrated in Tables 8.17 and 8.19.

8.4.8 EFFECT OF SULFATE CONTENT

There is usually found to be an optimum SO_3 content (2–3 per cent) for binders, beyond which (> 4 per cent) compressive strength begins to decline, particularly at early ages. Frigione and Marra[21] confirmed this statement using ISO-RILEM mortar prisms, for cements with a wide range of particle size distributions (gypsum was added to preground clinker), and found that the maximum in strength was not sensitive to particle size grading.

The compressive strength of 100 mm concrete cubes containing up to 2.2 per cent SO_3 additions (gypsum) were found to show significant strength regression at levels of addition above 4.2 per cent SO_3 for a Portland cement concrete, but incorporation of 20 or 40 per cent natural pozzolana allowed the strength level to be maintained up to and including 13.2 per cent SO_3. It was pointed out that the maximum allowable sulfate in a concrete is dependent on many factors, including the C_3A content, the curing temperature, the particle size of the gypsum and the presence of chloride in the mix.

The effects of increased sulfate content (total SO_3 2.26–5.26 per cent) on the early compressive strength of concrete cubes at up to 56 days were examined and showed a definite reduction at levels of SO_3 above 4.0 per cent for two Portland cements (3.8 and 8.9 per cent C_3A, 2.34 and 2.76 per cent SO_3) and fly ash blended cement mortars.[95] Similar data have been reported elsewhere.[84]

The variation in SO_3 level between about 1.5 and 4.5 per cent was found to have very limited influence on compressive strengths at 28 days or 1 year,[82] but had a very marked effect on the creep of concretes; the higher the sulfate level, the smaller the creep strain.[96] A fall in cement strength with increasing SO_3 content in low-alkali clinker by up to about 10 per cent has been reported.[90] The decrease in strength is less than could be expected from the reduction in the amount of alite forming, suggesting that activation of the belite phase is occurring.

The amount of SO_3 in clinker is generally low. Here SO_3 is present predominantly in the form of alkali sulfates. A larger fraction of SO_3 is added to cement in the form of calcium sulfate, either as gypsum, $CaSO_4 \cdot 2H_2O$, or anhydrite, $CaSO_4$. During cement grinding, a fraction of the gypsum may be decomposed to hemihydrate $CaSO_4 \cdot \frac{1}{2} H_2O$. The main role of calcium sulfate is to control cement setting, although strength may also be affected.

Data on the effect of calcium sulfate on the progress of hydration and on cement strength are not uniform, though it is generally believed that optimum strength values are obtained at an 'optimum gypsum' value, depending on the clinker quality, cement fineness and hydration time. A strength maximum occurred with increasing gypsum in the cement.[97] This maximum shifted to higher SO_3 values with increasing hydration time.

The effect of anhydrite added to ordinary Portland cement was found to form a strength maximum at about 5 per cent $CaSO_4$ (at room temperature).[98] This maximum shifted to higher values at 65°C. At optimum anhydrite addition, the early hydration of C_3S was retarded and the degree of hydration at later ages increased. The development of strength was accelerated.

The optimum gypsum value may depend on clinker composition and fineness and also on the hydration temperature, increasing with increasing temperature. The strength optimum shifted to higher gypsum values with increasing hydration time.[99] The effect on strength for six cement brands, manufactured in full-scale plants, of changes in SO_3 contents was reported.[82] The strength was usually independent of, or linearly related to, the SO_3 content of the cement. At longer ages the association between strength and C_3A content varied considerably with the content of SO_3. The effect of gypsum on strength was studied on laboratory-made cements, with variable C_3A/C_4AF ratios.[100] In all instances the amount of SO_3 had a considerable effect on strength; however, this effect and the optimum level of SO_3 depended on the C_3A/C_4AF ratio. In addition to strength, the progress of hydration was affected as the amount of gypsum present.

Only slight differences in strength were found by varying the content of gypsum in both Portland and Portland–blastfurnace slag cements.[19] At the same time,[95] other data showed a distinct optimum shifting gradually to higher SO_3 values if either hemihydrate or gypsum were used as set regulators.[95]

Soroka and Relis[101] compared the strength development of compacts made from identical ground clinkers with and without gypsum additions (2.93 per cent SO_3). The effect of gypsum on strength was most beneficial after 1 day, and exhibited a minimum after 7 days. The degree of hydration was decreased except after 1 day. It was shown that the higher strength was associated neither with a higher degree of hydration nor with lower porosity, but with an improved quality of the hydrates formed.

It has also been found that the resultant compressive strength may be affected by the rate of sulfate dissolution, which depends on the kind of calcium sulfate used and its fineness. Differences in both 1 and 28 day strengths have been found after adding identical amounts of different forms of calcium sulfate (gypsum, natural anhydrite, hemihydrate or phosphorgypsum) to the same clinker.[102] Greater strengths have been reported by using a gypsum with a fineness $554\,m^2/kg$ as compared with one with $10\,000\,m^2/kg$.[99]

It appears that the effect of calcium sulfate on strength is a rather complex one. Even though calcium sulfate may affect the rate of hydration, it appears likely that the observed variations of strength are mainly due to an alteration of the binding properties of the hydrates formed.

8.4.9 EFFECT OF ALKALI CONTENT

The strengths of 31 cements have been examined and correlation with their chemical composition has been attempted by multiple linear regression.[76] The highest correlation coefficient existed between 28-day strength and the calculated quantity of soluble alkali (i.e. alkali present in the clinker as sulfate); the higher the soluble alkali, the lower the strength. This correlation was much stronger than that between strength and C_3S or C_3A content. In contrast, the correlation between strength and quantity of alkali combined in the clinker minerals was very poor.

Alkali sulfate additions to laboratory-prepared clinker did not cause changes in the degree of hydration of the C_3A or C_3S components[24] but the strengths at times between 1 day and 28 days were significantly reduced (Table 8.20). The cements were ground to a specific surface of $300\,m^2/kg$, and made into pastes with water/cement = 0.5, and hydrated for various periods at 20°C. The development of strength was not altered by the alkalis present in the crystal lattices of the cement minerals (Table 8.21).[23]

It is recognised that the strength of Portland cement may also be affected by the presence of minor constituents in clinker. Of the various minor constituents, the effect of alkalis has been studied most extensively. It is accepted that the action of alkalis may depend on the form in which they are present in the clinker: in the absence of SO_3, alkali oxides are incorporated into the crystalline lattice of the clinker minerals, while in the presence of SO_3, alkali sulfates are formed. A decrease of both early and late strength

Table 8.20 Strengths of laboratory-made cement with added alkali sulfates[24]

Cement + sodium or potassium sulfate	Compressive strength (MPa)			
	1 day	3 days	7 days	28 days
Control	20.0	41.5	61.8	74.2
0.72% Na_2O as sulfate	18.8	29.6	39.8	56.5
1.26% Na_2O as sulfate	9.3	22.4	32.5	42.6
0.88% K_2O as sulfate	16.1	33.7	43.7	66.3
1.48% K_2O as sulfate	8.5	23.1	35.5	48.8

Table 8.21 Strengths of laboratory-made cement with added alkali in the clinker[23]

Cement + sodium or potassium oxides	Compressive strength (MPa)			
	1 day	3 days	7 days	28 days
Control	20.0	41.5	61.8	74.2
0.72% Na_2O in clinker	19.5	39.8	59.6	68.7
1.26% Na_2O in clinker	18.4	39.2	57.5	68.2
0.88% K_2O in clinker	21.9	44.8	60.7	72.1
1.48% K_2O in clinker	20.0	43.1	61.0	73.2

has been reported due to the presence of Na_2O or K_2O, either in the form of sulfates or incorporated into the crystalline lattice of clinker minerals.

Of the various minor constituents, the effect of alkalis, i.e. of Na_2O and K_2O has been studied most extensively. A review on the action of alkalis in cement has been published.[20] According to this document, high contents of alkalis in clinker generally result in a decrease of final strength while early strength is usually increased. Some workers, however, report an overall positive effect on strength development.

In a more detailed study of the subject, it has been recognised that the action on alkalis depends to a great extent on the form in which they are present in the clinker: in the absence of SO_3, alkali oxides are incorporated into the crystalline lattice of clinker minerals, while in the presence of SO_3, alkali sulfates (designated also as 'soluble alkalis') are formed.

Knöfel[103] reported a decrease of both early and late strength due to the presence of high amounts (1.6 per cent) of either Na_2O or K_2O present either in the form of sulfates or incorporated into the crystal lattice of the clinker minerals. Schmitt-Henco[104] reported an increase of strength due to alkali sulfate, while insoluble alkalis increased the final but lowered the initial strength.

The effect of alkalis on 31 industrial cements has been reported.[76] A decrease of strength after 7 and 28 days due to soluble K_2O in the clinker occurred, while the effect of this form of potassium oxide on strengths after 1 and 3 days was insignificant. At the same time, no significant effect of K_2O bound in clinker minerals on strength was observed.

In a subsequent study on laboratory-made cements, an increase of early strength and a decrease of late strength was observed, due to soluble K_2O.[106] Parallel to that, the hydration of the phases C_3S, C_3A and C_4AF was distinctly accelerated. An increase of early strength and a decline of late strength due to soluble alkalis was also reported.[107] The hydration of C_3S accelerated up to 36 h and reduced afterwards.

Only minor strength changes due to the presence of Na_2O or K_2O in the crystalline lattice of laboratory-made clinkers have been detected.[84] A decrease of strengths at 7 and 28 days due to K_2SO_4 occurred,[108] while data on 1-day strengths were inconclusive. C_3S hydration was accelerated while the hydration of C_3A was retarded.

A decrease of both early and late strength due to Na_2SO_4 or K_2SO_4 in cements has been reported.[24] The rate of C_3S hydration was not altered. In parallel work on alkalis incorporated into the clinker minerals,[23] no significant effect of either Na_2O or K_2O on strength was detected. The hydration rate of C_3S was not altered. The hydration of C_3A was retarded due to Na_2O doping and accelerated due to K_2O doping.

Studies were conducted on laboratory clinkers made from natural cement raw materials (limestone, clay and quartz) and iron oxide (reagent) as a corrective ingredient, or from industrial raw meal.[109] All clinkers were burned in a closed kiln with a raised SO_2 partial pressure at 1450°C for 2.5 h. They were then cooled in air. The free lime content of the clinkers was 1 per cent. The strengths (determined by crushing small paste prisms $15 \times 15 \times 60$ mm) of low-alkali cements (ground to $340 \pm 10\,m^2/kg$) at up to 28 days decrease with increasing SO_3 content in the clinker, by up to 10 per cent. This decrease in strength is less than could be expected from the decrease in alite; possibly the increased belite present is activated by the sulfate. By changing the chemical composition of the clinker, e.g. by raising the silica modulus, it is possible to avoid these strength losses caused by the incorporation of sulfur in the clinker. A loss in strength as a result of increased SO_3 content from 1.4 to 2.9 per cent can be offset, for example, by increasing the silica modulus from 1.6 to 2.4.

Table 8.22 Phase composition of laboratory clinkers for different rates of cooling[105]

MgO (%)	Alite	Belite	C_3A	Ferrite	Periclase
Potential composition (Bogue) (%)					
0	60	19	13	8	0
2	59	19	13	8	2
4	58	18	12	8	4
6	56	18	12	8	6
Phase composition determined microscopically (%)					
Rapidly cooled clinker					
0	64	10	15	11	0
2	68	5	13	14	0
4	69	5	10	14	2
6	70	5	7	14	4
Slowly cooled clinker					
0	61	16	14	9	0
2	63	12	11	13	1
4	63	11	9	14	3
6	64	9	8	14	5

8.4.10 INFLUENCE OF CLINKER SO_3 AND CALCIUM SULFATE ADDITIONS

The influence of SO_3 content in the cement on setting and strength development is well known. It is not possible to draw up a generally valid formula for the optimum sulfate content in the cement. For each cement it is necessary to determine an optimum SO_3 content for setting behaviour and strength development by trials, taking into account the chemical composition and structure of the clinker, the sulfur and alkali contents in the clinker phases, the sulfate phases, the formation of the clinker phases and their content of foreign ions, the fineness and particle size composition of the cement, and the type of calcium sulfate addition, etc.

The percentage of sulfatisation of the alkali was defined by the expression

$$SD = \frac{\% \, SO_3}{1.292 \times \% \, Na_2O + 0.850 \times \% \, K_2O} \times 100 \qquad (8.16)$$

The compressive strengths after 2 and 7 days were increased by K_2O up to about 1.5 per cent regardless of moduli. The compressive strengths after 28 and 90 days were reduced with increasing K_2O content. The reduction in the compressive strengths could be moderated by

- increasing the silica ratio;
- lowering the alumina ratio;
- increasing the lime saturation factor.

With an optimum degree of sulfatisation, the compressive strengths after 2 and 7 days were increased by Na_2O up to contents of about 1.5 per cent, regardless of the moduli.

The compressive strengths after 28 and 90 days are progressively reduced with rising Na_2O contents. The reduction in compressive strength is more marked in relation to Na_2O than with K_2O. As with clinkers containing K_2O, the drop in strength with increasing Na_2O content could be moderated by increasing the silica ratio, lowering the alumina ratio or increasing the lime saturation factor. Compensating for the loss in strength by an appropriate change of the composition ratios was not always satisfactory with cements containing Na_2O.

The optimum degree of sulfatisation was essentially dependent on the lime saturation factor. It was not possible to confirm a relationship between the optimum degree of sulfatisation and the level of the alkali content such as that established by Sprung.[110] When changing the composition ratios to improve the technological properties of cements, an attempt should always be made to achieve the degree of sulfatisation best suited to the lime saturation factor used.

8.4.11 EFFECT OF MINOR COMPONENTS

It is well known that cement strength may be affected by the presence of minor constituents in clinker. Such constituents may be present only in amounts of a few per cent, or a few tenths of a per cent, yet may affect the resultant properties of the binder noticeably.

The effect of MgO content on cement strength has been studied by several investigators and has been found not to be very significant.[84,100,104] The data produced[105] show that the effect of MgO content on strength is conditioned by the rate of cooling of the clinker (Table 8.23).

Free lime affected the cement strength mainly by inducing unsoundness, volume instability and cracking. According to Alexander *et al.*,[77] a negative influence of free lime on strength began to appear at about 2 days, reaching greatest significance at between 28 and 90 days. Schmitt-Henco also found a negative effect of free lime on 28-day strength.[104] On the contrary, a positive effect of free lime on strength has been reported.[75]

Table 8.23 Compressive strengths of laboratory cements after cooling the clinkers at different rates[105]

	Compressive strength (MPa)			
MgO (%)	2 days	7 days	28 days	90 days
Rapidly cooled clinker				
0	15.4	27.7	42.9	50.4
2	12.9	31.2	46.3	55.7
4	11.7	30.1	42.4	56.3
6	12.0	30.1	37.8	43.3
Slowly cooled clinker				
0	13.2	24.3	31.4	54.4
2	13.4	25.2	41.1	50.1
4	13.8	27.5	44.1	48.4
6	10.9	26.4	35.9	40.1

Table 8.24 Effect of cement specific surface area on strength[111]

Cement	Surface area (m^2/kg)	Compressive strength (MPa)			
		18 h	2 days	7 days	28 days
1	261	6.3	18.4	45.4	69.2
	343	13.9	36.2	58.6	77.0
	453	21.8	44.9	61.1	76.5
2	260	12.9	27.5	44.6	55.6
	367	14.4	36.0	52.5	64.2
	474	22.3	42.4	54.8	62.8

8.4.12 EFFECT OF SPECIFIC SURFACE AREA

It is generally believed that the ultimate strength, i.e. the strength of fully hydrated cement paste, is independent of the fineness of the original cement. On the other hand, the fineness of cement determines the progress of hydration and thus the rate of strength development. The strength data for two cements ground to a range of finenesses have been published.[111]

It has been well recognised that the progress of hydration and strength development, especially after short hydration times, is significantly enhanced with increasing specific surface area (Table 8.24). Data for two series of cements made from two clinkers ground to different surface areas are illustrated, in Table 8.24. Fineness of grinding of the cement, or specific surface area, correlates positively with early age strength development, as would be expected since the rate of hydration will be greater with increasing fineness of the cement. There is some additional evidence[94] that ultimate strength is also increased by fine grinding (tests were reported for cement specific surface areas of 250, 450 and 800 m^2/kg, for strength measured on 15 × 15 × 60 mm mortar prism specimens); this finding is accounted for by the proposal that a more uniform microstructure would be expected for the more finely ground cement and that this will lead to higher strengths.

8.4.13 EFFECT OF PARTICLE SIZE DISTRIBUTION

It has been recognised that, in addition to the surface area, the progress of hydration depends on the particle size distribution of the cement.[21,111–113] As a measure of particle size distribution, the inclination of the line characterising the size distribution in a logarithmic granulometric plot of percentages greater than a given particle diameter against particle diameters, according to Rosin, Rammler and Bennet (RRB), may be employed. The wider the particle size range of the sample, the smaller the value of n. The strength of RILEM mortars after 1, 3 and 7 days' hydration at 20°C increased as the value of n increased, that is, as the particle size range in the sample was reduced, at the same specific surface area (320 m^2/kg; SO_3 ~3.1 per cent).

The effect of n on cement strength has been studied;[21] all strengths between 18 h and 28 days increased with an increasing value of n, or with an increasingly narrow particle size distribution (at constant specific surface area) regardless of the fineness of the cement, i.e. for equal specific surface areas the strength increased as the granulometric distribution became narrower. This increase of strength was found to be predominantly the effect of a faster hydration under these conditions. A narrower particle size range can be attained in a ball mill by using very small grinding media.[114]

8.4.14 EFFECT OF CLINKER MICROSTRUCTURE

The parameters to be considered include the size, shape and orientation of individual grains, the distribution of grain sizes, the distinctness of their boundaries, areas, clustering colour and birefringence.

Even though the effect of alite size on strength has been generally recognised, opinions differ as to the relationship which exists between these parameters.[115,116] According to most investigators, the initial as well as the final strength increased with decreasing size of alite crystals.[117–119] In contrast, Butt and Timashev[120] reported an improvement in strength properties with increasing alite size. Suzukava *et al.*[121] reported no effect on strength due to differences in alite crystal size. Butt and Timashev[122] reported best strengths for alite crystal sizes in the range 35–45 µm. Okorov[123] reported optimum strength properties for alite crystals of 70–100 µm for strengths between 3 days and 3 months, while after 1 year the strength declined or became unchanged with increasing alite size.

It has been noticed that, in addition to clinker mineral grain size, the overall clinker structure may also have an effect on cement strength. It has been generally accepted that clinkers with relatively large, well-developed crystals with distinct grain boundaries lead to higher strengths than those with indistinct crystallisation, indistinct grain boundaries and aggregates of ill-formed minerals.[124–129]

The following four types of clinker microstructure can be distinguished:

1. monodoblastic, distinctly crystalline, coarse grained, with grain size > 30 µm;
2. monodoblastic, distinctly crystalline, fine grained with grain size < 30 µm;
3. glomerdoblastic, medium grained with relatively indistinct crystallisation and formation of belite aggregates;
4. glomerdoblastic, poorly crystalline with large aggregates of ill-formed minerals.

The strength obtained (at constant phase composition) declines from (1) to (4), whereby the difference in strength after 28 days may amount to 20 MPa.

The relationship between clinker structure and cement strength has been studied.[129,130] A set of multiregression linear equations (for strengths after 7 and 28 days have been presented) in which the following parameters were considered: free lime, Blaine specific surface area, size of alite, birefringence of alite, size of belite, birefringence of belite and colour of belite. Using these parameters the 28-day strength could be estimated with a standard deviation of ±15–3 MPa.

It appears that the effect of structural parameters, which may be influenced by conditions of burning, has to be taken into consideration in estimating the quality of clinker, and its effect on strength. Since they are determined mainly by conditions of burning,[129,131] the condition of burning is another major factor determining cement strength.

8.4.15 DISCUSSION

Strength generation is a necessary characteristic of cements and standard tests form the basic measurement for specification and compliance throughout the concrete industry. Usually, strength measurement means the crushing strength of concrete cubes, since this measurement is easier to obtain than tensile or bend strengths, and the variability of the data is not too great. Thus the testing of between three and six replicate specimens is usually adequate. Strength measurements can be used to monitor the behaviour of concrete in practical situations, for example where attack by aggressive species is taking place, or where high-temperature curing is employed.

More detailed study of concrete specimens has shown that a process of stable crack formation and growth starts at low loads and continues with increasing intensity as the load is raised. On restressing concretes, the capacity to resist load is reduced by stress, indicating that damage is occurring during first-time loading. Concretes and hardened cement pastes exhibit gross failure under triaxial compression provided that confining pressures exceed a low limit, near 2.5 MPa,[25] with cracks only rarely visible on external surfaces. The influence of the interfacial region between aggregate particles and cement paste within the concrete microstructure is a continuing field of investigation.

8.5 Instantaneous and time-dependent strains under load

The mechanism of creep in concrete has continued to be a subject of research for the past 60 years. Recent papers confirm that a complete understanding has not yet been achieved.[132–135] The strain exhibited when concrete is mechanically loaded is conventionally divided into instantaneous, or elastic, and time dependent, or creep. However, there is no clear separation between the two and strain continues to increase with the period under load from the earliest times. The rate of strain increase gradually reduces with the period under load. It is convenient to define elastic strain as that occurring within 0.001 days of application of the load. A small fraction of the long-term creep strain is slowly recovered on removal of the external load, but a proportion of the creep can be labelled as irrecoverable. Changes in aggregate volume fraction and aggregate stiffness can give rise to large changes in concrete elastic and creep strains, and theoretical models have been derived which predict the behaviour of elastic modulus, creep and drying shrinkage with increasing aggregate content.[44,136]

A recent review of proposed mechanisms of creep[132] has listed the basic ideas that retain support. An ageing process is strongly favoured as the underlying reason for the appearance of irrecoverable creep, the major component of creep. Parrott[137] first put forward the idea that polymerisation of the silicate anion in the calcium silicate hydrate (C-S-H) making up the bulk of the hydrated cement matrix was linked inversely to irreversible creep, from the similarity of the curves relating creep with the age of loading (creep decreased as the age at load was increased), and the effect of age on the fraction of silicate anion in C-S-H in hydrated cement in the form of polysilicates (the degree of polymerisation increased with storage time).[138] The relationship between the degree of polymerisation of the silicate anion and creep was explored further,[139,140] making use of a molybdate complexing technique for the determination of the monomeric silicate anion.

The magnitude of short- and long-term strains under load for cast materials based on Portland cement depends on the conditions of production and of testing,[141] these various conditions may be summarised as follows:

- Production conditions
  - mix proportions
  - stress history
  - cure
  - storage.
- Test conditions: constant or variable
  - load
  - humidity
  - temperature
  - carbonation.

In service, concretes are usually under variable load, temperature and humidity simultaneously, but strain measurements under constant test conditions have been adopted to elucidate basic processes.

8.5.1 CONSTANT TEST CONDITIONS

A detailed investigation which included creep measurements on concretes loaded in compression under water was published in 1931[142] (100 mm diameter cylinders, 355 mm long): creep strains were found to increase throughout the test period but the rate of increase gradually reduced[143,144] – for one concrete loaded at 6.2 MPa the creep strain was 1130 μstrain at 10 years and only slightly larger at 1170 μstrain at 25 years.[145,146] Creep for specimens with sealed-in moisture has been represented by a number of mathematical expressions, e.g.

$$\epsilon_c = at^n\varsigma \tag{8.17}$$

Where ϵ_c, the creep strain under imposed stress ς is governed by t, the time under load, and n, a factor nearly independent of age, water/cement ratio and moisture content, etc., which is approximately equal to 0.35; factor a is dependent on age at loading and moisture content.[137,147,148] An alternative expression derived from a simple rheological model (a Burger element, being a combination of springs and dashpots; Figure 8.14) has been proposed for concrete.[149] All four rheological parameters (E_m, E_k, Λ_m, Λ_k)vary with the age of concrete and period under load: expressions based on this model can be made to fit experimental data over a period of 900 days under load.[149,150] Irreversible creep, the more important component of creep, may be regarded as viscous flow (the coefficient of

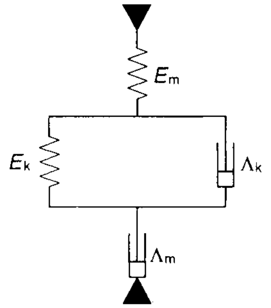

Fig. 8.14 A Burger element.

viscosity increasing as age increases). However, Poisson's ratio for creep (the lateral strain divided by the longitudinal strain) is very small at low stresses and well below the value (0.5) for viscous behaviour; Poisson's ratio rises above 0.5 at high stresses[146,151] but is equal to the instantaneous value (~0.17) for low stresses in either uniaxial, biaxial or triaxial loading modes[152] (200 mm concrete cubes). Creep is greater for mixes of high water/cement ratio and greater when specimens are loaded at an early age.[142]

8.5.2 STRESS HISTORY

Generally, the rate of irreversible creep development is claimed to be unaffected by the time under load (or previous stress history), either at room temperature or at elevated temperature, and is dependent only on the current age of a concrete, and the stress level.[149,153,154] A master creep curve can be constructed from creep data on specimens loaded at different ages (at a given temperature). However, several investigators have shown that previous stress history does modify creep.[155] The method of superposition may be used to predict creep and creep recovery when the load is removed. This implies that the state of strain of a specimen at any time is a function not only of the forces acting at the time but of the entire past stress history.

When a concrete is loaded (for 12 months) and then unloaded (for 1 month), its elasticity is modified,[142] elastic strains being smaller; however preloading for shorter periods apparently increases the elastic strain for both concretes and cement pastes.[25,35] Previous stress cycles are claimed to reduce creep strains on subsequent loading;[156] however, according to other investigators the strains due to a second stress cycle are unaffected by an initial cycle of stresses.[149,151]

8.5.3 WORK ON CEMENT PASTE SPECIMENS

Work on the creep of concrete has been supplemented by a number of studies of the creep of hardened cement pastes: in one investigation, paste specimens (150 × 150 × 20 mm slabs) cured for 7 days in a fog room at 20°C were sealed in copper foil either while wet or after drying under controlled humidity for 14 days.[157,158] Provided the hardened pastes had not been dried to relative humidities of <30 per cent and had not been allowed to carbonate, the axial creep strains induced by loading at room temperature to compressive stresses <40 per cent of the failure loads were a function of the elastic strains (defined as the strains produced after 0.001 days under load), the age of the hardened paste at loading, and the time under load.[159] These effects of age on creep strain had been noted previously;[160] the creep is reduced by a factor of two when specimens are stored for 200 days before loading.[137]

Elastic strains were found to be a function of imposed stress, hardened paste porosity and water content of the paste; paste age affected the elastic strain where partly dried material was considered. Stress versus elastic strain plots were curved; empirical relationships were established:

$$e_{\mathrm{el}} = \frac{\zeta^{1.1}}{(1-P)^3}(9.25 + (9.70 - 2.46\log_{10})V_{\mathrm{lw}}) \qquad (8.18)$$

where ζ is the imposed stress; e_{el} is the elastic strain; P, the porosity is given by

$$P=\frac{\mathrm{w/c}-0.175h}{\mathrm{w/c}+0.315} \tag{8.19}$$

where w/c is the water/cement ratio; h is the degree of hydration of the cement; t is the paste age (days) and V_{lw} is the volume of water lost during predrying per unit volume of hardened paste.

The elastic strains for partially dried pastes decreased as the age at loading increased. An expression similar in form to that quoted had been proposed previously, relating elasticity to porosity.[48]

The axial creep is related to the elastic strain by the expression

$$e_{\mathrm{c}}=e_{\mathrm{el}}^{1.2}(t-t_{\mathrm{l}})^{a}\cdot b \tag{8.20}$$

where t is the paste age (days), t_{l} is the age at loading (days), and a and b are given by

$$a=0.270+\frac{0.0125}{(0.156\log_{10}(t+5)-0.1)}$$

$$b=\frac{0.0136}{(0.156\log_{10}(t+5)-0.1)}$$

a typically varies between 0.37 and 0.30 while b falls from 0.12 to 0.05 as the age increases.

For lateral strains

$$\text{lateral creep} = \text{axial creep} \times \gamma$$

where $\gamma = 0.13$ for saturated paste and $\gamma = 0.275 - 0.214V_{\mathrm{lw}}$ for predried pastes.

The close relationship between elastic strains and creep strains revealed by these expressions is confirmed by the reported effects of the elastic properties of the aggregate on the elasticity and creep properties of the concrete.[161]

8.5.4 HUMIDITY AT TEST

The axial creep strain is increased slightly at intermediate humidities, according to the above equations, but not all investigators agree with this finding: some reported that humidity had no influence on creep[162] while others reported reduced creep when specimens were predried.[147,160] The elastic strain was increased slightly by predrying, according to the above equations. The axial creep of cement pastes which have been predried to relative humidities of <30 per cent were reduced below those given by the above equations.[148] Specimens which have been oven dried at 110°C exhibit little or no creep;[148,163–165] this observation has led some investigators to propose an absolute creep potential for concretes given by their drying shrinkage at zero relative humidity,[163] but this idea must be modified since drying shrinkage at zero relative humidity is not a single-valued parameter, but increases when humidifying/drying cycles are applied.[166] Elastic strains are usually increased by overdrying,[163] so that the proposed expression connecting creep strains with elastic strains breaks down under hard drying.

Investigations into the creep of specimens which were first dried at 105°C and then equilibrated to different relative humidities showed an increased creep as humidity rose above 45 per cent, in contrast to data presented for first drying. The relatively short time allowed for moisture content (and drying shrinkage) to reach equilibrium in Refs 159 and 167 (or 148) indicates a large hysteresis in the relationship of creep rate versus water content: creep rate during adsorption is less than during desorption. A hysteresis is also reported in the elastic strain versus humidity plot, but strains are greater during adsorption than during desorption.[168]

The relationship between creep and load for saturated specimens is not linear, creep at high humidities being progressively larger than that predicted by a linear relation;[142] on the other hand, plots of elastic strain versus load for oven-dried specimens (having no creep strain) were linear right up to fracture.[163]

8.5.5 TEMPERATURE AT TEST

The creep of specimens at elevated temperatures was greater than at room temperature;[165,169,170] prior creep at higher temperature did not influence subsequent creep at a lower temperature;[149] creep increased steadily with increasing temperature between −15 and 60°C[149] – raising the temperature from 20 to 40°C doubled the creep rate; the activation energy for creep was calculated at ~20 kJ/mol.[159] A creep Poisson's ratio of 0.2 was found for concrete under uniaxial and biaxial loading at temperatures between 20 and 96°C.[170] Two investigations found slight reductions in creep rate if the temperature was raised above 60°C when specimens remain saturated with water, but not when they were partly dried,[160,171] suggesting that an increased maturity was countering the expected decrease in viscosity with increasing temperature. Another investigator measured creep between 20 and 400°C and found that the creep rate reached a peak at about 50°C, then fell to a lower value at 105°C before rising again with further temperature increase.[172] Elastic strains were not affected by a rise in temperature,[159] so the relation between elastic strain and creep strain proposed above breaks down at other than room temperature. Specimens frozen at −18°C still exhibit creep,[164] so the presence of free liquid water is not essential for creep.

When concrete specimens were transferred to higher temperatures, the rate of creep was increased to a value associated with a concrete at the higher temperature, but younger than the actual age, since creep is related more closely to concrete maturity (equal to the product of age and temperature of storage) than to concrete age. In order to predict the creep rate at any temperature, an empirical parameter, the 'weighted maturity', was invented (equal to $\int \theta^2 \, dt$, where t is the time stored at temperature θ) and a combined single creep curve could be constructed from data collected at temperatures between 20 and 76°C, for creep strains against weighted maturity,[171] this curve allowed the prediction of creep after any combination of temperature/time storage conditions (temperatures of 20–76°C) but the relation could not be extrapolated to represent data on concretes at higher temperatures.

8.5.6 MIX PARAMETERS AND CURING CONDITIONS

Curing conditions have a marked influence on creep. Thus creep is reduced to 60 per cent after curing for short periods at elevated temperatures of up to 65°C.[139] Heating specimens at up to 95°C for a few days after the specimens have been cured for 28 days at room temperature also reduced subsequent creep.[173] The creep rate decreased with increasing maturity,[174] while steam curing and autoclave curing resulted in reduced creep – to between 50 and 20 per cent of room temperature-cured values (40 per cent of the cement of the autoclaved specimens was replaced by silica flour and specimens were loaded under drying conditions).[175] A linear relation was found between first drying shrinkage (at 60 per cent relative humidity) and creep,[139] and also between elastic strain (after drying) and drying shrinkage.[176]

The mix composition parameter which particularly increases creep is the presence of accelerators, especially $CaCl_2$.[177] The presence of triethanolamine also tended to increase creep. The presence of air-entraining agents[178] and the influence of the composition and fineness of cements[160,179,180] and the presence of lignosulfonates[178] have also been examined for their effects on creep. It has been found that the variation in SO_3 level between about 1.5 and 4.5 per cent had very limited influence on compressive strengths at 28 days or 1 year,[77] but had a very marked effect on the creep of concretes; the higher the sulfate level, the smaller the creep strain.[96]

Besides affecting the moisture content, storage conditions can also modify the degree of carbonation of specimens. Exposing specimens to CO_2 for 1 year before loading resulted in a 50 per cent reduction in creep when loading was on drying specimens.[181]

8.5.7 VARIABLE TEST CONDITIONS

The behaviour of concretes under variable stress has been investigated:[156] when the load was alternatively applied and released, the magnitudes of the elastic and creep deformations tended to become smaller as the number of cycles increased, but the residual deformations at the end of each load cycle increased;[140] periods of cycling between 2 days and 2 months were examined. The residual deformations after load cycling were independent of the frequency of loading and were approximately 50 per cent of the creep under sustained maximum load.[142] The rate of load cycling is found to be important when higher frequencies of loading are tried – reducing the frequency from 90 to 20 cycles/min increases creep.[182] Two investigations found increased creep when cyclic loading was adopted: after cyclic loading at 500 cycles/min for 24 h, a creep equivalent to 28 days under constant maximum load was obtained;[183] cyclic loading at 30 cycles/min led to twice the creep produced by static maximum loading.[155]

Changing the temperature of specimens while under load had a marked effect on creep (under both compressive and torsional loading) if the temperature of saturated or partly dried specimens was raised, provided the temperature reached was higher than that achieved by the specimen in its previous history (little or no extra creep is claimed to be induced if specimens have already been conditioned at the higher temperature).[154,184] No extra creep was produced if the temperature was reduced while under load (some enhancement of creep was indicated, however, on raising the temperature from 58 to 76°C even though a preheat at 76°C for 1 day had been applied).[171] Possibly the delay in reaching the new maturity appropriate to the higher temperature was long enough to allow creep at the higher temperature while paste maturity was still that appropriate to the lower temperature. The magnitude of this enhanced creep is claimed to be unaffected by concrete maturity, however, being a function only of temperature rise.[171] Creep at higher temperatures did not affect subsequent creep at lower temperatures.[149,183]

Loading specimens which have been both drying and shrinking has been the most common form of creep test in the laboratory: creep strains are generally larger (after subtracting the drying shrinkage) than those obtained under hygrothermally stable conditions[142] 100 × 100 mm section prisms, loaded at 5.5 MPa showed a creep of 0.027 per cent at 2 years at 100 per cent relative humidity, 0.063 per cent at 70 per cent relative humidity, and 0.089 per cent at 50 per cent relative humidity. Specimens which are rewetted (while under load) after drying also exhibit some enhancement of creep.[165] Creep under drying conditions appears to reach a limiting value in about 7.5 years.[185] The effect of drying on creep is greater for specimens loaded at 3 months than at 1 month; one explanation for the additional creep when drying under load is that the non-linearity of the plot of stress versus long-time strain results in proportionally greater strains when the external stress is augmented by drying shrinkage stresses.[147] Creep during drying is represented by a basic creep term, in which allowance is made for changes in basic creep rate with moisture content, together with a drying creep term which is simply proportional to the drying shrinkage. Basic creep can be represented by a power function

$$\xi_c = at^n\zeta \tag{8.21}$$

for non-drying conditions. Under drying conditions, the basic creep changes in step with drying shrinkage ξ_s:

$$\xi_c = (a_1 + a_2\xi_s)t^n\zeta \tag{8.22}$$

An additional drying creep term is also required:

$$\xi_{cs} = y\xi_s\zeta \tag{8.23}$$

to allow for the extra strain induced by the added drying shrinkage stresses. The drying shrinkage is represented by an exponential expression; these considerations lead to the calculation of a drying creep.[162] Using this approach, it is found that the ratio of ultimate specific drying creep to drying shrinkage is not constant; this ratio varies with different mixes from 32.99 to 323.04,[147] i.e. the best fit for the experimental data to this theoretical expression leads to a 10-fold range of magnitude for this ratio, which suggests that there is no physical basis for this method of analysis.[186] The fact that enhanced drying creep is observed when specimens are loaded in torsion, where drying shrinkage cannot induce extra torsional stresses, also seems to rule out this treatment.[160] Under drying conditions, creep is linearly related to stress, in contrast to creep under saturated conditions.[142,187] Cycling the environmental humidity while under load, between 50 and 70 per cent relative humidity, resulted in only slightly increased creep.[188] Lateral creep strains for drying concrete were zero for the first days under load – this fact was taken as evidence that basic and drying creep were essentially similar.[186] The drying creep of specimens was greatly increased by the presence of accelerators (in the case of $CaCl_2$ by a factor of two),[177] as is the drying shrinkage; rewetting of dried specimens while under load also resulted in some creep enhancement,[171,177] but the increased creep during first drying was particularly large.[149]

A theoretical interpretation based on sliding of submicroscopic gel particles over one another has been developed in which the contact zone between particles is lubricated by a layer of adsorbed water: temporary disturbance of the structure of this adsorbed layer during evaporation leads to increased creep.[159,165] Simply causing water to flow within specimens does not result in enhanced creep; extremely rapid drying from very thin specimens results in greatly increased rates of drying creep. Curing at elevated temperatures reduces drying creep and shrinkage.[173] Carbonation of cement paste specimens while under load leads to increased creep.[189] In contrast, carbonation before loading leads to reduced creep.

8.5.8 DISCUSSION

In contrast to the elastic strains, which are largely determined by the porosity of the system, the long term strains under load are dependent on the slowly developing microstructure and continuing chemical reactions. The proposed relationship between elastic strains and creep must break down for all environmental conditions apart from the simplest. Several examples are apparent where prediction of behaviour is impossible from formation parameters, the most striking being that of ageing. Some success seems to have been obtained in relating this ageing process to the slow increase in the degree of polymerisation of the silicate anion in the hydrated calcium silicates, an increase in the degree of polymerisation correlating with a decrease in creep.[140] Addition of $CaCl_2$ to a mix reverses this relationship, however, since creep is increased but the degree of polymerisation is also increased.

The effect of previous stressing is apparent in a subsequent reduction in creep; in other words, a stress ageing effect also occurs. It seems possible that chemical stressing is usually present during normal hydration so that stress ageing may occur even when external loads are absent.

Drying and carbonation creep are related to first-drying shrinkage and both may be the result of changes in the microstructure of hardened cement pastes during first drying. The length of time required by a drying specimen before enhanced drying creep is eliminated does not seem to have been established. Irreversible creep makes up the greater proportion of total creep, amounting to 80–90 per cent of the total.[132]

8.6 Drying shrinkage

No standard procedure exists for determining the drying shrinkage of concrete. Normally, drying shrinkage is determined on concrete or mortar prisms that are allowed to dry naturally in a controlled humidity environment and shrinkage is measured by monitoring changes in length using surface-attached strain gauges or by recording length changes at the axis of the prism. Automatic monitoring of the data is usually adopted.

The first-drying shrinkage for cement pastes amounts to 0.35–0.70 per cent, when drying is carried out at 47 per cent relative humidity[190] (0.5–3 mm cement paste wafers, $w/c = 0.3$, 0.4, 0.5 and 0.6, cured for 6–30 months). Prolonged curing reduces the first-drying shrinkage, especially of more porous pastes – porous pastes cured for 6.5 months shrink by 0.65 per cent while pastes cured for 30 months shrink by 0.45 per cent when drying at 47 per cent relative humidity. Work on thin wafers of cement, C_3S and alite pastes indicates that the rate of drying affects the first-drying shrinkage, slow drying resulting in smaller ultimate shrinkages (when drying stepwise to 92, 84, 75, 67, 58 and 47 per cent relative humidities, wafers shrank 20 per cent less than those dried directly to 47 per cent relative humidity). Shrinkage on first drying for 4 days at 40 per cent relative humidity is not dissimilar to stepwise first drying via intermediate humidities over a period of 6 months[191] (1.2 mm cement paste wafers, $w/c = 0.5$ and 0.8, cured for 1 year). On first drying, mass loss continues for several months even for 1 mm wafers; the degree of swelling on rewetting depends on the length of time for which specimens are dried[190] (cement paste wafers dried at 47 per cent relative humidity for 150 days showed swelling on rewetting half that of specimens dried for only 22 days). Swelling continues for several weeks after resoaking. With rapid, single-step drying, the relationship between first-drying shrinkage and mass loss can be represented approximately by two straight lines: (1) between 100 and 30 per cent relative humidity, the volume change of the specimens divided by the volume of water lost is 0.025; and (2) between 30 and 1 per cent relative humidity the specimen volume change divided by volume of water lost is 0.22 (6.8 × 6.8 mm cement prisms, w/c = 0.3, 0.5 and 0.7, cured for 1, 7, 28, 90 and 365 days).

The shrinkages of cement pastes and concretes are approximately twice as large on first drying as their respective swellings and shrinkages on resoaking and second drying[192] (25.4 × 22.2 × 285.8 mm prisms, w/c = 0.35 and 0.50, with 0–67 per cent aggregate, cured for 7 days). After first drying at between 11 and 47 per cent relative humidity, the shrinkage versus mass loss and swelling versus mass gain relationships approximate to a single straight line, which can be traversed repeatably without further significant irreversible shrinkage.[190,192] Drying to 7 per cent relative humidity, however, results in additional irreversible shrinkage amounting to 0.1 percentage points at 47 per cent relative humidity,[190] and repeated wetting/drying cycles which include very low humidities (produced by heating the specimen at 97°C under vacuum) generates additional irreversible shrinkage after each cycle; greater irreversible shrinkage develops if specimens are exposed to humidities greater than 55 per cent relative humidity during each cycle[184] (1.27 mm wafers).

8.6.1 CEMENT COMPOSITION

The components of cements which most influence shrinkage are the alkalis, C_3A and sulfate; these parameters interact with the fineness of grinding of the cement.[8] In addition, an increase in C_3A or alkalis increases the first-drying shrinkage; while this increase can be nullified by adding calcium sulfate, excess calcium sulfate can lead to a slight increase in shrinkage. Pure alite and C_3S pastes behave similarly to neat cement pastes.[190,193,195] High alkali concentrations in the cement reduce the rate of diffusion of water and so affect the uniformity of the shrinkage of specimens, and increase the tendency to crack[194] (64 × 64 × 292.6 mm mortar prisms).

The coefficients derived for the relative contributions of the different compounds to drying shrinkage are not satisfactory. There is some indication that cements with a high content of $2CaO \cdot SiO_2$ show somewhat higher shrinkage values than those with a high content of $3CaO \cdot SiO_2$. There is no consistent relationship with the content of $3CaO \cdot Al_2O_3$ or $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, and their effect seems to depend on the gypsum content of the cement. There is evidence[195–198] to show that the amount of gypsum required to minimise shrinkage increases with the content of $3CaO \cdot Al_2O_3$, and of alkalis in the cement, and that with amounts below the optimum, the shrinkage increases considerably. It has often been held that the replacement of $3CaO \cdot Al_2O_3$ by $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ tends to reduce shrinkage, but the evidence is too uncertain for valid conclusions to be drawn.

The effect of SO_3 on compressive strength, shrinkage and expansion of concrete under water has been known for a long time.[20,195,199] It has been found that an optimum SO_3 exists which produces the highest 28-day strength and the lowest drying shrinkage[49,197] and depends greatly on the phase composition of the clinkers and the cement fineness. Alkalis have been found to affect the optimum SO_3 content of cements. Lerch showed that the optimum gypsum requirement for a properly retarded cement increased with an increase in both C_3A and alkali content. Using Lerch's data, the following linear regression equations for optimum SO_3 content have been obtained[200]

$$\text{optimum } \% \text{SO}_3 = 1.841 + 0.095 \times (\% \text{C}_3\text{A}) + 1.6364 \times (\text{equivalent } \% \text{Na}_2\text{O}) \tag{8.24}$$

This treatment was extended to include cement fineness, or specific surface area m^2/kg[201]

$$\text{optimum } \% \text{SO}_3 = 0.556 \times (\% \text{Na}_2\text{O}) + 0.00177 \times \text{fineness} - 0.107 \times (\% \text{Fe}_2\text{O}_3) - 3.60 \tag{8.25}$$

It has been concluded[202] that optimum SO_3 content is related to cement fineness or, alternatively, to alkali and C_3A contents.

The influence of minor components, e.g. the alkalis and trace elements present in amounts mostly <0.1 per cent, on cement properties has been examined statistically for nearly 200 cements tested at the US Bureau of Standards;[80,203,204,205] their influence on properties, though statistically significant in many instances, was small compared with that of the major cement components. High-alkali cements were associated with higher shrinkages. An increase in either C_3A or alkali content, unless accompanied by an appropriate increase in gypsum, resulted in increased shrinkage.[197]

8.6.2 *WATER/CEMENT RATIO OR PASTE POROSITY*

The first drying shrinkage is approximately proportional to the water/cement ratio[155] (25.4 × 22.2 × 285.8 mm mortar prisms, cured for 7 days). Both mortar and cement paste prisms shrank more when the water cement ratio was increased, from 0.35 to 0.71 per cent shrinkage, on 25.4 × 25.4 × 254 mm prisms cured for 7 days. The relation between first-drying shrinkage and porosity (porosity given by

$$\frac{D(W_t - W_n)}{(W_t + C)} \tag{8.26}$$

where D = paste density, W_t = total water, W_n = combined water, C = mass of cement) is found to be linear. However, the subsequent swelling on rewetting and the second-drying shrinkage is found to be independent of porosity[191,206] for cement wafers, cured between 6 and 24 months.

8.6.3 *CURING TEMPERATURE*

An increase in the temperature of curing (up to 71°C) and an increase in the period of cure lead to a reduction in the first-drying shrinkage, but mass loss on drying is unaffected[166] (150 × 300 mm concrete cylinders cured for 32 days). Curing for a few hours at 70°C reduces the first-drying shrinkage from 0.22 to 0.136 per cent, while curing at 50°C reduces it to 0.176 per cent (12 × 12 × 110 mm prisms cured for 8 days). Autoclave curing at 185°C reduced shrinkage to 1–2 per cent of the room temperature cure value.[149,207]

8.6.4 *ADMIXTURES*

First-drying shrinkage is doubled by adding larger doses than usual of certain admixtures to normal cements, although swelling and shrinkage on resoaking and second drying are unaffected[191,208] (using as admixtures triethanolamine, carboxylic acids and lignosulfonate). The first-drying shrinkage of a 1:3 mortar in a CO_2-free atmosphere is reported to develop more rapidly when calcium lignosulfonate is present, though ultimate shrinkage is unaffected.[209] No increase in shrinkage was observed with a vinsol resin or sulfonated hydrocarbon air-entraining admixture, or for any of the above admixtures when adding to high-alkali cements.[191]

8.6.5 SPECIMEN GEOMETRY

A humidity gradient is set up within concrete specimens during drying which can be detected by humidity-measuring probes cast into specimens[205] (150 mm concrete slabs). An attempt to account for the overall data of mass loss versus drying time by means of diffusion theory[210] revealed a progressive reduction in diffusion coefficient as the water content of the concrete was reduced by drying[194,211] (the diffusion coefficient falls to 0.00005 from 0.0002 cm^2/s on drying to 50 per cent relative humidity). Diffusion coefficients increased with increasing water/cement ratio, increasing temperature and decreasing specimen age[194] (cement paste and concrete spheres; $w/c = 0.3$ and 0.55; sphere diameters 51, 64, 102, 127, 152, 178 and 229 mm, cured for 3–458 days). Because of the slow rate of drying, an extra hydration reaction during first drying may interfere with the interpretation of mass loss data for young specimens.[212] The relationship between mass loss and shrinkage depends on specimen size: for concretes cured for only 7 days, the shrinkage increased as specimen size increased for a given moisture loss;[213] for cement pastes and mortars cured for 28 days, the ultimate drying shrinkage increased as specimen's size decreased[214] ($12.7 \times 6.4 \times 127$, $12.7 \times 9.5 \times 127$ and $12.7 \times 12.7 \times 127$ mm specimens cured for 28 days; $w/c = 0.399$–1.025). Data have been fitted to expressions derived from diffusion theory, showing the diffusion coefficients falling as the concrete dries out.[215] The absolute values of diffusion coefficients are found to vary from one set of data to another (in this study only data for old concretes dried at uniform temperature were included); the diffusion coefficients fell 20-fold at about 75 per cent relative humidity, suggesting that the major transport mechanisms for moisture is by movement of liquid water. The shapes of mass loss versus time plots on second drying are substantially different from those on first drying,[192] suggesting that diffusion coefficients are modified by drying. Measurements on cement pastes subjected to gradual drying to 79 per cent relative humidity followed by resaturation show greatly increased permeabilities to water compared to undried material[216] (pastes with $w/c = 0.5$ cured for 63 and 141 days gave permeabilities between 400 and 1025×10^{-12} cm/s for dried/rewetted pastes and 15×10^{-12} cm/s for undried pastes). Diffusion coefficients were reduced by increasing the alkali content of the cement; specimens with high alkali content showed a much greater tendency to crack during drying.[191]

8.6.6 AGGREGATE RESTRAINT

It has been established experimentally that changes in aggregate size grading do not affect the first-drying shrinkage[217] (concrete prisms $76 \times 76 \times 154$ mm, $w/c = 0.47$, cured for 7 days). A theoretical relationship between aggregate volume fraction, V_a, cement paste shrinkage, S_p, and concrete shrinkage, S_c, has been derived[218]

$$S_c = \frac{S_p(1 - V_a)}{(1 + V_a)} \tag{8.27}$$

which is applicable when aggregate stiffness is much greater than paste stiffness, and when aggregate shrinkage is zero. This simple expression yields calculated paste shrinkages from concrete shrinkages which are smaller than experimental values[218] (25.4 × 25.4 × 254 mm prisms, w/c = 0.35–0.71, aggregate volumes 0–69 per cent, cured for 7 days). An alternative theoretical expression has been derived which adequately represents the data:

$$S_c = S_p(1 - V_a)^\alpha \tag{8.28}$$

where

$$\alpha = \frac{3(1 - \mu)}{1 + \mu + 2(1 - 2\mu_a)E/E_a} \tag{8.29}$$

and $\alpha \sim 1.7$, and where μ and E are Poisson's ratios and Young's moduli for the cement paste and aggregate.[192]

8.6.7 CARBONATION

The ultimate effect of carbonation is to replace hydroxyl ions (or combined water) in hydrated cement with carbonate ions; it was found that the shrinkage/water loss relationship by carbonation is similar to the shrinkage/water loss relationship on first drying.[49] The total shrinkage due to first drying and carbonation can be double the shrinkage due to drying alone. The effect of carbonation is most pronounced when mortars are first dried, to 50 per cent relative humidity, say, and then carbonated; simultaneous drying and carbonation produces about half the extra shrinkage given by first drying then carbonating[214] (12.7 × 12.7 × 127 mm mortar and paste prisms; w/c = 0.399–1.025; cured for 1 or 3 months). Carbonation improves the volume stability of cement pastes: the swelling and shrinkage on resoaking and second drying are decreased by 20 per cent for specimens carbonated at 50 per cent relative humidity.[214]

8.6.8 DISCUSSION

Those parts of the microstructure of cement pastes which are involved in the mechanism of drying shrinkage suffer a progressive and irreversible collapse during first drying; the degree of collapse depends on the length of time during which specimens are dried and on the humidity to which they are dried. An ageing effect in saturated pastes manifests itself as a progressive reduction in first-drying shrinkage as the curing period is extended. The behaviour subsequent to first drying may be independent of previous curing and drying histories; swelling and shrinking on resoaking and second drying are independent of the water/cement ratio and may only depend on curing temperature and cement composition. Admixtures may affect first-drying shrinkage but seem to have no influence on subsequent behaviour.

8.7 Durability

Excessive deflections of beams or floor slabs can be attributed to overloading of the structure or to deterioration of the concrete or steel reinforcement. Some knowledge of the stresses induced by the external loading on the structure, and consequent failure mode or crack pattern, has proved of value in recognising the deterioration processes involved.

Knowledge of external loading conditions and likely failure mode can identify crack patterns due to structural factors.

Expansive reactions (Table 8.25) within the concrete may give rise to signs of size increase in the structural member, i.e. displacement of supports, lack of alignment in

Table 8.25 Deduction of deterioration mechanism

Main observation	Additional factors	Deterioration mechanism indicated
Expansive reaction	Surface gel exudation, moist conditions, Isle of Man crack pattern, cracks penetrating only a few centimetres, surface concrete appears strong, pop-outs	ASR
	Precast concrete, heat-cured, mass pours, moist conditions, cracking may be very limited, surface concrete appears strong	DEF
Contraction	Deep cracks, drying slabs	Plastic shrinkage
	Deep cracks, deep sections	Plastic settlement
	Fine cracks well spaced, drying environment	Drying shrinkage, shrinking aggregate
	Fine cracks	Early thermal contraction
Surface disintegration, mushy concrete surface, pop-outs	Foundation concrete, buried concrete	Sulfate attack, pyrite-contaminated aggregate (brown staining)
	Porous mortar or render, carbonate aggregate, low to moderate temperatures	Thaumasite formation
	Concrete above ground, access to moisture, closely spaced surface cracks, freezing conditions possible	Freeze–thaw
Rust stains and wide cracks	Moist chloride-containing environment crack pattern following reinforcement mesh	Corrosion of reinforcement – chloride initiated
	Drying environment, concrete superstructure, porous concrete, low cover	Corrosion of reinforcement – carbonation initiated
Surface formations	Porous concrete	Leaching by groundwater percolation
Wear	Floor slabs	Mechanical wear
	Fast water flow	Cavitation damage
Flaking damage, broken arris, deep cracks	Vulnerable bridge or beam, load-bearing member	Structural damage, foundation movement construction damage

parapets, or displacement of retaining walls. Deterioration mechanisms likely to lead to expansion are ASR (alkali–silica reaction), where certain vulnerable aggregates contain a proportion of reactive siliceous material, e.g. opal, which forms a hydrous gel with high-alkali Portland cements, accompanied by expansion; and DEF (delayed ettringite formation), where calcium sulfoaluminate formation occurs as ettringite after an initial delay, accompanied by expansion and cracking, due to decomposition of ettringite by heat curing or unplanned elevated-temperature excursions of the setting concrete.[89] ASR may be accompanied by gel-like formations and a distinctive map-crack pattern. DEF is associated with steam-cured precast concrete members formed using Portland cement concrete. DEF may also occur in large sections and mass pours cured for non-heat-cured concrete, where the heat of hydration of the binder causes an early temperature rise to >70°C. Both ASR and DEF can require several months or years before significant expansions develop. Internal sulfate attack may sometimes develop from the use of sulfate- or sulfide-contaminated aggregates.

The durability of cement-based materials is often determined by the rate of ingress of deleterious species (acids, carbon dioxide gas, sulfates and chlorides) from the aggressive environment. Permeability measurements form a basis for an understanding of the subject to a large extent. The mathematical description of permeation of various types of aggressive species has been reviewed.[219] Whilst water itself is not usually deleterious to concrete, absorption of additional water is necessary for many types of deterioration to occur and the exclusion of free water prevents many problems appearing. Where soft water is flowing over concrete, the incongruent dissolution of $Ca(OH)_2$ from the cement hydrates in the continuously changing fluid may still be sufficient to result in significant leaching or erosion, in spite of their very low solubility.

Formations take the form of stalactites or general chalky growths on walls or the soffits of arches and slabs. Gel-like formations appear in certain circumstances. Rust staining on the surface of concrete is indicative of reinforcement corrosion, and may be associated with a limited thickness of concrete cover over the reinforcement. Brown stains can also be associated with oxidation of pyrite (FeS_2) to brown iron oxide (Fe_2O_3) impurity in the aggregate, in which case surface pop-outs may occur.

A summary of the commonly met deleterious mechanisms is presented in Table 8.25. The identification of the deterioration mechanism involved requires considerable expertise and should take into account the nature of the concrete, the nature of the physical and environmental loading, and an assessment of the physical and chemical deterioration observed in the concrete.

Surface disintegration may take the form of softening of the outer surface of the concrete, or of fine crazing and crumbling. Pop-outs of aggregate contribute to the disruption of the concrete surface. Comparison of the observed deterioration with standardised photographs of well-researched structures should enable a visual inspection to estimate the degree of deterioration to be assessed in a semi-quantitative manner and a good estimate of the mechanisms of deterioration.

8.7.1 MICROSTRUCTURAL DEVELOPMENT

The imperfect packing of aggregate particles within the fresh concrete mix leads to concentrations of cement mortar in certain regions, especially at the surface of concrete (Figures 8.15 and 8.16). The cement content was increased to a depth of about 5 mm when

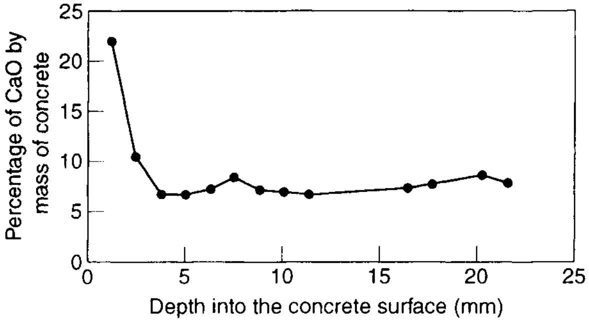

Fig. 8.15 Composition of the surface layers as cast of Portland cement concrete.

the maximum aggregate size was 15–20 mm. The permeability of the surface layers can be assumed to be different from that of the body of the concrete because of this effect.

In a similar manner, the packing of cement grains within the paste fraction is also disrupted by the presence of aggregate surfaces.[220] Experiments have been undertaken on polished sections using backscattered electron imaging in an SEM combined with quantitative image analysis. Composite specimens in which a single piece of aggregate was embedded in cement paste (w/c = 0.5, cured in moist air for 10 weeks) have been examined for three aggregate types: biotite granite, dolomitic limestone and grossular garnet. It was found that the content of anhydrous cement decreased close to the aggregate–paste interface, from 8–13 per cent at a distance of 40–50 μm to near zero at the interface, while the concentration in the bulk paste was about 8.5 per cent. The porosity of the hydrated material increased from 8 to 20–30 per cent over the same distance.

The main compounds in unhydrated Portland cement are tricalcium silicate, dicalcium silicate, tetracalcium aluminoferrite, tricalcium aluminate and gypsum. The overall hydration rate of the cement depends on the relative proportions of the cement minerals, the moisture conditions, the temperature, the fineness of grinding of the cement, the current degree of hydration and the pore space available for additional reaction products. The main hydration product is an ill-defined calcium silicate hydrate gel that exhibits a

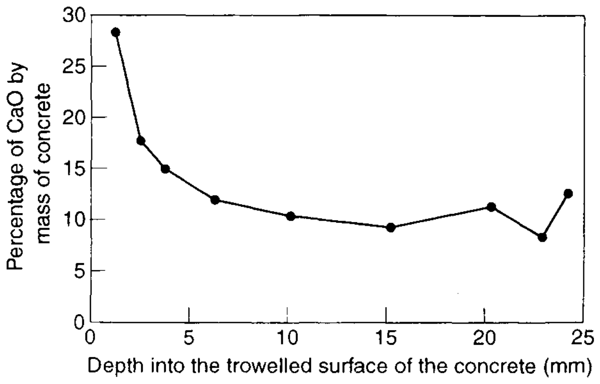

Fig. 8.16 Composition of the trowelled surface of Portland cement concrete.

fine pore structure and a high surface area. The microstructure is considered to be a highly disordered layer structure[221] composed of metasilicate chains, with average silicate chain lengths that increase with the period of cure from about 2.1 at 1 day to 4.8 at 26 years. Increasing the temperature of curing results in a modest increase in chain length and an increase in the lime/silica ratio. The increase in chain length with increasing temperature has been confirmed by high-resolution solid-state NMR investigations.[222]

Although the hydration of Portland cement is accompanied by an increase in volume of the solid phase, disruptive expansion does not occur. Hydrate particles generated at or near the cement grain surface are pushed into contact with adjacent cement grain hydrates, under the influence of the overall increase in solids volume during hydration. A readjustment of the hydration product, to fill the available pore volume and to increase the area of solid–solid contact, takes place.

The volume initially occupied by water in the fresh concrete can only be partly filled with hydration products: first, because the process of chemical combination of water involves an overall reduction in specific volume (solid + liquid), so that voids remain after combination of the water initially present; second, because any further potential for hydration of the cement is eventually stifled because of the very slow diffusion of the additional water needed to continue the hydration, through the rapidly densifying hydrates. Consequently, the lower the initial water (or air) filled void fraction in the mix, the lower the final void fraction remaining at ultimate hydration, and the higher the final strength.

This cementive hydration reaction may be contrasted with the generation of calcium sulfoaluminate hydrate which can lead to disruption. One basic distinction between these two situations seems to lie in the solubility of the reaction products: extreme product insolubility results in an inability to redistribute, and so expansion results (the solubility of ettringite is much less than that of calcium silicate hydrate in cement pore solutions). A second factor may be the speed of production of the hydrate; the slower the hydration process, the greater its ability to readjust and form a dense microstructure.

The formation of $Ca(OH)_2$ by hydration of hard burned lime leads to disruption, while its crystallisation during C_3S hydration is non-expansive, presumably because the speed of reaction of the free CaO is too great to allow adjustment of the product to the available pore space. The crystallisation of $Ca(OH)_2$ during the hydration of Portland cement has been reported to be expansive where high alkali hydroxide concentrations have depressed its solubility.[223]

Elevated temperatures accelerate the rate of the normal cementitious reactions and the density of the hydration product is increased.[90] The degree of silicate polymerisation in the calcium silicate hydrate is increased at higher curing temperatures, and the sorption capacity for heavy metal ions is reduced.[224] Long-term ageing experiments have shown that the calcium silicate hydrate gel is partly crystallised (Table 8.26).[225]

Table 8.26 The composition of calcium silicate hydrates formed from cements of different lime/silica ratios at increasing temperatures[225]

CaO/SiO_2	25°C	55°C	85°C
0.9	C-S-H	C-S-H	1.1 nm tobermorite
1.3	C-S-H	C-S-H	Jennite (afwillite, C-S-H(II))
1.7	C-S-H	C-S-H	Jennite (afwillite, C-S-H(I))

8.7.2 PERMEATION OF LIQUID WATER

A large number of techniques have been employed to investigate the microstructure of the resulting hydrated cement pastes, with somewhat mixed success because of the difficulties of interpreting the data. A more direct examination of the properties, from the point of view of durability, has been made by measuring the permeability of hardened pastes and concretes to a variety of agents.[226]

The movement of aggressive species into concrete plays an important and possibly controlling role for many durability problems. The fluid flow rate, Q, through concrete is described by Darcy's law:

$$Q = \frac{(KAP)}{(\eta L)} \tag{8.30}$$

where η is the viscosity of the fluid, A is the cross-sectional area of the specimen, L is its length, P is the fluid pressure head across the specimen and K is the permeability. Permeation of water through concrete, under the influence of a water pressure head is the traditional measurement of permeability in concrete technology. The expression above is simplified to

$$Q = \frac{(KAh)}{L} \tag{8.31}$$

where h is the pressure head in metres of water, and the viscosity of water is incorporated into the permeability, K, which in this case has the units of m/s. The method is subject to considerable experimental difficulty and uncertainty. The water/cement ratio, the time under measurement and the drying history influence permeability to water.

Concretes in the fully saturated state yield permeabilities between 1×10^{-13} and 100×10^{-13} m/s when properly compacted.[227] Specimens that have been allowed to dry out and then resaturated give much higher permeabilities. Initially these may be as high as $30\,000 \times 10^{-13}$ m/s but values fall over a period of 1–2 weeks down to near the fully saturated values. The influence of drying and storage history is probably the main reason for the very wide range of water permeabilities reported.

8.7.3 PERMEABILITY TO OXYGEN GAS

This involves the flow of a compressible fluid, and expressions (8.30) and (8.31) are modified to

$$Q = KA\frac{(P_2^2 - P_1^2)}{(2P_1 L\eta)} \tag{8.32}$$

where Q is the flow rate of oxygen in units of volume at the output pressure, P_1; K is now given in units of m^2. Specimens must be brought to a standard moisture level before measurement (e.g. drying at 65 per cent relative humidity).[227] This permeability is a much easier measurement to make; it is found to be sensitive to cement content and the water/cement ratio, and is particularly sensitive to the degree of cure, especially for weaker mixes. A single inverse relationship is observed between oxygen permeability and cube strength for a wide range of cements.

Although the time required to complete the permeability test is probably <1 h, the extended time scale required to bring concrete specimens to a standard relative humidity was a big disadvantage where assessment of site concrete was required. A cooperative programme of investigation of the oxygen permeability of concrete[228] found that reproducible results could readily be obtained when restricting the investigation to a single laboratory. However, comparison of data obtained from independent laboratories showed very poor results, and the use of the technique as a possible test of compliance of concrete quality with specifications intended to be relevant to durability performance had to be abandoned.

8.7.4 OXYGEN DIFFUSION

Gas diffusion rather than permeation under a pressure gradient is one mechanism by which deleterious reactions occur in practice. Measurements have been obtained in the laboratory using a partial pressure gradient across the specimen (again conditioned at 55 per cent relative humidity). The expression used to derive diffusivities is

$$Q = (DPA)\frac{(C_2 - C_1)}{(RTL)} \tag{8.33}$$

where P is the absolute gas pressure, R is the gas constant, T is the absolute temperature, $(C_2 - C_1)$ is the oxygen concentration difference across the specimen, in mole fraction, Q is the molecular diffusion rate for oxygen through the concrete (mol/s) and D is the diffusivity of oxygen through the concrete (in $\mathrm{m^2/s}$).

Diffusivities typically lie in the range $0.2\text{–}5.0 \times 10^{-8}\ \mathrm{m^2/s}$ for concretes dried at 50 per cent relative humidity. Both the water/cement ratio and degree of cure influence the rate of diffusion. In the case of the much smaller diffusivities for saturated concrete ($10^{-12}\ \mathrm{m^2/s}$), the mix proportions are unimportant but the degree of compaction may be critical. Simple relationships appear to exist between the permeability and the diffusion of oxygen through dried concretes.

8.7.5 DRYING AND WETTING

The rate of drying is controlled by the diffusion of water vapour through the concrete. This is found to be sensitive to the water/cement ratio, the degree of cure and relative humidity. Transmission of water through a partially dried concrete occurs mainly through the movement of liquid water condensate, and transmission rate increases with increasing humidity. The rate of wetting of dried concrete is controlled by pore size distribution and the surface tension of the water.

A theoretical approach to the rate of capillary absorption of porous solids has been developed for soils and for ceramics, and has been adopted for concretes; however, the situation here is more complicated since the pore structure of dried concrete is not stable under wetting conditions, tending to become finer with increasing period of wetting. Thus the simple model which works well for clay brick is not completely satisfactory for concrete, although it has been used for mortar prisms and for relatively thin slices of concrete. Wetting is generally rapid, although swelling of previously dried hydration products continues over an extended period of several weeks.

8.7.6 IONIC DIFFUSION

Chloride ion diffusion rates are dependent upon the water/cement ratio and on cement type. A similar expression to that used in the oxygen diffusion calculation is appropriate but some care is necessary in utilising ionic diffusivity values. The diffusivity may have been calculated using either the difference in concentration in the solution phases on either side of the specimen, or the concentration gradient within the concrete expressed as the quantity of chloride per unit volume of concrete.

The physical processes involved in the movement of chloride ions within cement-based products appear to be closer to an exchange of chloride for hydroxyl than to simple diffusion, and some chemical dissolution of the cement hydrates occurs in chloride environments. Particularly noteworthy is the low rate of movement of chloride in hardened blastfurnace slag or fly ash blended cement pastes. The lower rate of penetration of chloride for slag cement is possibly the result of a lower concentration of free hydroxyl, yielding a smaller OH^-–Cl^- exchange capacity.

Electrolytic resistivity values are related to the diffusivities of ions in the pore space in the concrete, particularly the hydroxyl ion. Chloride ion diffusivities lie in the range $0.1–1.2 \times 10^{-12}\,m^2/s$. The diffusion of sulfate ions through Portland cement-based material has been followed by a number of techniques, including radioactive tracer methods. Typically, sulfate ion diffusivities lie in the range $2–30 \times 10^{-14}\,m^2/s$.

A simple technique has been developed for measuring the chloride ingress into the surface layers of concrete exposed to chloride solutions, from which a chloride ion diffusivity can be derived. Work on the penetration of chlorides into concrete prisms immersed in salt water has indicated that the depth of penetration of chloride is not greatly influenced by cement type, but the quantity of chloride taken up by the surface layers is much greater for Portland cement than for sulfate-resisting Portland cement or slag cement concretes. Carbonation of the outer layer reduced the capacity for absorption of chloride, but a reduction in temperature greatly increased its absorption capacity for chloride. However, it is reported that carbonated concretes show a much increased diffusivity for chloride ions.

8.7.7 CRACKING

The vulnerability to attack by external agents is greatly increased by the presence of voids, honeycombing and wide cracks. Cracks occur in reinforced concrete subjected to external loading and the Codes of Practice provide for limitations in crack widths by specifying steel quantity and distribution.

Cracking also occurs where restraints oppose the normal tendency of the concrete to shrink.[229] Plastic settlement cracking usually takes place within the first 3 h after placing. The primary cause is excessive sedimentation or bleeding of the fresh concrete under the action of gravity, or capillary suction if the rate of evaporation exceeds the rate at which clear water appears on the concrete surface. The types of restraint producing plastic settlement cracking are reinforcement, wedging action of concrete in columns or marked variations in depth of formwork. Movement of formwork during setting also gives rise to plastic cracking.

Plastic shrinkage cracking usually takes place within the first 6 h after placing. The primary cause is too rapid early drying. Early thermal contraction cracking typically occurs within 2–3 weeks after placing. The primary causes are excessive temperature rise or temperature gradients during cement hydration. In the early stages of the hydration of the cement, the rate of heat generation may be greater than the rate of heat loss (especially in deep sections); the temperature rises initially, but at later ages, after setting has occurred, the temperature falls, producing a thermal contraction and cracking if the concrete is restrained.

Long-term drying shrinkage cracking usually occurs within a few months after placing. The primary cause is a lack of efficient contraction joints, although some aggregate rocks (e.g. certain dolerites) give rise to increased drying shrinkages and movements under moisture cycling. Various deleterious reactions also give rise to cracking.

8.7.8 PERMEABILITY OF CEMENT PASTE–AGGREGATE INTERFACES

It is clear that the interface at the cement paste–aggregate boundary presents a path of low resistance to the ingress of aggressive species. The packing of cement particles at the boundary is less efficient than in the body of the paste, thus locally providing a region of higher water/cement ratio and lower density. In addition, a chemical interaction between the aggregate and the cement occurs more often than is normally supposed, resulting in local changes to the chemical microstructure.

Computer modelling has been carried out to represent the intrusion volume observed by mercury penetration techniques.[230] Mercury intrusion experiments performed on mortars indicate that results change dramatically at a critical sand content.[231] It is considered that an overlap between adjacent interfacial zones occurs at this critical sand content, allowing the percolation of mercury to increase dramatically. An increase in the volume fraction of dense aggregate should lead to a reduction in the rate of permeation and diffusion of species through a mortar or concrete because the fraction of permeable cement paste is reduced and replaced by impermeable sand or gravel.[232] However, the volume of the interfacial zone will be increased by an increase in aggregate content and the rate of permeation might be expected to increase with increased aggregate content. Some evidence is provided from gas and water vapour diffusion measurements for a minimum permeability at an intermediate aggregate content, although the reported effect is quite small (Figure 8.17).

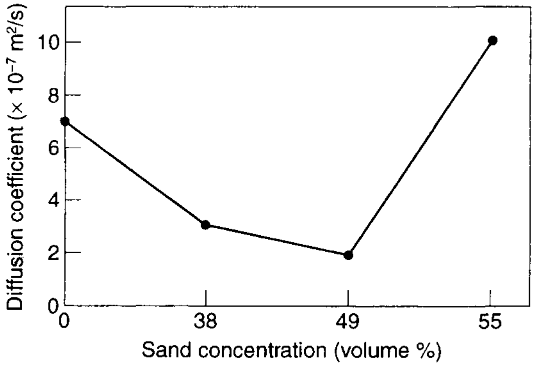

Fig. 8.17 Diffusion coefficients of oxygen through mortar as a function of sand content.[232]

8.7.9 FREEZE–THAW ATTACK

The subject of freeze–thaw attack on concrete has been a topic of investigation for many years and continues to attract research. An early theory for freeze–thaw damage was proposed by Powers[233,234] in which it was considered that the unique 9 per cent expansion of water during freezing was solely responsible. In saturated systems, the flow of water away from the advancing ice front generated transient pressure. This view was seriously questioned by the observation that disruption was possible where porous solids were saturated with organic liquids, not showing an expansion on freezing, but also developed disruption on freezing. Freeze–thaw testing may be carried out according to ASTM C 666, where freeze–thaw cycles may be imposed with the specimens under water (procedure A) or freezing in air at 100 per cent relative humidity and thawing under water (procedure B). Powers found that all cement pastes in the normal range of water/cement ratios were vulnerable to frost action. The importance of the volume of capillary pores and the degree of saturation of the concrete is well established:[235] the critical saturation method of testing concrete for frost resistance seeks to quantify the ease with which concretes reach the degree of water uptake which results in damage on freezing.[235] The standard procedures to counter freeze–thaw action are to employ mixes with a low water/cement ratio, as for pressed precast components, or to entrain small air bubbles in the fresh mix, which are largely retained in the set concrete and are difficult to fill with water. The spacing between entrained air bubbles is an important parameter and the type of air-entraining agent also has an influence;[236,237] it is determined (according to ASTM C 457) by microscopic point counting on a polished surface and represents approximately the average half-distance between two air-bubble walls. The critical spacing factor represents the spacing factor at which expansion of the concrete specimen begins to increase rapidly after a given number of freeze–thaw cycles.[238] A minimum air content of 5 per cent by volume of concrete is specified for concrete with a nominal maximum aggregate size of 20 mm, when the concrete grade is <50.

Litvan[239] has summarised the laboratory experimental observations relating to freeze–thaw damage:

- The severity of damage is proportional to the water content; in the fully saturated state, few systems can endure even a single freezing.
- The physical size of the porous solid influences its susceptibility to damage, and freeze–thaw resistance improves with reduction in specimen size.
- Damage is increased with increasing cooling rates. Even the most vulnerable system can be taken through a freeze–thaw cycle without injury if the freezing rate is very low. The critical spacing factor for entrained air bubbles is reduced as the freezing rate is increased.[240]
- Solids with either very high or very low porosity usually have a good service record. Brick and marble, are examples of such materials. Hydrated cement paste with an intermediate porosity is usually vulnerable unless special precautions are taken. This is particularly true in the case of pastes with a high water/cement ratio. A relationship was observed between nitrogen BET (the Brunauer, Emett and Teller procedure for deriving specific surface area from adsorption isotherms) surface area and vulnerability to freeze–thaw damage.[241]
- Air entrainment, which consists of the addition of a surface-active agent to the fresh mix and results in the formation of small air bubbles, has proved to be an excellent method of increasing the frost resistance of concrete.

- Repeated freezing and thawing under natural conditions usually results in desiccation and in the accumulation of the formerly pore-held liquid outside of the body in the form of ice lens.
- Mechanical damage is more severe if the porous solid contains a salt solution instead of a pure liquid. The severity of the damage is a function of the solution concentration, the most severe damage occurring at relatively low concentrations, in the range 2–5 per cent.

Litvan[242] proposed a fresh approach to deducing an explanation to the problem of freeze–thaw damage, based on the discovery that water adsorbed onto the surfaces of capillaries does not freeze at temperatures below 0°C due to the action of surface forces which restrict the ability of the adsorbed water to redistribute to form an ice crystal lattice. A degree of supercooling is required before ice can enter the finer pore structure, since a curved ice–water interface would then be formed, generating a hydrostatic pressure in the ice, caused by the ice–water interfacial tension, and lowering the freezing point. Helmuth[243] showed that nucleation of ice does not occur within the structure of hydrated cement pastes automatically, even at temperatures as low as −15°C; external ice seeds are necessary to initiate freezing. The degree of supercooling in any specimen before freezing occurs is dependent on random factors, such as surface conditions and mechanical vibrations. This supercooled adsorbed liquid has a higher vapour pressure than ice at the same temperature, and equilibrium between pure water and any external ice crystals can only be attained by expelling a proportion of the pore water. Continued reductions in temperature cause continued expulsion of water and the paste becomes desiccated and shrinks. Damage occurs when the required rate of water expulsion is higher than can be realised, thereby developing hydrostatic pressure within the paste.

The quantity of water that must be expelled from the paste during cooling is determined by the porosity of the paste (or its water/cement ratio) and this rapidly increases as the water/cement ratio is increased. The expulsion of water is not of itself damaging, but damage ensues when the process is impeded; a low permeability may create such a condition. Because the increase in permeability as the water/cement ratio is increased does not match the increase in volume of water to be expelled, pastes with a high water/cement ratio are more vulnerable to freeze–thaw damage than those with a low water/cement ratio. The mechanism by which entrained air bubbles increase the resistance of concrete to freeze–thaw damage is by creating large reservoirs into which the expelled pore water can escape without the need to migrate to distant external surfaces.

Pigeon has extended the range of concretes investigated to those containing microsilica and superplasticisers, and those capable of providing very high strengths when made at low water/cement ratios of 60–100 MPa.[246] Litvan[245] examined the effect of superplasticisers on the entrainment of air bubbles in mortar specimens and their freeze–thaw resistance. Some superplasticisers were found to be air entraining. It was found that good frost resistance was obtained for mixes containing air-entraining agents and superplasticisers even when the spacing factor for air bubbles was larger than the accepted limit. One question that required investigation was the need for air entrainment in mixes with such a low water/cement ratio, since air entrainment carries a penalty of a strength reduction. Air entrainment was found to be required if freeze–thaw damage was to be avoided, even at a water/cement ratio of 0.3. Pigeon *et al.* also examined the resistance to scaling for microsilica containing concretes.[246] Scaling tests were carried out according to ASTM C672. It was found that the presence of microsilica reduces the resistance to scaling but a limit of 8–10 per cent by mass of cement was acceptable. It was found that scaling cannot be prevented by air entrainment but a spacing factor of 200 μm provided some protection. Although air entrainment can completely protect against normal freeze–thaw action, the protection against surface scaling in the presence of de-icing salts is not complete because the degree of liquid filling of the pore space is increased at a given relative humidity when salt solution is present.[239,244]

Pigeon discussed the role played by the rate of freezing and the length of time under low temperatures on the damage incurred: the quantity of ice accumulating in capillary cavities is increased,[239] and possibly a decrease in the critical spacing factor is required for these concretes during the slower, more natural freezing cycles. The effect of superplasticiser dose on freeze–thaw durability of high strength concretes has been examined[247] for air entrained concrete, but no detrimental effects were found. However, non-air-entrained concrete was found to be less durable when high superplasticiser doses were employed.

Certain aggregates, for example those containing fine pores, are susceptible to freeze–thaw damage, especially when present as the coarse aggregate, e.g. cherts, shales and some limestones. Under freeze–thaw action, pop-outs or map cracking of the concrete surface can result.

8.7.10 WEAR RESISTANCE

An analysis of the abrasive wear of concrete floors has revealed that high-intensity crushing is the chief mechanism of deterioration, and hence the concrete crushing strength is the relevant parameter determining wear resistance.[248] Generally, the abrasion resistance of the coarse aggregate component is not related to the wear resistance of the concrete; rather, the properties of the mortar fraction are the determining factors. There is no correlation between the hardness or abrasion resistance of good-quality aggregates and the abrasion resistance of concrete of high strength. Soft aggregates, such as limestone and sandstone, do reduce abrasion resistance and the quality of aggregate is important in concretes in the strength range 20–35 MPa. Bleeding and segregation of concrete after compaction often lead to the formation of 'laitance' on the surface which, if left to harden, would very easily be abraded away.

The traditional finishing technique with plain and granolithic floors involves floating and trowelling to flatten and compact the surface mortar, so reducing the effective water/cement ratio at the surface. Surface abrasion resistance is very closely allied to the compressive strength of the outer skin of cement mortar; this may be enhanced by power trowelling the green concrete.[249] This process significantly increases abrasion resistance, and the great importance of curing is brought out in surface abrasion tests; the top few millimetres of the concrete slab are very important for wear resistance and also are greatly influenced by the type of curing employed. Even a short period of cure under polythene or the use of a sprayed-on curing compound produces a very large increase in performance for both plain Portland cement and blended cement concretes by ensuring that the degree of hydration of the cement is allowed to reach a satisfactory level.

Three causes of the removal of material from the surface of cement-based material have been identified: chemical action, abrasion by suspended solid matter in flowing water, and cavitation from the collapse of vapour bubbles formed by pressure changes within a high-velocity water flow.[250] Damage amounting to the removal of substantial depths (fractions of a metre) of concrete have been reported[238,248,251] from combined abrasion and cavitation.

Cavities form within the water flow where the local flow is increased, and the pressure consequently drops to a value that will cause the water to vaporise. This takes place near curves, protuberances or offsets in a flow boundary, or at the centres of vortices. The vapour bubbles travel with the water flow and then collapse or implode when the local uniform flow is restored. Damage occurs at this point and it is the result of the collapse of these vapour bubbles which causes high instantaneous impacts on the concrete retaining surface, resulting in pitting, noise and vibration.[251]

The erosion pitting is concentrated in the mortar matrix and undermines and loosens aggregate and other harder particles. The tendency for a system to cavitate is described by a cavitation index, which is the ratio of the local pressure drop within the water flow to the dynamic pressure existing in the flow, $\frac{1}{2}\rho V^2$, where ρ is the density of the water and V the fluid velocity; if the system operates above a critical value of cavitation index, the system does not cavitate. A way to avoid cavitation is to keep the cavitation index high by ensuring a high hydrostatic pressure and a low water flow velocity.

8.7.11 DISCUSSION

Physical aspects of durability have been examined in this section. Inevitably, long-term testing is the only certain method of investigation, but in the current economic climate this approach is only rarely possible. Much effort is being expended on computer simulation of durability problems as an alternative approach; however, this procedure assumes that the mechanism of deterioration has been fully established. The investigation of the chemical nature of hardened cement-based materials, including the microstructure involved, is also currently attractive to experimentalists, especially as great developments in instrumentation are regularly forthcoming. It is still necessary to relate these structural investigations to the performance of concretes under practical conditions before the full value of this work can be appreciated.

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9

The Production of Low-Energy Cements

C. David Lawrence

9.1 Introduction

Rising levels of 'greenhouse' gas in the atmosphere, and the associated increase in temperature of the environment, are potentially able to alter the ability of the planet to support present life forms.[1] These greenhouse gases are characterised by showing radiation absorption bands in the infrared region of the spectrum; examples are carbon dioxide, methane, ozone, NO_x and chlorofluorocarbons.[2] The most important greenhouse gas is carbon dioxide. Recent discussion has questioned the validity of the accepted mechanism of global warming;[3–6] however, most commentators find that greenhouse gases result in an increased temperature for the Earth's troposphere. Action is being proposed on a worldwide scale to limit the use of fossil fuels which release CO_2 on combustion.[7] The Intergovernmental Panel on Climate Change (IPCC) estimates that the average rise in temperature of the environment should reach between 1.9 and 5.3°C in the next 100 years. The EU is seeking to limit CO_2 emissions and has recommended (September 1991) that member states adopt a new energy and fuel tax, thereby restricting CO_2 emissions to 1990 levels.[8,9]

The cement production industry has been identified as one of the most important users of carbon-based fuels as a source of heat energy and also as an industry in which the technology exists for large savings in this respect.[10] More importantly, decarbonation of limestone constitutes an initial step in traditional cement production, thereby releasing additional CO_2 to the atmosphere. Portland cement production involves the sintering of raw feed (composed of limestone and clay) at about 1450°C and then grinding the cooled clinker with 5 per cent gypsum rock. A typical fuel energy requirement for efficient production may approach 3000 kJ/kg cement, of which 2000 kJ/kg is used in drying the feed and carrying out the chemical reactions, while 1000 kJ/kg is consumed by energy losses (radiation, evaporation, grinding, etc). The theoretical heat energy requirement to form Portland cement clinker is calculated to depend on the percentage of limestone employed, or the lime saturation factor,

$$\text{lime saturation factor} = \frac{100\%\,\mathrm{CaO} + 75\%\,\mathrm{MgO}}{2.8\%\,\mathrm{SiO_2} + 1.18\%\,\mathrm{Al_2O_3} + 0.65\%\,\mathrm{Fe_2O_3}} \tag{9.1}$$

rising from about 1570–1800 kJ/kg as the lime saturation factor is increased from 80 to 100 per cent.[11] The specific electrical energy consumption, which includes the power absorbed in grinding the cement, is ~110 kWh/t on average, (or an additional 396 kJ/kg electrical energy, which is equivalent to ~990 kJ/kg fuel energy).

Although energy use and release of CO_2 are closely related in the usual cement manufacturing industry, it is the release of CO_2 to the atmosphere rather than the consumption of energy which is of chief concern. Decarbonation of limestone ($CaCO_3$) results in the release of CO_2 and, since natural limestone and chalk are the only large-scale sources of calcium available to the cement industry, this CO_2 release is only reducible by changing the chemical composition of the cement. The rate of increase of cement production is much higher in the underdeveloped world, in China and India for example, than in the developed Western countries, and any attempt to limit CO_2 emissions (and Portland cement production) to the 1990 levels (as proposed) will penalise the developing world.[8]

Accepting that the thermal energy requirement for very efficient Portland cement production may be 2930 kJ/kg, and that 1 kg of Portland cement requires the decomposition of 1.209 kg of $CaCO_3$, then the production of 1 kg Portland cement clinker, or the decomposition of 1.209 kg of $CaCO_3$, releases $44/100 \times 1.209 = 0.5320$ kg CO_2 into the atmosphere since

$$\begin{array}{llll} CaCO_3 & = CaO & + CO_2 \\ 100 & 56 & 44 \end{array}$$

If carbon is the fuel used in firing the kiln

$$\begin{array}{lll} C + & O_2 = & CO_2; \\ 12 & 32 & 44 \end{array}$$

releasing 94052 cal/mol; or 7837.7 cal/g, equivalent to 32792 J/g. To burn 1 kg of Portland cement clinker requires $2930/32792 = 0.08935$ kg of carbon to be burnt, thus releasing $44/12 \times 0.08935 = 0.3276$ kg of CO_2 to the atmosphere.

The electrical energy required is additional to the above calculations. Reference 12 shows that up to 120 kWh/t may be required, or 432 kJ/kg of electrical energy. Assuming a 40 per cent efficiency in the generation of electricity, this amounts to 1080 kJ heat energy/kg clinker. If carbon is again burnt then $1080/32792.8 = 0.03293$ kg is required, or the release of a further 0.1208 kg CO_2 takes place. If fuel oil or natural gas is substituted for carbon in the burning of the clinker or the generation of electrical power, the quantity of CO_2 released is reduced. Waste organic solvent is a convenient fuel source with reduced CO_2 emission for a given heat output that has recently been developed for the burning of cement clinker.[13] It seems that usually more than half the CO_2 released in the process of Portland cement production arises from the decarbonation of the raw feed, with a smaller fraction resulting from the burning of fuel.

9.1.1 *ALTERNATIVE CEMENTS*

Electro-accretion processes in sea water, onto preformed wire-mesh reinforcement arranged in the shape of the required component, allows a concrete to be produced directly[14] by making this the cathode in an electrolytic cell. The deposit that forms on the reinforcement mesh, consisting of brucite $Mg(OH)_2$ and $CaCO_3$ in the forms of calcite and aragonite, may be used as a load-bearing structure.[2,15,16] Although this electrochemical alternative to the formation of concrete structures, avoiding the use of cements, has tentatively been proposed, most proposals for reducing energy consumption in the construction industry have accepted the need to continue to use a manufactured cement.

Presently, common cements or binders for concrete production and building construction are based on calcium compounds, either calcium silicates or calcium aluminates. The basis of modern concrete technology is a calcium silicate cement in the form of Portland cement. The forerunners of Portland cement were hydraulic limes and 'Roman' cement, the raw feed for the kilns being natural siliceous limestones in both cases. 'Roman' cement can be regarded as a low-energy cement since lower firing temperatures and lower CaO contents were involved. An important difference between 'Roman' cement and Portland cement lay in the firing procedure: 'Roman' cements were taken from that part of the fired charge which had not clinkered, and clinkered material was regarded as being non-cementive.[17] It seems likely that equilibrium (approached by clinkering) resulted in non-hydraulic calcium silico-aluminates being formed, while the more readily forming but non-equilibrium intermediate compounds, such as β-C_2S and CA, were required if hydraulic activity was to be achieved. 'Roman' cements were not as strong as Portland cements but were quicker setting due to a higher aluminate content.

A number of approaches to limiting the energy requirement (or reducing CO_2 release) in the production of modern construction cements have been proposed or adopted:

- Traditional Portland cement clinker formation may be made more efficient and the energy requirements in the different steps identified and minimised. The introduction of energy-efficient dry-process kiln systems has reached an advanced stage, and further developments can be expected to provide additional but possibly limited improvements. The quantity of CO_2 released is reduced because of the reduced thermal energy requirements, but the composition of the cement is not radically changed and the quantity of $CaCO_3$ to be decarbonated remains similar.
- More efficient use of the Portland cement produced can be achieved by increasing its hydraulic activity, and thus encouraging the use of leaner concrete mixes. A modification of the raw feed in Portland cement clinker production, to include minor percentages (0.25 per cent) of fluoride (F^-), for example, can lead to increased reactivity,[18] as can increasing the speed of cooling of the clinker. The reduced clinkering temperature possible by the use of mineralisers may bring about savings in energy, however the energy savings to be made by bringing the firing temperature down from 1450 to 1350°C in industrial practice amount to only 5 per cent.[19,20] Reduced firing temperature should allow low grade fuels to be utilised and will also reduce the emission of the greenhouse gas NO_x.

  If chloride is added, a salt melt forms and a modification to the clinker minerals is introduced, to give alinite [$Ca_{11}(Si_{0.75}Al_{0.25})_4O_{18}Cl$] rather than alite. The burning temperature of the clinker is stated to be reduced to between 1000 and 1100°C, and an overall saving in heat plus electrical energy of up to 30 per cent has been claimed.[19] The raw mix contains between 6 and 25 per cent $CaCl_2$ with the remaining composition similar to that of Portland cement raw feed.[21] The presence of chloride in the clinker raises doubts concerning the suitability of this cement for use in steel-reinforced concrete. Substitution of CaF_2 for the chloride removes this problem and has been shown to lead to satisfactory clinkers at 1150°C.[22]

Subsequent dilution of these highly reactive Portland cements with low-energy waste material or ground limestone can be made without a reduction in performance from accepted levels for the blend. Carbon dioxide emissions levels would be expected to show a significant fall, in line with the percentage of cement replacement materials employed. A development of blended cements or limestone-extended cements has been suggested which uses mineralised, highly active Portland cement clinker.[23,24]

- Cements in which up to 40 per cent of the Portland cement clinker is replaced by fly ash and other artificial pozzolanas are well established; larger replacement levels by granulated blastfurnace slag are also commonly employed (European Standard ENV 197[25]). The critical selection of natural pozzolanas and improved activity of waste materials and byproducts may increase the performance of blended cements and allow a greater dilution of high-energy Portland cement clinker (and thereby reducing energy requirement and CO_2 emission) without reducing performance. Dilution of Portland cement with 5 per cent limestone filler before grinding may allow a small saving in the energy of production with little decrease in quality of the cement.[26] The energy required for a slag cement can be expected to be reduced in proportion to the replacement level by the slag (i.e. up to 75 per cent). This approach to a reduction in the energy consumed in cement production has been offered as the preferred route to low-energy cements.[19] However, calculations show[8] that the improvement to cement supplies achieved by dilution of Portland cement with low-energy waste material will be insufficient to meet the future needs of the developing world if CO_2 emission (i.e. Portland cement production) is to be held at 1990 levels.
- Further reductions in CO_2 emissions must involve a reduction in CaO content of the final cement, resulting in belite ($2CaO \cdot SiO_2$) based cement rather than the present alite ($3CaO \cdot SiO_2$) based cement. The substitution of a high-lime by a low-lime cement should lead to both energy saving and a reduction in CO_2 emissions.[19,27] The belite formed normally has a low hydraulic reactivity with water and improvements are required if cement properties are to be maintained at present Portland cement levels. In order to increase the activity of the belite formed, it is frequently proposed that fast cooling should be adopted. This procedure leads to increased heat losses in the processing coolers, so the overall saving in fuel is questionable; however, CO_2 emissions will be reduced in line with the reduction in lime standard, i.e. by about 25 per cent.[19]
- Radically different methods of sintering cementive clinkers, using chemical systems based on sulfoaluminate, sulfoferrite or fluoraluminate to form the molten phase, have been proposed, leading to lower temperatures for clinker formation. In combination with a low-lime mix, a belite cement which contains hydraulically active sulfoaluminate or ferrite phases is produced, $C_{12}A_7$ or $C_4A_3\bar{S}$ and C_4AF, thereby giving both good short-term and good long-term strengths.[28] Setting and early hardening is based on the formation of ettringite (rather than the traditional calcium silicate hydrate). Alternatively, high-strength cements containing $C_{11}A_7 \cdot CaF_2$ may be formed; substitution of this aluminate by a ferrite results in a further reduction in temperature of formation and improved performance. A reduction in limestone utilisation of about 40 per cent appears to be possible.

Calculations suggest that 25 per cent savings in energy may be achieved. In China and Japan, commercial production of rapid-hardening, zero-C_3S cements containing large amounts of $C_4A_3\bar{S}$ is claimed to be in operation. A clinker containing C_2S, $C_4A_3\bar{S}$ and C_4AF, made at 1250–1300°C, gave compressive strengths of 29.4, 49.0 and 82.5 MPa at 3 h, 1 day and 28 days, respectively. Many of the restrictions on the use of waste materials and low-grade fuels in Portland cement clinker production no longer apply. Durability problems have been indicated from the decline in strength after a number of years of water storage, and increased vulnerability to carbonation has been suggested.

- Study of the activation of granulated hydraulic slags by alkalis to form cements has resulted in more than 30 years of commercial production of these low-energy cements in Eastern Europe. In this application, a wider range of slags can be utilised than is normally considered for traditional slag cements; the additional energy input and CO_2 release is very low given that the slag is a by-product of another industry.[29,30] Supersulfated slag cement is a well-established blastfurnace slag cement in Western Europe where the slag is activated by the inclusion of small percentages of Portland cement clinker and 10–15 per cent anhydrite.[31–33]

  Especially produced reactive aluminium silicates, for example by dehydroxylation of kaolin, have been developed more recently to allow a similar cementive action with alkaline solutions.[8] This class of cements has been termed 'geopolymeric'. Full production of these cements is in operation in the USA. The possibility of using other natural glassy aluminosilicates has been mentioned. High strengths and good durabilities have been reported. The low reserves of alkalinity in these cements increase their vulnerability to carbonation, and their ability to protect reinforcement steel from corrosion has been questioned.[34]
- Developments of construction cements have been proposed from blends of gypsum plaster, as the early-age cementive component, and a secondary siliceous components to improve durability and give adequate long-term strength. The energy required to form gypsum plasters has been quoted at only about 15 per cent of that required to form Portland cement clinker, and no decarbonation of limestone is involved. Blended cements containing 20 per cent Portland cement clinker with large proportions of plaster of Paris and reactive pozzolanas, in theory, can offer up to 70 per cent savings in energy while supposedly yielding similar cementive properties to Portland cement.[27] Highly reactive pozzolanas, such as microsilica or rice husk ash, are capable of forming calcium silicate hydrates rapidly, and it is claimed that their presence imparts the necessary water resistance in spite of the simultaneous formation of large quantities of $CaSO_4 \cdot 2H_2O$ during plaster hydration.[35,36] Doubts remain on the long-term durability of these very low-energy systems.

A number of other cementive systems may be mentioned, but the limited availability and high cost of raw materials is likely to rule them out of contention as replacements for Portland cement. High-alumina cements have been produced since the early 1900s and used in the construction industry. In recent years the durability problem of conversion of the hydrates, which results in a porous product and a long-term reduction in strength, has restricted their use.[37] The discovery that blending with blastfurnace slag can change the character of the hydrate formed, and eliminate the conversion process, has revived interest in this cement. A 1:1 blend of high-alumina cement with blastfurnace slag results in the hydrate strätlingite (C_2ASH_8) being formed, and strengths continue to rise (up to 65–70 MPa) over a period of up to 1 year at 38–40°C under water. Their resistance to external sulfate attack is very good.

Systems relying on the hydration or reaction of phosphate compounds have received some attention, due to their rapid development of strength[38,39] but shortage and cost of raw materials would be a serious problem. Phosphatic binders have been reviewed;[37] in these cements, a basic solid is reacted with an acidic fluid; at the present time, end uses are mostly concerned with the development of fast-setting repair systems. Magnesium oxide is a basic oxide which has been reacted with various acidic phosphate solutions to form quick-setting cements. Various polyphosphate solutions increase strength. Calcium phosphate cement bonds have been formed by the hydration of calcium phosphates or by reacting these with phosphoric or organic acids. Compressive strengths of up to 30 MPa have been claimed. Hydraulically reactive glasses in the $CaO–Al_2O_3–SiO_2$ system have been shown to develop good strengths (91 MPa after 28 days at water/solid = 0.4)[40] but there is some evidence for strength regression after 28 days water storage. Reactive $CaO–Al_2O_3–SiO_2$ glasses have also been prepared which can hydrate without activators. Cements based on aluminophosphate glasses ($Al_2O_3–P_2O_5–H_2O–SiO_2$) have also been explored.

9.2 Gypsum plaster cements

The apparent attraction of basing a building cement on gypsum plaster has been mentioned in Section 9.1. A considerable volume of experimental investigation has been carried out on these systems and the recent literature contains a surprising number of papers on their development and long-term stability.[41]

Many attempts to develop quick-setting cements based on mixtures of gypsum plaster and Portland cement have been reported, and repair systems based on this blend were in production in the 1970s. One system examined was based on a 50:50 mixture of sulfate-resisting Portland cement and autoclaved plaster of Paris; specimens were either cured at 70°C (for 5 h, 'B' or for 20 h, 'C') or at room temperature. All specimens cured at room temperature expanded and disintegrated within 1 year; specimens cured for 20 h were less expansive than those cured for 5 h, but were eventually found to expand and were of poor durability (Figure 9.1).[42] Certain specimens (labelled D) were dried for several days at 40°C before immersing under water for an extended period. The outer layers of specimens in contact with the storage water appeared to expand and form a mush, while the central regions remained hard. Heat curing and the inclusion of a range of admixtures only improved the durability to a limited extent. By drying out before testing, compressive strengths were increased by a factor of about two.

A blend of 75 per cent gypsum plaster (kettle dehydrated product) and 25 per cent Type I Portland cement, with partial replacement of Portland cement by microsilica, has provided a system with good strength levels and moderate wet strength, but tests were continued for only 200 days.[35] The inclusion of silica fume allowed a slow development of strength to occur between 28 and 200 days while, in the absence of silica fume, strength declined rapidly.

Combinations of calcined phosphogypsum, fly ash and hydrated lime or Portland cement resulted in strong products.[36] Compositions examined contained 40 per cent

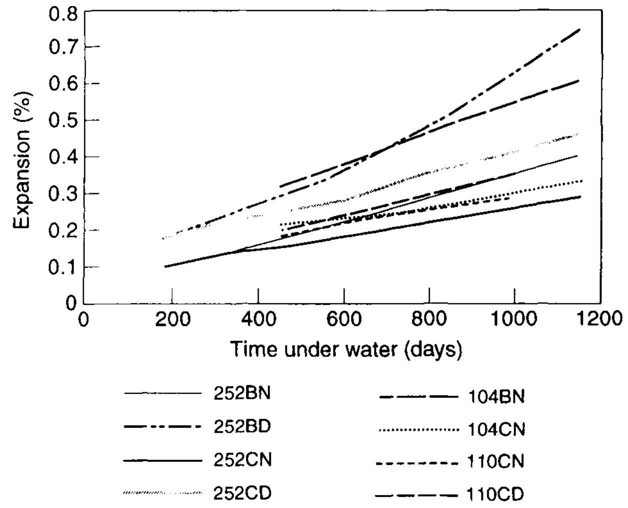

Fig. 9.1 Expansion of 50:50 plaster/sulfate-resisting cement pastes heat cured at 70°C for 5 or 20 h (source: Ref. 42).

plaster, 40 per cent fly ash and 20 per cent hydrated lime (binder A). A second binder was examined in which 10 per cent hydrated lime was replaced with Portland cement (binder B) (Table 9.1).

Combinations of Portland cement and gypsum plaster with added pozzolana were tested for strength at up to 90 days[27] (Table 9.2). The strengths obtained using rice husk ash or microsilica pozzolanas were comparable to those obtained from pure Portland cement. No strength regression was observed. Other studies of hemihydrate–Portland cement mixtures have found strength reductions beyond 75 days.[41] The energy input required to form plaster of Paris is given as approximately 15 per cent of that required to form Portland cement, with release of CO_2 related only to the burning of fuel for the appropriate dehydration reaction. The energy required to form these composite cements was calculated at 25–33 per cent of that required to form pure Portland cement.[27]

The system Portland cement–gypsum plaster–microsilica has been investigated in some

Table 9.1 Compressive strengths of plaster–fly ash–lime (A) or plaster–fly ash–lime–Portland cement (B) mixes[36]

		Compressive strength (MPa)				
Cement	Curing temperature (°C)	1 day	3 days	7 days	28 days	90 days
A	27	1.82	1.98	2.01	2.97	8.50
	40	1.85	2.45	5.35	16.32	18.70
	50	1.92	3.04	7.71	20.07	22.53
B	27	1.96	2.5	4.50	8.78	12.06
	40	2.00	3.78	10.43	18.71	19.95
	50	2.81	5.89	13.72	22.41	23.68

Table 9.2 Composition and strength of blended plaster cements[27]

Composition (%)									
Portland cement	Plaster of Paris	Pozzolana[a]			Time of set (min)	Compressive strength (MPa)			
		F	R	S		3 days	7 days	28 days	90 days
100					230	10.8	22.0	33.5	39.6
20	50	30			37	2.1	2.8	5.6	19.6
20	50		30		25	6.9	13.5	26.9	27.6
20	50			30	37	8.0	19.5	26.9	28.1
20	40	40			37	1.6	2.4	7.0	20.2
20	40		40		25	8.1	17.8	31.3	36.1
20	40			40	30	10.1	21.6	23.9	25.6
20	30	50			27	1.0	1.9	7.4	18.9
20	30		50		29	7.6	19.4	30.8	32.8
20	30			50	30	12.5	23.2	26.1	29.1
30	40	30			35	2.6	3.7	7.2	16.9
30	40		30		25	7.2	13.2	27.3	34.3
40	20		40		30	12.8	30.3	35.4	41.0
30			70		60	24.3	35.9	43.3	50.8
50			50		150	26.5	39.6	58.3	61.5

[a] F = fly ash; R = rice husk ash; S = microsilica.

detail.[41] Mixes containing 100 per cent gypsum plaster showed zero strengths after 1 year under water while 50 per cent plaster sulfate-resisting Portland mixes retained some strength after 1 year (14.6–22.0 MPa). Sulfate-resisting Portland cement was substituted for the ordinary Portland cement in some mixes and a reduced expansion resulted, but strengths were reduced to zero after 1 year in both cases. The addition of 10 per cent microsilica seemed to delay the disruption of the set material, but strength regression was observed at 1 year.

The mechanism of deterioration of Portland cement–gypsum plaster–fly ash set material has been considered.[43] Not surprisingly, the expansion of the specimens (at 20°C) is associated with the crystallisation of ettringite–thaumasite solid solutions, the CO_2 requirement for thaumasite formation being absorbed during curing from the natural atmosphere.

9.3 Blended cements

Table 9.3 illustrates concrete strengths that can be achieved in the laboratory from comparable simple Portland cement, and fly ash and slag blended mixes. Strengths after 1 day for blended cement concretes are invariably much less than those for the simple Portland cement mixes, while strengths at 1 year can be very similar. Higher strengths can be obtained from blended strengths if full advantage is taken of the reduced mix water demand.

Other active pozzolanic materials have been described: one is based on calcined kaolin (metakaolin) formed in the temperature range 450–800°C.[44] The activator may be

Table 9.3 Concrete mix proportions and 100 mm cube strengths

	Mix composition (kg/m^3)				Free water/ Portland cement	Free water/ total cement	Air (%)	Slump (mm)	Compressive strength (MPa)			
Mix	Portland cement	Fly ash slag	Total cement	Total water					1 day	28 days	56 days	1 year
Slag blends												
3724	364	–	364	183	0.47	0.47	–	–	16.5	53.7	59.5	68.0
3738	182	182	364	187	0.95	0.47	0.3	40	5.8	40.7	50.3	60.4
3759	277	–	277	186	0.62	0.62	0.4	37	8.1	33.6	38.4	43.1
3776	140	140	280	187	1.23	0.62	0.25	24	3.7	28.0	33.8	44.4
3792	199	–	199	185	0.86	0.86	0.65	18	4.8	20.2	23.4	27.3
Fly ash blends												
3836	279	–	279	187	0.62	0.62	0.3	75	9.1	36.5	39.3	43.0
3809	182	98	280	185	0.94	0.61	0.1	173	4.5	21.4	27.0	44.5
3850	217	115	332	184	0.78	0.51	0.2	135	6.8	30.0	37.3	58.8
3901	367	–	367	183	0.46	0.46	–	35	19.9	57.9	63.6	71.4
3883	234	127	361	185	0.74	0.48	0.2	155	7.6	32.0	41.9	61.7
3890	278	149	427	184	0.62	0.40	0.3	77	11.5	46.4	58.9	80.4

$Ca(OH)_2$, NaOH or $CaSO_4$. Strengths of up to 50 MPa were reported for 50:50 blends with $Ca(OH)_2$ mixed at water/solid ratio of 0.35. A further active pozzolana has been based on rice husk ash.[27]

9.4 Portland cements with improved reactivity

Pure C_3S exhibits seven distinct polymorphic forms, depending on the formation temperature and pressure. Although all forms of alite are metastable at temperatures below about 1252°C[45] and slowly transform to C_2S plus CaO, transition temperatures for rapid transformations between the polymorphic forms have been established. The slow decomposition of C_3S to C_2S and CaO normally occurs at temperatures below about 1250°C:

$$T_1 \xrightarrow{620^\circ C} T_2 \xrightarrow{920^\circ C} T_3 \xrightarrow{980^\circ C} M_1 \xrightarrow{990^\circ C} M_2 \xrightarrow{1060^\circ C} M_3 \xrightarrow{1070^\circ C} R$$

The pure compound when cooled to room temperature is T_1C_3S. In production clinkers, due to the incorporation of foreign ions, the form present at room temperature is normally M_1 or M_3C_3S. The introduction of minor amounts of other components into the crystal composition enables the retention of higher-temperature forms at lower temperatures.

The quantities of foreign ions that can be inserted into the crystal structure are limited. Detailed studies have been published on the maximum quantities of Mg^{2+}, Al^{3+} and Fe^{3+} that can be inserted. In general, greater quantities of foreign ions can be inserted at higher temperatures than at lower temperatures, so that the rhombohedral form is expected to be able to accommodate more foreign ions than the triclinic or monoclinic forms. Boikova[46] reported the stabilisation of the different forms of C_3S with ZnO (T_1 at up to 1 per cent, T_2 and T_3 from 1 to 2 per cent, M_1 from 2 to 2.5 per cent, M_2 from

2.5 to 4 per cent, and R from 4 to 5 per cent). The greatest hydration activity was at 4 per cent ZnO where the crystal structural arrangement was changing to the rhombohedral form.

Between 3 and 4 per cent of the composition of Portland cement clinker can be designated as composed of minor components. The minor components P_2O_5, Na_2O, K_2O and SO_3 primarily enter into solid solution with belite and the rate of combination of CaO to form alite is slowed down. The role of CaF_2 in the formation of cement clinker from phosphatic limestone has been examined in detail: the tolerance for phosphate is substantially greater in the presence of fluoride.[47] The effects of some additives (fluorspar, anhydrite, sodium and potassium sulfate) on the rate of the reaction $C + C_2S = C_3S$ have been studied under isothermal conditions between 1350 and 1500°C.[48] Fluorspar acts as an accelerator while the others retard the formation of alite. A compound $(C_3S)_3 \cdot CaF_2$ is formed at ~1100°C.[49] A technical raw feed was given various additions of MgO, SO_3 and ZnO, and the specimens were burned at 1500°C.[50] Additions of SO_3 made sintering more difficult due to the increased viscosity of the liquid melt, and the alite crystals became larger. Addition of MgO reduced the viscosity of the melt, and the alite crystals became smaller; at least 1.5 per cent MgO can be absorbed by the clinker minerals. ZnO was easily absorbed by the silicate minerals and the alite became more stable.

The use of combined fluoride and sulfate mineraliser has been explored.[51-54] The compound fluorellestadite ($3C_2S \cdot 3CaSO_4 \cdot CaF_2$) appears as an intermediate phase and results in a decrease in the maximum clinkering temperature to 1175°C. Clinkers with high alite content can be obtained at 1300°C and a melt is formed at 1180°C. For a synthetic alite raw feed,[55] it was established that the most effective sintering aids were ZnO, CaF_2 and MnF_2, allowing burning to be completed at ~1100°C. Low-temperature alite cements have been prepared using 2 per cent additions of ZnO or CaF_2 as fluxing agent,[55] firing at 1150 and 1250°C, respectively. The reactivity of alites produced at lower temperatures is enhanced and the microstructures of the clinker allows easier grinding.

The effects of fluxes and mineralisers upon phase equilibria in the system $CaO–Al_2O_3–Fe_2O_3–SiO_2$ have been investigated.[48,56] In the presence of CaF_2, the temperature for first liquid formation is reduced and the primary phase field area of $C_{12}A_7$ is expanded, while the phase area for C_3A is greatly decreased.[57] The effects upon phase relations and related kinetic phenomena appear to be favourable to cement clinker manufacture, resulting in greater kiln efficiency.

The amount of clinker melt has an effect on the rate of formation of alite,[11] and the beneficial effects of fluoride arises partly as a result of the increased quantity of melt. A linear relationship has been found between the amount of melt liquid and the rate of formation of alite. Segregation of the melt into two liquid phases, which may have very different viscosities and surface tensions, may complicate the above relationship. For clinker melts containing 1–5 per cent fluoride, chloride or sulfate, the tendency to form two liquid phases increases in the following order:

$$S \rightarrow Cl \rightarrow F, \quad Mg \rightleftarrows Ca \rightarrow Na \rightarrow K$$

Sulfated melts separate only in the presence of alkali metal ions. The addition of MgO or Mn_2O_3 to the liquid phase changes its properties and, when the amount of Mg^{2+} is large, separation into two liquid phases is suppressed. For melts containing chloride or fluoride, separation into two melts takes place more readily than with sulfate additions.

These salt melts have viscosities which may be half those of the usual oxide melts found in Portland cement clinker, and may have surface tensions one-quarter the value of the normal melt.

The effect of MgO content on unsoundness has been studied in relation to the speed of cooling and the C_3A content.[58] Rapidly cooled clinker forms smaller alite and belite crystals, exhibits faster strength growth during hydration, and is able to accommodate the hydration of periclase (MgO). Slowly cooled clinkers containing 3 per cent MgO are sound when containing 7 per cent C_3A but are unsound when C_3A contents rise to 15 per cent. The addition of 25 per cent secondary cements (fly ash) effectively stabilises high MgO (10 per cent) Portland cements.

Fluorine-containing additives have a major influence on the composition of the liquid phase, and accelerate silicate mineral formation between 1200 and 1300°C, permitting the formation of C_3S below the usual stability range. MgO and K_2SO_4 influence the partitioning of fluoride between silicate and interstitial phases, and have a further fluxing effect; the presence of MgO favours the partitioning of fluoride into the silicate phase while K_2SO_4 increases volatilisation. The crystallisation of C_3S results in the removal of fluoride from the interstitial phases, and causes a compositional shift from $C_{11}A_7{\cdot}CaF_2$ to C_3A in the interstitial phase as the temperature is increased from 1100 to 1300°C.

The strength performance of about 50 commercial cements has been analysed in terms of the types of alite and belite present:[59] high temperature forms (alite with high birefringence, and α-belite with a pale coloration) prove to be more hydraulically active and result in higher strengths. It is suggested that extended retention of the clinker at high temperatures, followed by quenching, allows crystal growth to occur and so restrains the crystal transformations and exsolution of impurities from the alite and belite crystals. Exsolution of dissolved Fe_2O_3 results in the formation of orange-coloured particles of iron oxide within the belite crystals. The possibility of preparing cements with enhanced reactivity has been confirmed by the discovery of the exceptional properties for rhombohedral alite, the polymorph stable at the highest temperatures.[60,61] Surprisingly, the content of minor components in the high-temperature metastable transform (M_3) is claimed to be less than in the low-temperature metastable transform (M_1). The high-temperature metastable transform, with smaller amounts of minor and trace components, had a higher hydration reactivity and also a higher birefringence.[62]

Strength tests on mortar cubes have been reported for both pure and mineralised systems;[63] in all cases, mixes containing 0.5 per cent F^- were substantially weaker than the corresponding mixes without F^-, and this effect seemed unrelated to the polymorphic form produced. In contrast, the inclusion of fluoride plus Al_2O_3 in the crystal lattice improved the stability range for the rhombohedral form of alite, and allowed its retention in quenched material;[60] micro-concrete cube strength tests showed rates of strength growth up to twice that shown by the low-temperature (triclinic) form of alite (Figure 9.2). The presence of fluoride causes a loss in hydraulic activity, but this can be restored by adding SO_3.[24,51] The use of combinations of SO_3 and fluoride additions has been proposed[51] to allow the production of highly reactive Portland cements having increased alite content, with alite in the more reactive rhombohedral form (Table 9.4).

The effects of fluoride-containing mineralisers and fluxes on the burnability of a series of synthetic raw mixes, ranging from the quaternary system $CaO-Al_2O_3-Fe_2O_3-SiO_2$ to more complex mixtures and industrial mixes, were determined.[57]

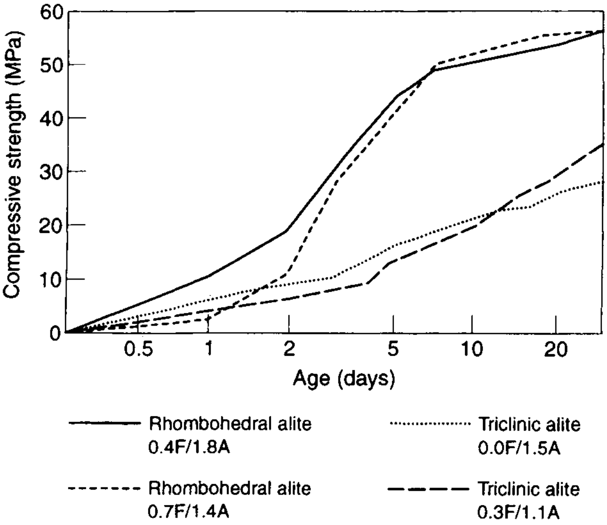

Fig. 9.2 Compressive strength of alites (source: Ref. 60).

Table 9.4 Influence of clinker fluorine content on cement quality[51]

Factor	1	2	3	4	5	6	7
K_2O (%)	1.0	1.2	1.4	1.5	1.4	1.2	1.5
SO_3 (%)	2.9	3.4	3.3	3.6	3.2	2.8	3.9
F_2 (%)	0.06	0.10	0.14	0.22	0.39	0.80	1.7
Free lime (%)	3.3	2.0	1.7	1.7	1.6	1.5	1.1
Standard consistence (%)	25.3	31.0	29.0	29.5	27.5	27.5	29.5
Initial set (min)	90	140	155	170	240	210	540
Final set (min)	110	175	205	220	310	260	660
Concrete compressive strength (*MPa*)							
8 h	6.7	5.4	3.7	4.6	1.7	1.8	
16 h	17.7	20.8	19.7	22.2	15.6	14.5	1.6
24 h	22.9	30.0	29.3	33.2	26.6	19.4	11.6
3 days	33.9	41.9	43.2	46.5	47.5	44.6	38.6
7 days	42.3	48.2	50.2	52.0	55.3	57.1	46.8
28 days	51.9	54.0	56.2	60.7	65.9	66.4	56.0

Factors that influence hydration and strength development (up to 28 days) have also been examined;[57] in most cases a significant increase in strength was obtained where mineralisers (CaF_2, 0.5 per cent F^-) were present (Table 9.5), but a mix containing a high alumina content 'C' showed reduced strength development at 1 and 28 days in the presence of CaF_2.

The action of different mineralisers has been investigated:[22] the use of mineralisers can be expected to reduce the burning temperature by over 100°C and give an energy saving of

Table 9.5 Compressive strengths of mortar cubes made from synthetic clinkers[57]

	Compressive strength (MPa)		
Cement compositions (5% gypsum)[a]	1 day	7 days	28 days
A + MgO + SO_3	6.2	23.1	31.6
A + MgO + SO_3 + CaF_2	10.1	29.2	34.8
B + MgO + SO_3	7.3	22.6	33.6
B + MgO + SO_3 + CaF_2	9.1	26.7	38.4
C + MgO + SO_3	5.6	28.1	38.3
C + MgO + SO_3 + CaF_2	1.2	20.8	32.5
Raw Mix I + H_2SIF_6 (0.3% F^-)	10.8	31.1	35.6
Raw Mix II + H_2SiF_6 (0.6% F^-)	6.3	28.1	33.6

[a] Synthetic clinkers, 1% additions of MgO, SO_3 as K_2SO_4, 0.5% F^- burnt for 30 min at 1450°C.

2–3 per cent. A reduction in the sintering temperature by 200°C and in the calcining temperature by 50°C would be expected to give an energy saving of about 6 per cent.[22] The performance of low-energy cements formed by mineralisation with CaF_2 and gypsum in sulfate solutions and sea water was reported to be satisfactory[64] and to be better than ordinary Portland cement. The mineralised clinker did not require the addition of gypsum to control the set since sufficient calcium langbeinite ($2CaSO_4 \cdot K_2SO_4$) was present in the high-SO_3 clinker (2.6 per cent SO_3 and 0.27 per cent F^-). It was concluded that only a limited saving of energy can be accomplished by the use of mineralisers and fluxes.[19] In one commercial production, the kiln temperature was reduced by 100°C and the fuel requirement by 3 per cent. However, much larger savings were realised from the much longer life of the kiln linings and the 50 per cent reductions in NO_x emissions brought about by the reduced firing temperature. The mineralised cement was found to exhibit slightly reduced early strength, due to the reduced lime saturation factor; however, the 28-day strength was increased as a result of the increased activity of the additional belite forms formed.[18]

The use of Portland cement clinkers which have enhanced activity due to the use of mineralisers allows the performance of blended cements to exceed those of normal pure Portland cements, (Figure 9.3).[23] Recent evidence has shown that mineralised Portland cement clinker can be blended with limestone filler to give a cement with an exceptionally high early strength.[18]

The European Standard, ENV 197-1, for common cement types allows up to 5 per cent addition of secondary cement or filler to Portland cement clinker.[25] A significant acceleration in setting and a reduction in bleeding has been found to occur where limestone is used for this 5 per cent filler, but the most important result of the adoption of the use of 5 per cent additions has been the possibility of grinding modern, highly active Portland cement clinkers to a reduced fineness, thereby reducing the degree of hydration and early strength development without causing increased bleeding and segregation of the concrete mixes, since the limestone filler provides the fine material necessary for this desirable result. The introduction of 5 per cent filler enables overall cement fineness to be maintained and 28-day strengths to be controlled over a range of levels, as required.

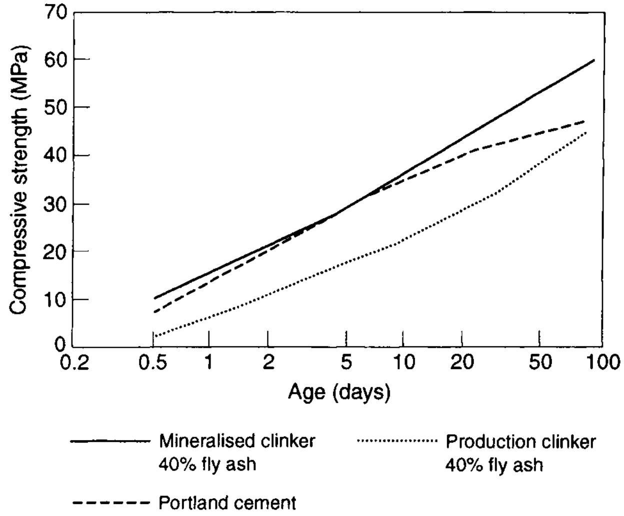

Fig. 9.3 Comparison of blended cement concrete strengths for mineralised and normal Portland cement clinker (source: Ref. 23).

9.4.1 JET CEMENT (REGULATED SET CEMENT)

Regulated set cement was invented at the Portland Cement Association (USA) in the early 1970s; however, the main development work occurred in Japan, where it is known as Jet cement. The cement is derived from a fluoride-modified Portland cement clinker and contains $C_{11}A_7 \cdot CaF_2$ (or $C_{11}A_7\bar{F}$) instead of C_3A.[37] The hydration of mixtures of $C_{11}A_7\bar{F}$, C_3S and $CaSO_4$ have been studied using isothermal calorimetry: the initial peak is considered to be due to the hydration of $C_{11}A_7\bar{F}$, or the formation of ettringite; the hydration of C_3S is retarded. The $C_{11}A_7\bar{F}$ was generally fully hydrated within the first day. Investigations have been made of the sulfate resistance of mortars made with this cement:[65] sulfate resistance was poor, and worse than for ordinary Portland cement. The sulfate resistance of concretes made with Jet cement could be improved by blending with fly ash. Strength results were presented for up to 2 years water storage, with no strength regression (Table 9.6). Two types of clinker have been studied (both with about 1.9 per cent F^-), $C_{11}A_7 \cdot CaF_2$–C_3S–C_4AF and $C_{11}A_7 \cdot CaF_2$–C_2S–C_4AF. It was found that the hydration activity of $C_{11}A_7 \cdot CaF_2$ was increased with increase in clinkering temperature (1250, 1350 and 1450°C) and that it was higher when formed in the presence of C_3S (15 per cent) than when formed with C_2S (15 per cent) clinkers.[66]

By varying the proportion of this compound in the resultant clinker, the desired setting times and compressive strengths could be obtained. The product is used extensively in patch repairs and in the precast concrete industry.[67] Fibre reinforcement, with steel or glass fibres, has been employed in shotcrete applications[68] for repair work. The inclusion of organic polymers (styrene–butadiene rubber) improved the bond strength to old concrete[69] in repairs and overlay systems.

The hydration of rapid-setting cements formed in the system C_2S, $C_{11}A_7\bar{F}$, and $C_2(AF)$ have been studied with different admixtures of $CaSO_4$ and Portland cement.[70] The $C_{11}A_7\bar{F}$ hydrated the most rapidly and formed ettringite in the presence of sulfate. If calcium carbonate has been added to the mix, an aluminate carbonate hydrate is readily formed. As the SO_3/Al_2O_3 ratio is increased (by adding gypsum) from 0.26 to 0.51, the

Table 9.6 Compressive strengths for 1:3 mortar cubes made with commercial Jet cements A and B[65]

Cement	Cement content (%)	Fly ash content (%)	Compressive strength (MPa)							
			1 day	3 days	7 days	28 days	3 months	6 months	1 year	2 years
A	100	0	22.0	33.5	36.0	44.0	52.5	55.5	53.0	57.0
	90	10	12.0	37.5	41.5	50.0	56.5	60.5	61.0	53.0
	80	20	7.5	31.5	36.0	49.0	50.5	62.0	63.5	65.5
	70	30	6.0	19.0	29.5	41.5	55.0	62.5	63.5	66.0
	60	40	4.0	10.0	22.5	35.0	47.0	56.0	59.0	61.0
	50	50	3.0	3.5	14.5	25.5	40.5	45.0	49.0	51.0
B	100	0	29.5	34.5	42.0	46.5	55.5	59.5	58.0	57.0
	90	10	26.5	24.5	35.0	45.0	54.0	61.5	64.5	63.0
	80	20	22.5	18.5	31.0	39.0	54.0	60.0	66.5	68.5
	70	30	16.5	14.5	25.0	33.5	45.0	55.0	60.5	66.0
	60	40	13.0	11.5	19.0	26.5	41.0	53.5	50.5	60.5
	50	50	11.0	9.0	14.5	20.5	36.5	45.5	51.0	52.5

very early compressive strength (after 2 h and 1 day) is increased; however, a further increase in this ratio to 0.76 results in a drastic reduction in strength and the system expands in an uncontrolled fashion.

In the CaO–SiO_2–Al_2O_3–Fe_2O_3–SO_3–CaF_2 system, three quick-setting clinkers (A, B and C) (Table 9.7) have been developed based on the phases C_3S, C_2S, $C_{11}A_7\bar{F}$, $C_4A_3\bar{S}$ and $C_2(AF)$.[71] The burning temperatures required to produce low free CaO for the clinkers lay between 1250 and 1350°C, while setting times were in the range 6–16 min. It was demonstrated that blending these cements with secondary binders or fillers (limestone dust and blastfurnace slag) could lead to viable products (cements 1 to 5 in Table 9.8). The quick-setting cements show high strengths at very early ages and also at 28 days (45–64 MPa).

Table 9.7 Potential compound content of quick-setting clinkers (per cent)[71]

Clinker	C_3S	$C_{11}A_7\bar{F}$	$C_4A_3\bar{S}$	C_2S	$C_2(A,F)$
A	70	25	–	–	5
B	–	60	–	30	10
C	–	5	60	30	5

Table 9.8 Chemical composition of quick-setting cements (per cent)[71]

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	SO_3	F^-	TiO_2	LOI
1	16.6	11.9	1.12	56.0	1.85	1.09	7.84	1.29	0.07	2.03
2	14.2	19.0	1.25	48.7	2.57	0.86	7.12	0.96	1.17	4.05
3	12.2	21.1	1.00	44.9	1.67	1.11	12.8	0.49	0.69	4.17
4	19.7	18.0	1.14	46.8	4.01	0.87	7.63	0.76	1.06	–
5	5.78	21.0	1.40	51.0	0.48	1.06	9.21	1.25	1.32	7.93

Table 9.9 Ranges of composition for alinite and Portland cements[74]

Oxide constituent	Alinite cement	Portland cement
CaO	45–55	62–67
SiO_2	13–19	18–24
Al_2O_3	9–12	4–8
Fe_2O_3	4–10	1.5–4.5
MgO	1–10	0.5–4
$CaCl_2$	6–18	–
Limestone used to form clinker (%)	60–70	75–80

9.4.2 ALINITE CEMENTS

Alinite cement was developed in the former USSR and patented in 1977.[72] $CaCl_2$ added to the Portland cement clinker raw feed forms chloralinite ($Ca_{11}Si_3AlO_{18}Cl$) in the temperature range 1000–1100°C.[22,73] A class of cement based on this new cementitious phase has been produced commercially by clinkering at 1150°C, after adding 6–18 per cent $CaCl_2$ as a sintering aid (Table 9.9). The overall saving in energy in the production of alinite cements is ~1250 kJ/kg, amounting to a 30 per cent saving. Some chloride evaporates in the kiln and gives rise to a chloride cycle in the kiln. The strength properties of these cements are comparable to those of Portland cements. Magnesium is considered to be an indispensable ingredient of alinite, $Ca_{9.9}Mg_{0.8}\square_{0.3}[Si_{3.4}Al_{0.6}O_{16}]O_{1.9}Cl_{1.0}$.

The formula for alinite has been revised to $Ca_{10}Mg_{1-x/2}\square_{x/2}[(SiO_4)_{3+x}(AlO_4)_{1-x}/O_2/Cl]$.[75] Optimum quantities of MgO are claimed to be 3–4 per cent.[76] Production of Portland cement clinker at reduced temperatures (1000–1300°C) in $CaCl_2$ melts has been described:[72] diffusion constants of calcium, silicon, and aluminium ions are several orders of magnitude greater in these melts than in the normal Portland clinker melts, in spite of the lower temperatures, and the rate of production of the clinker minerals is 4–10 times higher than in the usual aluminoferrite melt. A lower lime component was obtained in mixes where the molar ratio CaO/SiO_2 was 2, with the composition $Ca_{2.15}SiO_{4.15}Cl_{0.07}$. A high lime component was obtained in mixes where the $CaO/SiO_2 = 3$ of composition $Ca_{3.06}Mg_{0.1}Al_{0.09}SiO_{5.2}Cl_{0.08}$.

The clinkers obtained from chloride melts could be formed into cements by simple grinding to cement fineness without the addition of calcium sulfate, and were found to be quick setting and to exhibit higher early and later strengths compared to the usual products at the corresponding low or high lime/silica ratio. Alinite cement production has been discussed in conjunction with refuse incineration.[21,77] Flue gas from refuse incineration contains acidic gas constituents HCl and SO_2 which are removed by reaction with $Ca(OH)_2$ and which results in solid residues containing chloride that can be used in the production of Alinite cement.

9.4.3 FLUORALINITE CEMENT

In an analogous manner to $CaCl_2$ melts in the alinite process, CaF_2 additions have been used to produce low-energy cements,[22,52] firing at temperatures from 950–1100°C for 20 min

Table 9.10 Potential phase composition of raw feeds 1, 2 and 3[22]

Raw feed	1	2	3
$C_{19}S_7 \cdot 2CaF_2$[a]	34.0	81.37	60.39
C_3S	39.4	–	–
C_2S	7.06	–	21.18
$C_{11}A_7 \cdot CaF_2$	6.6	6.32	6.32
C_4AF	9.87	9.31	9.31
Lime saturation factor III	95.9	94.3	86.8
Alumina ratio	1.68	1.68	1.68
Silica ratio	2.49	2.54	2.78
CaF_2	3.5	8.0	6.0

[a] Fluoralinite.

(Table 9.10). The fluoride contents are increased over that used for Jet cement. In contrast to the alinite process, with fluoride the problems of reinforcement steel corrosion in concrete do not occur.[78] Fluoralinite cement was prepared at ~1100°C from an industrial raw meal with additions of CaF_2;[22] the grindability of the clinker was improved.

The possibility of reducing the temperature of burning for the synthesis of calcium silicates is opened up by the results of a study.[55] In addition, the energy of grinding may be reduced. The use of sintering agents ZnO and CaF_2 permitted the formation of alites at 1150–1250°C. The presence of CaF_2 alone resulted in a slight retardation of the hydration, but this could be corrected by the inclusion of SO_3 in the feed.[78]

9.5 Low-energy clinker production

The development of low-energy cementive systems has been particularly active in China. Reviews of energy-saving cements which are being produced in China have been published,[79–81] together with their practical applications. Six types of cement have been briefly described.

- $CaO–SiO_2–Al_2O_3$ system (NA). The amount of CaO in the system is only enough to form minerals with a lower lime content, such as $CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$ and $2CaO \cdot SiO_2$. The object of the raw mix design is to limit the quantity of the unreactive product $CaO \cdot Al_2O_3 \cdot SiO_2$ by limiting the amount of silica in the charge, which is composed of limestone and high-grade alumina. The clinkering temperature is 1400°C.
- $CaO–SiO_2–Al_2O_3–CaCl_2$ system (LC). Eutectic mixtures of CaO and $CaCl_2$ are formed which greatly decrease the clinkering temperature. At 600°C an intermediate compound $2CaO \cdot SiO_2 \cdot CaCl_2$ is formed which is transformed at ~975°C to a high-temperature type. Both the low- and high-temperature types are non-hydraulic. At about 1050°C, high lime mixes begin to form alinite (approximately $21CaO \cdot 6SiO_2 \cdot Al_2O_3 \cdot CaCl_2$). Alinite remains stable between 1050 and 1250°C. Al_2O_3 in the system forms $11CaO \cdot 7Al_2O_3 \cdot CaCl_2$, starting at 750°C and remaining stable up to 1300°C. Starting from a raw feed made up of limestone, fly ash and alkali slag, the cement clinker is found to contain alinite, $11CaO \cdot 7Al_2O_3 \cdot CaCl_2$ and α'-$2CaO \cdot SiO_2$. The clinkering temperature is 1200°C.

- $CaO–SiO_2–Al_2O_3–CaF_2$ system ($\bar{\mathrm{F}}$A). The introduction of CaF_2 greatly reduces the clinkering temperature: α'-$2CaO\cdot SiO_2$ forms at 800°C and the inactive $2CaO\cdot SiO_2\cdot CaF_2$ forms at 900°C, remaining stable up to 1040°C when it decomposes to CaO and liquid. At 1100°C, a second fluoride mineral, $11CaO\cdot 4SiO_2\cdot CaF_2$, forms which is non-hydraulic, but melts and decomposes to give hydraulically active $3CaO\cdot SiO_2\cdot CaF_2$. Thus a form of alite is produced at a temperature 200°C below the normal formation temperature of alite. Al_2O_3 can form two minerals, $11CaO\cdot 7Al_2O_3\cdot CaF_2$ or $3CaO\cdot Al_2O_3$, the formation temperature of the fluoride compound being 1050°C. This fluoraluminate cement is formed from limestone, alumina and fluorite. The clinkering temperature is 1300°C.
- $CaO–SiO_2–Al_2O_3–CaSO_4$ system ($\bar{\mathrm{S}}$A). $CaO\cdot Al_2O_3\cdot SiO_2$ first forms and is then converted to $4CaO\cdot 3Al_2O_3\cdot SO_3$ ($C_4A_3\bar{S}$) and α'-$2CaO\cdot SiO_2$ at 1000°C; the sulfoaluminate is decomposed at 1200°C and $2CaO\cdot SiO_2\cdot CaSO_4$ is formed as an intermediate in the temperature range 1200–1280°C. Sulfoaluminate cement is formed from raw feed composed of gibbsite, limestone and gypsum, at a clinkering temperature of 1350°C.
- $CaO–SiO_2–Al_2O_3–Fe_2O_3–CaSO_4$ system (FA). The introduction of Fe_2O_3 promotes the conversion of $2CaO\cdot Al_2O_3\cdot SiO_2$ to $4CaO\cdot 3Al_2O_3\cdot SO_3$ and α'-$2CaO\cdot SiO_2$, and reduces this conversion temperature to 1250°C. The clinker contains a ferrite which is similar to that of the solid-solution series $2CaO\cdot Fe_2O_3$–$6CaO\cdot 2Al_2O_3\cdot Fe_3O_3$ in Portland cement, together with free $CaSO_4$, $4CaO\cdot 3Al_2O_3\cdot SO_3$ and α'-$2CaO\cdot SiO_2$. It can be formed from raw mixes composed of limestone, ferroalumina slags and gypsum, at a clinkering temperature of 1300°C.
- $CaO–SiO_2–Al_2O_3–Fe_2O_3–CaSO_4–CaF_2$ system (HCA). In contrast to the fluoride-free system, $3CaO\cdot SiO_2$ can form in this system. By changing the ratios of components, a clinker containing $3CaO\cdot SiO_2$, $4CaO\cdot 3Al_2O_3\cdot SO_3$, $6CaO\cdot Al_2O_3\cdot 2Fe_2O_3$ and $11CaO\cdot 7Al_2O_3\cdot CaF_2$ or $3CaO\cdot Al_2O_3$ can be formed. A high-calcium sulfoaluminate cement clinker is made from a raw feed composed of limestone, high-alumina clay, gypsum and fluorite (or slag). The clinkering temperature is 1300°C.

The compressive strengths of the above cement types are illustrated in Table 9.11. All appear to give high early strengths and show no evidence of strength regression during the

Table 9.11 Compressive strengths of six rapid-hardening cements[80]

	Compressive strength (MPa)			
Cement type	12 h	1 day	3 days	28 days
NA	31.3	43.6	51.5	80.0
$\bar{\mathrm{S}}$A	37.3	67.2	81.8	–
FA	–	57.9	77.6	85.4
HCA	–	34.3	46.3	63.5
$\bar{\mathrm{F}}$A	31.4	40.9	–	53.8
LC	–	38.6	54.5	83.4

28-day water storage period examined. Practical applications of these cements have been quoted.[80]

Winter concreting has been carried out at −25°C using cement $\bar{S}$A. Quick-hardening cement FA has high resistance to sea water and has been used to carry out rapid repairs and construction in marine conditions. Cements NA and $\bar{F}$A have been used for repairs of airport runways. The slightly expansive cements $\bar{S}$A and FA were used to repair damaged cellars. Shotcreting has been applied using cements $\bar{S}$A and FA. Self-stressing cements NA, $\bar{S}$A and FA have been used to make pressure pipes of various diameters. A detailed review of the development of low-energy cements throughout the world has been published.[20]

9.5.1 BELITE CEMENTS

Work on the subject of belite cements can be split into three groups:[82]

1. hydraulic activity of the C_2S phase;
2. hydraulic activity of belite-rich cements without additional cementive components;
3. hydraulic activity of belite-rich cements with additional components such as $C_4A_3\bar{S}$.

In group 3, low-energy production of a rapid-hardening, belite-rich cement is possible as a result of the sulfoaluminate content, even where the belite is in the usual β form having a low hydraulic reactivity.

The chemical composition of the blended raw feed and the final clinker may be represented using a number of component ratios in order to aid in the selection and control of manufacture. The lime saturation factor or lime standard is the most important of these ratios. It expresses the maximum amount of lime that can be combined with the various oxides present, based on the chemical formulae for the cement minerals being formed (C_3S, C_2S, C_3A, C_4AF) and on the high-temperature phase diagram. A number of definitions of lime saturation factor are used in the literature,[83] for example:

$$\text{lime saturation factor} \equiv \frac{100\%\ \mathrm{CaO}}{2.8\%\ \mathrm{SiO_2} + 1.1\%\ \mathrm{Al_2O_3} + 0.7\%\ \mathrm{Fe_2O_3}} \tag{9.2}$$

One approach to a reduction in energy consumption and to a reduction in the release of CO_2 in the production of cements, is to reduce the lime saturation factor of the raw feed.[84] A reduction in lime saturation factor leads automatically to an increasing belite content and a decreasing alite content.[82] With lime saturation factor = 75 per cent, a virtually alite-free clinker is obtained and $C_{12}A_7$ is formed instead of C_3A.

A reduction in lime saturation factor from 100 to 75 results in a 12 per cent reduction in theoretical heat requirement; however, a reduction of only 6 per cent in CO_2 emission occurs (Figures 9.4 and 9.5). This result appears to arise because of the reduced heat evolution during crystallisation of silicate minerals if they consist of belite rather than alite.

A predominantly belite cement has a theoretical heat of formation ~150 kJ/kg less than a conventional alite cement.[82] In forming these cements, raw materials of lower lime content can be exploited. The reduction in $CaCO_3$ content of the raw feed reduces the energy demand (by about 10 per cent for a lime saturation factor of 80–85 per cent) and allows a satisfactory clinker to be formed at lower temperatures (lower by 150°C)

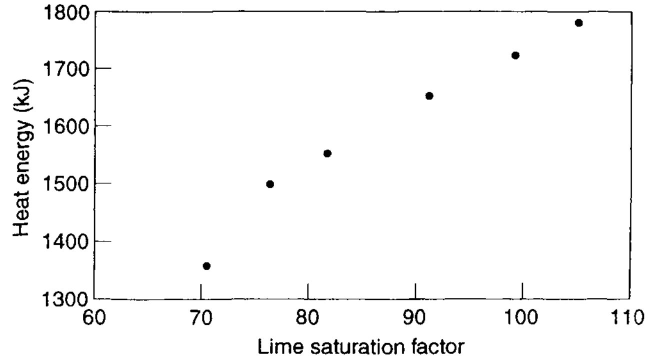

Fig. 9.4 Effect of lime saturation factor on heat energy required (after Ref. 85).

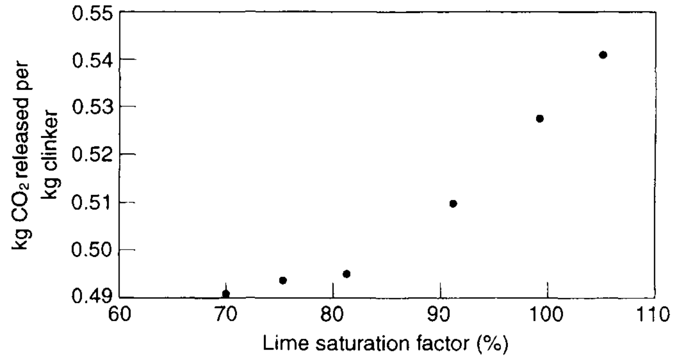

Fig. 9.5 Effect of lime saturation factor on the CO_2 released during clinker production (after Ref. 85).

(Figure 9.6).[84] Laboratory investigations have been carried out on cement raw feed based on natural marls, by heating 11 mm pressed cylinders up to clinkering temperature at 50°C/min, holding them at that temperature for 20 min, and then cooling at 800°C/min. Figure 9.6 shows the reduction in firing temperature which is possible by reducing the lime saturation factor; however, clinkers with lime saturation factor III > 80 per cent still need to be fired at temperatures >1250°C.

A reduced lime saturation factor results in easier grinding. The compressive strength development for mortars made from laboratory cements of different lime saturation factor is shown in Figure 9.7 fired at different temperatures according to Figure 9.6.[84] The strength development for cements with lime saturation factors of 84 per cent and above is adequate, even in the early period of hydration. The marked drop in reactivity for the cement with a lime saturation factor of 80 per cent cannot be compensated by increased cement grinding or increased sulfate level. It is argued that a certain minimum percentage of alite is required in the cement (~15 per cent) for the cement to perform in a near-normal manner;[19] this alite content may be derived either from the low-energy clinker or from normal Portland cement clinker blended with the low-energy clinker.

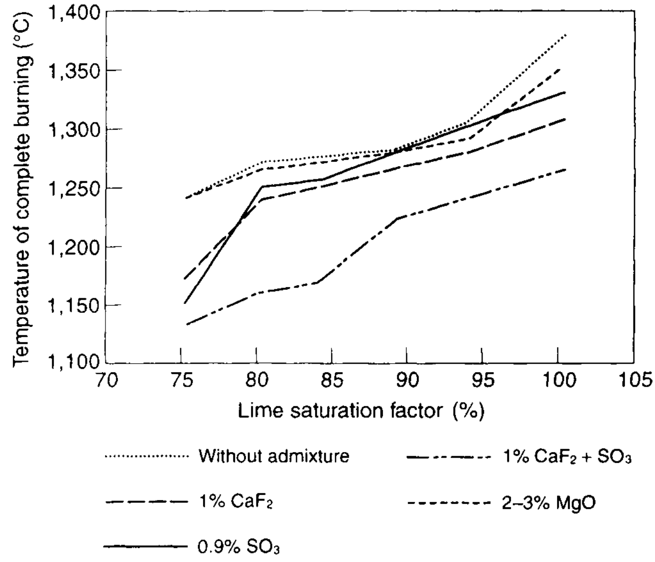

Fig. 9.6 Burning temperature for complete combination (<2 per cent free lime) versus lime saturation factor of cement raw feed based on natural marls (source: Ref. 84).

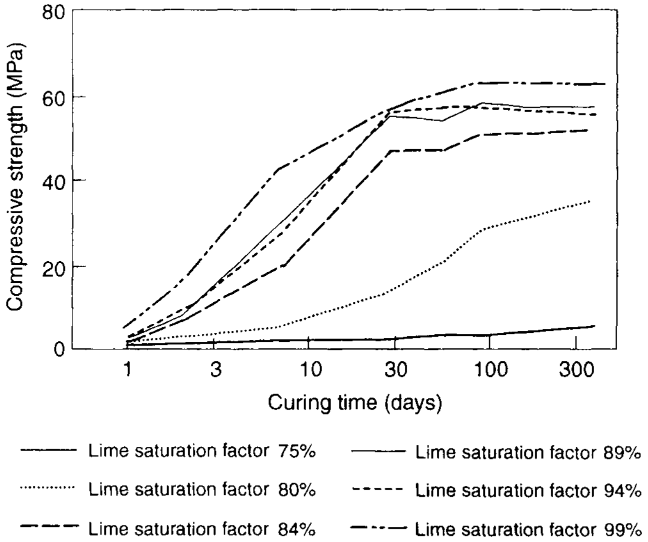

Fig. 9.7 Effect of lime saturation factor on compressive strength (source: Ref. 84).

The most effective cement feed for forming cement clinker at 1250°C is one containing CaF_2+SO_3 as a flux, but the use of this mineraliser does not result in cements showing adequate strength when the lime saturation factor is below about 90 per cent. The rheological properties of belite cement pastes have been examined.[86]

9.5.2 *ACTIVE BELITE CEMENTS*

In order to produce Portland cements with adequate strength at lime saturation factors below about 85 per cent, a belite which has improved reactivity is required. Several possible approaches to the improvement in reactivity of C_2S have been suggested:[84]

- rapid quenching of the clinker, in order to stabilise a high-temperature polymorph;
- the introduction of impurity ions during formation at high temperature (alkalis, sulfate, etc.) into the crystal structure, again to stabilise a high-temperature polymorph;
- the addition of normal Portland cement clinker to the C_2S clinker in order to accelerate the rate of hydration.[19,84]

Pure C_2S exhibits five polymorphic forms, depending on temperature and pressure during formation;[87] all are metastable except the γ form.

$$\alpha \xrightarrow{1425°\text{C}} \alpha'_H \xrightarrow{1160°\text{C}} \alpha'_L \xrightarrow{680°\text{C}} \beta \xrightarrow{<500°\text{C}} \gamma$$

In Portland cement the equilibrium temperature between α and α'_H is 1280°C and the conversion reaches a maximum rate at 1100°C. With decreasing cooling rate, the α'_H phase tends to dominate, and finally the belite is composed entirely of this form, which transforms into β-C_2S after passing through the α'_L form.[88]

The β form exists in Portland cement and is slowly reactive with water to form cementive hydrates. The α and α' forms are also hydraulic. The speed of hydration of β-C_2S can be increased by imparting a stressed condition through thermal shock, or through the formation of small crystallites using gel techniques or spray drying in the preparation of the raw feed, followed by firing at temperatures in the range 750–940°C. For cement raw feed with lime saturation factor II of 80–90 per cent, and different alkali contents, quenching yields α-belite at high alkali content (1.49 per cent equivalent Na_2O) at the fastest cooling rate, while at lower alkali contents a new polymorph β^* is identified, having increased hydraulic properties (Table 9.12).[89] The introduction of impurity ions into the crystal lattice has been explored.[46]

The most important aim for the development of active belite cement is to reduce the energy consumption for cement manufacture. However, the maximum burning temperature may be reduced, leading incidentally to reduced NO_x formation. The

Table 9.12 Compressive strengths (MPa) of cement paste cubes (water/cement = 0.6) formed from belite-rich clinkers (lime saturation factor = 70–80%)[89]

Main belite phase	Cooling rate (°C/min)	3 days	7 days	28 days	90 days
α	50 000	3.1	8.9	20.9	29.6
α'	3 000	1.4	2.0	6.7	10.0
β^*	50 000	–	2.8	8.2	21.8
β	2.0	2.2	3.3	3.9	8.3
β^* annealed for 2 h at 850°C giving α'	50 000	1.4	2.0	2.4	13.5

production of active belite cement allows the use of lower grade limestone, the belite formed being activated either by thermal or by chemical means. Typically, the lime saturation factor lies in the range 75–85 per cent: thermal activation is achieved by quenching in the temperature range 1300 to 900°C, with a cooling rate of at least 800°C/min. This quenching procedure results in stabilisation of α'-belite by the incorporation of alkalis or other foreign ions in amounts up to 5 per cent. The deliberate addition of alkali sulfates fails to stabilise the α'-belite modification and only quenching is able to achieve a high-strength belite. Pilot plant investigations yield cements with strengths between 16 and 22 MPa after 3 days and 50–60 MPa after 28 days. Production of an active belite cement with lime saturation factor between 80 and 82 per cent allows a reduction in energy consumption of 10–14 per cent, and a decrease in burning temperature of 100°C. Both β- and α'-belites have also been stabilised by P_2O_5; α'- form was found to hydrate faster than the β form.[90]

Belite is a major phase in active belite cements and is chiefly present in the α and α' modifications, stabilised either by rapid cooling in the temperature range 1300–900°C,[20] or by the use of higher alkali levels.[78] It has been suggested that the hydraulic activity of β-C_2S is related to the calculated strength of the Ca–O ionic bond.[28] A study of the relationship between crystal structure and hydraulic activity, including synthetic β-C_2S and samples separated from Portland cement, indicates that the electric field strength at the site of the Ca^{2+} ions in the crystal lattice determines the hydraulic activity.[91] The ease of early hydration increases for samples of pure C_2S that have been quenched in CCl_4. Hydration rates of impure belite extracted from Portland cement are lower than those for pure C_2S quenched in CCl_4.

The work of Ono[92] shows that rapid cooling may result in 40 per cent of the belite remaining in the α modification sandwiched between fine lamellae of disordered β-C_2S; exsolution of impurities fails to occur on cooling. The overall result from these studies led to the suggestion that among belites there is no hydraulic activity sequence of general validity (e.g. $\alpha > \alpha' > \beta > \gamma$), and that the measured strength generation depends on the actual experimental conditions (burning temperature, cooling rate, foreign oxide content, etc.). In principle, it is claimed that both hydraulically highly active and nearly inactive forms may be possible for all belite modifications.[89]

Experiments have been conducted, using industrial limestone and clay, on kiln feeds designed to lime saturation factors between 70 and 101 per cent. A range of firing temperatures from 1150 to 1450°C, and a range of clinker cooling rates between 20 and 3000°C/min, in the temperature interval 1350–700°C, were applied. An increase in strength is achieved for the lower range of lime saturation factors by increasing the cooling rate of the fired clinker (Figure 9.8).[82] Strength is increased at both 3 and 28 days. Comprehensive investigations of the conditions necessary for the production of active belite have indicated that the rate of cooling of the clinker plays the important role where the lime saturation factor is below about 90 per cent, especially as far as the 28-day strengths are concerned.[78,82] The increase in strength between quenched and slowly cooled clinker with a lime saturation factor of 80 per cent, was 5 MPa after 3 days and 40 MPa after 28 days. In agreement with this result, rapid cooling of low-lime clinkers improved hydraulic activity[93] but had no influence on the activity of high-lime clinkers.[82] The difference in phase composition of clinkers cooled at different rates is shown in Table 9.13.[94,95] A lime saturation factor of 80–82 per cent allowed a reduction in energy of production of at least 10–14 per cent, and a reduction in temperature of clinkering of >100°C. The rate of cooling of the clinker in the temperature range 1300–900°C, in which

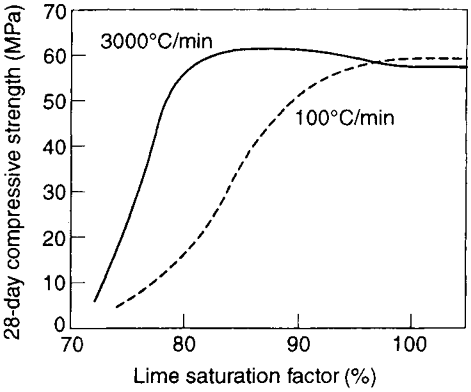

Fig. 9.8 Effect of the quenching rate of clinkers of different lime saturation factors on their strength generation capacity (source: Ref. 82).

belite is the main mineral, is the most important factor affecting the development of strength.[94] A cooling rate of 1000°C/min was achieved in a pilot plant and resulted in high early strengths of 16–22 MPa at 3 days and 50–60 MPa at 28 days. This high cooling rate was achieved by crushing the hot clinker. An addition of anhydrite rather than gypsum was made in order to control the setting.

An active belite cement has been produced in sufficient quantities to enable a concrete road to be constructed (in 1984). The concrete was tested for durability performance after 4 years[96] and found to have similar degrees of carbonation and frost resistance to a concrete using Portland cement. The compressive strengths after 4 years were virtually identical, but somewhat smaller for the belite cement after 3 days (16.7 and 22.4 MPa) and after 28 days (45.9 and 53.0 MPa). The cement [95] exhibited a lime saturation factor (I) between 80.5 and 81.7. Its silica ratio lay between 2.7 and 2.9 and its alumina ratio lay between 2.3 and 2.6. Its mineralogical composition (in per cent) was alite 27–29, α'-C_2S 21–30, β-C_2S 14–30, C_3A 6–7 and ferrite 16–18. The theoretical heat required to form the cement was 1630–1680 kJ/kg of clinker. Rapid cooling was achieved in an air-fluidised trough, giving rates of temperature change of 1100°C/min, in a rotary cooler, or by hot comminution in an impact mill attached to the rotary kiln. Highest strengths were achieved using the air-fluidised bed cooler (28-day strengths varied between 43 and 59 MPa depending on the cooling rate).

Table 9.13 An example of the phase composition of low-lime clinkers cooled at high and normal rates[94]

Cooling rate (°C/min)	1000	100
Alite	30	24
α'-C_2S	48	7
β-C_2S	0	44
C_3A	10	15
C_4AF	9	6
MgO	3	4
Amorphous glass	0	0

The frost resistance of cement paste and mortar specimens has been measured for cements formed from clinkers with lime saturation factors between 69 and 97 per cent. The clinkers were burnt at temperatures between 1380 and 1430°C.[97] The phase composition had C_2S contents of 25–71 per cent and alite contents of 0–43 per cent. It was found that the strength retained after freeze–thaw cycles was higher for the high-belite cement than for Portland cements. It was proposed that the weak link in the microstructure was provided by the $Ca(OH)_2$ crystals and, as belite cements produce less $Ca(OH)_2$ on hydration, they are consequently better able to resist frost damage. This view is based on the fact that reduced temperatures increase the solubility of $Ca(OH)_2$ and thus cause an increase in the porosity of the microstructure at the surface of the portlandite crystals during freeze–thaw cycling.

In another investigation, the normal processes of cement technology were adopted, except that the clinkering temperature was reduced by 100°C, at 1365°C.[98] The influence of lime saturation factor and quenching rate are investigated: for a lime saturation factor of between 70 and 101 per cent, cooling rate affects the hydration rate up to a lime saturation factor of 90 per cent; beyond this, the cooling rate does not affect strength. Strengths after 3 and 28 days of approximately 15 and 60 MPa, respectively, can be achieved. The firing temperature is reduced to 1350°C and quenching at a rate of 1000°C/min is employed.

The role of alkali in the stabilisation of β-C_2S has been reviewed.[23] The influence of alkali on the stabilisation of high-temperature forms of dicalcium silicate, and the increased hydraulic activity of the dicalcium silicate phase has been studied.[99,100] K_2O is found to be incorporated into the C_2S phase and results in the stabilisation of the α' form. It is stated that the α'_L form can be stabilised by the inclusion of barium, magnesium, manganese and boron oxides, or by inclusion of $CaNPO_4$. Rapid cooling of the clinker assists in the stabilisation of this hydraulically active phase. The highest 7-day strengths are recorded for high-alkali samples, and generally water or air quenching improves the strength levels, the improvements being greatest for the highest alkali levels.

Alkali oxide in C_2S-rich clinkers (particularly Na_2O) induces an increase in the compressive strength for the corresponding cements, and modest strength enhancement is attained by high cooling rates for the low-lime clinkers at all alkali levels (Table 9.14). In general, active-belite cements have lower early and higher late strengths compared to alite-rich Portland cement.

Active-belite cements, stabilised with chromium oxide as a component in the raw feed, have also been examined.[101] Low- to medium-grade limestones are employed to produce clinkers in the laboratory, firing the mixes at 1350, 1400 and 1450°C. The cements (with 4–5 per cent Cr_2O_3 giving the highest strengths at 1 day and 28 days) were observed to be sound; the β-C_2S does not undergo dusting to the γ modification. The lime saturation factor was maintained between 95 and 100 per cent, the silica ratio between 1.7 and 1.8, and the alumina ratio between 1.2 and 1.3. An active belite can be produced from barium-contaminated waste.[102] Raw feed with lime saturation factors of 70, 85 and 90 per cent are blended with 1 per cent barium waste. After firing at 1350 or 1450°C, compressive strengths are determined up to 28 days. The strengths of the clinker containing barium are somewhat higher for the mix with a lime saturation factor of 70 per cent. A reduction in heat consumption during manufacture is observed.

In some investigations, the presence of pozzolanas, and to a lesser extent blastfurnace slag, has been found to accelerate the hydration of β-C_2S.[103] In contrast, other investigations find the presence of blastfurnace slag reduces the rate of hydration of belite.[105] γ-C_2S is normally regarded as non-hydraulic,[20] although a slow hydration has been reported;[104] in the presence of silica fume, no hydration of γ-C_2S took place.

Table 9.14 Effect of alkali content and cooling regime of low-lime clinkers[a] on the strength of the corresponding cements[101]

Alkali oxide (%)			Cooling mode[b]	Compressive strength (MPa)			
K_2O	Na_2O	Equivalent Na_2O		2 days	7 days	28 days	90 days
0.23	0.04	0.193	a	5	6	32	42
0.25	0.04	0.192	b	4	7	31	40
0.28	0.04	0.206	c	4	7	29	41
0.57	0.04	0.226	a	5	10	51	56
0.54	0.04	0.419	b	3	10	43	50
0.50	0.04	0.399	c	4	9	30	46
1.01	0.04	0.373	a	3	11	47	50
1.01	0.04	0.712	b	4	12	42	44
1.02	0.04	0.712	c	5	12	38	45
1.46	0.04	1.001	a	6	17	53	56
1.42	0.04	0.974	b	4	17	42	48
1.46	0.04	1.000	c	5	16	39	46
0.23	0.63	0.781	a	6	14	60	59
0.22	0.65	0.794	b	5	14	47	55
0.24	0.65	0.808	c	5	9	31	47
0.25	1.08	1.245	a	5	17	59	59
0.24	1.11	1.268	b	5	15	48	58
0.26	1.10	1.271	c	4	9	38	55
0.25	1.65	1.815	a	6	22	64	64
0.25	1.63	1.795	b	6	17	45	47
0.24	1.61	1.768	c	5	9	33	45
0.26	0.15	0.321	a	5	11	50	57
0.27	0.18	0.358	b	6	11	50	48
0.27	0.17	0.348	c	5	8	30	41
0.53	0.49	0.839	a	5	11	54	60
0.54	0.47	0.825	b	6	11	47	58
0.48	0.49	0.806	c	5	10	39	54
0.76	0.80	1.300	a	7	15	60	62
0.75	0.77	1.264	b	6	13	48	56
0.77	0.81	1.317	c	5	11	32	46

[a] Lime saturation factor II = 80%, silica ratio = 2.4, alumina ratio = 2.0.

[b] a, cooling in water; b, cooling in air; c, cooling in furnace.

Synthetic belite and alite (as well as 70:30 and 30:70 mixtures) were hydrated with 2 per cent SO_3 added as pastes at a water/cement ratio of 0.4, after casting as $10 \times 10 \times 60$ mm prisms.[105] The influence of replacing these synthetic cements with commercial blastfurnace slag was explored by measuring compressive strength development and heat of hydration after curing for periods up to 365 days under water at 20°C. The hydration of belite was significantly retarded by the presence of blastfurnace slag. The presence of alite, or normal Portland cement clinker,[20] greatly accelerated the hydration of the belite and it was suggested that the presence of $Ca(OH)_2$ is required to ensure a full hydration rate for both blastfurnace slag and belite.

9.5.3 BELITE–ALUMINATE AND –SULFOALUMINATE CEMENTS

The development of an aluminous-belite cement (Table 9.15) was described by Zakharov[106,107] in which avoidance of the formation of hydraulically unreactive C_2AS and CAS_2 was the guiding principle. This was achieved by rejecting any attempt at equilibrium through sintering, reliance being placed on the rapidity with which CA (or $C_{12}A_7$) and β-C_2S could be formed through solid–solid interactions at relatively low temperatures (below 1250–1300°C). The inclusion of mineralisers was of value; gypsum was found to be a useful compound in this respect, and also a stabiliser of β-C_2S. It is reported that $C_4A_3\bar{S}$ is formed at ~1270°C. An effective mineraliser is a molar mix of CaF_2 with $CaSO_4$, when firing in the temperature range 700–1200°C. Equally effective is a mix of CaF_2 and roasted pyrites ($FeSO_4$). Strength tests for aluminous-belite cements show a continuing increase in strength up to 3 years' hydration (Table 9.16). Mortar specimens show good resistance to sulfate solutions and to freeze–thaw cycles.

In the presence of sulfate, two ternary compounds, $C_4A_3\bar{S}$ and $C_5S_2\bar{S}$, can form in the C–S–A–$\bar{S}$ system;[20] $C_5S_2\bar{S}$ is stable in a narrow range of temperature, 1100–1180°C, and decomposes to form C_2S and $C\bar{S}$; the phase $C_4A_3\bar{S}$ is stable up to 1400°C. The sequence of reactions that take place is

1. formation of C_2S at 800 to 900°C, with the formation of C_2AS;
2. above 1000°C, $C_4A_3\bar{S}$ and $C_5S_2\bar{S}$ are formed and C_2AS disappears;
3. the phase $C_5S_2\bar{S}$ disappears above 1180°C to form α'-C_2S and $C\bar{S}$.

The quantity of $C_4A_3\bar{S}$ reached a maximum at 1200°C. The phase $C_5S_2\bar{S}$ does not have hydraulic properties, while $C_4A_3\bar{S}$ does and forms ettringite on hydration in the presence of $C\bar{S}$ and lime. The preferred temperature for formation of these cements lies above 1200°C. Depending on the composition of the mix, the phases $C_{12}A_7$ or CA also appear.

Studies of long-term properties of Portland cements with added $C_4A_3\bar{S}$, were carried out during the development of expansive cements.[108,109] Compressive strengths were reported for periods up to 5 years and showed a decline beyond 3 years (Table 9.16).

Cement clinker may be produced in the system CaO–Al_2O_3–SiO_2–SO_3 with $C_4A_3\bar{S}$ and β-C_2S as the main components.[79] The SO_3 present inhibits the formation of C_2AS. By adjusting the added gypsum content, a series of cements ranging from rapid-hardening to self-stressing can be produced. These cements are manufactured on an industrial scale in China[79] and used for the production of self-stressing concrete pipes and other concrete products, and for rapid-repair systems. Strength test results up to 2 years have been presented. Compressive strengths are found to increase over the period to 1 year,[109] but

Table 9.15 Compressive strength development in aluminous-belite cement mortar (1:3)[106]

Storage condition	Compressive strength (MPa)									
	1 day	3 days	7 days	28 days	2 months	3 months	6 months	1 year	2 years	3 years
Water	19.6	26.5	27.5	27.5	28.4	31.4	38.3	38.3	39.2	40.2
Air	19.6	21.6	25.5	28.4	29.4	36.3	46.1	46.1	51.0	53.0
Combined air and water	19.6	26.5	27.5	29.4	31.4	44.1	66.7	66.7	71.6	76.5

Table 9.16 Compressive strength of expansive cement mortars[108]

Storage condition	Compressive strength (MPa)								
	1 day	3 days	28 days	6 months	1 year	2 years	3 years	4 years	5 years
Stiff-consistency mix									
Water	31.3	33.5	33.7	37.9	51.2	50.7	52.5	53.3	46.2
Air	31.3	37.8	46.9	45.3	46.8	46.3	39.0	35.9	34.4
Plastic-consistency mix									
Water	16.0	20.8	29.8	33.6	31.9	33.6	34.3	28.1	30.5
Air	16.0	17.7	28.6	27.1	30.9	27.7	24.5	23.2	21.2

a decline in strength follows at later ages, and specimens show accelerating expansion in sulfate solutions.

A notable property of C_2S–$C_4A_3\bar{S}$ cements is a very high early strength (15 MPa after 2 h). A sulfoaluminate–C_2S cement has been reported in which the C_2S was stabilised in the α' form by SO_3 in the lattice.[52] The raw materials for cement manufacture are blastfurnace slag and gypsum, together with some limestone and alumina, the system being fired at 1200 or 1300°C. For the highest strengths, cements are fired below the solidus temperature; if melt is allowed to form, hydration is retarded.[52] Rapid-hardening, high-strength cements are formed in the CaO–Al_2O_3–SiO_2–SO_3 system by burning at between 1250°C and 1300°C.[110] The minerals produced are $C_4A_3\bar{S}$ and C_2S. A commercial cement named Porsal cement has been produced based on 55–60 per cent β-C_2S, 10–20 per cent $C_4A_3\bar{S}$, 5–10 per cent CA and 0–17 per cent $C_{17}A_7$, which has a strength similar to that of Portland cement.[111]

Cements based on $C_4A_3\bar{S}$ can be produced at temperatures much lower than those required by Portland cement.[20,112] The clinkers are relatively friable after firing and require little energy to be ground. High early strength, low-energy cements containing $C_4A_3\bar{S}$, β-C_2S or $C_5S_2\bar{S}$ and $C\bar{S}$ can be synthesised from both pure chemicals and industrial by-products, such as fly ash and blastfurnace slag. Phosphogypsum greatly increases the rate of $C_4A_3\bar{S}$ formation, owing to the presence of phosphate mineraliser. Cements which contain $C_5S_2\bar{S}$ rather than β-C_2S are found to show very high early and late strengths; however, strength loss is observed at ordinary humidity levels because carbonation leads to decomposition of the ettringite hydration product. A loss of strength amounting to between 35 and 70 per cent has been reported within 1 year under normal atmospheric conditions.[112] The blending of fly ash or slag with the cement based on $C_4A_3\bar{S}$ reduces the 1-day strength but enhanced the 28-day strength. The dimensional stability of pastes based on $C_4A_3\bar{S}$ cement is similar to that found with Portland cement pastes. When $C_4A_3\bar{S}$ and gypsum are present, ettringite forms rapidly.[67]

Calcium sulfoaluminate cements have been developed for low temperature applications and have been shown to exhibit high resistance to sulfates.[67]

The phase composition of the five-oxide system CaO–SiO_2–Al_2O_3–Fe_2O_3–SO_3 has been described.[113] There are three sulfate phases, $C_5S_2\bar{S}$, $C_4A_3\bar{S}$ and $C\bar{S}$. Laboratory mixes can be prepared by heating in a sealed platinum crucible at 1000–1200°C for 4–20 h. The practical formation of sulfoaluminate cements have been developed using limestone, fly ash and gypsum as raw materials.[114] Fly ashes with high sulfate contents provide a valuable raw material for the production of sulfoaluminate belite clinkers.[114,115] These cements can be synthesised at temperatures 200–300°C lower than Portland cement clinkers and are easier to grind to cement fineness. Clinkers containing $C_4A_3\bar{S}$, $C_5S_2\bar{S}$ and anhydrite can be synthesised by a single firing at 1200°C of mixes composed of natural minerals or industrial wastes (fly ash, phosphogypsum, blastfurnace slag).[116] The readily ground clinker hydrates rapidly, giving good wet strengths (after 1 day, 35–50 MPa; 28 days, 58–76 MPa). Strengths are greatly increased in dried-out specimens, measured on 25 mm cubes; shrinkage/expansion data have been collected on 100 × 12.5 × 12.5 mm bars, at a water/solid ratio of 0.4. Strengths reach a maximum after 100 days and then either remain constant or tend to slowly fall. Specimens which are kept wet expand slowly; unfortunately, results were only presented for periods up to 1 year. Significantly, accelerated carbonation tests (in 4 per cent CO_2) show that the specimens have only moderate resistance to carbonation. Under normal atmospheric conditions, strength is reduced from a peak value after 6 months to about 90 per cent of this value after 1 year. Under accelerated carbonation for 28 days, the strength dropped to about 67 per cent of the initial value and the quantity of ettringite present fell from 47.9 to 18.5 per cent. The $C_5S_2\bar{S}$ present may hydrate, but only very slowly.

Belite clinkers with good hydraulic properties can be produced from raw feed materials with a reduced content of Fe_2O_3 by increasing the MgO content (to 10 per cent) and increasing the SO_3 content to 5 per cent. Firing temperatures are up to 200°C lower than for Portland cement clinker.[117] The high activities of the clinker were attributed to the formation of $(C,M)_4A_3\bar{S}$.[118] The possibilities of producing a white belitic cement have been explored.[118] Firing temperatures lie between 1170°C and 1350°C, depending on the starting materials employed. The compressive strength (at ages up to 28 days) of the ground clinker after hydration is increased by the presence of 7 per cent MgO, but falls away for the 10 per cent MgO clinkers. Strengths are increased by increasing the firing temperature and by increasing the lime saturation factor. Sol–gel technology has been used to form white cements at 1280°C from the $CaO–Al_2O_3–SiO_2–CaF_2$ system showing high early strengths (29, 36, 42 and 74 MPa at 1, 3, 7 and 28 days).[67]

Sulfoaluminate belite cements have been synthesised from raw feed containing fly ash, limestone and gypsum by clinkering at 1200°C for 30 min.[119] Free lime contents are high but this was found to have no harmful effects. Compressive strengths at ages up to 28 days are presented in Table 9.17. Waste products from the water purification industry have been examined as a source of alumina.[120]

Incorporation of CaF_2 lowers the clinkering temperature, and α'-C_2S formation occurs at about 800°C. This compound reacts with CaF_2 at ~900°C to form $2C_2S \cdot CaF_2$, which is non-hydraulic. It decomposes eventually to give C_3S (containing ~1.5 per cent F^-). In the presence of Al_2O_3 another ternary compound, $C_{11}A_7 \cdot CaF_2$, is formed at ~1050°C.[20] The influence of a wide range of mineralisers on the formation and hydration of belite–sulfoaluminate cements has been studied.[121]

9.5.4 BELITE–ALUMINOFERRITE AND –SULFOFERRITE CEMENTS

The hydraulicity of C_4AF is reported to be dependent on the conditions of formation, formation at lower temperatures (1200°C) resulting in a more hydraulic cement.[27] The hydration of pure calcium aluminoferrite has been investigated;[122] high strengths are found to result from its hydration. The cements were formed by melting at 1360°C and then

Table 9.17 Compressive strengths of mortar specimens after storage in humid conditions (MPa)[119]

	Water/cement = 0.5			Water/cement = 0.4			
Number	1 day	7 days	28 days	1 day	7 days	28 days	Fineness (m^2/kg)
1	6.8	10.5	18.3	19.8	22.5	25.0	380
2	7.8	9.0	17.8				390
3	1.5	3.0	5.0				400
4	17.7	26.5	36.3	31.0	35.0	37.0	370
5	11.2	19.0	21.9				395
6	7.5	13.0	18.3				390
7	7.5	30.5	36.8	20.3	42.5	50.0	400
8	7.8	8.5	15.0				365
9	9.6	12.8	19.5				380
10	18.8	28.0	36.0	27.5	18.7	38.5	390
11	5.0	15.5	20.0				370

hydrated after cooling and grinding with 3 per cent gypsum (Table 9.18) to 300 m^2/kg. High early strengths were obtained from high-iron mixes containing C_4AF.[122] The hydration of C_4AF synthesised by solid-state reaction at 1200°C, was faster than that for C_4AF synthesised from the melt.[124] Compressive strengths have been reported for ferrites prepared by the separate burning of pure compounds;[123] the ferrites were fired at temperatures such that the free lime was reduced to zero (1230–1350°C). It is postulated that more structural vacancies exist in material burned rapidly than in normally fired products, and this leads to higher hydration rates and increased strength. Hydration studies in the system C_2F–C_4AF–$C_4A_3\bar{S}$ showed that C_4AF hydrated more rapidly than C_2F and that the presence of $C_4A_3\bar{S}$ accelerates the hydration of the ferrite. The character of the ferrite phase was found to alter with cooling rate and Na_2O content;[125] the Fe_2O_3/Al_2O_3 ratio in the ferrite phase is increased by slow cooling and by the presence of Na_2O. The hydration of samples of C_3A and $C_2(A,F)$ (obtained by extraction from Portland cements) show that the ferrite hydrates more rapidly in the presence of calcium sulfate. The reaction rate of the ferrite phase in Portland cement is increased by the presence of 1–3 per cent potassium citrate or potassium carbonate, or combinations of the two. A normal Portland cement and a sulfate-resisting Portland cement clinker were examined.[126] Compressive strengths of cement mortars were

Table 9.18 Compressive strengths (MPa) of C_2F and C_6AF_2[123]

	3 days	7 days	28 days
R–C_6AF_2	18.3	19.4	25.3
O–C_6AF_2	12.2	14.7	24.2
R–C_2F	6.1	8.8	22.0
O–C_2F	0.7	0.9	14.8

R = rapid heat, O = ordinary heat.

measured on 40 × 40 × 160 mm prisms between 4 h and 28 days; after 28 days, strengths lay between 56 and 81.5 MPa. Strength increases were very marked at ages up to 1 day in the presence of citrate.

Ferruginous bauxite plus limestone and gypsum may be used to produce (at 1350 ± 50°C) ferroaluminate cement clinkers in the C–S–A–F–$\bar{S}$ system.[127] These materials belong to a group of special cements whose relatively low energy consumption in manufacture results mainly from the low CaO content of their main phases, i.e. belite and calcium aluminoferrite, and in the lower clinkering temperatures required. The mineral composition is $C_4A_3\bar{S}$ (35–60 per cent), C_4AF (15–45 per cent) and C_2S (15–30 per cent). By adjusting the feed proportions, a high early strength, an expansive or a self-stressing cement could be produced. The cements gave a high resistance to sulfates (tested over 12 months). The energy consumption for the production of these cements was about 65 per cent of that required for Portland cement production. The lattice distortions present due to impurities and the low temperature of burning contribute to their hydraulic properties[128]. The compressive strengths of high early strength cements produced industrially attained 19.7 MPa after 1 day and 101.8 MPa after 3 days.[127] The $Ca(OH)_2$ content of the hydrated cement was low, with a pH for the set paste between 12 and 12.5; FH_3 is present in the set material, both factors leading to a high sulfate resistance. Firing temperatures were low, in the region of 1250°C, leading to good grindability; their properties could be adapted by varying the proportions of clinker minerals to give either high early strengths or expansive cements. The phase composition, for example, of a Chinese cement[127] was stated to be 15 to 45 per cent C_4AF, 35–60 per cent $C_4A_3\bar{S}$, and 15–30 per cent C_2S. The SO_3 content of the clinker is up to 10 per cent.[78] The designation C_4AF does not imply a particular member of the ferrite solid-solution series. Increasing the Fe_2O_3 content in the feed resulted in a lowering of the clinkering temperature.

Four-component clinkers containing Al_2O_3, Fe_2O_3, CaO and SiO_2 with additions of SO_3 and MgO may be synthesised, at varying Al_2O_3/Fe_2O_3 ratios, at 1350°C followed by either slow cooling or air quenching. When this ratio is high (1.75), the sulfate is first consumed to form $C_4A_3\bar{S}$ and a high Fe_2O_3 aluminoferrite phase (C_6AF_2), in spite of the high aluminate composition of the clinker, as well as β- and α'-belites. When the Al_2O_3/Fe_2O_3 ratio is low (<1.0), belite and a high ferruginous ferrite, C_6AF_2 is formed containing significant amounts of SO_3 in solid solution. With increasing additions of SO_3 the amounts of $C_4A_3\bar{S}$ and α'-belite increase while the amount of aluminoferrite phase decreases, and this phase becomes more ferruginous. The hydraulic character of these ferrites is greatly influenced by the speed of quenching.[128] The possibility of forming $C_4F_3\bar{S}$ was not confirmed.[128] Compressive strengths were measured on 10 mm cubes, at water/cement = 0.3 and the degree of hydration is established by quantitative X-ray diffraction. Hydration kinetic measurements showed that both the belites and the ferrites were more reactive for clinkers with lower Al_2O_3/Fe_2O_3 ratios. The belites in these clinkers contained significant amounts of SO_3 (3–4 per cent) in solid solution, and possessed a strongly distorted structure. Maximum strengths were obtained when the ratio (C_4AF or C_2F)/$C_4A_3\bar{S}$ equalled 3:1. The hydration products formed from calcium aluminoferrite cements in the presence of gypsum have been studied:[129] the hydration products were essentially similar to those formed from C_3A. $Fe(OH)_3$ was found as a gel phase and Fe^{3+} ions were incorporated into the AFm hydration products.

The hydration of calcium sulfoferrites and the addition of sulfoferrite clinker to Portland cement results in improved properties for the cement.[130] In the C–F–C$\bar{S}$ system, clinkering starts at 800°C with the formation of CF initially. Within the interval

Table 9.19 Composition and properties of modified Portland cements[27]

Parameter	Item	Rapid hardening		Normal	Slow hardening	
		#3	#6	#5	$\#K_b$	$\#K_a$
Oxides (%)	CaO	48.3	49.0	51.8	52.9	55.8
	SiO_2	8.7	10.5	15.7	16.7	22.0
	Al_2O_3	18.4	16.3	13.1	11.3	8.2
	Fe_2O_3	13.2	9.9	5.0	9.9	5.0
	SO_3	11.4	14.4	14.4	7.2	7.2
Percentage compound composition (%)	C_2S	25	30	45	50	65
	$C_4A_3\bar{S}$	20	20	20	10	10
	C_4AF	40	30	15	30	15
	CS	15	20	20	10	10
Surface area	Blaine surface	405	380	374	420	387
Compressive strength of mortars (N/mm)	8 h	–	15.6	0	0	0
	1 day	34.8	28.3	9.5	5.6	5.2
	3 days	36.9	33.8	19.3	7.6	8.9
	7 days	37.4	35.7	27.1	11.7	12.4
	28 days	–	–	49.8	14.1	14.5
	90 days	–	–	–	21.4	22.4
	120 days	51.8	53.8	86.2	–	–

950–1205°C, CF and $CaSO_4$ interacted to form calcium monosulfoferrite ($C_4F_3\bar{S}$), which decomposes at 1205°C to form $C_3F\bar{S}$ in clinkers of high basicity. CF hydrates slowly to form C_3FH_6, which has little or no strength. Commercial clinkers containing sulfoferrites can form at temperatures between 1200 and 1350°C, to produce cements showing high resistance to sea water, and 28-day strengths of >80 MPa.[130]

The aluminoferrite phase has a variable composition, even within individual clinker nodules,[131] and this phase can accommodate ~10 per cent by oxide mass of impurity ions.[46] Heterovalent substitution in the lattice leads to greatly increased hydraulic activity and to a near-amorphous structure. The aluminoferrite phase in Portland cement clinker contains considerable quantities of MgO, Mn_2O_3 and TiO_2.[46]

Iron-rich cements in the system C_2S–$C_4A_3\bar{S}$ have been examined; Table 9.19 summarises the results of an early investigation.[26] Cements fired at the lower clinkering temperatures possible (1200°C for 1 h), show that C_4AF is formed with increased hydraulic activity and practically no free CaO. Similar experimental cements have been prepared again more recently[132] from a range of waste materials; setting times were about 45 min. The clinkers are very easy to grind, partly as a result of the very low temperature of firing. The hydraulic activity of these cements is closely related to the poor crystallinity and high impurity content, arising from the low temperature of formation. Limestone is added as setting control rather than gypsum. The hydrates forming are AFt, AFm, AH_3 and C-S-H; strengths in the range 50–90 MPa at 1 day are achieved, with good frost resistance.

A review of cements formed in low CaO systems has revealed that high early strengths can be attained[20] for systems containing certain additions, for example TiO_2, CaF_2, $CaCl_2$ and $CaSO_4$.

Cements containing the series of compounds C_2S, $C_4A_3\bar{S}$, C_4AF, $C\bar{S}H_2$ and free CaO have been prepared.[20,110,127] It is observed that free lime can be accommodated in these cements without resulting in unsoundness. Hydration studies showed very high early strengths (1-day strength up to 40 MPa) and good durability. Systems that incorporated MgO were important in that high-magnesium limestones and dolomites are commonly available and not normally useful in the production of Portland cement. Systems were found to be able to accommodate up to 10 per cent MgO without expansion; high strengths were obtained on rather coarsely ground cements (250–300 m^2/kg) (37 and 49 MPa at 1 and 28 days, respectively).[133] Natural raw minerals combining limestone, dolomite, bauxite, laterite and gypsum are ground and blended to contain 5–12 per cent MgO, and 35–49 per cent CaO. They were burned in an electric oven at 1350°C for up to 35 min. The phases β-C_2S, $C_4A_3\bar{S}$, C_4AF, $C\bar{S}$, C_3MS_2 and C_2AS were present. On hydration, ettringite was the main product.

9.5.5 *IRON-RICH FLUORALUMINATE BELITE CEMENTS*

The introduction of fluoride brings about a further reduction in the clinkering temperature, to ~1050°C.[20] CaF_2 is an efficient mineraliser but a combination of $CaSO_4$ and CaF_2 is more effective. The phase $2C_2S \cdot 3CaSO_4 \cdot CaF_2$, calcium fluorellestadite, is found to appear as intermediate during clinkerisation, beginning to form at 900°C and remaining stable up to 1240°C. Fluoraluminate cement (based on $C_{11}A_7 \cdot CaF_2$) was developed in America and blended with Portland cement to form regulated set cement. The setting time of this cement was very fast and required organic retarders in its application. The development of an iron-rich fluoraluminate cement has overcome these difficulties[66,67,81,122] and has been produced on an industrial scale (Tables 9.19–21). The ferrite content of the new cements lies between 20 and 80 per cent and has the formula C_6AF_2. The clinker can be burned at <1000°C. The hydration rate of $C_{11}A_7 \cdot CaF_2$ is increased with increasing clinkering temperature and is greater when prepared in clinkers

Table 9.20 Mineral composition and physical properties of high early strength cement[122]

Item		a_{32}	F_{10}	F_1	F_9	F_{12}	F_{15}
Mineral composition (%)	C_4AF	30	35	40	50	60	75
	C_2S	23	20	18	12	8	0
	C_4A_3S	34	33	32	27	23	17
	$C_{11}A_7 \cdot CaF_2$	12	12	10	11	9	8
Blaine surface area		366	274	377	340	422	–
Water/cement		0.267	0.267	0.267	0.267	0.267	–
Setting time (min)	Initial	20	10	12	47	40	–
	Final	25	19	26	93	60	–
Compressive strength (MPa)	1 day	44.5	47.5	41.3	31.4	34.4	24.9
	3 days	61.1	51.0	48.2	53.8	67.6	52.5
	7 days	64.0	67.2	62.5	61.1	64.9	58.1
	28 days	80.8	77.5	77.4	64.4	75.4	56.0

Table 9.21 Compressive strengths of 1:1 mortars made from C_4AF (water/cement = 0.3)[122]

No.	Compressive strength/MPa 3 days	7 days	28 days
1	30.3	42.4	54.8
2	41.4	47.0	54.3
3	43.7	55.3	65.9

Table 9.22 Strength and setting of paste (F1, F3 and F5; laboratory cements) and mortar samples (G1 and G2; cement produced in industrial kiln)[81]

	Proportion (%)				Setting time (min)		Compressive strength (MPa)				
Sample	Clinker	Gypsum	Water/ cement	Blaine surface area	Initial	Final	6 h	1 day	3 days	7 days	28 days
F1	100	20	0.39	454	26	48	31.0	65.8	69.3	72.3	86.7
F3	100	10	0.37	420	38	63	21.6	45.3	53.4	75.2	88.3
F5	100	10	0.31	405	44	104	10.7	41.3	49.6	59.0	68.2
G1	100	10	0.41	425	29	43	19.8	35.4	41.3	49.5	56.4
G2	100	15	0.41	455	26	45	17.5	36.5	49.6	55.0	63.5

containing C_3S than those containing C_2S. The clinker can be burned to acceptable free-lime levels at temperatures <1050°C. The strength of this series of cements is dependent on gypsum content.

The setting time and strengths up to 28 days hydration of mortar samples have been recorded in Table 9.22. An increase in the $C_{11}A_7 \cdot CaF_2$ content results in an increased strength. The inclusion of ZnO in the raw feed resulted in an increased setting time. An iron oxide-rich belite cement[125] formed in the presence of CaF_2 may contain the mineral $C_{11}A_7 \cdot CaF_2$.

The reactions leading to clinker formation are given as

Bauxite $\rightarrow Al_2O_3 + SiO_2$	530°C
$CaCO_3 \rightarrow CaO + CO_2$	860°C
$CaO + Fe_2O_3 \rightarrow CF \rightarrow C_2F$	860°C
$CaO + Al_2O_3 \rightarrow CA \rightarrow C_{12}A_7$	900°C
$C_2F + Al_2O_3 \rightarrow C_6AF_2$	980°C
$CaO + SiO_2 \rightarrow C_2S$	950°C
$C_{12}A_7 + CaF_2 \rightarrow C_{11}A_7 \cdot CaF_2$	1000°C

The mineral $C_{11}A_7 \cdot CaF_2$ in conjunction with $C_4A_3\bar{S}$ brings about very high early strengths.

The main hydration products are AFt, AH_3, FH_3, C-S-H, C_4AH_{13}, C_2AH_6 and AFm. Because of the relatively low firing temperature, the ferrite phase appeared in the form C_6AF_2. The composition of ferrites in iron-rich fluoraluminate cement depended on the burning temperature. Iron-rich fluoraluminate cements burned at low temperatures were wholly C_6AF_2, which apparently guarantees a high rate of hydration and high strength.[124] The increased setting time is attributed to the increased content of minor elements; Zn is mentioned in particular. Mineralisers may be used to reduce the final free lime content of the clinker.

9.6 Alkali-activated slags and other aluminosilicates

Alkali-activated slag cements using granulated blastfurnace slags were invented by Glukhovsky and patented in 1958. A review in 1980[134] commented that alkali-activated slag cements had been introduced into construction practice in the USSR in 1960 and in Poland in 1972, including the use of steam curing. Alkali-activated slags have been employed on a limited scale as oilwell cements and as a roof support system in mine applications in South Africa and Canada. Industrial experience of precast products utilising these cements is widespread in Eastern Europe, Finland and France, and has extended in some cases for periods up to 30 years involving severe exposure conditions.[135] Research in China[136] has confirmed the high strength of these systems and their tendency to rapid setting. A wide range of industrial slags has been found to be suitable: blastfurnace slag, phosphorus slag, and other metallurgical slags including some which are not useful for incorporation with Portland cement (Table 9.23). Several alkali solutions can act as activators. The cement has proved to be of a lower cost than Portland cement and a saving in energy of 60 per cent is claimed over that required by Portland cement.[137] Detailed reviews of the performance of these cements have been presented, based on laboratory investigations and full-scale work.[135,138] It was commented that a small amount of silicate in the activator resulted in a large increase in strength.[138] Strength results have been obtained over a period of 2 years and the set material exhibited good frost resistance and low drying shrinkage. The finely ground slag, usually granulated blastfurnace slag, may be activated by a solution of sodium or potassium hydroxide, or carbonate, but preferably by silicate (water glass). Part of the slag can be substituted by fly ash. The strengths developed can lie between 40 and 120 MPa. Mortar strength tests up to 2 years under water and in air at 70 per cent relative humidity showed no indication of strength regression.[139] The cement is very reactive and the fresh mix loses slump rapidly; setting times are short and the fresh mixes are somewhat sticky – effective demoulding agents must be used. It is claimed that a conventional precasting plant can be utilised to produce activated slag concrete units, and that savings of 30–55 per cent in energy and 40 per cent in cost can be made.

Table 9.23 Chemical composition of slags[30]

No.	Description	SiO_2	Al_2O_3	CaO	MgO	TiO_2	K_q[a]	K_b[b]	Fe_2O_3	MnO
M	Basic	35.5	12.6	40.3	9.0	0.7	1.69	1.02	0.6	0.5
Cl	Basic	33.6	11.3	41.8	5.8	1.7	1.65	1.06	2.9	0.3
W	High K_q	32.8	16.1	35.1	11.0	–	1.90	0.96	0.75	–
KP	Phosphorus slag	37.6	9.4	45.2	1.6	–	1.37	1.00	1.6	–
C2	Acid	41.8	11.7	32.9	3.8	1.1	1.13	0.69	2.7	–
C3	Acid	38.6	10.8	33.3	4.3	2.4	1.18	0.76	2.4	–

[a] $K_q = (CaO + MgO + Al_2O_3)/(SiO_2 + TiO_2 + P_2O_5 + F + MnO)$
[b] $K_b = (CaO + MgO)/(SiO_2 + Al_2O_3)$

The effect of different curing conditions on the performance of alkali-activated slag mortars has been investigated:[135,139] temperatures between −15° and 105°C have been studied, together with water storage conditions ranging from under water to air curing at 100, 70 and 50 per cent relative humidity. The basic slag can be an aluminosilicate, such as synthetic ashes or natural ashes, burned clays, or ground basalt rock. Depending on the type of aluminosilicate, the activation by alkali may take place at room temperature or may require higher temperatures. The choice of activator is more important for room temperature curing. The optimum quantities of Na_2O lie between 3 and 6 per cent by mass of slag. The hydration products are zeolitic in character, with general formulae of $R_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot nH_2O$, with $x \sim 2$ rising to 4 if steam curing is used ($R \equiv$ *metal*).

The cements show substantial advantages where early strength development and resistance to sulfates and chlorides[137] are important, but a number of disadvantages are listed, including unpleasant handling characteristics, the development of skin irritation, the inconvenience of mixing more than one component, the sticky consistency of the fresh mix, the short setting time of plain mixes without retarder, and the existence of serious efflorescence on concretes cured in dry air. Specialist applications are illustrated under three headings:[140] railway sleepers, immobilisation of waste and high resistance to aggressive conditions. Experimental work was described on the immobilisation of the metal ions Zn, Cd, Cr and Pb which was being carried out in the University of Krakôw. Strength development was good in general and leaching tests were carried out according to the German Standard (EDVS4) over a period of 360 days. A more serious weakness is the vulnerability to carbonation[141] and sensitivity to drying which results in loss of strength. An increased tendency to alkali–silica reaction is also noted.[141,142] These observations were discounted by Malolepszy *et al.*,[140] who claimed that good reinforcement protection was obtained. Tenoutasse supported the view that these concretes were vulnerable to carbonation.

Supersulfated cements may be regarded as alkali-activated slag cements: they are composed of 80–85 per cent granulated blastfurnace slag, 10–15 per cent anhydrite, and about 5 per cent Portland cement clinker. The British Standard for this type of cement is BS 4248: 1974 and a minimum SO_3 content of 4.5 per cent is included in the specification. The cement is ground to a fineness $>400\,m^2/kg$. The cement exhibits good durability in sea water and sulfate environments. The main hydration products are ettringite and calcium silicate hydrate, although the amount of sulfate present is insufficient to convert all the aluminate available to ettringite, so monosulfoaluminate and aluminate hydrates are probably also formed. The resistance to saturated $MgSO_4$ is poor, compared to that shown by sulfate-resisting Portland cement and high-alumina cement mortars.[33] Thomas[32] measured the durability of a supersulfated cement containing 13.8 per cent Al_2O_3: the supersulfated cement cubes remained effectively at 100 per cent strength in Na_2SO_4 solution while sulfate-resisting Portland cement cubes fell to 20 per cent of the water-stored value in 8 years. The performance of supersulfated cement cubes in 3.5 per cent SO_3 $MgSO_4$ solution (42 000 mg/L) was poor, the strength falling to <25 per cent of the water-stored strength in 8 years, which was about the same as that shown by sulfate-resisting Portland cement.

Harrison and Teychenne[33] found that supersulfated slag cement concrete was less resistant to $MgSO_4$ (18 000 mg/L) than to Na_2SO_4 solution (18 000 mg/L). A disadvantage of supersulfated slag cement is reported to be its behaviour during natural carbonation:[143] the set concrete tends to dust, since one of the bonding agents, ettringite, is decomposed by carbonation to give aragonite ($CaCO_3$), gypsum and hydrous alumina.

Table 9.24 Chemical composition (per cent) of slags used in alkali-activated cements[145]

Slag	CaO	SiO_2	FeO	Al_2O_3	MgO	LOI	P_2O_5	Cr_2O_5	MnO
Synthetic slag SI	44.72	32.41	4.76	15.79	1.18	1.4			0.1
Synthetic slag SII	37.4	36.09	3.56	20.93	1.05	0.37			0.1
Synthetic slag SIII	35.1	38.26	5.6	18.12	1.19	1.54			0.1
Commercial slag SB	33.2	31.0	1.8	23.6	8.72	0.81			1.73
Commercial slag SR	33.36	32.83	2.4	26.53	3.18	0.89			3.86
Commercial slag SD	35.96	30.35	1.69	22.4	5.32	0.94			0.1
Phosphatic slag	49.02	40.1		4.06	1.94	3.72	0.56		
Alloy slag	40.32	37.84	4.5	11.76	6.0	1.7		2.3	0.1

A number of alkali-activated cementitious systems have been developed in China.[144] Blastfurnace slags, steel slags and phosphorus slags have been found to yield strong cements. Fly ash can be incorporated into the cement.

Steam curing has been employed with these cements.[144] Carbonates, silicates, fluorides or hydroxides of the alkali metals can be used as the alkaline components.[30] The cements have been found to be rapid hardening, and strengths of 30–35 MPa at 1 day, 40–55 MPa at 2 days and 65–75 MPa at 3 days are reported. The cements are characterised by low heats of hydration, which makes them very suitable for mass concrete. Large savings of energy can be made by substituting alkali-activated slag cements for Portland cements and further release of CO_2 to the environment is avoided. Strength data for a range of cementive systems have been published (Tables 9.24 and 9.25).[145]

Granulated blastfurnace slags are employed in geotechnology as injection grouts, activated with sodium carbonate, water glass, or mixtures of the two at a rate of 5 per cent Na_2O by mass of slag.[146] Alkali activation has been employed with slags and fly ashes.[147] The alkali solutions examined included NaOH, Na_2CO_3, water glass, Na_2SO_4, and $KAl(SO_4)_2 \cdot 12H_2O$. Strengths of between 40 and 50 MPa were recorded at 3 months. Blends of fly ash and slag were also examined.[145]

Table 9.25 Characteristic properties of alkali-activated slag cements[145]

Type of slag	Percentage activator	Fineness (m^2/kg)	Compressive strength of 1:3 mortars (MPa)					Setting time (min)
			1 day	3 days	7 days	28 days	90 days	
Synthetic SI	3	400	19.3	22.1	26.5	33.6	35.7	37
	3	500	21.5	25.2	32.4	35.3	44.3	45
Synthetic SII	3	400	3.92	6.1	9.91	11.3	–	101
Synthetic SIII	3	400	2.75	4.22	5.3	7.65	–	140
Commercial SB	3	400	7.46	–	20.9	25.7	–	69
Commercial SK	3	400	6.28	10.8	16.4	22.1	31.9	90
	3	500	8.63	14.4	20.6	22.9	32.7	88
Commercial SD	3	500	–	15.7	31.4	41.0	–	–
Phosphatic	3	400	10.6	12.5	25.8	35.7	–	232
Alloy	3	400	7.46	12.7	18.3	24.6	28.9	85

Table 9.26 The strength of paste specimens (10 × 10 × 30 mm) made with granulated blastfurnace slag (w/s = 0.3) and sodium silicate solutions[150]

	Compressive strength (MPa) at 28 days		
M_s[a]	3.0% Na_2O	3.7% Na_2O	4.5% Na_2O
1.35	52.8	79.0	96.6
1.50	58.4	94.8	121.3
1.60	62.8	92.6	120.8
1.70	76.9	106.6	113.6
1.80	87.6	99.6	101.4
1.90	87.9	111.3	100.5
2.00	92.6	109.0	98.9
3.30	104.1	96.5	93.0

[a] $M_s = SiO_2/Na_2O$ (molar ratio) in the water glass solution.

The hydration products for alkali-activated slags are largely calcium silicate hydrates, similar to those for Portland cements.[147–149] The factors determining strength of alkali-activated slag cements have been investigated in the laboratory.[30] An important point determining strength is the type of alkaline activator: water glass (sodium silicate solution) was found to be the best activator. A study of the performance of blastfurnace slags activated with sodium silicate solutions[150] has examined the effect of sodium silicate composition and concentration (Table 9.26). The relationship is complex; however, strengths up to 121 MPa are reported after 28 days' moist cure. The use of pure NaOH solution resulted in very low strengths (<20 MPa), while the use of Na_2CO_3 solution resulted in strengths up to 42 MPa. The strengths of mortar specimens were reported after moist or water cure for 28 days. No zeolitic hydrates were observed;[148] however, it was considered that an increase in silicate content resulted in the formation of zeolites. A number of zeolites are expected to be formed in activated slag systems, depending on the overall chemical composition,[159] including sodalite, phillipsite, chabazite and zeolite P (giomondite). Calcium silicate hydrate was the main hydrate, having a low cement/solid ratio of 1–1.1 and Al in solid solution. Hydrotalcite, AFm or hydrogarnite (after elevated-temperature curing) was sometimes found. The inclusion of other mineral phases (e.g. fly ash) gave rise to zeolitic hydrates.

The use of natural aluminosilicate clay (kaolinitic or lateritic soils) in conjunction with alkalis (3–6 per cent NaOH and KOH) to form high-quality building materials has been the subject of long-term investigations by Davidovits.[152] The stabilisation of kaolinitic soils with lime [$Ca(OH)_2$] and added Na_2CO_3 yielded a strong 'geopolymeric' binder, containing hydrosodalite, analcime and various synthetic calcium and sodium silico-aluminates. Chemical investigations are claimed to have replicated ancient concretes in use in Egypt for the construction of the Pyramids of Cheops, Chefren, Teti and Sneferu, in 2500 BC. A modern adaptation of this ancient process[153] involves the calcining of kaolinitic clay at 750°C, then reacting with alkali polysilicate solution, or blending with the solid polysilicate and using it as a conventional cement. The cement hardens rapidly at room temperature to give compressive strengths of 20 MPa after 4 h and 70–100 MPa after 28 days. It is claimed that a similar investment of energy and identical CO_2 emission allows the production of 5–10 times the quantity of cement as that formed from the Portland cement process. In another investigation, calcined kaolin (metakaolin), formed in the temperature range 450–800°C,[44] developed strengths of up to 50 MPa for 50:50 blends with $Ca(OH)_2$ mixed at water/solid ratio of 0.35. Geopolymeric binders have been proposed for radioactive waste containment.[154] Durability testing has shown that Na^+-based geopolymers have increased zeolitic behaviour compared to K^+; however, frost resistance is increased for K^+-based cements.

Alkali-activated cementitious components have been shown to generate high early strengths.[155] A review of the position in regard to the development of special cements was published in 1992.[37] In connection with the concept of making alkali-activated cement from slags, commercially available products are mentioned (pyrament, F cement, introduced in 1988) based on finely ground aluminosilicate slags. Zeolites can be synthesised from mixtures containing 80 per cent Class F fly ash and 20 per cent Portland cement, when mixed with 5 M NaOH solution,[156] and cured at 60–90°C. High compressive strengths, up to 30 MPa, were observed when curing was continued for 26 days for 50 mm paste cubes made at a water/solid ratio of 0.4.

Davidovits[8] has reviewed the potential of geopolymer cements (alkali-activated aluminosilicate cements) and also holds the patents to a number of these. NMR has been employed since 1987 to investigate the crystal structure of the hydrates which form, and to distinguish between polymer chains and three-dimensional networks. These cements consist of a mixture of minerals, and contain 10–28 per cent blastfurnace slag. The hardening mechanism involves the chemical reaction of, for example, $Si_2O_5 \cdot Al_2O_3$ with solutions of alkali polysilicates to give polymeric—Si—O—Al—O—bonds. The microstructure of these hydrates has been investigated by ^{29}Si and ^{27}Al NMR spectroscopy. The aluminosilicate component is formed by calcinating kaolinitic clays at 750°C, and is given the name 'kandoxi' rather than metakaolin. The name kandoxi is an acronym for kaolinitic, nacrite, dickite oxide. The other component is a slag (alkali mellilite glass). The cements hydrate rapidly at room temperature and provide compressive strengths of 20 MPa after only 4 h at 20°C; at 28 days the strength reaches 70–100 MPa. The potential for alkali–aggregate reaction using geopolymer cements has been examined and found to be minimal. Geopolymer cements are not dissolved by acid solutions and are able to resist 5 per cent HCl or H_2SO_4 solutions.

A series of synthetic glasses in the system $CaO–Al_2O_3–SiO_2$ has been found to be hydraulically active without the need for the presence of alkali.[157] The composition range found to be hydraulically active contained 45–55 per cent CaO, 30–40 per cent Al_2O_3 and 15–25 per cent SiO_2. Compressive strengths on cement pastes using water/cement = 0.4 were up to 73 MPa, obtained on 10 × 10 × 60 mm specimens. After longer hydration times, the strength started to decline.

The binding potential of combinations of fluidised-bed combustion by-products and fly ash has received considerable attention.[158] No Portland cement is involved and the material can be described as a low-performance, low-cost and low-energy binder. The main reactive components are $CaO/Ca(OH)_2$, anhydrite and dehydroxylated clays from the fluidised-bed bottom ash and fused aluminosilicate glass from the fly ash. Ettringite is the main hydration product resulting in strength generation. There is uncertainty over the long-term stability of these systems.

9.7 The future of cement production

The need to reduce the consumption of energy and the release of CO_2 is recognised in the Portland cement industry, and much effort and resources have been expended in improving the traditional manufacturing processes. A reduction in the release of CO_2 to the atmosphere, in general, will accompany any reduction in the use of energy in the industry. The increased emphasis on the use of blended cements, which incorporate secondary cements developed from waste by-products, has been encouraged by the introduction of the new European Standard for cement, and automatically leads to further, and major, reductions in energy use and CO_2 release (up to 75 per cent reduction in both energy requirement and CO_2 release may be expected if granulated blastfurnace slag is employed as the diluent). However, a reliance on waste materials as cements may introduce difficulties in ensuring continuing and consistent high performance, and will not provide the increased output requirement expected by the developing world.

The production of cements with enhanced reactivity developed by the introduction of small percentages of mineralisers has reached the production stage, and in combination with low-energy cement components can result in a low-energy blend with acceptable early age strengths. The formation of alinite cements which contain substantial quantities of chloride again leads to a high early strength cement that can be formed at much lower temperatures than Portland cement, thus reducing energy requirements and minimising pollution. The problem of chloride-induced corrosion of reinforcement steel may be averted by employing fluoride rather than chloride.

Further developments to yield greater savings can be made in theory by limiting the lime content of the clinker, and several encouraging lines of research have been explored in the literature. Cements based on belite are attractive as a way of reducing the temperature of formation and consumption of calcium carbonate (emission of CO_2) as the present production plant can be adapted. Many of the restraints currently placed on the use of low-grade fuels and alternative source materials, especially lime because of a lack of purity, would disappear. The major difficulty is the low hydraulic reactivity of belite compared to alite. A number of methods of increasing the reactivity of belites have been examined. The most interesting way round this difficulty seems to lie in rapid quenching of the clinker. Perhaps a saving of 10–20 per cent in energy and CO_2 emission may be expected.

Cements prepared at reduced temperatures may have other benefits, apart from the reduction in energy input. The ferrite phase becomes more hydraulic when prepared at low temperature, and cements can be formed to give reactive systems containing combinations of CA and β-C_2S, which have good long-term performance. The abandonment of sintering in favour of solid–solid interaction in the production of cements seems to deserve further attention.

Cements based on sulfoaluminates are already successful and are attractive from the point of view of their special quick-setting and hardening properties; applications such as repair mortars are already finding commercial outlets. They require further assessment in their long-term stability and strength. These systems may be vulnerable to long-term expansion, and extensive testing for expansion beyond 12 months is required. The stability of these cements towards carbonation, sulfate attack and general swelling by water seems to be open to doubt. The leaching behaviour of these cements does not seem to have been investigated, and the ease of removal of sulfate and aluminate should be established. The resistance to ingress of chloride is a vital parameter in the protection of reinforcement steel against chloride-initiated steel corrosion. The use of calcium fluoraluminate as a component in shrinkage-compensated mortars and concretes is well established and good long-term performance data exist. Possibly improvements may be developed by the use of sulfoferrites, thus providing additional confidence in this type of cement by avoidance of high contents of aluminate and sulfate. The longer-term strength performance of iron-rich fluoraluminate cements has yet to be established. Energy savings of 25 per cent have been mentioned, with somewhat greater savings in CO_2 emission.

The present successful concrete technology involving the employment of alkali-activated slag can allow the use of a variety of waste slag types which at present are not permitted in cements. A high-alkali Portland cement clinker as activator would increase the potential further for utilisation of a wider range of raw feeds in the production of the presently dubious Portland cements to be adopted in this combination. Alkali activation of aluminosilicates also forms the basis of other successful cement systems. Further testing on the resistance towards carbonation of these relatively reduced alkalinity systems, and their ability to protect reinforcement steel, is required. The saving in energy may be as high as 80 per cent with an even greater saving in CO_2 emission.

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10

Pozzolana and Pozzolanic Cements

Franco Massazza

10.1 Pozzolanas

The term 'pozzolana' has two distinct meanings. The first one indicates the pyroclastic rocks, essentially glassy and sometimes zeolitised, which occur either in the neighbourhood of Pozzuoli (the ancient Puteoli of the Roman times) or around Rome.[1] The second meaning includes all those inorganic materials, either natural or artificial, which harden in water when mixed with calcium hydroxide (lime) or with materials that can release calcium hydroxide (Portland cement clinker). In this chapter the term 'pozzolana' will be referring to the latter meaning, definitely wider than the former, and will therefore embrace a large number of very different materials in terms of origin, composition and structure.

For a long time the use of pozzolanas has been mostly restricted to Italy, where considerable reserves of natural pozzolanas are found and to Greece (Santorin earth). In other countries the interest in these materials is of relatively recent date and has arisen from the need for reusing some waste materials such as fly ashes and silica fume. This historical background can help explain why so many countries have long distrusted pozzolana-containing cements, despite the millenary use of lime–pozzolana mortars and the almost 100-year experience in pozzolanic cements. In any case, results of a variety of studies have substantially confirmed that pozzolanic cements can yield concrete showing a high ultimate strength and great resistance to the attack of aggressive agents.

In addition to the previous edition of this book,[1] the properties and applications of pozzolanas have been exhaustively covered in the proceedings devoted, either partly[2-9] or completely,[10-17] to pozzolanic materials. Establishing a precise classification of pozzolanas proves difficult since this common name includes materials which are very different in terms of chemical composition, mineralogical nature and geological origin and which are related only by the general property they have to react and harden when mixed with lime and water.

The more commonly accepted classification concerns the origin of pozzolanas and therefore a first subdivision is between natural and artificial materials. Natural materials do not require any further treatment apart from grinding; artificial pozzolanas result from chemical and/or structural modifications of materials originally having no or only weak pozzolanic properties. The latter can be residues of certain production methods or products manufactured from selected raw materials.

The division between natural and artificial pozzolanas is not well defined, since there are materials, as Danish moler, French gaize and some rhyolitic tuffs from the USA which, besides typically pozzolanic constituents such as opal or volcanic glass, also contain variable amounts of clay minerals which take on a clear and strong pozzolanic character only by firing.

The classification of pozzolanas shown in Figure 10.1[18] is basically identical to that proposed at the 6th International Congress on the Chemistry of Cement held in Moscow in 1974. The only significant change concerns the introduction of silica fume into the artificial pozzolanas which began to be used after the Moscow Congress.

10.1.1 NATURAL POZZOLANAS

Materials of volcanic origin (pyroclastic rocks)

Pyroclastic rocks result from explosive volcanic eruptions which project minute particles of melted magma into the atmosphere. The rapid pressure decrease occurring during the eruption causes the gases originally dissolved in the liquid magma to be released. As a consequence, each particle will contain a number of microscopic bubbles and ducts forming a microporous structure.[19] Simultaneously, the particles are subject to a quenching process which is responsible for their glassy state. The material can be deposited either on the ground or in water. Generally, the ground deposits, which are loose and heterogeneous, are composed of ashes mixed with fragments coming from the volcanic duct walls or the base of the volcano. The microstructure of three typical Italian volcanic pozzolanas is

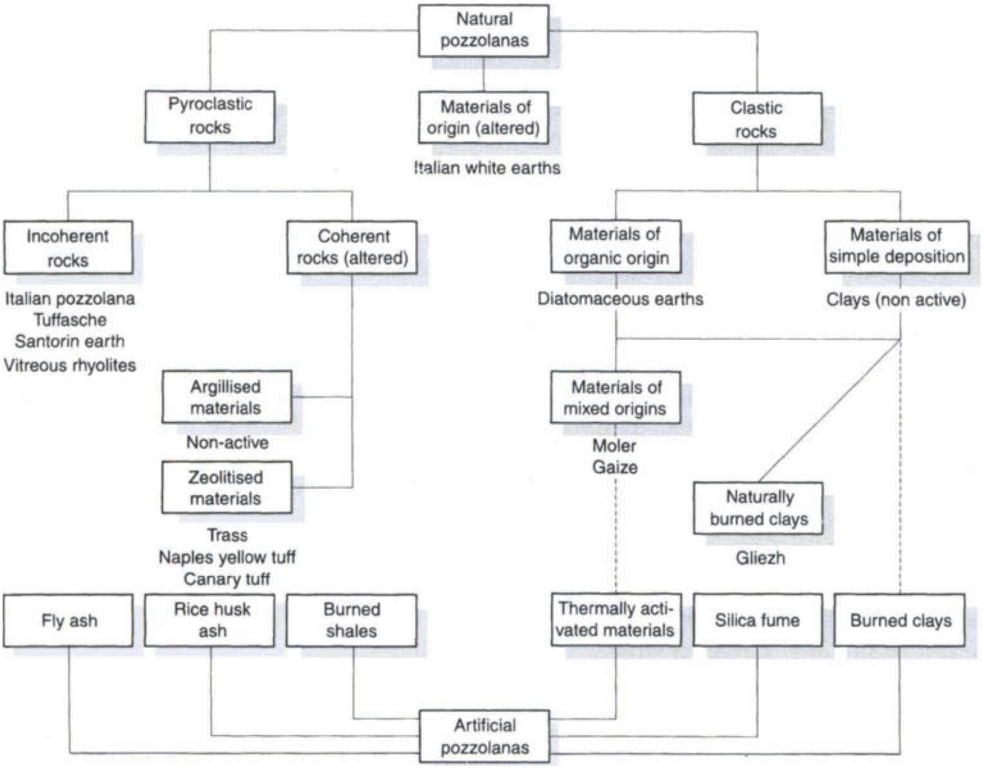

Fig. 10.1 Classification of pozzolanas (source: Ref. 18).

shown in Figures 10.2–10.4. Non-explosive eruptions produce volcanic ashes with no or little pozzolanic activity since quenching is not sufficiently rapid to prevent crystallisation of the melt magma.[20]

Incoherent materials. This group includes typical Italian pozzolanas from Campania (Naples) and Latium (Rome), the so-called Santorin earth, widely used since ancient times; the incoherent glassy rhyolites, to be found in the USA,[21] India (Bombay)[22] and Turkey.[23] Rhine trass is commonly included among the tuffs, i.e. compact, coherent materials, but its deposits also contain incoherent layers mainly made up of glass.[24] The Japanese Furue shirasu and Higashi Matsuyama pozzolanas belong to the group of glassy volcanic pozzolanas.[25]

Table 10.1 shows that the chemical composition of incoherent volcanic pozzolanas varies within wide limits and that silica (and alumina) prevails over other constituents. The alkali content is rather high with peaks exceeding 10 per cent (pozzolana from Bacoli, Naples and Rhine trass).[24] Loss on ignition, generally low in Neapolitan pozzolanas, can reach as much as 10 per cent in Roman ones as well as in Rhine trass.

The structure and mineral composition of the Neapolitan pozzolanas are very simple. Here the fundamental constituent is a pumiceous glass containing sanidine and, rarely, plagioclase and pyroxene inclusions.[30] In Latium pozzolanas, leucite appears both as clear, unaltered as well as turbid altered crystals. Augite is another common mineral contained in Latium pozzolanas, where traces of mica, olivine and zeolitic minerals,[31] fluorite and

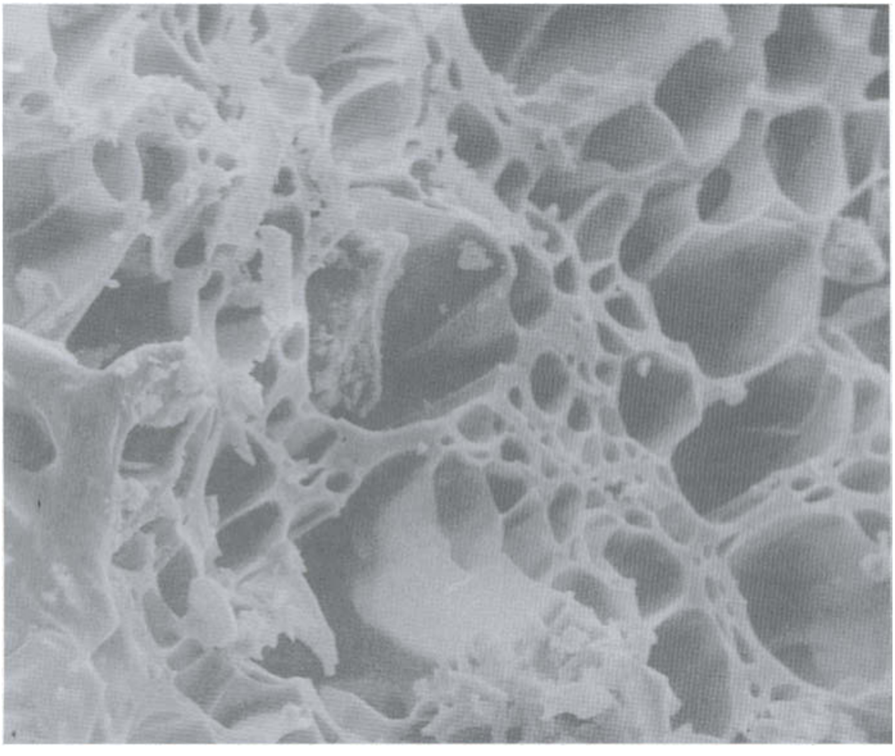

Fig. 10.2 SEM image of Bacoli pozzolana (Italy) (600×).

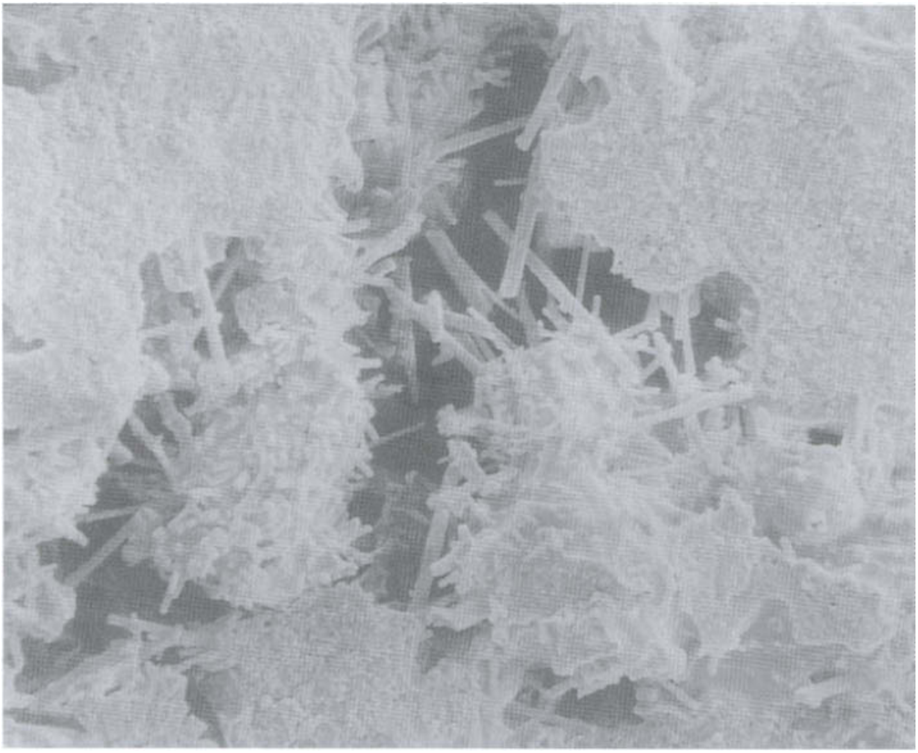

Fig. 10.3 SEM image of Salone pozzolana (Italy) (300×).

clay minerals are also present.[32] The various crystals are cemented by an isotropic groundmass consisting of deeply altered glass.

The natural pozzolana from Volvic (France) has a vitreous matrix containing andesite and, in lesser quantities, quartz, diopside and magnetite. The loss on ignition is very low.[27]

In the incoherent layers accompanying the true lithoid German trass, the most important constituent is glass, whereas the crystalline portion – mostly composed of quartz and, to a lesser extent, of sanidine – represents a smaller portion.[24]

The incoherent or slightly coherent rhyolites found in the USA contain from 65 to 95 per cent glass and variable amounts of calcite, quartz, feldspar, sanidine, hypersthene, hornblende and montmorillonite.[21]

The eruptive material forming the Japanese Furue shirasu and Higashi Matsuyama pozzolanas is mainly made of glass and small quantities of quartz, feldspars and plagioclase. The Higashi Matsuyama pozzolana also contains small quantities of clay minerals and zeolites, which would indicate the beginning of a diagenetic process.[25]

The mineralogical composition of some volcanic pozzolanas is shown in Table 10.2.

Compact materials (*Tuffs*). The deposits of volcanic pozzolanas are often associated with compact layers (tuffs) which originate from weathering and cementation of loose particles by diagenetic or other natural processes. Weathering can cause zeolitisation or argillation, that is, it can transform the glass of pozzolana into zeolitic minerals or clay minerals. The degree of transformation reached by the original deposit depends on the intensity of the

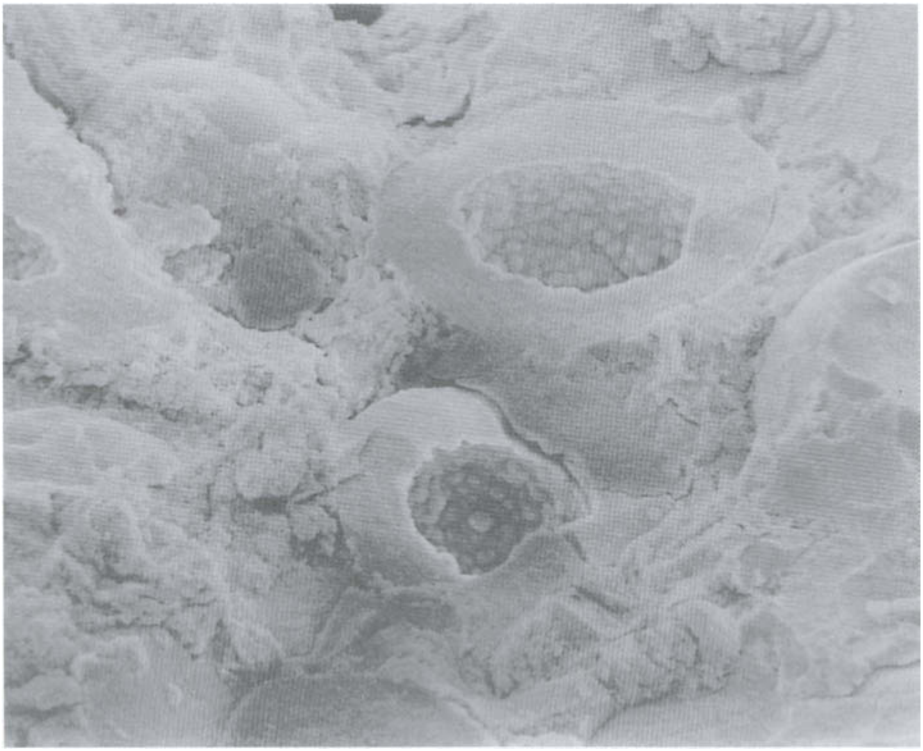

Fig. 10.4 SEM image of Vizzini pozzolana (Italy) (300×).

Table 10.1 Chemical analyses of some incoherent volcanic pozzolanas (per cent)

Pozzolana	Country	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	LOI	Ref.
Bacoli	Italy	53.08	17.89	4.29	9.05	1.23	3.08	7.61	0.31	0.65	3.05	26
Barile	Italy	44.07	19.18	9.81	12.25	6.66	1.64	1.12	0.97	tr.[a]	4.42	26
Salone	Italy	46.84	18.44	10.25	8.52	4.75	1.02	6.35	0.06	tr.	3.82	26
Vizzini	Italy	50.48	16.77	11.59	4.86	5.24	0.87	0.17	0.08	0.15	9.68	26
Volvic	France	54.30	16.80				4.47	2.60				27
Santorin earth	Greece	65.1	14.5	5.5	3.0	1.1					3.5	28
Rhine tuffash	Germany	58.91	19.53[b]	2.85	2.48	1.33	6.12	4.53			2.21	24
Rhyolite pumicite	USA	65.74	15.89	2.54	3.35	1.33	4.97	1.92			3.43	21
Furue shirasu	Japan	69.34	14.56	1.02	2.61		3.00	2.39	0.25		1.85	25
Higashi Matsuyama	Japan	71.77	11.46	1.14	1.10	0.54	1.53	2.55	0.14		6.50	25

[a] tr. = trace.

[b] $Al_2O_3 + TiO_2$.

Table 10.2 Minerals in some volcanic pozzolanas

Pozzolana	Country	Active phases	Inert phases	Ref.
Bacoli	Italy	Glass	Quartz, feldspars, augite	26,27,30
Barile	Italy	Partially decomposed glass	Pyroxenes, olivine, mica, analcime	26
Salone	Italy	Glass, analcime	Leucite, pyroxenes, alkali feldspars, mica	26,31
Vizzini	Italy	Glass	Feldspars, quartz, olivine, clay minerals	26
Volvic	France	Glass	Andesine, quartz, diopside	27
Santorin earth	Greece	Glass	Quartz, anorthite, labradorite	28
Rhine trass	Germany	Glass (55–60)	Quartz (9%), feldspar (15%)	29[a]
Bavaria trass	Germany	Glass (62–67) Chabasite (3%) analcime (5%)	Quartz (19%), feldspar (15%)	29[b]
Rhyolite pumicite	USA	Glass (80%)	Clay (5%), calcite, quartz, feldspar, etc. (15%)	21
Furue shirasu	Japan	Glass (95%)	Quartz (1%), anorthite (3%)	25
Higashi Matsujama	Japan	Glass (97%)	Quartz (1%), anorthite (1%)	25

diagenetic actions as well as on their duration. Zeolitisation improves pozzolanic properties, whereas argillation reduces them.[33,34]

The yellow Neapolitan tuff[33,34] and the compact tuff to be found in Grand Canary (Spain)[35] are typical examples of pozzolanic tuffs. They belong to the alkali-trachytic type like the Rhine tuff, whereas those from the volcanic region near Rome (Latium) are of the leucitic type.[36 38]

The chemical composition of some pozzolanic tuffs is shown in Table 10.3. The silica or the silica plus alumina contents are most similar to pyroclastic pozzolanas. Loss on ignition is generally high and minor element contents are very variable. In contrast, the mineralogical composition of tuffs is more complex[31] since the glass or the original pozzolana is transformed by an autometamorphic process[43] in zeolite compounds such as hershelite, cabazite and phillipsite.[44] Bavarian trass is not of volcanic origin since this material formed as a result of the impact (shock) of a large meteorite that produced the Ries crater.[29]

The main minerals in Rhine trass and Bavaria trass are glass (55–60 per cent), quartz (9 per cent), feldspar (15 per cent) and glass (62–67 per cent), quartz (19 per cent), feldspar (15 per cent) respectively.[29] The tuffs contain also variable amounts of zeolite and clay minerals.

In some deposits the transformation of volcanic pozzolana, incoherent and mostly glassy, into compact and zeolitised tuffs, is most evident. In typical examples the pozzolana is separated from tuff by an intermediate layer. The chemical composition of the three layers is similar, even though some differences occur (Table 10.4).[43] In moving from pozzolana to tuff, trivalent iron and water contents increase, while the alkali amount decreases.[39]

The association of loose material rich in glass with compact, stony material is found also in Rhine trass deposits (Kretz).[24] Here the chemical composition of the various layers forming the deposit is quite similar, but the microscopic structure is different.

The so-called 'Tuffasche' contains large amounts of glass, little quartz and sanidine, but

Table 10.3 Chemical analyses of pozzolanic tuffs (per cent)

Pozzolana	Country	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O		K_2O	SO_3	LOI	Ref.
Rhine trass	Germany	52.12	18.29	5.81	4.94	1.20	1.48		5.06		11.10	29[a]
Bavaria trass	Germany	62.45	16.47	4.41	3.39	0.94	1.91		2.06		7.41	29[b]
Selyp trass	Hungary	55.69	15.18	6.43	2.83	1.01				0.26	16.33	39
Ratka trass	Hungary	73.01	12.28	2.71	2.76	0.41				0.10	6.34	39
Yellow tuff	Italy	54.68	17.70	3.82	3.66	0.95	3.43		6.38		9.11	33
Dacite tuff	Romania	67.70	11.32	2.66	3.73	1.64				0.18	7.27	40
Gujarat tuff	India	40.9	12.0	14.0	14.6	1.45					12.06	22
Trass K	Bulgaria	71.63	10.03	4.01	1.93	1.22		2.35		3.05		41
Zeolite (clinoptilolite)	Japan	71.65	11.77	0.81	0.88	0.52	1.80		3.44	0.34	9.04	42
Zeolite (mordenite)	Japan	71.11	11.79	2.57	2.07	0.15	1.66		1.33	0.27	9.50	42

no trace of zeolitic compounds. On the contrary, in the compact tuffaceous layer beneath the loose 'Tuffasche', the groundmass appears to be glassy since it is isotropic under transmitted light microscopy, but it contains large quantities of 'diffused' zeolites which are detectable only by XRD analysis. The zeolitic minerals present in the compact trass are mainly analcime and, to a certain extent, cabazite and phillipsite.[24]

The relationship between loose pozzolanas and the underlying layer of compact tuff was proved by reproducing in the laboratory the pozzolana → Neapolitan yellow tuff transition

Table 10.4 Chemical composition of three adjacent layers of Naples pozzolana (per cent)[43]

	Pozzolana	Intermediate layer	Yellow tuff
SiO_2	56.04	54.30	51.36
TiO_2	0.42	0.42	0.42
ZrO_2	0.03	0.05	0.03
Al_2O_3	17.79	17.40	16.84
Fe_2O_3	2.07	2.65	3.90
FeO	2.80	2.12	0.84
MnO	0.12	0.15	0.14
MgO	1.19	0.92	0.99
CaO	3.47	3.61	3.47
BaO	0.06	0.08	0.05
K_2O	7.43	6.93	6.57
Na_2O	4.17	3.00	2.57
Cl_2	0.05	0.06	0.09
SO_3	0.05	0.05	0.04
P_2O_5	0.10	0.08	0.13
CO_2	–	–	0.44
H_2O^-	0.60	2.65	4.96
H_2O^+	3.79	5.70	7.55
Total	100.18	100.17	100.39

occurring near Naples (Italy). Bacoli pozzolana underwent a hydrothermal treatment which resulted in a material similar to the yellow tuff. The chemical composition did not change but the original volcanic glass was transformed into zeolitic minerals.[45] Autoclaving was also carried out on other materials, such as a pumiceous lapillus, artificial glasses obtained by melting and quenching natural lavas,[45] and leucite crystals.[46] In any case, the original component was transformed in zeolitic minerals, thus confirming that volcanic materials have a considerable capacity for zeolitisation. The rate of transformation, as well as the type of mineral formed, depends on the autoclaving conditions and on the chemical activators used. In some tuffs the original volcanic glass is completely transformed into zeolitic minerals (Table 10.5).[47]

The presence of clay minerals in many volcanic pozzolanas means that diagenesis or metamorphism can follow different paths.[48] In contrast to zeolitisation, argillation has not been assessed in the laboratory.

Materials of sedimentary origin

Clays and the so-called diatomaceous earths are sedimentary rocks which are capable of combining with lime. The former originates from the alteration of igneous rocks whereas the latter form from the siliceous skeletons of microorganisms (diatoms) deposited in fresh or sea waters. Since both materials result from deposition in water in spite of their different origin, it is not surprising that diatoms and clay minerals occur mixed together.

Clay minerals, especially those belonging to the montmorillonite group, can react with lime giving calcium silicate and aluminate hydrates[49-52] but they cannot replace pozzolana as they increase the water demand and lower the strength of mortar and concrete.

The largest deposit of diatomites occurs in California, USA. Other important deposits are found in former USSR, Canada, Algeria and Germany[1] and in other countries. A diatomaceous earth, the so-called 'moler', which consists mainly of a mixture of montmorillonite and amorphous opal, is found in Denmark, where it has been used either as it is or calcined.

Table 10.5 Minerals in zeolitic materials (per cent)[47]

	Content (%)			
Mineral	ZG[a]	G 1[b]	T[c]	He (pure)[d]
Clinoptilolite	62 ± 3		68 ± 3	
Heulandite	18 ± 1		11 ± 1	100
Analcime		45 ± 2		
α-Quartz	19 ± 1	28 ± 2	15 ± 1	
Cristobalite			5 ± 1	
Montmorillonite			Traces	
Illite	Traces			
Andesine		24 ± 1		
Chlorite		Traces		

[a] Tuff from Zaloška gorica (Yugoslavia).
[b] Tuff from Gorenje (Yugoslavia).
[c] Tuff from Tokay mountain chain (Hungary).
[d] Heulandite crystal from Theigarhorn, Berufjord (Iceland).

Table 10.6 Chemical analyses of silica-rich pozzolanas of different origin (per cent)

Pozzolana	Country	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	LOI	Ref.
Diatomaceous earths												
Moler	Denmark	75.6	8.62	6.72		1.10	1.34	0.43	1.42	1.38	2.15	53
Diatomite	USA	85.97	2.30	1.84		trace	0.61	0.21	0.21		8.29	21
Diatomite	USA	60.04	16.30	5.80		1.92	2.29				11.93	21
Mixed origin												
Sacrofano	Italy	85.50	3.02	0.44	1.22	0.58		0.16	0.26	0.77	7.94	26
White hearth (a)	Italy	90.00	2.70	0.70		0.20					6.10	57
White hearth (b)	Italy	84.25	4.50	1.55		2.40					8.40	57
White hearth (c)	Italy	78.40	12.20	1.50		1.55					8.60	57
White hearth (d)	Italy	56.80	21.40	1.70		2.35					7.50	57
Beppu white clay	Japan	87.75	2.44	0.41	1.10	0.19	0.23	0.11	0.11			25
Gaize	France	79.55	7.10	3.20		2.40	1.04			0.86	5.90	55

The pozzolanic properties are remarkably improved if moler is burnt in order to decompose the clay minerals.[53]

Table 10.6 shows the chemical composition of some diatomaceous earths. The silica content increases as the clay mineral content decreases. The opposite occurs for alumina. The opal content in diatomites ranges from 25 to 100 per cent, the remainder being formed by clay minerals and other minerals as quartz and feldspars.[21]

Diatomaceous earths are highly reactive towards lime owing to their high content of amorphous silica and high specific surface area. In spite of the strongly pozzolanic behaviour, the use of diatoms in pozzolanic cements is hampered by their huge specific surface area which causes the water demand of cement to increase. Small additions of diatomites to concrete improve plasticity and reduce bleeding.

Gaize is a sedimentary rock which is found to the east of Paris, in the Ardennes and the Meuse valley. It contains 30–35 per cent of active silica, which is easily soluble in potassium hydroxide solutions and confers a certain pozzolanic activity to the rock.[55] Gaize contains up to 50 per cent quartz and substantial amounts of clay minerals. Since these minerals can reduce the workability of mortars, gaize is used after burning at about 900°C.[55,56]

Materials of mixed origin (hybrid rocks)

North of Rome there are stratified deposits of a crumbly rock (Sacrofano earth; Figure 10.5) composed of materials of different origin (volcanic, sedimentary and organic).[26,54,56,57,58] The upper layers show a silica content up to 90 per cent, considerable loss on ignition and small amounts of other oxides (Table 10.6). As far as the innermost deeper layers are concerned, the silica content is appreciably less; alumina can reach about 20 per cent, but other oxides are present only in very small amounts.[57] The low iron content explains the light colour of these materials, generally known as 'white earths'.

For the layers that are richer in silica, XRD analysis shows a band at ~0.405 nm that is typical of dried silica gel, which is attributed to the groundmass. In the patterns of the high-alumina layers, this band fails to occur and peaks of montmorillonite-type clays attacked by acid solution appear.[54] The crystalline minerals, sometimes clear but often

Fig. 10.5 SEM image of Sacrofano pozzolana (Italy) (300×).

altered, consist of feldspar (sanidine or plagioclase), biotite, quartz, calcite, zeolites and diatom skeletons.[53]

The presence of diatoms with fragments of volcanic rocks shows that these deposits probably originated from the deposition of materials of different origin in stagnant water, followed by acid attack. For the minerals of the upper layers, the destruction of the crystalline structure took place with the formation of silica gel; for the minerals of the lower layers the transformation was only partial, and zeolite and clay minerals formed.

Within the Oita prefecture (Japan) there is a high-silica deposit (the Beppu white clay; Table 10.6), essentially made of opal. Other minor minerals are quartz, cristobalite and opaque constituents.[25] The silica gel deposit originated from the neighbouring rocks made of hornblende and andesite which were decomposed by hot springs.

In Central Asia, Jurassic shales are found which were calcined by natural subsurface coal fires. This material, called gliezh, is rich in SiO_2 and Al_2O_3 owing to its clay origin and shows a clear pozzolanic activity.[59]

10.1.2 Artificial pozzolanas

Fly ash

Fly ashes consist of finely divided ashes produced by burning pulverised coal in power stations. They are removed from the combustion gases and collected by special mechanical

Table 10.7 Analyses of low-lime fly ash (per cent)

Country	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	C	LOI[a]	Ref.
France	51.68	27.01	6.25	1.72	1.88	0.54	4.49			4.70	60
France	48.10	24.68	6.50	1.41	1.82	0.56	4.06			11.70	60
Belgium	55.74	24.14	6.02	2.47	2.22			1.04		2.74	61
Taiwan	48.75	23.21	4.15	3.93	1.00	0.24	1.10			10.39	62
UK	50.09	28.1	11.7	1.62	1.54	0.28	0.62			1.27	63
Poland	50.8	23.9	8.6	3.6	2.8	0.8	2.9	0.8		2.9	64
Denmark	53.98	22.27	11.60	3.95	1.97	2.71	eq.	0.73		2.13	65
Netherlands	50.46	25.74	6.53	4.32	2.24	2.04	4.43			3.95	66
Canada	47.0	17.7	25.3	2.1	1.0	0.7	2.3	0.3		2.4	67
Japan	57.5	26.1	4.0	5.1	1.3	1.50	1.35	0.4		1.6	68
UK	48.0	38.2	4.5	3.3	1.5	0.3	1.7	0.37		2.3	69
Japan	53.53	23.55	6.23	5.85	1.60	2.20	1.75		2.14	3.44	42
USA	52.24	19.01	15.71	4.48	0.89	0.82	2.05	1.34		0.92	70
Canada	43.8	22.1	16.2	3.5	0.8	4.4	eq.	1.1		5.0	71
Germany	51.2	29.6	6.8	3.4	1.2	0.6	3.1	0.5		3.3	72

[a] Often includes carbon content as well.

devices and electrostatic precipitators. Owing to the high temperature reached during the instantaneous burning of coal, most of the mineral component contained in the coal melts and forms small fused drops. The subsequent sudden cooling transforms them partly or entirely into spherical glass particles.

Fly ashes result from the burning of bituminous or subbituminous coal as well as of lignite.[59] Their chemical composition depends on the mineral composition of the coal gangue, i.e. the inorganic part of the coal.

As shown in Table 10.7, the chemical composition of bituminous fly ashes (class F according to the ASTM classification[73]) varies within rather wide limits. Silica and alumina prevail, as in natural pozzolanas. Silica usually varies from 40 to 60 per cent and alumina from 20 to 30 per cent; the iron content also varies quite widely. The lime content is low, ranging between 2 and 5 per cent. Alkalis are present in appreciable amounts and potassium prevails over sodium. TiO_2, not shown in the table, is always present at ~ 1 per cent together with minor oxides. Carbon is also present to a lesser or greater degree depending on the burning process. Loss on ignition values, summarised in Table 10.7, are rather low when compared to the composition of common fly ashes. In practice LOI is generally higher and can exceed 12 per cent.[74] In general, the chemical composition of fly ashes from the same source shows little variability.

Fly ashes are considered to be composed of relatively few mineral phases, since the coal mineral matter does not contain more than five or six components; clay minerals, pyrite, quartz and one or two calcium, iron and magnesium carbonates.[75] Moreover, considering the mineral distribution in the coal and the burning conditions in the boilers, every particle is probably produced by coal fragments containing only one or two mineral species.[75]

Microscopic examination and electron probe microanalysis confirm these conclusions. In fact, besides the prevailing vitreous ground mass, only four compounds are present to any appreciable extent: quartz, mullite, hematite and magnetite.[75,76,77] Magnetite may possibly be a mixture of ferrites.[78] Examples of mineralogical composition of class F fly

Table 10.8 Mineral analyses of fly ashes (per cent)

Fly ash source	Country	Quartz	Mullite	Hematite	Magnetite	Carbon	Glass	Anhydrite	Ref.
Dunston	UK	4.5	11	2.7	1.4	3.1	77		75
Ferrybridge	UK	2.8	6.5	1.6	1.9	1.5	86		75
Hams Hall	UK	3.5	10	1.6	1.2	0.6	83		75
Rye House	UK	8.5	14	2.1	2.5	2.4	71		75
Skelton Grange	UK	4.1	10	2.4	2.6	2.1	79		75
Northeast P26	UK	7	28	9	7	4.0	45.0		79
Northeast P27	UK	2	9	7	7	3.0	70.0		79
EFA	NL	1.8	2.1		0.7		95.4		66
LM	NL	5.1	22.8		0.5		71.6		66
Lubbenan	D	17.1			10.4	2.7	75.8	11.4	80
Eophenhain	D	1.4			1.9	3.8	74.3	12.9	80
Swarze Pumpe	D	2.0			5.7	1.0	74.3	16.9	80
Vackarode	D	2.0			6.2	2.2	80.2	9.4	80
Hagenwerder	D	0.3			5.1	6.1	85.1	3.3	80
Hirshfeld	D	1.8			3.8	5.1	93.6	0.7	80

Table 10.9 Elementary compositions obtained by electron microprobe analysis for single grains of the same fly ash[81]

No.	SiO_2	Al_2O_3	Fe_2O_3	CaO
1	58	36.1	3.0	2
2	53.1	33.1	6.3	-
3	51.1	42.9	5.1	–
4	43.5	24.2	9.6	18.4
5	42.5	30.2	12.9	7
6	42.1	29.3	17.9	4.6
7	42.1	24.2	26.8	–
8	42	29.5	20.8	–

ashes are given in Table 10.8. Although the overall chemical composition of fly ash does not vary appreciably, the microprobe analysis still shows a notable chemical heterogeneity of the particles (Table 10.9).[81]

Fly ash particles are typically spherical and glassy, but they also show other typologies. An ash particle classification, based on criteria such as shape, colour, crystallinity and texture, is given in Table 10.10.[75] The finest glassy particles are generally thick but many are hollow. Sometimes the biggest ones look like empty spheres filled with other smaller, spherical particles. Other types of particles are irregular and sometimes contain a variable amount of bubbles, which makes them take on a spongy aspect, or a high content of crystalline minerals. The morphology and behaviour of fly ashes depend on the burning process.[82]

The particle diameters of fly ash range from <1 to $>150\,\mu m$. Specific surface area is extremely variable, ranging from <2000 to $>8000\,cm^2/g$ (Blaine),[75] but sometimes lower and higher values occur.

Table 10.10 Types of fly ash particles characterised by microscopic examination[75]

Type	Shape	Colour	Crystallinity and texture	Characteristic size range (μm)	Comments
1	Spherical and rounded	Colourless	(a) Glassy, clear, solid (b) Glassy, containing small bubbles (c) Glassy, with crystal traces (d) Predominantly crystalline, solid	0–20 10–50	
2	Spherical and rounded	Light brown to black	Lighter coloured ones, glassy; all solid	5–30	Deepening colour suggests increasing iron content
3	Rounded	White in reflected light	Glassy, spongy	10–200	Small and large bubbles, giving a range from foam to cenospheres
4	Irregular	Light brown	Partly crystalline, solid	10–100	Irregularity of profile and surface very marked
5	Irregular	Varicoloured in reflected light	Partly crystalline, solid	50–500	Agglomerated particles, apparently sintered; generally containing red particles and areas
6	Irregular	Black	Solid or porous	20–200	Partially burnt coal particles, sometimes containing mineral matter
7	Angular	Colourless	Crystalline, solid	10–100	Probably quartz
8	Angular	Red	Crystalline, solid	5–50	Probably hematite

Table 10.11 Analyses of high-lime fly ash from bituminous coals and lignite (per cent)

Country	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O		K_2O	SO_3	LOI	Free lime	Ref.
Saudi Arabia	52.3	25.2	4.6	10.0	2.2				0.6	0.4		83
Poland	44.4	16.4	6.00	22.10	1.0	0.1		0.5	4.6	3.9		64
Canada	38.67	18.56	5.89	22.96	4.99	1.74		0.41	1.87	6.26		70
Spain	49.8	17.3	8.7	24.9	1.9	0.3		1.7	4.30	2.3	11.4	52
Greece	26.00	10.60	6.59	42.1	1.48	0.17		0.8	5.57	4.55	10.0	85
USA	51.3	20.9	6.00	7.98	1.05		0.25[b]		0.52	0.17		86
USA	44.6	15.5	7.70	20.9			0.89[b]		1.50	0.05		86
USA	32.8	22.9	5.10	27.4	4.82		1.56[b]		2.21	0.53		86
Turkey	27.4	12.8	5.5	47.0	2.5	0.2		0.2	6.2	2.4	18.6	87
Turkey	40.6	9.1	7.7	19.9	8.1	0.9		0.7	10.6	1.4	5.5	81
Turkey	39.9	22.3	4.4	25.4	1.9	0.1		0.4	4.8	0.4	9.8	81
Italy	55.42	23.41	7.71	3.16[a]	3.82	0.90		2.87	0.18	1.06		88
Canada	47.9	21.9	4.91	13.3	2.92	6.05		0.96	1.16	0.14		89

[a] Low-lime lignite.
[b] Na_2O equivalent.

As shown in Table 10.11, subbituminous coal and lignite combustion generally results in high-calcium fly ashes (class C[73]). This is not a general rule since lignite can be low in lime (see Ref. 88 in Table 10.11). Class C fly ashes are generally poor in alkalis, but sometimes they may show high contents (see Ref. 86 in Table 10.11). High lime contents in fly ashes can be attributed to the high limestone content of the gangue.

The crystalline phases occurring in class F fly ashes are few, whereas many phases can be found in class C fly ashes as a consequence of a more variable chemical composition. Some of them have a hydraulic character. Analysis of XRD has evidenced the following crystalline phases in lignite fly ashes: quartz, lime (free), periclase, anhydrite, ferrite spinel, merwinite, alkali sulfates, melilite, mullite, sodalite and hematite.[90]

The presence of C_3A was detected by XRD analysis[91] but in some cases tricalcium aluminate (C_3A) and bredigite (C_2S) were only assumed to be present, as their occurrence was not clearly evident due to the overlapping of their strongest reflections with those of

Table 10.12 Mineralogical compositions of high-lime fly ashes[87]

Mineral	HL1	HL2	HL3
Quartz	4.5	5.6	5.1
Lime	18.6	5.5	9.8
Anhydrite	12.2	9.3	7.4
Plagioclase	~28[a]	~15	~20
Hematite	4.0	6.0	2.0
Magnetite	0.8	2.5	0.6
Mullite	1.0	1.2	4.3
Amorphous and glass	~30	~50	~50

[a] Includes gehlenite.

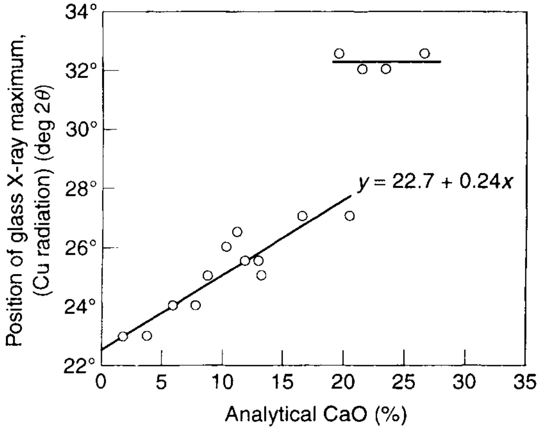

Fig. 10.6 Positions of glass X-ray maxima versus analytical CaO contents for 16 fly ashes (source: Ref. 92).

other compounds.[79] Examples of the mineral composition of lignite fly ashes are given in Table 10.12.[87]

Differences between low- (class F) and high-lime (class C) fly ashes concern the chemical and mineral composition and the chemical composition and structure of the glass. These differences are highlighted by the change occurring in the X-ray diffraction background induced by the glass. For fly ashes containing up to 20 per cent CaO, a striking statistical relationship emerges between the CaO content and the position of the X-ray maxima in the background (Figure 10.6).[92] For fly ashes with about 20–27 per cent CaO, the relationship is no longer valid and invariable maxima appear at 32–32.5° 2θ (Cu radiation).[92]

The position of maxima of low-calcium fly ashes is indicative of a siliceous glass structure, whereas that of high-calcium fly ashes (CaO > 20 per cent) is typical of a calcium aluminate glass structure.[92]

IR, NMR and TMS (trimethylsilylation) investigations have pointed out that the degree of condensation of silicate ions increases as the lime content in the glass decreases. Thus the monomer + dimer content is as high as 7–8 per cent in 27.3 per cent CaO fly ash, but it is < 1 per cent in 2.8 per cent CaO fly ash. Silica fume and rice husk ash contain only polymers.[93]

Burned clay and shale

Clay minerals gain a distinct pozzolanic activity when burned at temperatures between 600 and 900°C. The use of burned clays for the preparation of hydraulic mortars dates back to ancient times and is particularly widespread in India.[22] Owing to the chemical composition of clay and related materials, these artificial pozzolanas are mostly composed of silica and alumina.

The loss of combined water due to the thermal treatment causes the crystalline network of the clay minerals to be destroyed, while silica and alumina remain in a messy, unstable, amorphous state. Heating does not affect anhydrous minerals such as quartz or plagioclase, so that pozzolanic activity depends only on the clay mineral content as well as on the thermal treatment conditions.[21,94 96]

The burning or retorting of certain oil shales produce ashes which harden when mixed with water. Their chemical composition varies largely according to their origin. The silica content can vary between 22 per cent[97] and 42 per cent[98] and conversely lime can vary between 55[97] and 22 per cent.[98] Hardening results from the presence of cementitious compounds such as C_2S, CA and CJ.[97–99] Burned shales have a more complicated mineralogical composition than burned clays depending on their composition, temperature and duration of burning. As an example, shale burned at temperatures ranging between 750 and 840°C contains β-quartz, β-cristobalite, calcite, α-Fe_2O_3 and muscovite, which are already present in shale, and gehlenite, anorthite, wollastonite, orthoclase, anhydrite, β-C_2S, CA and CaO formed during the burning process.[98]

In any case, oil shale ashes should possess pozzolanic properties as they consume lime when they are mixed with water and hydrated lime or Portland cement.[99]

Microsilica

The manufacturing processes of silicon metal and ferrosilicon alloys in an electric arc furnace occur at temperatures up to 2000°C. They generate fumes containing spherical microparticles of amorphous silicon dioxide. This is the reason why the product is called 'silica fume' or, owing to its form and chemical composition, 'microsilica', 'condensed silica fume' and 'volatilised silica'.[100]

The reduction of quartz to silicon releases gaseous SiO. This is transported by combustion gases to lower-temperature zones where it is oxidised by air and condenses in the form of tiny particles of silicon dioxide.

The main features of microsilica are a high silica content, high specific surface area and amorphous structure. These characteristics account for the substantial pozzolanic activity of microsilica, in terms of both its capacity of binding lime and rate of reaction. The chemical composition of microsilica varies with the type of alloy produced within the ranges shown in Table 10.13.[101] The silicon metal process gives purer products whereas the production of silicon alloy results in more complex compositions, the minor element content being as high as 30 per cent.[102]

Microsilica particles are spherical and have an average diameter of 0.1 µm. The BET specific surface ranges from 15 to 25 m^2/g, with typical values of 20 m^2/g.[101] Microsilica may contain traces of quartz.[93] Low-lime silica fume shows a high degree of condensation of silicate ions since it is formed only by polymeric species.[93]

Table 10.13 Chemical analyses of microsilica from the production of silicon metal and 75 per cent ferro-silicon alloy (per cent)[101]

	Si metal	75% FeSi
SiO_2	94-98	86-90
C	0.2-1.3	0.8-2.3
Fe_2O_3	0.02-0.15	0.3-1.0
Al_2O_3	0.1-0.4	0.2-0.6
CaO	0.08-0.3	0.2-0.6
MgO	0.3-0.9	1.0-3.5
Na_2O	0.1-0.4	0.8-1.8
K_2O	0.2-0.7	1.5-3.5
S	0.1-0.3	0.2-0.4
LOI	0.8-1.5	2.0-4.0

Table 10.14 Typical chemical composition of rice husk, rice straw and bagasse ash compared with that of trass and fly ash[103]

	Chemical composition (%)				
Chemical component	Rice husk ash	Rice straw ash	Bagasse ash	Trass	Fly ash
SiO_2	79.5	82.0	75.0	50.0	66.8
Al_2O_3	0.09	0.3	6.7	17.8	7.2
Fe_2O_3	0.06	0.3	6.3	6.8	5.1
CaO	0.64	1.5	2.8	4.5	2.7
MgO	0.83	1.8	3.2	1.0	2.7
Na_2O	0.07	5.3	1.1	3.9	0.9
K_2O	3.75	4.9	2.4	2.6	4.5
P_2O_5	0.31	0.8	4.0	–	–
Loss on ignition	14.3	–	0.9	2.5	9.8

Other materials

Ash exhibiting a marked pozzolanic character can be obtained by burning rice husk within certain temperature ranges. Rice husk ash contains >80 per cent silica[103] (Table 10.14) and its BET specific surface area is as high as 50–60 m^2/g[91] or over 152 m^2/g.[103] Crystalline silica, such as quartz and cristobalite, can be present in large amounts depending on the burning conditions.[93]

The pozzolanic activity of rice husk ash depends on the firing temperature and the retention period. The sensitivity to burning conditions is the primary reason which prevents the widespread use of this material as pozzolana.[104] The amorphous fraction of rice husk contains silica in polymeric form only.[93]

10.2 Lime–pozzolana mixes

Until the nineteenth century, lime–pozzolana mixes were the only hydraulic mortars capable of hardening in water and, at the same time, of resisting the attack of aggressive waters, including sea water. Due to their slow rate of hardening, lime–pozzolana mixes have gradually been replaced by pozzolanic cements. The lime–pozzolana–water system is in any event simpler than the clinker–pozzolana–water system, thus its thorough investigation can help to formulate a correct interpretation of both the behaviour and properties of pozzolana-containing cements.

10.2.1 POZZOLANIC REACTION

The term 'pozzolanic activity' covers all reactions occurring among the active constituents of pozzolanas, lime and water. The definition, although approximate, is however acceptable from a technical and practical viewpoint. Notwithstanding the difficulty in following the evolution of pozzolana's active phases throughout the hydration process, the progress of pozzolanic reaction is commonly evaluated in terms of diminution of the free lime in the system or increase in the silica + alumina soluble in acid[105] by using the Florentin attack method.

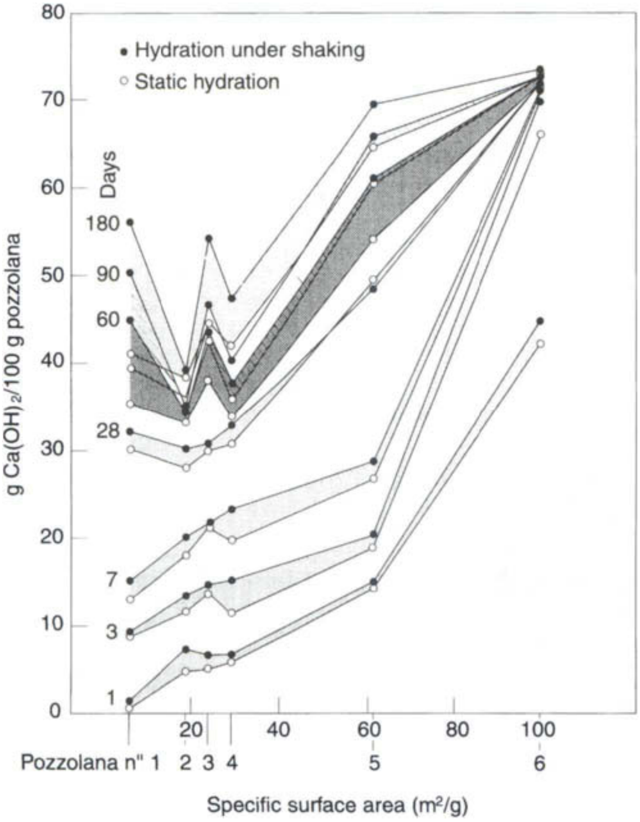

Fig. 10.7 Combined calcium hydroxide versus specific surface area of pozzolana (source: Ref. 26). Lime/pozzolana ratio = 80:100, water/binder ratio = 2:1.

The term 'pozzolanic activity' includes two parameters, namely the maximum amount of lime that a pozzolana can combine and the rate at which such combination occurs. Both factors depend on the nature of pozzolanas and, more precisely, on the quality and quantity of the active phases. The heterogeneity of the pozzolana family, as well as the complex phenomena occurring during hydration, do not allow a model of pozzolanic 'activity' to be defined and only enable general trends to be identified.

Figure 10.7 shows that, should water be in excess, the amount of combined lime may vary appreciably according to the different types of pozzolana.[26] After 180 days of reaction, pozzolanas have been able to combine 45–75 per cent of lime with respect to their mass. In pastes, lime combination is lower inasmuch as the hardened mass hinders the attainment of equilibrium conditions.[106]

There is a general agreement that the overall amount of combined lime essentially depends on the following:

1. the nature of the active phases;
2. their content in pozzolana;
3. their SiO_2 content;

4. the lime/pozzolana ratio of the mix;
5. length of curing;

whereas the combination rate also depends on

6. the specific surface area (BET) of pozzolana;
7. water/solid mix ratio;
8. temperature.

These conclusions are briefly illustrated below.

1. Within the zeolite family, herschelite and clinoptilotite are considered to be more active than analcime.[107,108] Zeolitic pozzolanas are regarded as more reactive than glassy ones.[44] Glass contained in the Bavarian trass combines less lime than that of the Rhine trass.[29] The glasses of different pozzolanas have different capabilities of combining lime. As an example, glasses of the Rhine and Bavarian trasses, as well as those of an obsidian, combine respectively 0.364, 0.272 and 0.176 CaO g/g of pozzolana.

   Table 10.15 shows that the phases present in volcanic pozzolanas contribute to the combining lime to different extents.[109]
2. It is evident that, other properties being equal, the larger the amount of combined lime, the higher the content in active phases and the lower the content of inert or crystalline phases (quartz, sanidine, mullite, magnetite, etc.).
3. The amount of combined lime is related to the SiO_2 content in the active phases, which ranges between 45 and 75 per cent in volcanic glass[106] and in fly ash,[73] but reaches and sometimes exceeds 95 per cent in very active amorphous microsilica, such as natural silica gels[106] or silica fume.[101] However, the glass of the Rhine trass combines more lime than the Bavarian trass, in spite of the fact that their silica contents are about 55 and 67 per cent, respectively.[109] This means that in addition to the silica content, other

Table 10.15 Lime-binding capabilities of the principal trass minerals and their contributions to trass–lime binding[109]

Mineral component	Lime reaction (mg CaO/g)	Free alkali Na_2O (mg/g)	Free alkali K_2O (mg/g)	Average amount in trass (%)	Calculated lime reaction (mg CaO/g trass)
Rhenish trass					
Quartz	43	1.5	0.4	13	5.5
Feldspar	117	1.1	0.2	15	17.5
Leucite	90	1.3	1.8	6	5.4
Analcime	190	10.7	3.0	7	13.3
Kaolin	34	0.3	2.1	2	0.7
Glass phase	364	18.0	24.0	55	200.0
Total	–	–	–	98	242.5
Glass phase					
Bavarian	272	6.0	6.0	66	179.0
Obsidian glass	176	3.7	3.1	–	–

chemical and structural factors play an important role in determining pozzolanic activity. Also, the glasses of fly ashes can have a different composition and structure and this can cause different reactivity levels.[92]

Figure 10.7 shows that pozzolana 6, containing ~85 per cent of silica, combines most of the available lime within 28 days, whereas other natural pozzolanas and fly ashes, containing about 50–60 per cent silica, are capable of chemically binding from 31 to 51 per cent of the lime contained in the mix.[26]

4. Within certain limits, the amount of combined lime increases as the lime/pozzolana ratio increases (Figure 10.8).[25,26,110]
5. Combined lime also depends on the curing time (Figure 10.9), but the rate of combination varies widely between one pozzolana and another. Figure 10.9 shows that after a 90-day curing, the reaction of fly ashes is far from being complete, whereas that of natural pozzolanas is more or less complete.[111] The behaviour of sample 6, a very active natural microsilica, is different since the reaction appears to be complete after only 28 days.
6. Figure 10.7 shows that the short-term activity essentially depends on the specific surface area (BET) of pozzolana, while the long-term activity seems to be better referred to the chemical and mineralogical composition of pozzolana.[25] The reaction

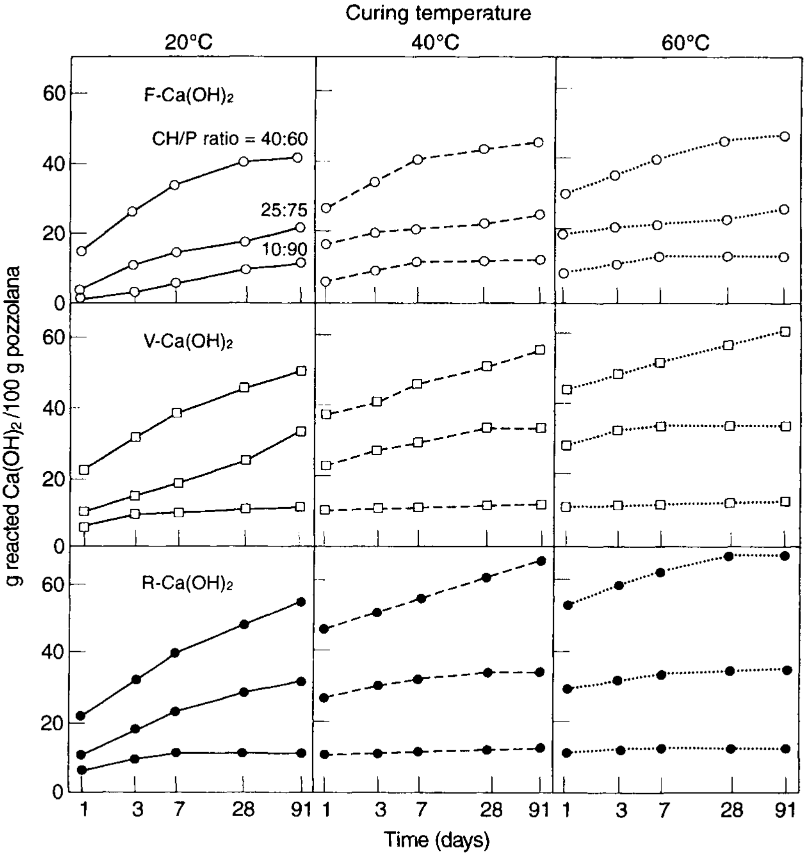

Fig. 10.8 $Ca(OH)_2$ reacted with pozzolanas F, V and R estimated by X-ray diffraction analysis varying the mixing ratio and curing temperature (source: Ref. 25). Water/binder = 0.56.

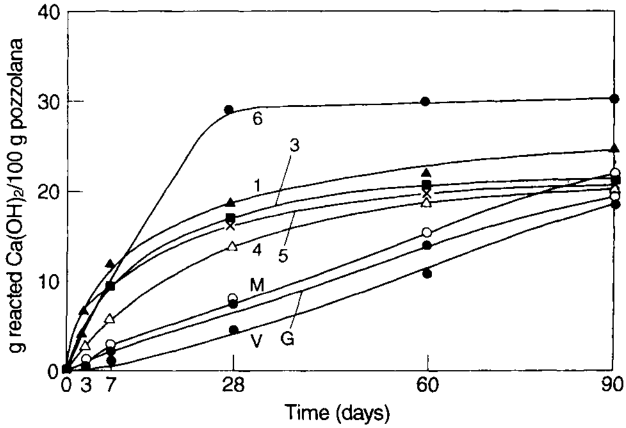

Fig. 10.9 $Ca(OH)_2$ combined by pozzolanas; pozzolana/hydrated lime = 70:30; w/s = 0.6 (source: Ref. 111). 1–6 are natural pozzolanas; M, G and V are fly ashes.

rate of pozzolanic materials is reportedly proportional to the square of the specific surface area.[25] The role played by the specific surface was also evident in pastes containing calcium hydroxide and two samples of microsilica (obtained by hydrolysis of $SiCl_4$) and silica fume having specific surface areas of 200 and 20 m^2/g respectively. The calcium hydroxide was fully consumed by the finer silica within 1 day, but part was still uncombined after 28 days when coarser silica was used.[112]

7. The larger the water content of the mix, the higher the rate of lime combination.[88] Thus the pozzolanic reaction is slower in paste than in dispersion and it is still incomplete after many years.
8. The rate of pozzolanic reaction increases with temperature (Figure 10.8).[25,110,113] Between 50 and 90°C, 1:3 lime/natural pozzolana mixes, compacted with 10 per cent water under a compressive load of 130 N/mm^2, react quickly, so that most lime is already fixed after 1 day of reaction.[113] Above 70°C, however, combined lime tends to stop increasing or to decrease.[110,113] As shown in Figure 10.10, evidence of this inversion is also found in fly ashes at ~60°C[110] and is likely to be due to the variation in the composition of the hydrated phases.

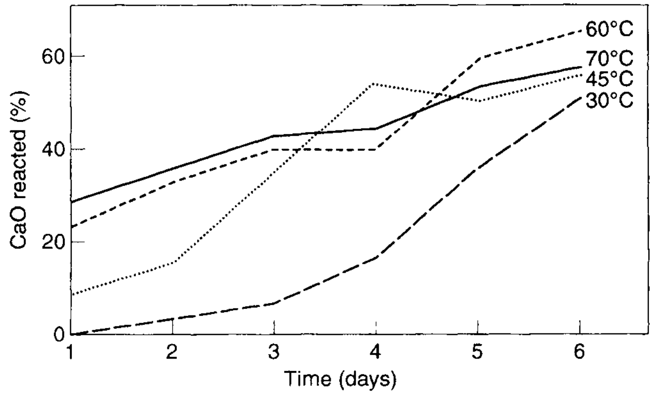

Fig. 10.10 Lime reacted at various times and temperatures (data from Ref. 110). CaO/fly ash = 1:4; water/binder = 0.5.

Temperature substantially increases microsilica reactivity: depending on the lime/silica ratio, after 2.5 h of treatment at 55°C, combined lime is as high as 25–55 per cent of the added CaO and at 90°C it attains 68–90 per cent. After 24 h of hydration, unreacted lime stabilises at 3–8 per cent independently of both temperature and C/S ratio of the mix.[114] Conversely, the amount of combined pozzolana, expressed in terms of silica which becomes soluble in acid, always increases with the temperature of hydration.[110]

The pozzolanic reaction is also influenced by other parameters. The addition of gypsum to the pozzolana–lime–water (in excess) system improves the rate of lime combination.[115,116]

Some natural pozzolanas display an initial reaction rate higher than that of some low-lime fly ashes. Afterwards, the rate in natural materials slows down whereas that in fly ashes accelerates (Figure 10.9). This different behaviour can be attributed to many factors, one being certainly the higher BET specific surface area of natural pozzolanas, which favours a higher initial rate of lime combination.[111]

10.2.2 THERMAL TREATMENT OF POZZOLANAS

When heated, many pozzolanas undergo chemical and structural transformations which may change, to a positive or negative extent, their reactivity to lime. The positive effects cover the loss of water in glassy or zeolitic phases and the destruction of the crystal structure in clay minerals; the negative effect is evidenced by the decrease in the specific surface area, devitrification and crystallisation. The resulting effect, an increased or decreased pozzolanic activity, depends on the nature of the pozzolana, the temperature and the duration of heating.[117]

The opposite effects induced by temperature explain the apparent contradictions that sometimes occur in the same material. For example, it was reported that combined lime decreases[118] or increases[117] by heating a Latium pozzolana at 700°C. If the temperature of calcination is increased step by step, combined lime initially increases and later decreases (Figure 10.11).[117] The same figure shows that heating is followed by a decrease in the specific surface area of pozzolana. This means that for every pozzolana, the optimum thermal treatment has to be established by means of appropriate testing. For several natural pozzolanas the optimum temperature is about 700–800°C. A higher temperature would enhance devitrification, crystallisation and densification and, generally, the formation of

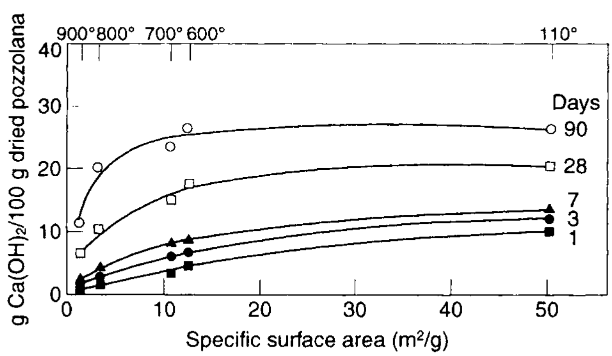

Fig. 10.11 Combined lime versus specific surface area of pozzolana no. 2 dried at 110°C and then fired at the indicated temperature (source: Ref. 117). Lime/pozzolana = 0.8; w/s = 0.6; temperature = 20°C.

more stable phases.[117] This fact is evidenced by a decrease in the amount of silica + alumina dissolved through acid attack.[118]

Microstructural changes induced by calcination are evident in natural pozzolanas, due to the variation of the refraction index. In glassy rhyolitic pozzolanas the index decreases with increasing temperature up to 550–650°C and then increases.[21] The amount of lime combined by pozzolanas containing mainly zeolites gradually decreases with increasing temperature.[21]

At up to 700°C, heating does not modify the pozzolanic behaviour of natural microsilica, which essentially consists of opal[119] or is slightly contaminated by clay.[21] In contrast, calcination improves the reactivity of diatomites containing high quantities of clay minerals.[21] In this case the pozzolanic activity of burned clays is associated with the activity of diatoms.

The reactivity of burned clays and kaolin depends on the firing temperature, as well as on the type of material. For example, combined lime reaches a maximum (0.8 g CaO/g kaolin) when kaolin is burned at between 600 and 800°C.[120]

10.2.3 REACTION PRODUCTS

The reaction of pozzolana–lime mixes produces the same compounds as those which are found upon hydration of Portland cement since the overall chemical composition of the two mixes falls in the same field. For the same reason, different types of pozzolana produce the same aluminate and silicate hydrates. Differences are minor and, in general, affect the amount rather than the nature of the hydrated phases. Thus any distinction made with regard to the different groups of pozzolanas is a matter of clarity rather one of different chemical behaviour.

Natural pozzolanas, dispersed in saturated or almost saturated lime water react with lime and form calcium silicate hydrate (C-S-H) and hexagonal aluminates, C_4AH_{13}.[95,121,122] Similar results have been obtained by testing zeolitic compounds[107,108] and pozzolana–lime pastes.[30,31,123] With excess water, the combination of lime is accelerated by the addition of gypsum.[115]

Table 10.16[124] shows that the hydration of the paste gives rise to certain differences in comparison with hydration in excess water. This is probably due to the fact that excess

Table 10.16 Hydrates formed in pozzolana–lime mixed by reaction of pozzolana with $Ca(OH)_2$ in saturated lime solution (a) and in paste (b)[124]

	Bacoli pozzolana		Segni pozzolana		Dehydrated kaolin		Neapolitan yellow tuff		Rhine trass	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
C-S-H	+	+	+	+	+	+	+	+	+	+
C_2ASH_8	+	+	+	+	+	+	+	+	+	+
C_4AH_{13}	−	−	−	−	−	−	+	−	+	+
$C_3A \cdot CaCO_3 \cdot H_{12}$	−	+	+	+	−	−	−	+	−	−
C_3AS_3–C_3AH_6	−	−	+	−	−	−	−	−	−	−

[a] Reaction time: 90 days.

[b] Water/solid ratio = 0.40; pastes cured for 5 years.

Table 10.17 Hydrates formed in the paste hydration of pozzolana-$Ca(OH)_2$ mixes[25]

Pozzolana	Curing temperature (°C)	Age (days)	C-S-H	C_3AH_6 $C_3AS_2H_2$	$C_3A{\cdot}CaCO_3{\cdot}H_{12}$ C_4AH_{13}	C_2ASH_8
Furue shirasu (F)	20, 40, 60	7	+	−	+	−
	20, 40, 60	180	+ + +	(+)	+ + +	(+)
Higashi Matsuyama tuff (G)	20	7	−	−	(+)	−
	20	180	+ + +	−	+	−
	40	7	(+)	−	(+)	−
	40	180	+ + +	−	(+)	−
	60	7	+	−	−	−
	60	180	+ + +	−	−	−
Kanto (Hachiōji) loam (R)	20	7	−	(+)	+ + +	+
	20	180	(+)	−	+ + +	+ + +
	40	7	(+)	+ + +	+	(+)
	40	180	(+)	+ + + + +	(+)	(+)
	60	7	(+)	+ + + +	(+)	−
	60	180	+	+ + + + +	−	−
Beppu white clay (V)	20, 40, 60	7	+	−	−	−
	20, 40, 60	180	+ + +	−	−	−
Tominaga masa soil (M)	20	7	−	(+)	+ + +	−
	20	180	−	−	+ +	−
	40	7	−	(+)	+	−
	40	180	−	+ +	+	−
	60	7	−	+	+	−
	60	180	(+)	+ + +	(+)	−
Takehara fly ash (T)	20, 40, 60	7	+	−	−	−
	20, 40, 60	180	+ +	−	+	(+)

water accelerates the attainment of the final stage of reaction. Moreover, the hydration products formed in the paste are smaller in size and more irregular.[125]

By extending the duration of reaction between pozzolanas and lime solutions, besides hexagonal calcium aluminate and calcium silicate hydrate, other compounds are recognisable: carboaluminate, gehlenite hydrate and hydrogarnet.[25,126] Hydrogarnet appears after 70–150 days when combined lime represents 40–60 per cent of the initial mass of pozzolana.[52] Table 10.17 shows that the nature of hydrated compounds also depends on the composition of pozzolana, and thus a high-opal pozzolana (Beppu White Clay) can only give calcium silicate hydrate (C-S-H).[25]

When gypsum occurs in pozzolana-lime pastes, ettringite also forms.[127] Whenever the content of calcium sulfate exceeds specific values, the formation of ettringite causes paste to crumble.[128]

The C/S ratio of C-S-H is variable and seems to depend on the type of pozzolana, the time and the temperature of curing, the lime/pozzolana ratio as well as the analytical method used. As an example, with an opal-based pozzolana, ratios in the range 0.75–0.87 have been obtained; they are also a function of the curing temperature. On the other hand, with a glassy pozzolana, ratios are substantially higher, between 1.35 and 1.75.[25] It may be interesting to notice that the opal pozzolana consumed all the available lime, whereas the glassy one did not and free lime was still present in the mixes at the time of testing. In other cases, electron microprobe analysis has given values ranging between 0.75 (opal-based pozzolana) and 0.85 (glass-based pozzolana), whereas values calculated by chemical analysis ranged between 1.2 and 1.7.[106] Optical microscope examination of pozzolana–lime pastes has evidenced the coexistence of calcium silicate hydrates having different optical properties.[31] The variability of the C/S gel ratio can be ascribed to the non-stoichiometry of the C-S-H, depending on the chemical composition of the pore solution.

The progress of pozzolanic reaction is marked by changes in the distribution of silicate ions in the reaction products. The monomer content appears to fluctuate around a certain level, the dimer content increases up to a maximum value and then decreases, while the content of polymer species always increases.[129]

At temperatures between 50 and 90°C, the main product of the pozzolanic reaction is amorphous C-S-H, similar to that obtained upon hydration of Portland cement, and poorly crystallised tobermorite.[113]

SO^{4-} contained in low-lime fly ashes dissolves in lime water and after a certain period causes ettringite and gypsum to precipitate. The rate of ettringite formation depends on the rate of dissolution of alumina. If ashes are washed with water, the two compounds do not form and this means that sulfate occurs in a soluble form.[130]

Low-lime fly ashes mixed with lime and water form C-S-H, C_4AH_{13} and C_2SAH_8,[25] and sometimes carboaluminate as well.[131] If fly ashes contain sulfates, ettringite also appears.[27,129] C_4AH_{13} decreases with time wheres the $C_4A\bar{c}H_{11}$ content increases.[131] The presence of quartz (from fly ash) and calcite (by carbonation) in the mix can hinder the X-ray determination of C-S-H.[131]

High-lime fly ashes may contain variable amounts of free lime which, upon mixing, are transformed into $Ca(OH)_2$ and can thus harden without any further addition of lime.[132] From a practical viewpoint, these fly ashes correspond to the artificial hydraulic limes obtained by mixing hydrated lime with pozzolana.[133] If fly ash releases lime and sulfate, the formation of ettringite occurs without external additions.[79] If fly ashes contain high percentages of sulfate fly ash–lime paste will swell.[134]

Depending on the chemical composition of the fly ashes and the burning temperature of coal, high-lime fly ashes may also contain C_2S.[131,134] In this case hardening is the outcome of the pozzolanic reaction and the hydration of a hydraulic compound. In any case C-S-H, tetracalcium aluminate hydrate, carboaluminate, gehlenite hydrate and ettringite are formed.[135] However, if lime is entirely or mainly combined with Al_2O_3 and SiO_2, the glass is either not or only slightly reactive. As a consequence, no prominent pozzolanic reaction is evidenced and, for at least 3 months, no C-S-H is formed.[131] After 3 days the surface of the fly ashes appears to be slightly covered with hydrates, some of which protrude from the surface of the particles.

Little data concerning the reaction occurring between silica fume and $Ca(OH)_2$ is available. The reaction with $Ca(OH)_2$ solutions is very rapid and causes a phase to precipitate on the silicon dioxide particles as a high-silica hydrated layer. This layer is unstable and turns into C-S-H very quickly.[136] In pastes of normal consistency, owing to the high reactivity of silica fume, free lime disappears generally between 7 and 28 days[128] and in some cases even sooner[75]. Thus, it shows up earlier than in natural pozzolanas and fly ashes. The reaction product (C-S-H) is much more crystalline than the calcium silicate hydrate found in Portland cement paste.[137] In the 1:1 mixes of $Ca(OH)_2$ and SiO_2, the C/S ratio of C-S-H increases in the first days up to 1.30 and then decreases, reaching 1.10 after 70 days of reaction.[75]

Other types of pozzolana can also give the compounds mentioned above. The products from the reaction of burned kaolin with lime are mainly calcium silicate hydrate (C-S-H), gehlenite hydrate (C_2ASH_8) and small quantities of calcium aluminate hydrate (C_4AH_{13}).[95,138,139] At higher temperatures and suitable lime concentrations, the tetracalcium aluminate hydrate turns into C_3AH_6,[95] but traces of the cubic aluminate are also observed after reaction at normal temperature.[138]

The presence of both the tetracalcium aluminate hydrate and gehlenite hydrate is considered to be in contrast with the phase relations existing in the $CaO-Al_2O_3-SiO_2-H_2O$ system.[140] This coexistence might, however, result from some difficulty in attaining final equilibrium. This view is supported by the transformation of gehlenite hydrate into hydrogarnet when the former is shaken with a calcium hydroxide saturated solution.[120]

10.2.4 POROSITY AND MICROSTRUCTURE

The specific surface area (BET) of lime–natural pozzolana pastes increases gradually with time up to 35–100 m^2/g after 90 days of curing.[106] In bottle hydration (water/binder = 12.5) the specific surface area of the hydrates is higher and can be as high as 150 m^2/g after 1 year of curing, depending on the type of pozzolana and lime/pozzolana ratio.[141] For a lime/pozzolana ratio up to at least 0.6, combined lime progressively increases. In addition, the specific surface area initially increases too but, once it has attained a peak value, it sometimes decreases dramatically. The peaks of two Italian pozzolanas and two fly ashes occur at a lime/pozzolana ratio of 0.45,[141] whereas the peaks of other pozzolanas may be shifted. Whatever the type of pozzolana, a direct relationship exists between the porosity and the specific surface area of the paste when mixes of pozzolana and lime are hydrated in a sealed bottle.[141]

Between 3 and 90 days of curing, paste porosity does not change much, but some differences are still found among different pozzolanas.[106] For pozzolana/lime ratios ranging between 2:1 and 1:2, the porosity of the paste increases with increasing lime content. This is true for many natural pozzolanas, but not for the silica gel, since the porosity of the paste decreases when the lime content increases.[40]

Tests carried out with low-lime fly ashes have given the same results. A difference has, however, been found between a typical natural pozzolana and a fly ash: natural pozzolana–lime mixes show a well-defined discontinuity in pore radii between 1.5 and 2.0 nm, whereas fly ash–lime mixes show only a slight discontinuity.[141]

10.2.5 STRENGTH OF LIME–POZZOLANA MIXES

A practical consequence of the pozzolanic reaction is the gradual hardening of pozzolana–lime pastes. Strength increases as the amount of combined lime increases.[25,106] However, as shown in Figure 10.12, there is no general relationship between the two parameters, just a simple correlation within each pozzolana. The lack of correlation is also found when combined lime is compared with strength of Portland cement–pozzolana blends.[111]

For this reason the technical assessment of pozzolana must be carried out by measuring the strength of the lime mix (or Portland cement mix) and not by determining the amount of fixed lime present. The determination of combined lime is only a helpful tool in explaining

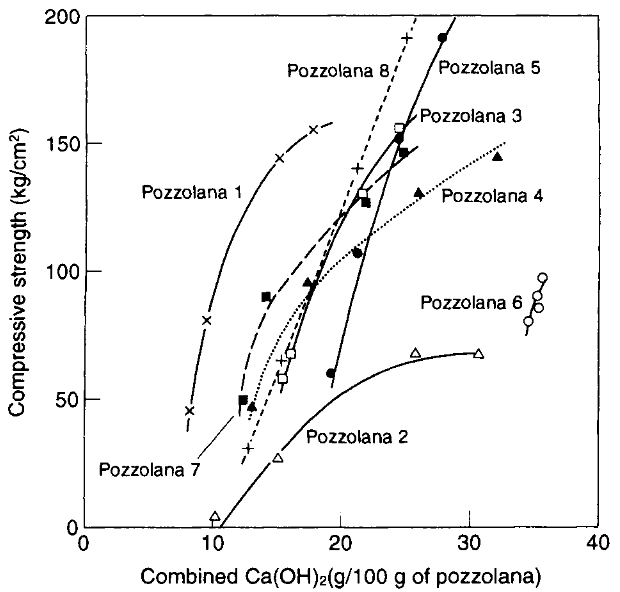

Fig. 10.12 Compressive strength versus combined calcium hydroxide (source: Ref. 106). Pozzolana/calcium hydroxide = 100:40; w/s = 0.6. Samples stored in water at 40°C and cured for 3, 7, 28 and 90 days.

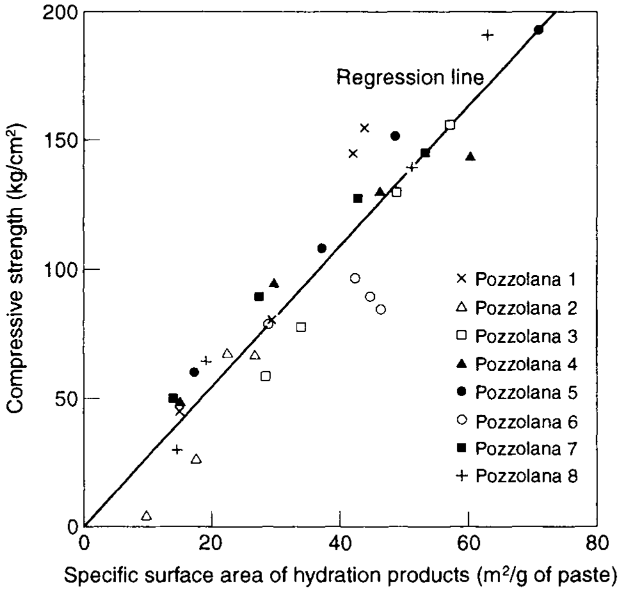

Fig. 10.13 Compressive strength versus surface area of hydration products (source: Ref. 106). Pozzolana/calcium hydroxide = 100/40 (correlation coefficient $r = 0.93$).

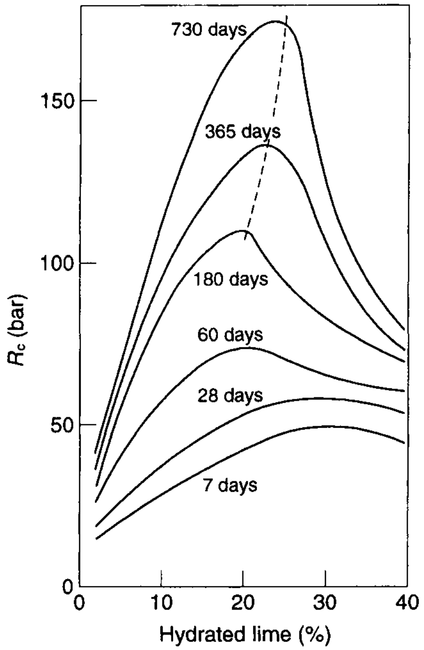

Fig. 10.14 Influence of lime content on the compressive strength of hydrated lime–pozzolana mixes (source: Ref. 142). Water/binder = 0.08.

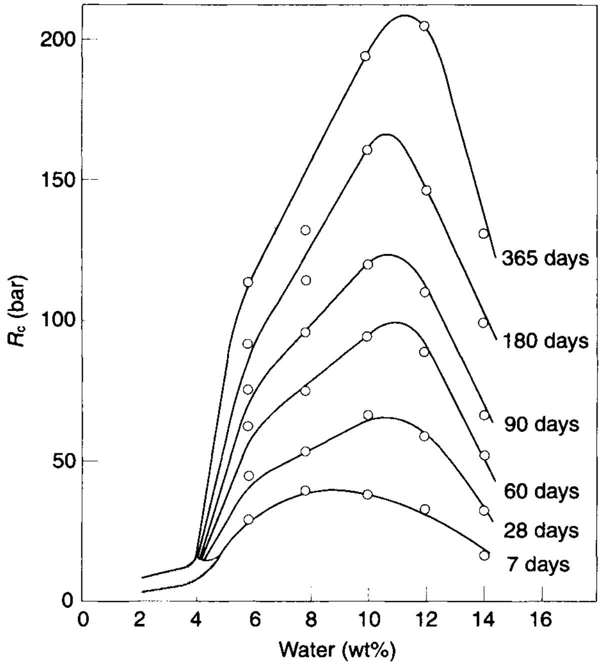

Fig. 10.15 Influence of water content on the compressive strength of binder (source: Ref. 142). Hydrated lime/pozzolana ratio = 0.20.

the hardening phenomenon of mortars and cements.[18] In this respect a typical example is provided by the behaviour of clay-based materials which, despite their ability to fix lime, do not harden appreciably. An interesting example referred to in Ref. 25 shows that the strength of a material rich in clay minerals can be as high as about one-third of the strength of materials having a true pozzolanic behaviour. A good correlationship has been found between compressive strength and specific surface area of the hydration products. Figure 10.13 shows that only pozzolana with high silica and a high surface area deviates from this empirical rule.

The strength of lime–natural pozzolana pastes increases with increasing the lime/pozzolana ratio but, beyond certain values, it decreases[142,143] (Figure 10.14). The addition of gypsum does not change this behaviour.[116] Strength increases with increasing fineness but the effect appears only after 28 days.[142] The influence of water content can be observed in Figure 10.15 which shows that the highest strength is reached at specified water contents.[142]

Hardening of a pozzolana–lime mortar is slow but long-lasting and thus compressive strength at 2 years can be as high as three times the 28-day strength.[143] The addition of gypsum increases strength[127] (Table 10.18), but it should not exceed certain levels if disintegration of specimens[128,116] (due to the formation of large quantities of ettringite[139]) is to be avoided.

A good linear correlation has been found between the Blaine fineness of a natural pozzolana and the compressive strength of 20:80 lime–pozzolana mixes. Benefits of higher fineness are more pronounced at early than at late ages.[144a] A similar relationship has been observed in mixes made up of fourteen different fly ashes and lime.[144b]

Table 10.18 Compressive strength of two lime–Segni pozzolana mixes of different gypsum content[127]

	$CaSO_4$ (%)				
Curing time	0	2.5	5	7.5	10
			$Ca(OH)_2 = 15\%$		
7 days	16	31	28	56	65
14 days	24	47	66	102	118
28 days	51	85	108	120	140
3 months	87	120	170	163	160
6 months	122	138	175	170	180
1 year	135	156	180	181	163
2 years	150	165	187	186	148
			$Ca(OH)_2 = 25\%$		
7 days	8	22	30	28	51
14 days	20	35	58	62	68
28 days	49	55	125	144	150
3 months	110	105	198	208	181
6 months	168	175	233	239	215
1 year	190	208	266	268	202
2 years	212	230	280	275	187

Early strength and 180-day strength of lime–pozzolana mixes are improved by adding KOH or NaOH, as well as Na_2SO_4 or $CaCl_2$.[144a,145] The 28-day paste strength can be as high as ~30 MPa, but rapid setting can occur.[134,146] Similar results have been obtained with lime–fly ash mixtures. Paste strength attains the highest level for 10–15 per cent lime content and increases with increasing fineness of fly ash.[132]

After 4 months the strength of fly ash–lime mortars is ~40 MPa depending on the sand/lime/fly ash ratios, the water/binder ratio, the curing conditions and so on. It may be affected, either positively or negatively, by the addition of chemicals. These products widen the small gap in strength observed in mixes having different lime/fly ash ratios, by causing it to increase from 10 to ~90 per cent. Addition of gypsum is effective in improving strength.[147]

High-lime fly ashes can behave like hydraulic binders. In fact, if they have a suitable composition, they need neither lime nor cement to harden.[85,134,146,148] The addition of gypsum (~6 per cent) improves the compressive strength of the paste, from 33.4 to 44.6 MPa.[134] After 28 days the compressive strength of concrete made with plain high-lime fly ash can be as high as 15–25 MPa.[85]

Burned kaolin (metakaolin),[139] as well as other clay materials,[196] harden gradually when they are mixed with lime and water. The strength attained after 28 days' curing strongly depends on the burned clay/lime ratio and water/solid ratio. The strength of metakaolin and burned clay shows a sharp peak for mix ratios ranging between two and three. The duration and temperature of the burning process affect the strength. Thus, it is necessary to select the correct thermal treatment in order to achieve the best results.[94,142,149]

The strength also depends on the nature of the clay minerals. The highest strength was obtained with mixes made with burned kaolin (27 MPa) and the lowest with burned illite

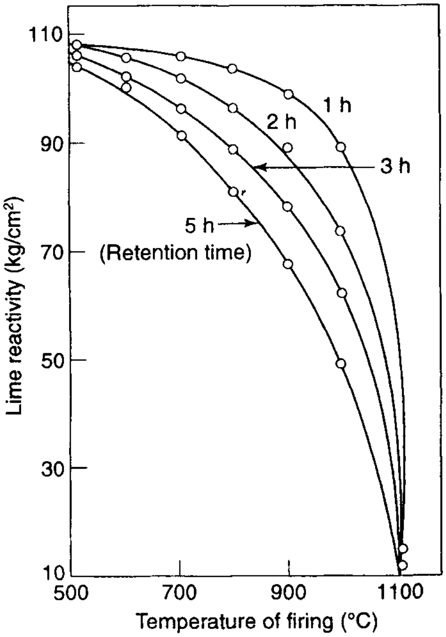

Fig. 10.16 Lime reactivity (a measure of pozzolanic value) of rice husk ash produced at different temperatures and firing times, according to Standard IS 1727: 1967 (source: Ref. 104).

(8 MPa).[196] Mechanical properties of calcined clays can be improved by incorporating admixtures, such as 0.01 per cent ZnO, to the mix.[150]

The compressive strength given by rice husk ash depends on the pozzolana/lime ratio and it shows a maximum when the ratio ranges between 1:1 and 1.5:1. The best result obtained according to the ASTM C 109 standard specification was 8.5 MPa. Unlike other types of pozzolana, the strength of rice husk ash–lime mortar do not increase beyond 28 days.[103]

The strength of rice husk ash blended with hydrated lime depends on the firing temperature and the firing length (Figure 10.16).[104] Thus a pozzolanic material having good and constant properties can be obtained only by burning rice husk under well-defined conditions. The practical difficulty in assuring such conditions is the primary reason which has prevented the production and use of rice husk ash on a large scale.[104]

Strength values between 10 and 14 MPa have been reached after curing mortar made of lime and diatomaceous earth for 28 days. Due to their high specific surface area, diatomite mortars have a high water demand.[151]

Hardening of burned shales occurs without the presence of lime. Nevertheless, the addition of up to 10 per cent of calcium hydroxide increases strength proportionally to the lime content.[98] Hydraulic oil shale ashes give the best performances when they are burned at a certain temperature. The highest strength occurs at burning temperatures of 800–850°C.[98]

10.3 Pozzolana-containing cements

10.3.1 POZZOLANIC CEMENTS AND POZZOLANA CEMENTS

When mixed with Portland cement and water, pozzolana reacts with the calcium hydroxide formed during hydration of the calcium silicates in the clinker. As a result of this reaction, the final portlandite content in the hydration products is always lower than that found in the control Portland cement. This applies to all pozzolanas, both natural and artificial, as well as to suspensions, pastes, mortars and concretes. The simultaneous presence of Portland cement and pozzolana modifies the respective reactions of hydration. This mutual influence needs to be thoroughly investigated in order to determine the conditions which allow the best technical performance to be obtained.

Pozzolanic cements are by definition mixes of Portland cement and pozzolana which, if dispersed in excess water and kept under certain conditions, eventually give rise to unsaturated calcium hydroxide solutions.[152–154] Conversely, pozzolana cements do not comply with this requirement inasmuch as their pozzolana content is insufficient – in terms of both quality and quantity – to combine all the portlandite which forms during the hydration of the clinker calcium silicates and to give unsaturated lime solution. As a consequence, whilst hardened pozzolanic cements lack, at least theoretically, free lime, pozzolana cements do not. The residual portlandite content depends on the activity of pozzolana, the amount of lime released by the clinker, as well as the pozzolana/cement ratio. As far as pozzolanic cements containing natural pozzolanas or silico-aluminate fly ashes are concerned, the pozzolana/Portland cement ratio is approximately 1:2. Pozzolana-containing cements are classified by CEN, the European Committee for Standardisation, as shown in Table 10.19.[155]

In principle, pozzolana can be added to Portland cement either at the cement plant or at the building site. In the first case, pozzolana undergoes either simultaneous grinding with clinker and gypsum or separate grinding followed by mixing and homogenisation

Table 10.19 Chemical types containing pozzolanic material according to CEN prEN 197-1[a][155]

Main cement type	Designation	Notation	Clinker K	Blastfurnace slag S	Silica fume D[b]	Pozzolana		Fly ashes		Minor additional constituents
						Natural P	Artificial Q	Siliceous V	Calcareous W	
II	Portland silica fume cement	II/A-D	90–94	–	6–10	–	–	–	–	0–5
	Portland pozzolana cement	II/A-P	88–94	–	–	6–20	–	–	–	0–5
		II/B-P	65–79	–	–	21–35	–	–	–	0–5
		II/A-Q	80–94	–	–	–	6–20	–	–	0–5
		II/B-Q	65–79	–	–	–	21–35	–	–	0–5
	Portland fly ash cement	II/A-V	80–94	–	–	–	–	6–20	–	0–5
		II/B-V	65–79	–	–	–	–	21–35	–	0–5
		II/A-W	80–94	–	–	–	–	–	6–20	0–5
		II/B-W	65–79	–	–	–	–	–	21–35	0–5
	Portland composite cement[c]	II/A-M	80–94	←6–20→						0–5
		II/B-M	65–79	←21–35→						0–5
IV	Pozzolanic cement[c]	IV/A	65–89	–	←11–35→				–	0–5
		IV/B	45–64	–	←36–55→				–	0–5
V	Composite cement[c]	V/A	40–64	18–30		←18–30→			–	0–5
		V/B	20–39	31–50		←31–50→			–	0–5

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[a] The values of the table refer to the sum of the main and minor additional constituents.

[b] The proportion of silica fume is limited to 10%.

[c] In portland-composite cement CEM II/A-M and CEM II/B-M, in pozzolanic cements CEM IV/A and CEM IV/B and in Composite cements CEM V/A and CEM V/B the nature and kind of the constituents besides clinker shall be declared by designation of cement.

[d] Portland composite cement can contain burnt shale.

with suitable equipment. In this latter case, pozzolana is introduced with Portland cement into the concrete mixer. This procedure improves the quality of concrete, both in terms of strength and durability, when pozzolana is added with the purpose of improving grading of the fine aggregates, but it causes a certain decline in the properties of concrete when pozzolana is used as a partial replacement for Portland cement.

The reasons why this procedure is not recommended can be summarised as follows:[156]

- generally, the degree of homogenisation that can be reached by mixing pozzolana with Portland cement at the building site is lower than that reached by using the facilities of a cement plant;
- replacing a relatively large portion of Portland cement with pozzolana reduces early strength;
- building yards rarely have all the personnel, equipment and time required for checking the properties of pozzolana and the mixes.

10.3.2 HYDRATION OF CLINKER PHASES IN THE PRESENCE OF POZZOLANA

Knowledge of the systems formed by pozzolana and clinker compounds makes it easier to study more complex systems containing Portland cement. Clinker compounds have the advantage of being pure and can be tested one at a time, thus limiting the interferences arising from simultaneous reactions such as those occurring when Portland cement hydrates.

The presence of pozzolana modifies to some extent the reactions of hydration of Portland cement, as well as the reactions of the single compounds. Any chemical and microstructural modifications can affect the engineering properties of cement.

Kinetics of hydration

The kinetics of early hydration can be investigated advantageously by isothermal transmission calorimetry, whereas the progress of hydration at advanced ages is best monitored through XRD, DTA, DSC, and optical and electron microscopy. For determining the portlandite content in the paste, chemical methods such as the extraction of free lime with appropriate solvents are used.

An important contribution to interpreting hydration of pozzolana-containing cements is given by the results of investigation concerning the hydration of the pure cement compounds in the presence of pozzolanic materials. The main findings are summarised below.

C_3A. The addition of natural pozzolana to C_3A changes the initial rate of evolution of the heat of hydration since it causes the intensity of the second peak to decrease. Lowering of the peak is seen as corresponding to a diminution in the hydration rate of the aluminate.[157,158]

The decrease of the second peak on the heat evolution curve is influenced by the type of pozzolana employed, and this could be related to the BET specific surface area of the pozzolana. In fact, the delay brought about by Sacrofano pozzolana (BET specific surface area $\sim 60\,\mathrm{m^2/g}$) is greater than that of the Segni pozzolana (BET specific surface area $\sim 30\,\mathrm{m^2/g}$).[157] Of course, the delay could be due to other causes, such as the dissolution of alkalis and the surface activity,[159] but these factors have not been investigated.

The retarding effect of fly ashes is quite similar to that shown by natural pozzolanas.

The addition of fly ash to C_3A (mass ratio 30:70) suppresses hydration during the first few minutes and then lowers the rate constants by approximately seven times.[159] Also, the addition of an inert material such as ground quartz reduces the hydration rate and delays the beginning of C_3A hydration, although its effect is less marked than that caused by fly ashes.[159]

Pozzolana reduces the hydration rate of both the C_3A produced in the laboratory and the tricalcium aluminate extracted from ground cement clinker by selective dissolution, the former hydrating more quickly than the latter.[159] The reasons for the delay caused by pozzolana to the early hydration of C_3A have not been resolved.

Gypsum, or gypsum and lime, decrease the rate of tricalcium aluminate hydration but the addition of pozzolana to these systems accelerates the hydration of C_3A, the formation of ettringite and its conversion into monosulfate.[157,158] By assuming that the decrease in intensity of the peaks of C_3A on the XRD trace is proportional to the volume of the hydrated compounds, it is possible to follow the hydration of aluminate with time by X-ray analysis.[159]

After 7 days of curing, the degree of hydration of C_3A attains $\sim$90 per cent, irrespective of the presence of pozzolana.[158] When the mixes contain gypsum and lime, the degree of reaction of pozzolanas increases slowly with time, typically reaching 20 per cent after 180 days.[158]

As far as the different behaviour of the two aluminates contained in the Portland cement clinker is concerned, the industrial tricalcium aluminate hydrates approximately six times more rapidly than C_4AF.[159]

C_3S. The presence of pozzolanic materials affects many aspects of C_3S hydration, i.e. the kinetics of reaction, formation of portlandite and composition of the hydrates. The determination of the heat evolution rate is a sensitive and useful tool to characterise the way in which pozzolana influences the early hydration of C_3S. Figure 10.17 shows that pozzolana modifies the curves of the rate of heat evolution to an appreciable extent. On the whole, natural pozzolanas have an accelerating effect on the hydration of C_3S. More

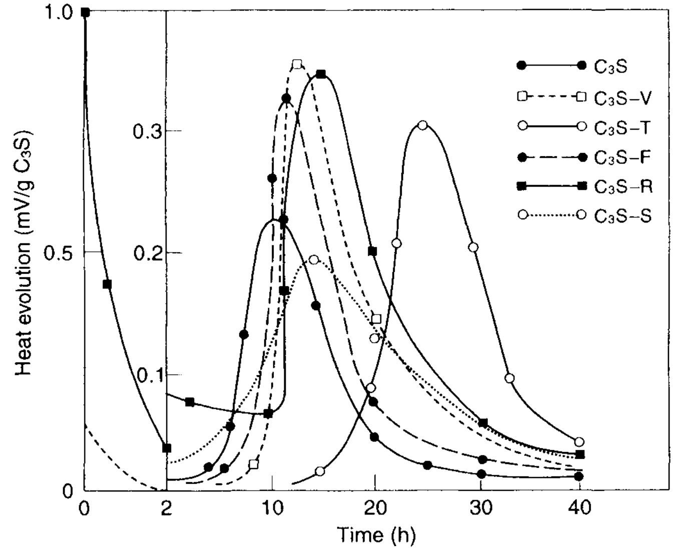


Fig. 10.17 Heat evolution curve in 6:4 C_3S–pozzolana blends (source: Ref. 160). V, F, R and S are natural pozzolanas, T is fly ash. w/s = 0.4.

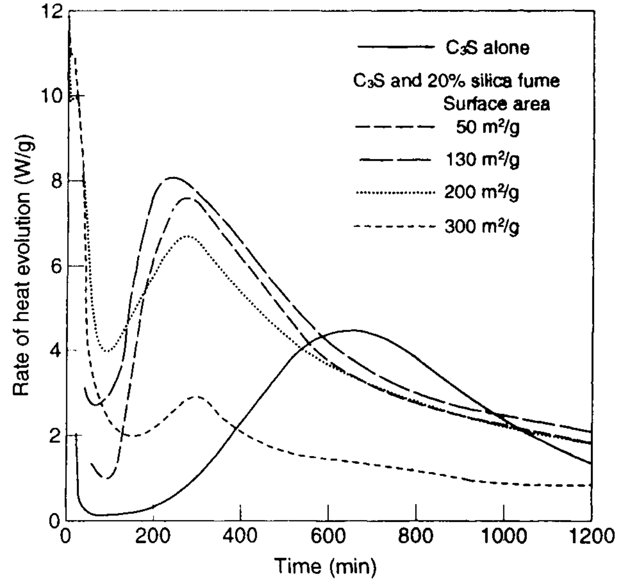


Fig. 10.18 Calorimetric curves from the hydration of C_3S with 20 per cent by weight of amorphous silica of various surface areas ($w/C_3S = 1$) (source: Ref. 164).

precisely, the dormant period does not vary: the second peak is only slightly delayed but its height is strongly increased.[160]

Fly ashes lengthen the dormant period and increase the height of the second peak,[160] though a slight decrease has also been reported.[161] These results can be interpreted as an initial retarding effect followed by an accelerating one. However, since the overall heat of hydration evolved in the first 48 h is higher for blends containing fly ash than for plain C_3S, it can be concluded that fly ash has an accelerating effect on the hydration of tricalcium silicate.

Very fine amorphous silica (Aerosil, BET specific surface area = 207 m²/g) reduces the length of the dormant period and increases the intensity of the main peak.[162] If the C_3S/S ratio decreases beyond a certain level (~0.67), the dormant period and the second peak will disappear, the Ca^{2+} concentration in solution will increase[163] and the curve of heat evolution will show only an initial peak whose height increases as the ratio decreases.[163] When mixed with alite, amorphous silica having the same specific surface area (20 m²/g) behaves like Aerosil.[164] The slight differences observed can depend on the composition of the tricalcium silicate and the different C_3S/S ratios used.

The reduction in the induction period has been observed in blends with microsilica having a specific surface area in the range 50–380 m²/g,[164] but not when microsilica had an unusually low specific surface area (i.e. 19 m²/g).[165] The height of the second peak initially increases as fineness increases, but then decreases, as shown in Figure 10.18.[164] Increasing amounts of microsilica will reduce the length of the induction period of C_3S.[75]

In general it would seem that, in the course of the first 24 h, natural pozzolanas and microsilica accelerate the initial hydration of C_3S both in terms of shortening the dormant period and of increasing the intensity of the second peak of the heat evolution curve.

The acceleration of the early hydration of C_3S caused by pozzolanas has been ascribed to the fineness of pozzolana particles, which would provide C-S-H with preferential nucleation sites.[73,160] More simply, the pozzolana particles offer a surface for the precipitation of C-S-H from the pore solution. In any case, the removal of calcium and silicate ions from the solution would result in a reduction of the thickness of the relatively impermeable C-S-H growing on the C_3S grains.[165] The precipitation is most likely to be due to the rapid adsorption of Ca^{2+} ions onto the high-silica surface of pozzolana. The partial removal of Ca^{2+} from the vicinity of C_3S grains should accelerate the transformation of the relatively impermeable, high-lime layer formed on the surface of C_3S by the first hydrate in more permeable C-S-H.[162] This view is supported by the following arguments:

- acceleration does not result from the pozzolanic reaction, as this becomes evident in pastes only after some days;
- in spite of the acceleration of C_3S hydrolysis, the Ca^{2+} concentration in the pore solution does not significantly change in the presence of pozzolana;[160]
- the formation of Ca(OH) and C-S-H on the pozzolana particles occurs through a dissolution and precipitation mechanism[160] which requires Ca^{2+} to move from the C_3S to the pozzolana surface.
- unlike pozzolanas, the partial replacement of Portland cement with ground silica sand[162] or graphite and titanium[164] produces either no or only minor changes to the heat evolution curve.

Amorphous microsilica accelerates the hydration of C_3S more than natural pozzolanas since, depending on the C_3S/S ratio, it causes an early decrease in the Ca^{2+} and OH^- concentrations[162,163] in the mixing water. The decrease occurs in water dispersions[162,163] as well as in the paste.[162]

As shown in Table 10.20, the higher pozzolanic activity of microsilica is in agreement with its calcium adsorption capacity (CAC), which is definitely higher than that of fly ashes. CAC is the difference in the Ca^{2+} concentration measured before and after dispersing pozzolana in a lime-saturated solution for 3 h.[166] As a matter of course, the transfer of calcium ions from the C_3S grains to the microsilica particles could also be accelerated by an early pozzolanic reaction, caused by the high specific surface area and high silica content of the microsilica. This view is supported by the roughness which appears on the particles

Table 10.20 Calcium adsorption capacity (CAC) and zeta potential of blending component dispersed in $Ca(OH)_2$ saturated solution[166]

No.	Blending component	Content (%)	BET (m^2/g)	Blaine (cm^2/g)	Calcium adsorption capacity (mmol Ca/g)	Zeta potential (mV, water suspension)
1	Coarse slag	20	2.67	4000	0.055	−18
2	Fine slag	20	2.86	5900	0.053	−9
3	Ordinary fly ash	20	0.44	3840	−0.026	−8
4	Ordinary fly ash ground	20	1.91	8400	−0.005	−14
5	High calcium fly ash	20	0.57	3730	−0.005	10
6	Rice husk ash	20	0.75	–	0.027	−20
7	Silica fume	20	20.91	–	0.203	−33
8	Aerosil	5	167	–	0.326	–

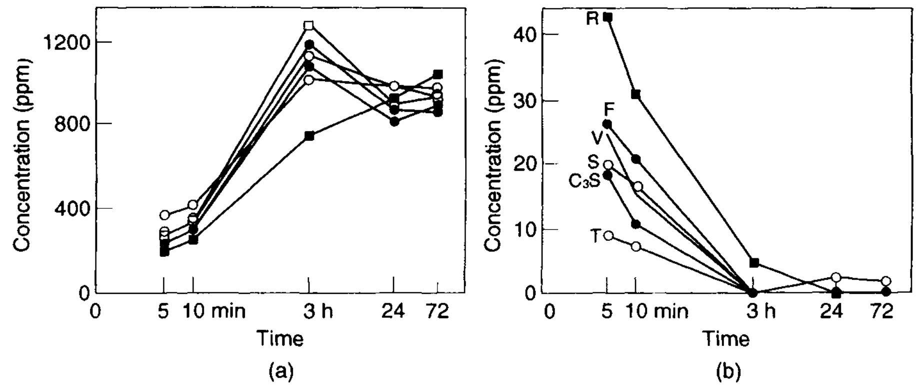


Fig. 10.19 Concentration of (a) Ca^{2+} and (b) Si^{4+} in water. 6:4 blends of C_3S and natural pozzolanas (V, F, R) fly ash (T) and blastfurnace slag (S) (source: Ref. 160). Samples dispersed in water and then shaken for fixed times.

of microsilica after only 1 h of hydration[164] and the shortening of the induction period.[162] Adsorption of calcium ions onto the surface of microsilica grains before the beginning of the pozzolanic reaction could also explain why the initial rate of crystallisation of portlandite is greater than the rate of consumption of calcium hydroxide with microsilica.[75] In this case Ca^{2+} ions adsorbed onto the silica fume could act as nuclei of crystallisation for portlandite.

The delay to the early hydration of C_3S caused by fly ashes has been tentatively attributed to the release of aluminate from the fly ash.[161] In fact, when the solution contains aluminate ion, the transformation of the 'first hydrate' ($C/S = 3$) into a 'second hydrate' ($C/S = 0.8-1.5$) is delayed.[167] However, aluminate ions are not present in the pore solution of fly ash–C_3S mixes except in the case when NaOH solution is used as gauging water.[161]

According to another assumption, the soluble compound contained in fly ashes (1–5 per cent) could interfere with the hydration of C_3S. In fact, lime mortars prepared from ashes washed with water reportedly gave strengths two to three times greater than those of mortars made with raw ashes.[75] However, these results were attributed to the increase in the specific surface area caused by the breaking down of the agglomerates of fine particles occurring in the fly ash. The prolonged dormant period observed in fly ash mixes could be attributed also to the presence of carbon compounds acting as retarders.

The evolution of the composition of the gauging water is the same both with suspensions (solid/water ratio 1:10) containing only C_3S and with mixtures of C_3S and pozzolana (Figure 10.19).[160] In the suspensions, the Ca^{2+} concentration first increases up to a certain supersaturating level and then decreases with time. Natural pozzolanas and fly ashes behave similarly. Figure 10.19 shows that the initial concentration of Si^{4+} in the liquid phase depends on the type of pozzolana, but after 3 h no differences can be detected.[160] In the presence of microsilica the Ca^{2+} concentration first increases and subsequently decreases, but it always remains lower than that observed in plain C_3S. If the C_3S/S ratio drops to 0.4, the solution never attains saturation in Ca^{2+} (Figure 10.20).[163]

For evaluating the medium- and long-term influence of pozzolana on the hydration of C_3S, other criteria have also been used, such as the determination of the integral heat of hydration, the diminution with time of the unreacted C_3S as well as the uncombined

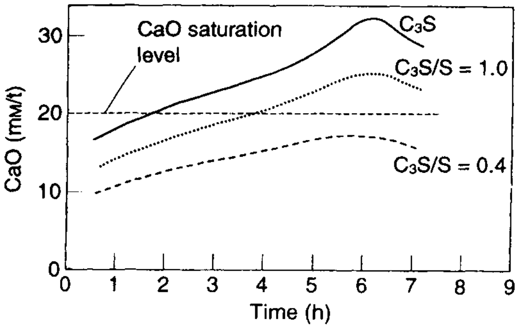


Fig. 10.20 Blends of C_3S and "Aerosil" microsilica dispersed in water (source: Ref. 163). Ca^{2+} ions concentration in the liquid phase as a function of time for different C_3S/S ratios; w/s = 10.

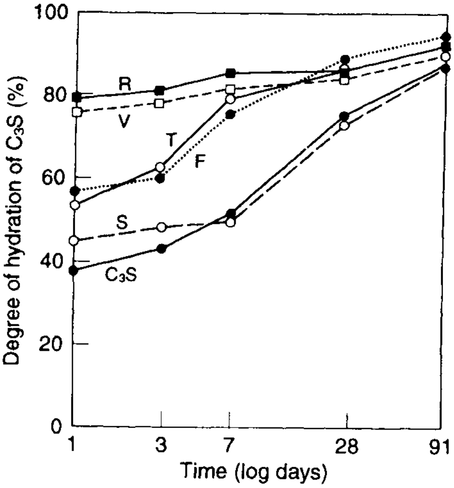


Fig. 10.21 Degree of hydration of C_3S as determined by XRDA (source: Ref. 160). Composition and symbols as in Figure 10.17.

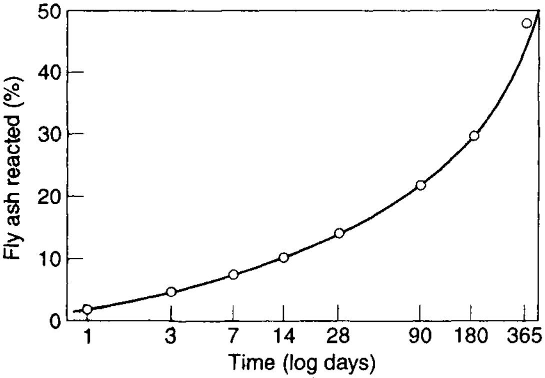


Fig. 10.22 Amounts of fly ash reacted (source: Ref. 168). C_3S/fly ash = 3, w/s = 0.5.

pozzolana content. XRD analysis reveals that after only 1 day, natural pozzolanas,[160] fly ashes[160,168] and microsilica[166] cause a definite reduction of unreacted C_3S content. The degree of hydration of tricalcium silicate strongly depends on the type of pozzolana at first[160] but any difference becomes negligible after ~91 days (Figure 10.21).[160,168]

The pozzolanic reaction starts slowly, thus the decrease in the unreacted pozzolana content becomes apparent only after 3–5 days.[160,168] The amount of reacted pozzolana increases as a function of time (Figure 10.22)[168] and reaches a value which depends, other conditions being equal, on the type of pozzolana.[160] As a consequence, pozzolana–C_3S pastes have a lower $Ca(OH)_2$ content than C_3S ones.

Paste microstructure and composition of hydrates

C_3A. Pozzolanas do not change the kinds of hydrates that form in the hydration of C_3A. However, if the mixes contain calcium hydroxide, C-S-H forms as a consequence of the pozzolanic reaction. In the presence of calcium sulfate and pozzolana, C_3A hydration gives ettringite, monosulfate hydrate and calcium aluminate hydrate hexagonal solid solutions, although at different ages.[158]

C_3S. The paste hydration of C_3S results in the formation of C-S-H on the tricalcium silicate grains, in the form of a high C/S ratio layer, and on the pozzolana particles as porous, low C/S ratio layer.[160]

After 3 days, C_3S grains appear to be surrounded by a hydrated layer, 2 μm thick, having a C/S ratio of 2.5. Nevertheless, near the pozzolana grains, the C/S ratio can be as high as 4, indicating an enrichment in lime or the presence of some portlandite.[160]

After a certain period of time, which depends on the characteristics of the pozzolana, the water/solid ratio, the temperature, etc., pozzolana grains are attacked by H_3O^+ protons contained in the basic solution resulting from the hydrolysis of the calcium silicates. The attack brings about a gradual dissolution of Na^+ and K^+ and produces an amorphous layer rich in both Si and Al on the surface of the pozzolana grains. This layer reacts with the Ca^{2+} ions present in the solution and transforms into calcium silicate and calcium aluminate hydrates. Dissolved alkalis intensify the protonic attack of water.[160]

In aged pastes made up of C_3S and fly ashes, the morphology of the hydration products of tricalcium silicate are not different from those of pure C_3S pastes. The hydration products surrounding the residual unreacted C_3S particle core form an 'outer' and an 'inner' layer of C-S-H. The 'outer' product often appears as fibrillar under TEM.[169] No foreign elements are found in the inner region of C_3S hydration products, whereas the outer region can contain other elements, especially potassium, obviously coming from the fly ash.[169]

After a curing period of 1 year, a rim of dense C-S-H is formed along the edges of the reacted fly ash particles, from which radial fibres of lower density C-S-H branch off. In the C-S-H forming the rim and in that forming the fibres, the C/S ratio is roughly the same, although it is lower than in the C-S-H formed in plain C_3S pastes.[169] The existence of different concentric regions or shells of dense C-S-H around a fly ash particle is attributed to a rhythmic precipitation.[169] In other parts of the reaction zone, dense plates made up of hydrogarnets occur. This phase should reportedly gather both Fe and Al released by the fly ash.[169]

During the first month, the alumina, iron and SO_4^{2-} contained in fly ashes are to be found in the form of small amounts of AFt and AFm.[168,169] Within 90 days, however, the three elements are incorporated into C-S-H[168] or hydrogarnet.[169]

The composition of C-S-H can be determined by direct and indirect methods. Microanalysis carried out by electron microprobe (EPMA), scanning electron microscope (SEM) and transmission electron microscope equipped with suitable analytical devices belong to the first methods. Chemical determinations, based on selective dissolution, form the second group.

The potential causes of analytical errors are many. They come from incorrect sampling and specimen preparation, the value of the accelerating voltage chosen for the microanalysis, poor selectivity of the analytical method, etc. Considering all these factors, it seems that the most probable value of the C/S molar ratio of C-S-H is 1.7. This value is in agreement with the indirect chemical determination of the ratio, which has given 1.7–1.8.[170] As a matter of fact, C/S ratios ranging between 1.5 and 1.9 have been found.[160,171-176] This variability is due to the difficulty of the analysis and to the variability of the C-S-H composition. A C/S molar ratio of 1.56 was typically obtained within a range of 1.21–1.96. This means that the variation of composition between the particles is highly significant and, in any case, higher than that found in crystalline substances.[171] No significant differences, possibly associated with time, degree of reaction or morphological type of C-S-H, were found.[171]

Some results had suggested that the outer and inner product would have different composition but microanalysis of ion beam-thinned section of pure tricalcium silicate paste, carried out by TEM (transmission electron microscopy), have shown that inner and outer products of hydration have the same C/S ratio of ~1.7.[175]

In the presence of pozzolana, the composition of C-S-H appears to change. Electron microscope analyses have shown that after 2 weeks, in the presence of fly ashes, the C/S ratio was on average 1.43, i.e. slightly lower than that found in pure C_3S pastes (1.51).[168] In the pastes of C_3S and fly ash, the C/S ratio of the inner product around anhydrous C_3S was 1.56 ± 0.05 after 2 weeks and 1.45 ± 0.01 after 1 year of hydration. After 1 year, the outer product had a C/S ratio of 1.6 ± 0.16 but contained some alumina and potash.[169]

Field emission scanning electron microscope (FESEM), featuring a higher resoluting power than other types of electron microprobe, provided more detailed results. In the hardened paste of plain C_3S the C/S ratio of the hydrated mass extending between adjacent C_3S grains reaches a constant value of 2 after 3 days of curing.[160] This value almost coincides with data reported by other workers,[173,174,177] but it is higher than the value specified in previous works.[172] However, the possible presence of portlandite crystals may locally increase the apparent C/S ratio up to 3.[160]

The C/S ratio changes in the presence of natural pozzolanas. After 3 days the hydrates filling the space between C_3S and the pozzolana grains have a C/S ratio as high as 2.5–3.00. However, near the pozzolana edge, the ratio can attain the value of 4, indicating the probable presence of portlandite.[160] After 91 days the Ca distribution in the paste is more regular, and outside the C_3S surface the C/S ratio decreases gradually, reaching a mean value of 1.7. Figure 10.23 shows the abrupt ratio decrease on the pozzolana surface.[160] Also, in the presence of microsilica, the hydration of C_3S forms an outer and an inner product. The reaction of microsilica is evident in the fracture surface of pastes because the boundary between the silica particles and the outer C-S-H becomes less distinct. The smaller particles appear to be eaten away.[165] The silica grains can be observed in the outer regions of C-S-H, but not in the inner product that has formed on C_3S grains.[165] Generally, the paste fracture takes place between the inner and the outer hydration product formed on the C_3S grains.[165]

TEM has revealed that the composition of C-S-H which forms in the presence of microsilica is different from that formed in plain C_3S paste. The inner product of plain

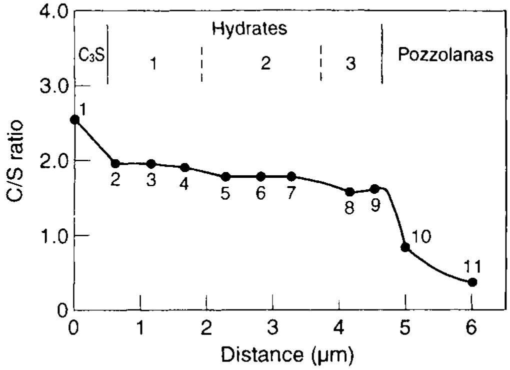


Fig. 10.23 Blends of C_3S and pozzolana (V) (source: Ref. 160). Mix ratio = 6:4, w/s = 0.4, curing = 91 days. Distribution of C/S ratio between two C_3S and pozzolana grains is shown.

C_3S paste had a C/S ratio equal to 1.68 ± 0.07 in the first case, and 1.60 ± 0.15 in the second. However, in the presence of microsilica, there are some areas in the paste which consist entirely of C-S-H having a ratio of 0.92 ± 0.09. These areas presumably contain microsilica particles which had completely reacted with Ca^{2+} ions.[165] This C/S ratio is lower than that occurring normally, but it corresponds to the low C/S recognised in a low-Ca^{2+} environment.[178] These results suggest that the overall C/S ratio of C-S-H decreases as the pozzolanic reaction proceeds and most of the silica reacts.[165]

Analysis by ^{29}Si MAS-NMR (magic angle spinning nuclear magnetic resonance) of 2 year old mixtures of silica fume, lime and water, have suggested the existence of two structurally distinct forms of calcium silicate hydrates having a C/S ratio ranging between 0.65 and 1.00 (low-lime C-S-H) and between 1.1 and 1.3 (high-lime C-S-H).[179] These results were obtained in dispersions (water/solid = 200) and thus they cannot apply directly to compounds formed by cement hydration. Nevertheless they give an important contribution to understanding the hydration phenomenon.

Presumably, a C-S-H of normal composition forms initially, but when all the locally available calcium hydroxide is consumed, the excess silica reacts with the hydrate already formed and produces another kind of C-S-H with a lower C/S ratio and which is highly polymerised.[220]

After 1 day of hydration, the paste made of 80 per cent C_3S and 20 per cent microsilica showed that the inner product developed on the surface of C_3S grains had a C/S ratio of 1.6 ± 0.1, but after 28 days the inner and the outer product had the same 1.2 ± 0.1 ratio. This indicates that some C_3S remained unreacted since the overall C/S ratio of the mixture is 1.5.[164]

The different compositions of C-S-H reflect the degree of silica polymerisation, calculated by determining the trimethylsilyl derivatives of C-S-H. As can be seen from Figure 10.24, pastes made up of C_3S and pozzolana show a higher content in polymers and a lower one in dimers than for pure C_3S pastes.[129,168,180] The degree of polycondensation of the polymer, expressed by the number average of the silicon atoms in the anion, depends on the type of pozzolana, although variation is not very significant, as it ranges between 11.0 and 12.9 after 180 days of curing.[180]

The dimer content begins to decrease after a certain period of time, varying between 3–7,[180] 90[168] and 270[129] days. Although very different, these results are not always

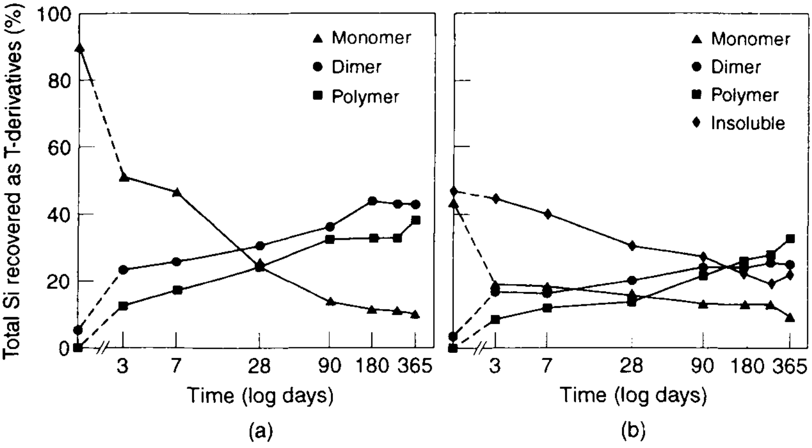


Fig. 10.24 Proportions of total Si present as monomer, dimer, polymer and insoluble in C_3S pastes (a) and C_3S-pozzolana pastes (b) as determined by trimethylsililation (source: Ref. 129). Specimens cured for 365 days at 20°C; w/s = 0.5.

meaningful since the difference could be attributed to different experimental conditions, water/solid ratio, C_3S/pozzolana ratio, curing temperature, etc. In other terms, these factors may influence the degree of polycondensation as much as they do the degree of hydration.

The influence of the C_3S/pozzolana ratio on the polysilicate content of C-S-H is evident in C_3S-microsilica hardened pastes. For a S/C_3S ratio of up to 0.16, the polysilicate content rises slowly with the degree of hydration to ~40 per cent, but at a ratio of 0.5 and a degree of hydration of 60 per cent, it grows rapidly and reaches about 80 per cent, the remainder being dimer.[73] After a 28-day hydration in the presence of microsilica, the average length of the silicate chain (3.6) is greater than that of the plain tricalcium silicate paste and the C/S ratio drops from 1.7 to 1.50.[165] The addition of silica gel modified with 1–10 per cent of Fe_2O_3 is claimed to increase the polymerisation of silicate anions of C-S-H.[181]

More precise determinations of the polymeric species, as well as the degree of hydration, have been carried out by using ^{29}Si MAS-NMR. This method is a valuable tool for quantitative analysis of synthetic and natural minerals[182] and for detecting structural differences in C-S-H. As a matter of fact, in the silica–lime–water system the higher-silica C-S-H (C/S = 0.65–1.0) predominantly consists of long chains of silica tetrahedra, formed by two Q_1 end units and Q_2 middle units, whereas the less rich C-S-H (C/S = 1.1–1.3) consists of dimer (Q_1) and shorter chains (Q_1 end units and some Q_2 middle units).[179]

After a 24 h hydration, the intensity of the peak Q_0 (corresponding to C_3S) is 60 per cent of the original value in the plain C_3S paste and <20 per cent in the presence of microsilica. In agreement with this, Figure 10.25 shows that the height of Q_1 (end units) and Q_2 (middle units) peaks is higher in the presence of microsilica than in plain C_3S.[165]

The study of the hydration of a mixture of C_3S and microsilica by solid-state ^{29}Si NMR and selective isotopic enrichment has shown that silicon atoms from silica and from C_3S occupy different positions in the C-S-H gel. Silicon from the two sources initially forms dimeric C-S-H, but later on silicon from silica takes part in the formation of C-S-H which has a longer chain length and a slightly better-ordered structure than calcium silicate hydrate from C_3S.[183]

Portlandite is generally present in hardened C_3S-pozzolana pastes in spite of the progress

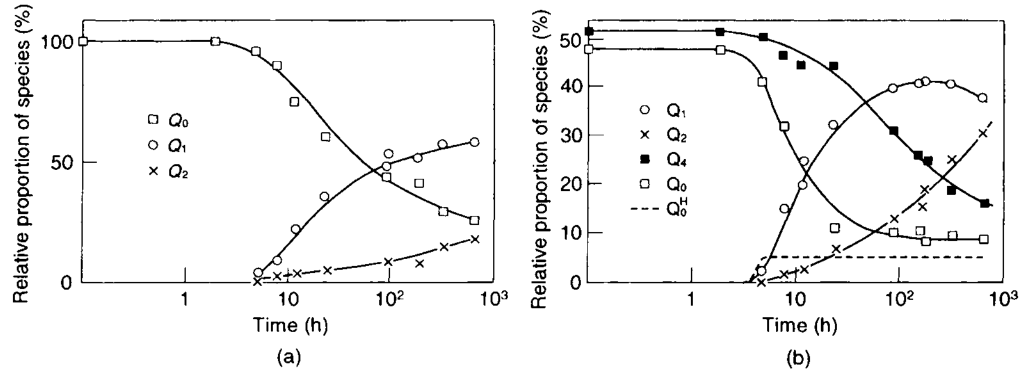


Fig. 10.25 Relative proportions of silicate species present during the progressive hydration of (a) doped C_3S and (b) doped C_3S and finely divided silica calculated from NMR spectrum peaks of ^{29}Si nucleus (source: Ref. 165). Q_0 = monomer units (hydrated), Q_1 = ends units, Q_2 = middle units, Q_4 = silica network.

of the pozzolanic reaction and the pozzolana content which is more than sufficient to combine all the lime released by hydration of C_3S. By means of a transmission electron microscope (TEM), CH crystals surrounding fly ash particles which show no sign of pozzolanic reaction have been observed.[169] This occurrence is presumably due to restricted access of the pore solution, i.e. to very low local permeability.[169] Also, in the presence of 20 per cent silica, the C_3S hydrated paste shows large lamellar crystals of portlandite running between the fibrillar mass of the C-S-H gel.[165]

10.3.3 HYDRATION OF POZZOLANA-CONTAINING CEMENTS

Kinetics of hydration

Clinker (plus gypsum) and pozzolana follow different reaction processes and react at different rates. However, both materials have a reciprocal influence. It is generally agreed that pozzolanic reaction becomes apparent, at least with the most common pozzolanas (natural and artificial), 3–14 days after mixing with water has occurred, that is to say, as soon as 70–80 per cent of the alite contained in the ordinary Portland cement has reacted.[184,185] The rate of the pozzolanic reaction depends on the properties of the pozzolana and of the mix, as well as on the temperatures. Thus, in the case of microsilica, which has a BET specific surface area higher than that of other pozzolanas, the reaction starts earlier.

The incubation period of the pozzolanic reaction is explained by the strong dependence of the solubility of the glassy part of the fly ash on the alkalinity of the pore solution. Thus the pozzolanic reaction will not start as long as the pH has not reached the required value.[186]

The kinetics of Portland cement hydration (clinker + gypsum) is modified by pozzolana even at the beginning of the process and its influence is revealed by changes occurring in:

- heat of hydration
- portlandite content
- combined water
- degree of hydration of alite
- degree of reaction of pozzolana.

It is obvious that there are also other phenomena which show the effect of pozzolana on hydration, such as the degree of silica polymerisation, but the above mentioned-parameters are those most frequently considered.

Heat of hydration. The hydration process can be monitored by recording the rate of heat evolution and the total heat of hydration released by the mixes. The determination of the rate of heat evolution is a sensitive method for detecting and recording the changes induced by pozzolana in the early hydration of cement up to 3–7 days. The cumulative heat of hydration is the algebraic sum of all the enthalpy variations related to every reaction occurring in the hydrating cement. It increases with time up to a certain asymptotic value following a typical path.

The effect of pozzolana on the heat evolved by hydrating cement becomes clearer when the measured parameters, namely the rate of heat evolution and the cumulative heat of hydration, are referred not to the whole system formed by clinker + gypsum + pozzolana, but only to the Portland cement fraction. Such a correction modifies neither the duration of the dormant period nor the delay (or acceleration) with which the second peak reaches its maximum value.

In cements containing natural pozzolanas, the dormant period is shortened and the height of the main peak is increased (Figure 10.26). This results in an accelerated rate of clinker hydration.[25] Also, the normalised height of the second or main peak is greater than that given by the control Portland cement,[25] and this would support the accelerating effect of pozzolanas on the hydration of alite. The acceleration induced by natural pozzolanas has not yet been exhaustively explained by experimental evidence. Adsorption of Ca^{2+} ions onto the surface of pozzolana may possibly favour their removal from the solution and this would accelerate the hydration of alite. Of course, all pozzolana properties, e.g. BET specific surface area, chemical composition and physical state of the surface, the more or less rapid release of alkalis, could contribute to the acceleration of the initial hydration rate of the cement.

With bituminous fly ashes, all calorimetric parameters prove to be very variable, since the duration of the dormant period can be lengthened[25,187-189] or remain unchanged[190,191] and the intensity of the main peak can be increased[25] or decreased.[187-191] The rate of heat evolution varies with the type of fly ash used[191] and the length of the induction period

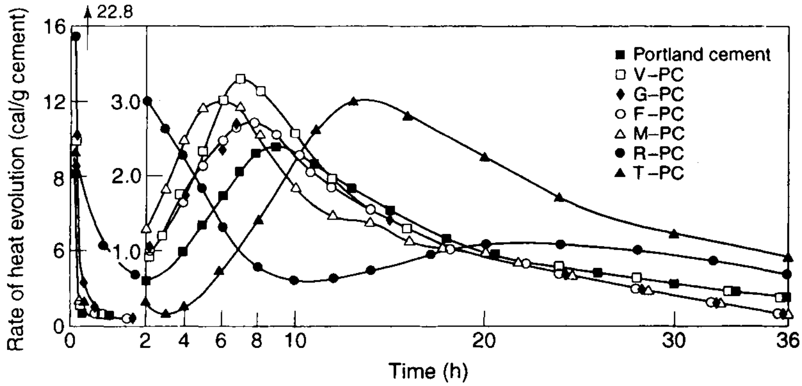


Fig. 10.26 Calorimetric curves from the hydration of some pozzolanic cements (source: Ref. 25). w/s = 0.4, temperature = 20°C.

increases with increasing the water/cement ratio.[187] If the height of the second peak is referred to the content of Portland cement of the blend, it can be slightly lower,[188] lower,[191] slightly higher[25,187,190] or definitely higher[184] than that of the parent Portland cements.

The prolongation of the dormant period caused by 30 per cent replacement of different fly ashes by a Portland cement has also been recorded by a quasi-adiabatic calorimeter. The temperature increase obtained with two low-lime and two high-lime fly ashes was lower than that of the control Portland cement, but that of a third high-lime fly ash was higher, probably owing to the dissolution of other compounds.[192] Water-leached fly-ashes have demonstrated a retarding effect on the second peak lower than that shown by as-received fly ashes.[191]

The cumulative heat of hydration released by the cement accounts for the overall reactions occurring during hydration. It depends on the height and the width of the main peak of the heat evolution curve. The total heat released from blended cements (clinker + gypsum + fly ash) in the first 2 days is always lower than that of the control Portland cement (clinker + gypsum), but it is generally higher[188,193] when referred to the Portland cement fraction (Figure 10.27). This means that fly ashes, similarly to other pozzolanic materials, accelerate the hydration of the Portland cement.

Generally, mixes of Portland cement and microsilica (up to 30 per cent) show a slight prolongation of the dormant period and a marked increase in the height of the second peak.[193] However, it has also been reported that cements containing up to 20 per cent microsilica have shown no changes in the dormant period and a small reduction in the height of the main peak.[188]

A 15[194] or 20 per cent[188] replacement of Portland cement by silica fume results in a lower total heat of hydration released in the first 2 days, as compared to the heat evolved by the plain control Portland cement paste. However, if calorimetric data are referred to

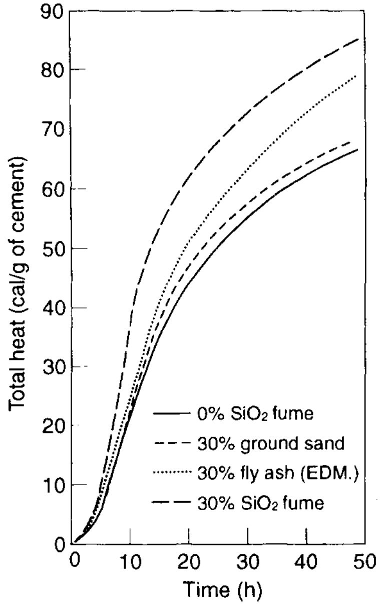


Fig. 10.27 Total heat evolved by various cement blends during hydration (source: Ref. 193). Heat referred to the Portland cement fraction.

the Portland cement fraction, the heat evolved can turn out to be higher[193] or roughly the same.[188,194] During the first 24 h the cumulative heat of hydration remains unchanged or increases, for a small silica fume content (5 per cent) and decreases for higher (10–15 per cent) contents,[194] while it is strongly affected by the water/cement ratio.

As a matter of fact, by increasing the silica fume content, the hydration rate of clinker increases when the water/cement ratio is as high as 0.6;[193] it is unaffected when the water/cement ratio is in the range 0.35–0.5,[188,194,195] and is reduced, in spite of the presence of the superplasticisers, when the water/cement ratio is as low as 0.28.[195] Also, ground silica sand increases the total heat evolved by the Portland cement fraction, but the effect is quite negligible (Figure 10.27).[195]

Portlandite content. The progress of hydration in Portland cements has often been followed by measuring the increase in portlandite content with time. However, the values must be used carefully when expressing the degree of hydration of Portland cement, inasmuch as after 28–91 days the portlandite content decreases slightly[196] or distinctly[197] in spite of the progress of hydration.

The presence of pozzolana modifies the ordinary course of the hydration of cements. Thus the portlandite content depends not only on the degree of hydration of clinker, but also on the progress of the pozzolanic reaction, the composition of the hydrates and of the mix, the type of pozzolana, the temperature, the water/cement ratio, the pozzolana/clinker ratio, etc. Table 10.21 shows that the portlandite content of blended cements is lower when it is referred to the cement as a whole, but it is higher when it is referred to the Portland cement fraction.[198]

The behaviour of natural pozzolanas and fly ashes is quite similar but, on comparing various cements containing 30 per cent of different pozzolanas, fly ashes and ground limestone, it has been found that samples of natural pozzolanas can fix more lime than fly ashes.[111]

In spite of these reservations, the determination of free lime provides useful information concerning the hydration process, when it is carried out simultaneously on pozzolanic cement and the corresponding plain Portland cement.

Bound water. The degree of hydration of Portland cement is often estimated by determining the non-evaporable water content of the paste, that is, the weight loss occurring in dried specimens burnt between 105 and 1000°C. Non-evaporable water includes inputs from all the products of hydration, and thus from calcium hydroxide too. The non-evaporable water content is only an 'indicator' of the extent of the hydration of Portland cement since the composition of hydrates is not accurately known and some bound water is lost during the preliminary drying of samples at 105°C.

By subtracting the water bound in $Ca(OH)_2$ from non-evaporable water, the content of water that is chemically combined in silicates and aluminate hydrates is obtained. Owing to the changes caused by pozzolanic materials in the amount of the different hydrates, as well as in their chemical composition, the determination of non-evaporable water is far from being useful in determining the degree of hydration of blended cements.[199] Also, in the case of chemically combined water, the variability in composition of the hydrated phases does not allow a good estimate of the degree of hydration to be obtained. Nevertheless, comparison of the results obtained from the blended and the parent Portland cements reveals the differences in the hydration process of these two types of cement.

The contents of non-evaporable and bound water in fly ash cement pastes are lower

Table 10.21 Portlandite and bound water contents for Portland cement–fly ash pastes from TGA–DTG data[198]

		Ca(OH)$_2$ content		Bound water content	
Paste	Age	per 100 g total binder	per 100 g Portland cement	per 100 g total binder	per 100 g Portland cement
Control Portland cement	2 h	0.94	0.94	2.82	2.82
	5 h	6.05	6.05	9.00	9.00
	1 day	15.05	15.05	14.75	14.75
	3 days	18.12	18.12	19.53	19.53
	7 days	19.16	19.16	21.39	21.39
	28 days	23.94	23.94	26.85	26.85
4515[a]	2 h	0.40	0.46	2.34	2.69
	5 h	1.53	1.76	4.13	4.75
	1 day	11.16	12.84	13.56	15.61
	3 days	17.76	20.44	19.55	22.49
	7 days	18.57	21.37	20.95	24.11
	28 days	18.94	21.79	24.34	28.01
4530	2 h	0	0	2.44	3.33
	5 h	2.45	3.35	4.54	6.20
	1 day	8.70	11.89	12.17	16.62
	3 days	12.84	17.54	17.21	23.51
	7 days	12.94	17.68	19.25	26.29
	28 days	15.06	20.57	23.14	31.60
1015	2 h	1.08	1.24	2.80	3.23
	5 h	1.34	1.55	4.72	5.43
	1 day	11.02	12.70	13.82	15.93
	3 days	16.47	18.98	19.93	22.97
	7 days	16.35	18.84	20.60	23.74
	28 days	20.73	23.89	27.91	32.16
1030	2 h	0	0	2.23	3.05
	5 h	0.96	1.32	3.54	4.85
	1 day	8.91	12.21	14.13	19.36
	3 days	12.77	17.49	18.94	25.95
	7 days	12.53	17.16	19.50	26.72
	28 days	19.42	26.60	22.38	30.66

[a] Pastes are identified by the shorthand forms 4515, 4530, 1015 and 1030 representing 15% 45 μm ash, 30% 45 μm ash, 15% 10 μm ash and 30% 10 μm ash, respectively.

than in the parent Portland cement,[190] but are greater if they are referred to the Portland cement fraction[190,196,198,200,201] (Table 10.21). The data show that the non-evaporable water content is already higher in blended than in parent Portland cement after 3 days, but the difference has been recorded even after 1 day.[196] At early ages this difference can be interpreted as an acceleration of the hydration of the Portland cement fraction and, at longer ages, as a consequence of the progress of the pozzolanic reaction, which causes an increase in the C-S-H content. In general, high-lime fly ashes ($\sim$30 per cent CaO) give cement paste with a higher non-evaporable water content.[192]

The increase in the non-evaporable water content could also be due to an increase in the chemically bound water in C-S-H. After a 180-day hydration of a fly ash cement, by apportioning the non-evaporable water content of the Portland cement fraction, a degree of hydration of the fly ash cement of about 100 per cent was calculated. Since this is impossible, the water content of the hydrates in the blended cement should be higher than that of the parent Portland cement paste. This conclusion is more evident in the case of cements containing high-lime fly ash, for which the calculated degree of hydration of the Portland cement fraction should be >100 per cent.[196]

By increasing the silica fume content by up to 25 per cent, the amount of non-evaporable water, referred to the whole cement, decreases, whereas the amount of combined water in hydrates increases. The results are strongly influenced by the water content of the paste since non-evaporable water decreases with decreasing water/cement ratios.[193,195,199]

Most of the chemically bound water is released below 450°C, which is the temperature at which $Ca(OH)_2$ decomposes.[198] By comparing the weight loss between 100–200°C and 200–300°C, a straight line is obtained, suggesting that the hydrates are substantially alike, irrespective of whether or not fly ashes are present in the paste.[184]

Degree of hydration of alite and other clinker compounds. The determination of unreacted alite in the cement paste is a useful method for comparing the progress of hydration in the blended and the parent Portland cement. The degree of hydration of alite increases when the cement contains pozzolanic materials.[25,184,190,202]

After 28 days of curing, four cements containing 25 per cent fly ash showed that the amount of alite reacted was greater by 3–9 per cent as compared to that found in the plain Portland cement paste. The accelerating effect depends on the type of fly ash[190] and increases by increasing the amount replacing Portland cement.[184] The change in the rate of hydration of alite has been also recorded at ages of <1 day,[184,190] but it is normally ascertained only after several days.[184]

The determination of the residual C_3A content in hydrated pastes is not a useful method for evaluating the influence of pozzolanas on the hydration of tricalcium aluminate because of the low content of C_3A in the parent Portland cement, the uncertainties associated with the analytical determination of tricalcium aluminate by XRD and the rapid disappearance of the compound. Nevertheless, the results obtained would suggest that fly ashes may slightly increase the rate of hydration of the aluminate,[184] as they do when plain C_3A is hydrated in the presence of gypsum.[157,158]

The rate of hydration of belite does not change in the presence of fly ash until 14[184] or 28[202] days, but at later ages it is reduced.[202]

Degree of reaction of pozzolanas. The unreacted content of natural or artificial pozzolanas can be quantitatively determined in cementitious systems by using selective dissolution methods such as salicylic acid–methanol,[168] salicylic acid–methanol and potassium hydroxide–sugar–water solutions,[184] or picric acid–methanol–water solution.[203] With these methods the reacted fraction of pozzolana is calculated as the difference between the insoluble residue determined before and after a given hydration period.

The glass of a fly ash contained in a blended cement reacts gradually (Figure 10.28). However, after 1 year the unreacted fraction can still be as high as 50 per cent.[184] Table 10.22 shows that silica fume is more reactive than low-calcium fly ash, but that after 3

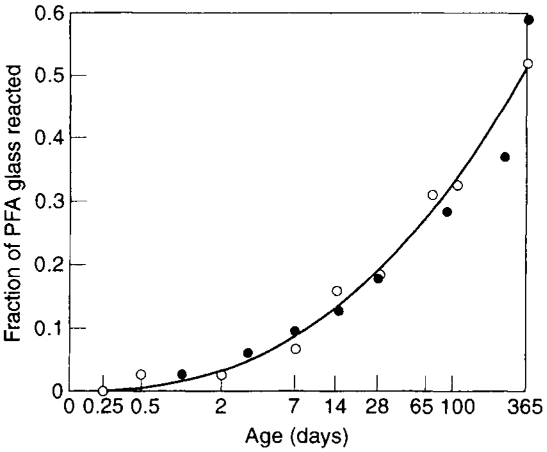


Fig. 10.28 Fraction of PFA glass reacted as a function of age (source: Ref. 184). Fly ash blended with Portland cement (filled circles[168]) or C_3S (open circles[184]).

days the amount of reacted silica rises very slowly, in spite of the fact that the water/binder ratio of the microsilica cement is higher than that of the fly ash cement.[203] Table 10.22 suggests that the reactivity of a pozzolana can be underestimated if calcium hydroxide cannot migrate and react with pozzolana particles owing to certain possible hindrances.[204]

Compounds occurring in pastes of pozzolana-containing cements

The reaction products resulting from the hydration of pozzolanic cements are the same as those occurring in Portland cement pastes. The differences solely involve the ratios of the various compounds as well as their morphology. The main hydrates found in the hardened pastes are:

- ettringite
- tetracalcium aluminate hydrate (often carbonated)
- monosulfoaluminate
- C-S-H
- C_2ASH_8
- $Ca(OH)_2$
- $CaCO_3$.

Table 10.22 Degree of hydration of pozzolanas in cement pastes, for blends containing 30 per cent of fly ash (fa) or 10% of silica fume (sf)

	Hydration time				
Specimen	1 day	3 days	7 days	28 days	90 days
C + fa	7.0	8.5	14.3	36.3	61.59
C + sf	53.1	67.9	68.7	69.0	78.47

These compounds can be detected by DTA, DSCA, XRDA, optical and electron microscopy, and by selective dissolution attacks, as the case may be.

Ettringite. Ettringite forms rapidly in cements containing natural pozzolanas[205] or fly ashes.[198,206] Ettringite was observed from 5 h up to 28 days in cements containing fly ash,[198] and at 1 year in cements containing natural pozzolanas.[205] Ettringite can disappear after 3 days[25] and be transformed into monosulfate. Its conversion was observed in low-SO_3, but not in high-SO_3 fly ashes.[190] The conversion of ettringite into monosulfate depends on the amount of SO_3 available and on the CO_2 content of the cement paste. In fact, carbon dioxide reacts with excess calcium aluminate hydrate and gives carboaluminate, thus preventing it from reacting with ettringite to form monosulfate.[207] This is the reason why ettringite is often found with carboaluminate hydrate.

Similar results have been obtained with a cement containing 15 per cent of microsilica (flame hydrolysis silica) cured for 10 years. The AFt phase was associated with a medium content of calcium carbonate whereas the AFm phase was associated with a low calcium carbonate content.[208] Analysis carried out by analytical electron microscope has revealed that the AFt phase of Portland cement and blended cement paste significantly deviates from the composition of pure ettringite. Table 10.23 shows that the atom ratio of plain Portland cement pastes and those with 15 per cent silica substitution deviates from the theoretical values.[208] In particular, the CaO/SO_4 ratio is significantly higher than the theoretical value of 2.0. These figures imply that a substitution in the SO_4 sites by silica and presumably by CO_3^{2-} anion has occurred.[208]

Tetracalcium aluminate hydrate. Tetracalcium aluminate hydrate can be present in the pastes, depending on the Al_2O_3/SO_3 ratio of the cement, but it is generally carbonated, either because it has been contaminated by the CO_2 of the atmosphere[205] or because of the presence of calcite as filler in cement.[198]

C-S-H. C-S-H is already visible after 24 h,[166] because the hydration of alite is accelerated by the presence of the pozzolanic materials. Its content increases with time. Uncertainties regarding the composition of C-S-H as observed in the products of C_3S hydration are again found when considering the composition of the calcium silicate hydrate formed by hydration of Portland cement and pozzolana-containing cements.

C-S-H formed by hydration of Portland cements shows some differences with respect to the calcium silicate hydrate from C_3S hydration. The variation in composition within

Table 10.23 Pastes of ordinary Portland cement (OPC) and Portland cement + 15% Degussa silica produced by the flame hydrolysis process. Atom ratios of the AFt phase for OPC and OPC + Si, as determined by analytical electron microscopy: figures in parentheses give range of values found.[208]

	Atomic ratios		
Sample	Ca/Al	Ca/SO_4	$Ca/(SO_4 + Si)$
OPC: AF_t $n = 10$	2.73 ± 0.15	2.66 ± 0.86 (1.87–4.40)	2.55 ± 0.78 (1.86–4.19)
OPC + FHS: AF_t $n = 10$	3.06 ± 0.39	2.73 ± 0.69 (1.87–3.82)	2.39 ± 0.58 (1.87–3.43)

specimens is comparable to that found in C_3S pastes, but the range of C/S ratios is greater, extreme values being 1.0 and 2.8.[209] The reasons of this variability in composition are the same as those concerning the formation of C-S-H by the hydration of C_3S, but in the case of cements the influence of other elements such as Al, Mg, Fe and S has to be taken into account.[210] Moreover, in Portland cement pastes, the C/S ratio has been found to increase with the increasing voltage of the electron probe microanalyses[176] and curing time.[209] The latter effect has not always been observed;[211] however, if it takes place this could be due to changes in the sulfate content of C-S-H.[212]

Several workers have highlighted some compositional differences between 'inner' and 'outer' products. The inner product appeared to be pure C-S-H with a median C/S ratio of 1.5,[213] 1.7,[214,215] 2.1,[216] or 1.75.[217] The C/S ratio of the outer product appears to be higher than that of the inner one as it ranges between 1.60[213] and 2.70.[216] Such a high ratio perhaps reflects the mixture of C-S-H with the CH and AFm phases or changes in composition due to the presence of foreign elements coming from the interstitial clinker phases.

If the inner product generally appears to be pure or almost pure calcium silicate hydrate, the outer product contains several other elements such as Al, K and sulphate.[213] In any case, the outer and inner products have been shown to have a different composition only when the cement is partially hydrated, i.e. when chemical equilibrium is far from being attained. As a matter of fact, in the C-S-H of a 10 year old concrete, presumably fully hydrated, just a single composition ($C/S = 1.82$–1.97) was found to predominate.[216]

The C/S ratio increases by decreasing the water/cement ratio,[217] and this could be one of the major causes of variation of C-S-H composition and the reason why C/S is lower in concrete than in the paste.[217,218] Using EMPA, other workers have identified the outer and inner products in a 23-year-old paste but without any significant deviation in the C/S ratio of the two layers, the mean value being estimated at 1.67.[215] The difference between the inner and the outer product has been demonstrated through the magnesia content: in the outer product, the Mg/Ca ratio was very low (<0.01), whereas in the inner one a very variable ratio has been found (0.00–0.08).[215]

The minor elements contained in the C-S-H vary to a large extent,[212] and this could account for the high variability of the C/S ratio. Incidentally, the (Ca + Mg)/(Si + Al + Fe + S) ratio was less variable than Ca/Si.[216]

EPMA carried out on concrete made of Portland and blended cement has shown that the C/S molar ratio in the hydrates varies irregularly from one point to another, but it is statistically normally distributed at the level of volume sampling (μm^3).[218]

In brief, the uncertainty and variability in the C-S-H composition revealed by electron microanalysis can be due to several reasons:

- incompletely attained chemical equilibrium;
- replacement in Ca and Si sites by different quantities of foreign elements;
- an intimate mixture of C-S-H and other hydrated compounds;
- faults in the preparation techniques of specimens and in the answers provided by the instruments.

It is worth noting that the majority of indirect determinations of the Ca/Si ratio have given values ranging between 1.7 and 1.8, thus the largest deviations from these figures should be considered to be a consequence of certain errors which occur in the analytical determinations and of the influence of the elements replacing Ca and Si in the structure of C-S-H hydrate.

In pozzolana-containing cements, besides the C-S-H deriving from the hydration of

Table 10.24 Composition of C-S-H in cement pastes with and without 40 per cent blending component (w/c = 0.40, t = 293°K, age 4 years) by EMPA[166]

	C/S	A/C	C/(S + A)	Na_2O (%)	K_2O (%)
OPC	2.03	0.06	1.81	0.03	0.11
Fly ash cement	1.01	0.21	0.84	0.24	0.33
Slag cement	1.62	0.44	0.96	0.23	0.30

clinker silicates, C-S-H from the reaction between pozzolana and hydrolysis lime is also found.

Table 10.24 shows that active blending components, such as fly ash and blastfurnace slag, change the composition of C-S-H.[166] Similar reductions in the C/S and C/A ratios are also found in concrete.[218]

The composition of C-S-H formed from pozzolanic reaction is different from that originating from alite and belite, the reason being the different conditions of formation. After an 8-day hydration, the presence of fly ash causes the C/S ratio of the C-S-H around the alite grains to decrease from 1.71 to 1.55.[214] The lower C/S ratio of the C-S-H is associated with a higher potassium content.[214] In mature pastes of cement containing 30 per cent fly ash, inner and outer products having a slightly lower Ca/Si ratio than those of plain cement have been found (1.49–1.50 and 1.45–1.60, respectively).[213] However, definitely higher differences have been reported also. After 4 years of curing, a 40 per cent fly ash cement and the parent Portland cement have given a C-S-H with Ca/Si ratios of 1.01 and 2.03, respectively. Such a large difference also persists in the Ca/(Si + Al) ratio.[166]

The Ca/Si molar ratio of the C-S-H formed in fly ash cement pastes decreases by increasing the percentage of the blending component.[213,219] Reported values of the C-S-H composition are averages since, for each mix, the Ca/Si ratio decreases by increasing the distance of C-S-H from hydrated alite or portlandite crystals.[219] The lower Ca/Si ratio of C-S-H found in pozzolana-containing cement could be related to the different degree of polymerisation of the silicate anion, which is greater in pozzolanic cement than in Portland cement pastes.[129]

Microsilica, which is constituted of amorphous SiO_2, reacts with hydrolysis lime and gives additional C-S-H. The resulting C/S molar ratio of C-S-H ($\sim$1.1) is lower than the overall ratio of the cement paste ($\sim$1.2). The C/S ratio of C-S-H markedly decreases as the content of microsilica increases.[221] Typically, a replacement of 13 and 28 per cent gives C/S ratios of 1.3 and 0.9, respectively.[222]

Electron microscope analysis, carried out on 10 year old pastes, has shown that the mean C/S ratio is higher in the parent Portland cement (1.54 ± 0.21) than in cement with 15 per cent microsilica replacement (1.36 ± 0.19). The analytical values are rather scattered, thus C-S-H of both high and low C/S ratio could coexist. This result and the presence of noticeable amounts of portlandite imply substantial chemical imbalance.[208]

The incidental presence of unusually large (35–80 μm), rounded silica particles in a silica fume-containing cement has given the opportunity to examine a simple but significant example of pozzolanic reaction. A cement containing 10 per cent silica fume was cured for 1 year and the polished surfaces of the paste were examined by SEM and analysed by EDXA. SEM revealed that the silica particles had reacted totally or partially, forming C-S-H while retaining their original outline. The results of EDXA analyses showed that the C/S ratio of C-S-H was more or less the same (1.7–2.0) around the silica particles, although it decreased linearly from the periphery to the centre (0.3–0.6).[223] Figure 10.29

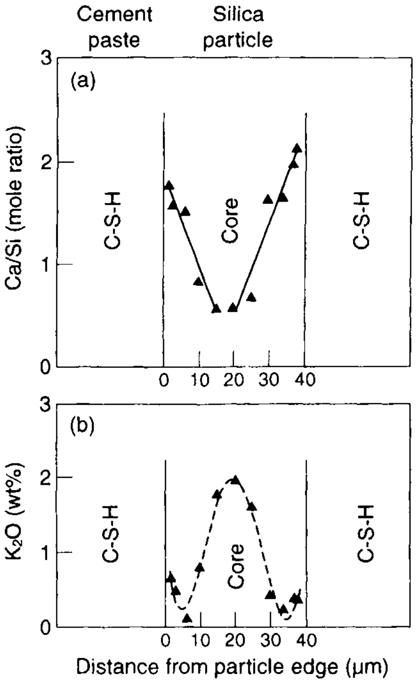


Fig. 10.29 Schematic representation of a siliceous particle immersed in cement paste with Ca penetration to the centre (source: Ref. 223). (a) Ca/Si mole ratio determined by EDXA along traverse A–B. (b) Weight per cent K_2O determined by EDXA along traverse A–B.

shows a plot of C/S molar ratio along the cross-section of a silica particle. The central core can be completely calcium-free or may contain some calcium. The rate at which the C/S ratio decreased ranged from 0.036 to 0.095 (C/S)/μm.[223]

EDXA data prove that calcium silicate hydrates of different composition can coexist for a long period, possibly on account of their similar chemical potential and the difficulty for the Ca^{2+} ions to travel across the rim of hydrates. The morphological differences occurring between the C-S-H formed around the clinker grains and that formed around the natural pozzolana particles have also been observed by means of optical microscopy in pastes of cement containing natural pozzolanas.[224] No sign of expansion of particles was detected[223] in spite of the penetration of Ca^{2+} and OH^- in the silica particles and the change of density from 2.2 (silica)[101] to 1.9–2.1 (C-S-H).[221] The volume stability of particles results from diffusion processes affecting the different ionic species involved in the growth of hydrates.[224]

The differences in chemical composition between C-S-H from pozzolana-containing cements and from the parent Portland cements are reflected in the degree of polymerisation of the silicate anion, which is greater for the former than for the latter.[129]

^{29}Si NMR investigations have shown that Q_2/Q_1 ratio is higher in the silica fume-containing cement than in parent Portland cement. This means that the average chain length of silicate anion is increased by the presence of microsilica.[66]

C_2ASH_8. In cements containing high-lime fly ashes, besides C-S-H, C_2ASH_8 (gehlenite hydrate) also forms.[206] In any case, if gypsum is added to cements, gehlenite hydrate gradually decreases and eventually disappears after 60 days.

Table 10.25 Free lime content in cement pastes cured for 4 years, for cements containing different amounts of a natural pozzolana[225]

	$Ca(OH)_2$	
Pozzolana content (%)	ATD method (%)	Franke method (%)
	10.2	9.65
10	7.6	7.20
20	5.3	5.4
30	2.9	3.1
40	1-1.5	1.3
50	1	0.9

Calcium hydroxide. XRDA is a sufficiently sensitive analytical method to detect the presence of portlandite after 5 h, while optical and electron microscopy gives information on the morphology and distribution of calcium hydroxide crystals. The SEM can detect CH crystals as early as 4 h and can identify relatively large crystals after 12–18 h.[187] Deposits of CH crystals have also been seen in intimate contact with apparently untouched fly ash particles,[196] as well as particles showing the presence of an interface reaction.[187]

In 28-day old pozzolanic cement pastes, CH has been detected by etching polished sections with appropriate micrographic reagents and by examining them under the reflected light microscope.[224]

In pozzolana cements, the amount of pozzolana present is not sufficient to combine all the CH released by the calcium silicates of the clinker, so the occurrence of portlandite even after 10 years is justified.[208] On the contrary, the presence of free calcium hydroxide in pozzolanic cements cured for a long period can only be attributed to the slow rate of the pozzolanic reaction and to the difficulties encountered by Ca in reaching pozzolana particles and reacting with them. Table 10.25[225] shows that although portlandite decreases with time, it is still detectable after 4 years of curing.

The occurrence of portlandite will be covered in detail below.

Carbon dioxide. Carbon dioxide can react with the hydrated cement compounds, forming calcite (calcium carbonate). Carbonation occurs also in pozzolana-containing cements but it seems to involve only portlandite, not other hydrates. By transforming the actual $CaCO_3$ into equivalent $Ca(OH)_2$, the portlandite content does not change between 90 days and 10 years.[208]

Pore solution

The solution contained in the pores of the cement paste can be partially squeezed using a high-pressure device[198,226 228] and then analysed by atomic absorption spectroscopy, plasma photometry, ion chromatography and other sensitive methods. The analytical data obtained from squeezed solutions must be considered with care for two main reasons:

- squeezing removes 10–20 per cent of the total free water, that is, only the water contained in the larger pores;
- the uniaxial external pressure applied to the sample is not equally transferred to every point of the cement paste.[201]

In spite of the above reservations, determining the free water contained in paste or mortar is at present the only method available for separating and analysing the pore solution.

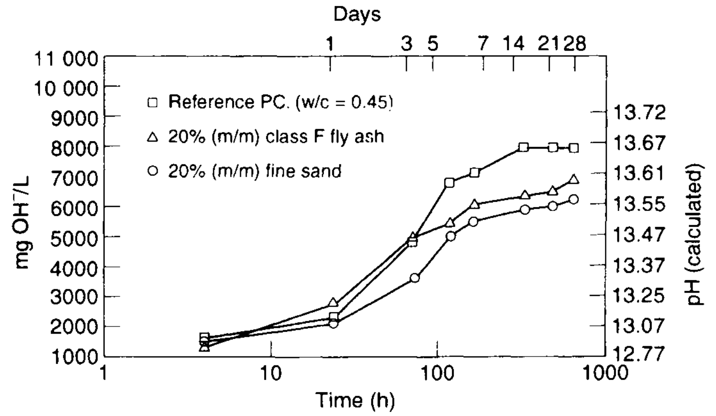


Fig. 10.30 OH^- concentration as a function of time in the pore solution of plain Portland cement paste and blended cement paste (source: Ref. 186). Portland cement replaced with 20 per cent fly ash or fine quartz sand. Temperature = 20°C, water/binder = 0.45.

The presence of pozzolanic material in the cement changes the composition of the pore solution and this can have some consequences on the durability of concrete and reinforced concrete. Up to an age of 28 days, the OH^- concentration in the pore solution of cements containing 20 per cent of fly ash has proved to be lower than that of the parent Portland cement, but higher than that of the cement containing ground sand (Figure 10.30).[186,198] This reduction occurred even if the alkali content in the fly ash was markedly higher than that in clinker. It may possibly depend on the low dissolution rate of alkali contained in the fly ash glass. Nevertheless, the difference between the curves of fly ash and ground sand suggests that after about 10 days, fly ash has contributed to increasing the pH whereas ground sand has caused only a dilution effect.

At a later stage the hydroxyl concentration decreases in the blended cement paste and increases in the plain cement paste until it reaches an asymptotic value (Figure 10.31).[229]

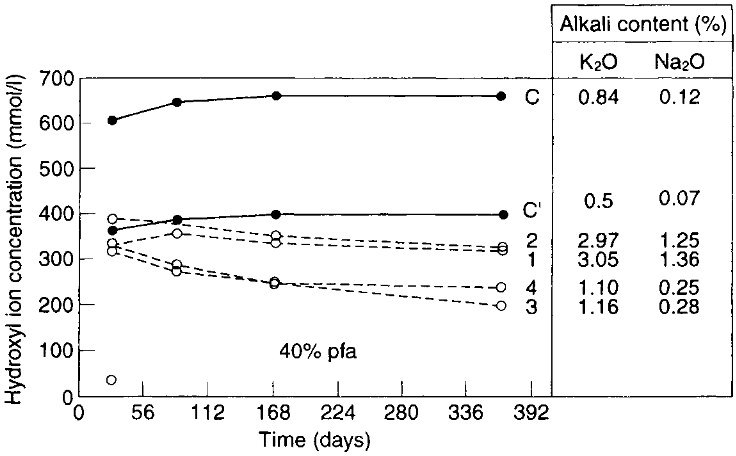


Fig. 10.31 OH^- ion concentrations in pore solutions of Portland cement paste (C) and blended pastes containing 40 per cent of various pulverised-fuel ashes (1, 2, 3, 4) or 40 per cent of hypothetical cement of zero alkali content (C') (source: Ref. 229). Alkali content of the parent Portland cement and four fly ashes is indicated.

The reduction in the alkalinity of the pore solution caused by the presence of fly ash has been recorded at up to 1 year.[218,229] Since the alkali content of the four fly ashes of Figure 10.31 was higher than that of the control of Portland cement, the reaction could be due to an incorporation of alkalis into the C-S-H gel formed by pozzolanic reaction.[229]

It is worth noting that after 1 day of hydration the alkalinity is higher in blended cement than in the parent Portland cement pastes (Table 10.26).[198] This may be due to an accelerated early hydration of the Portland cement fraction caused by the presence of fly ash or to the dissolution of some alkaline compounds from the pozzolana. The later decrease in alkalinity could instead be due to the removal of alkalis from the solution by reaction with the glass of the fly ash.

Table 10.26 Chemical data for pore fluids extracted from PC–fly ash pastes[198]

Fly ash				Ionic concentrations (mmol/L)							
Fineness (µm)	Content (%)	Age	pH	Si	Ca	Al	Na	K	SO_4^{2-}	OH^-	Cations/ Anions[a]
	Control	2 h	13.24	0.3	3.5	<0.1	46	426	177.8	175	0.91
		5 h	13.26	0.4	0.5	<0.1	45	473	166.6	180	1.02
		1 day	13.61	0.9	3.1	<0.1	61	549	88.0	403	1.07
		3 days	13.79	1.0	5.5	0.1	68	581	8.4	617	1.05
		7 days	13.80	1.0	3.9	0.1	66	605	8.9	629	1.06
		28 days	13.83	0.8	3.7	0.2	58	607	9.5	677	0.97
<45	15	2 h	13.25	0.4	0.7	<0.1	48	424	150.9	176	0.99
		5 h	13.24	0.4	4.7	<0.1	51	406	152.2	172	0.98
		1 day	13.68	0.8	4.7	<0.1	63	492	32.8	474	1.05
		3 days	13.77	0.8	5.4	0.1	69	472	6.3	589	1.09
		7 days	13.78	1.1	5.4	0.1	75	558	7.3	599	1.06
		28 days	13.80	1.0	2.9	0.2	69	473	9.5	627	0.86
<45	30	2 h	13.23	0.3	14.1	<0.1	55	335	144.0	168	0.89
		5 h	13.26	0.3	4.4	<0.1	54	339	124.0	184	0.93
		1 day	13.69	0.7	1.8	<0.1	73	434	10.4	487	1.01
		3 days	13.72	1.0	3.4	0.1	78	445	5.9	523	1.00
		7 days	13.73	0.9	4.2	0.1	77	444	5.2	539	0.97
		28 days	13.70	0.9	2.9	0.2	63	364	4.0	497	0.86
<10	15	2 h	13.28	0.3	16.8	<0.1	48	386	166.6	190	0.90
		5 h	13.27	0.3	2.7	<0.1	56	396	161.4	184	0.91
		1 day	13.73	0.8	4.7	<0.1	69	492	15.4	540	1.00
		3 days	13.78	1.0	4.2	0.1	81	516	6.2	607	0.98
		7 days	13.81	1.5	5.5	0.1	90	510	7.3	641	0.94
		28 days	13.81	1.0	3.7	0.2	82	486	8.1	645	0.88
<10	30	2 h	13.23	0.2	12.1	<0.1	60	313	143.1	168	0.88
		5 h	13.26	0.3	3.4	<0.1	63	336	156.2	183	0.82
		1 day	13.71	0.4	3.0	<0.1	74	393	1.3	510	0.93
		3 days	13.72	0.8	3.1	0.1	79	428	1.9	528	0.97
		7 days	13.74	0.5	3.1	0.1	82	434	3.6	546	0.95
		28 days	13.73	1.6	2.9	0.3	102	435	6.9	537	1.00

[a] Ion balance $= \dfrac{2Ca^{2+} + Na^{+} + K^{+}}{2SO_4^{2-} + OH^{-}}$.

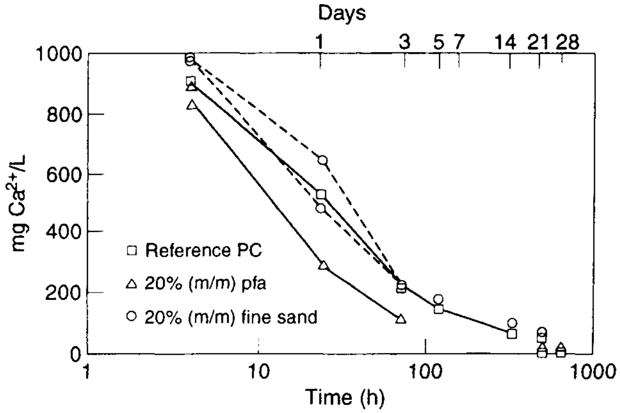


Fig. 10.32 Ca^{2+} concentration in the pore solution of plain Portland cement paste and blended cement paste (source: Ref. 186). Portland cement replaced with 20 per cent fly ash or fine quartz sand. Temperature = 20°C; water/binder = 0.45.

Figures 10.30 and 10.32 show that the increase in OH^- is matched by the decrease in Ca^{2+}, so the alkalinity of the pore solution is mainly due to the alkalis released by the Portland cement and the fly ash.[186] The Na^+ concentration in the pore solution of the blended cement paste is slightly higher than that of the parent Portland cement while the K^+ concentration is definitely lower (Table 10.26).[198] Taking into account that fly ash has a higher alkali content than the Portland cement, one can reasonably conclude that the decrease in K^+ indicates a take-up of potassium in the hydrated solid phases. Moreover, since the free water available in the pores decreases with time, an unchanged concentration

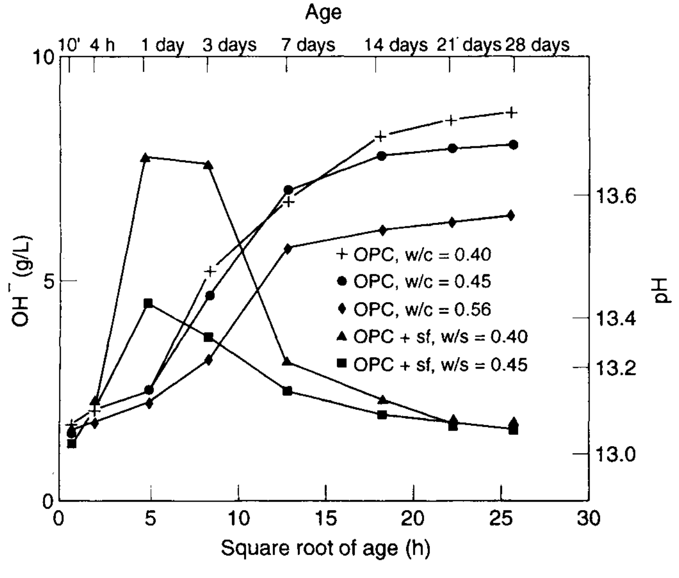


Fig. 10.33 OH^- concentrations in the pore solution of pastes as a function of age and w/(c + sf) ratio (source: Ref. 231). Silica fume content = 20 per cent.

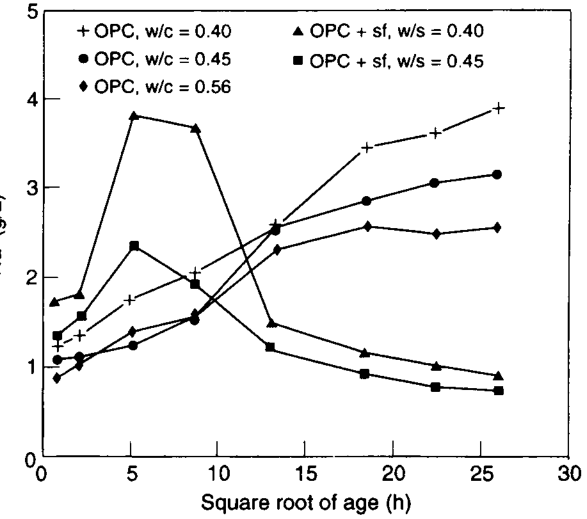


Fig. 10.34 Na^+ concentrations in the pore solution of pastes (source: Ref. 231). Samples as in Figure 10.33.

also means that increasing amounts of Na^+ are collected by the solid phases. Alkali and hydroxyl concentrations in the pore solution decrease by increasing the percentage of fly ash in the mix and also depending on the type of fly ash.[218,229] Concentrations of Si and Al in the pore solution are very low.

Unlike fly ashes, natural pozzolanas do not change the pH of the pore solution when the Portland cement has a high alkali content, but increase it if the Portland cement has a moderate alkali level.[230] In Portland cement pastes OH^-, Na^+ and K^+ increase with time until constant values are reached, but in a cement containing a considerable amount of silica fume (20 per cent) the evolution of concentrations is different. Figures 10.33–10.35 show that the evolution curve of concentration are similar and that a peak appears after

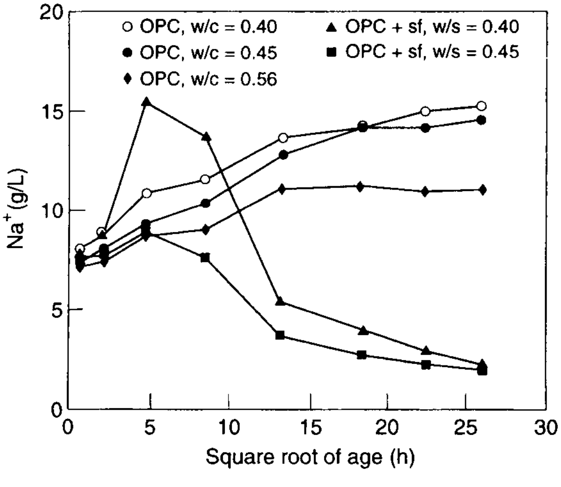


Fig. 10.35 K^+ concentration in the pore solution of pastes (source: Ref. 231). Samples as in Figure 10.33.

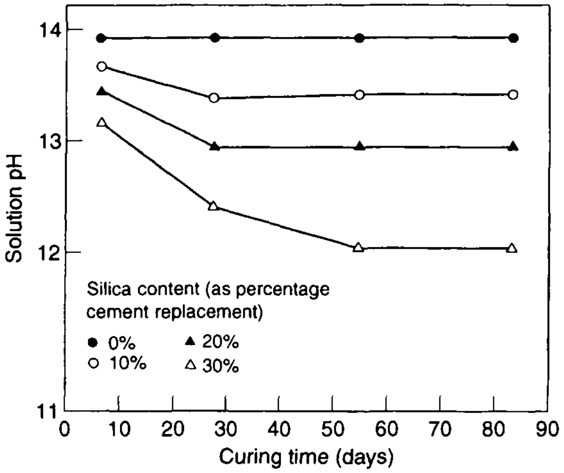


Fig. 10.36 Influence of the silica fume content on pH values of the pore solution from cement pastes (ordinary Portland cement and blended cements) (source: Ref. 226). w/(c + sf) = 0.50.

Table 10.27 Calculated total OH^- concentrations and pH values of pore solution measured in 10 year old pastes[208]

Cement paste	Total OH^- (m/ML)	pH
OPC	202	13.17
OPC + 15% FHS	96	12.87
HAPC	510	13.55
HAPC + 15% FHS	198	13.15

OPC = Portland cement; HAPC = high-alkali Portland cement; FHS = flame hydrolysis silica.

5 days of hydration.[231] The height of the peak depends on the water content of the mix[231,232] but after 24 h the influence of the water/cement ratio on the concentrations seems to have disappeared. The peaks can be explained by admitting an acceleration of the hydration of the Portland cement fraction caused by the silica fine particles whereas the descending branch of the curve should be the consequence of the incorporation of alkalis into the solid phases.[231] The actual concentration values decrease by increasing the silica fume content in the mix.[219,232] It is worth noting that the decrease in the alkali concentration caused by microsilica is not counterbalanced by an increase in Ca^{2+}

The reduction in OH^- and the corresponding pH must be taken into account by engineers when deciding the mix design.[233] Figure 10.36 shows the consequence of high silica replacement for Portland cement since the pH can drop below 12.5, which is the value of a saturated calcium hydroxide solution.[226] The decrease in pH has been recorded at up to 10 years (Table 10.27).[208]

In 10 year old pastes, the alkali concentration is definitely lower than in a 3 month old paste, although the decrease is only slight (Table 10.28).[208] Taking into account the reduction of free water that occurred after a 10-year hydration, the same table confirms that microsilica

Table 10.28 Measured composition (mM/L) of pore solution from 10 year-old pastes (figures in parentheses are for 90 days of cure, symbols as in Table 10.27)[208]

Solution	Na	K	Ca	SO_4	Al	Si	Mg
OPC	47.8	155.4	2.06	1.04	0.087	0.131	<0.004
	(64)	(200)	(2.75)				
OPC + 15% FHS	46.7	50.0	0.18	0.716	0.168	1.025	–
	(70)	(63)	(3.0)				
HAPC	78.8	432.7	0.75	7.55	0.240	0.369	<0.004
	(66)	(551)	(1.2)				
HAPC + 15% FHS	59.8	139.4	1.22	1.46	<0.15	0.142	–
	–	–	(1.45)				

(FHS) favours alkali incorporation into the solid phases and that Al and Si concentrations are very low in the pore solution.

Briefly, the partial replacement of Portland cement with microsilica causes

- a marked decrease in the concentration of Na^+, K^+ and OH^- dissolved in the pore solution of the paste;
- an incorporation of alkalis, and especially K^+, in the hydrates.

Portlandite in the paste

The evolution of the portlandite content is more complex for pozzolana-containing cements than for Portland ones. As shown in Figure 10.37, after 1 h of hydration the portlandite content in the fly ash cements is higher than that calculated on the basis of a dilution criterion.[191] At later stages it decreases but after 8 h it starts increasing until after 24 h it reaches the calculated value.[191] The decreasing branch of the curve could be due to a retarding effect on cement hydration or a pozzolanic action of fly ash. Taking into account

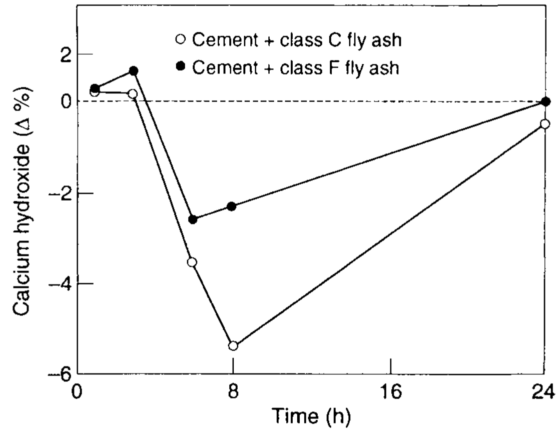


Fig. 10.37 $Ca(OH)_2$ in normalised fly ash/cement (40:60) pastes minus $Ca(OH)_2$ in neat cement pastes (source: Ref. 191).

what is shown on the heat evolution curve, the second explanation should be more correct.

At a later stage the portlandite content is expected to decrease gradually with respect to the values calculated after dilution as a consequence of the progress of the pozzolanic reaction. Actually, the overall $Ca(OH)_2$ content of pozzolana-containing pastes is always lower than that of the control Portland pastes when referred to the binder (Portland cement + pozzolana), but at 28 days it may be higher,[190,196,198] lower[111,190,198,234] or even the same[196,235] when the content is referred to the Portland cement fraction alone. In practical terms, in the first month the portlandite content of paste is more or less equivalent to that formed in the control Portland cement multiplied by the dilution factor, even though this equivalence has been claimed to persist for 180 days.[196]

The behaviour of natural pozzolanas and fly ashes is quite similar but, when comparing various cements containing 30 per cent of different pozzolanas, fly ashes and ground limestone, it has been found that the samples containing natural pozzolanas fix more lime than the samples with fly ashes.[111]

The long-term persistence of remarkable percentages of portlandite in hardened pozzolanic cements may seem unjustifiable. Common volcanic pozzolanas, as well as fly ashes, can combine an amount of $Ca(OH)_2$ which may be as much as about 50 per cent of their weight (Figure 10.7).[26] Henceforth, by using a pozzolanic cement having a pozzolana content of 35–40 per cent and taking into account that the portlandite content in the mature plain Portland cement paste is ~22 per cent CaO, the amount of pozzolana present should be sufficient to combine all or almost all the portlandite formed during the hydration of calcium silicates. On the contrary, the portlandite content in pozzolanic cement pastes made with different volcanic pozzolanas ranges between 3 and 8 per cent[111,236] after 90 days' curing. Of course the actual calcium hydroxide content depends on many factors and particularly on the nature of pozzolana.

In cement pastes, the calcium hydroxide content decreases with increasing microsilica content,[194,197,199,237,238] but small additions (~1.3 per cent) increase the 1-day free lime content.[238] This fact suggests an accelerating effect of microsilica on the rate of hydration of cements. Extrapolation of experimental curves referred to portlandite versus the age of pastes indicates that 20–22 per cent silica fume is sufficient to combine all the calcium hydroxide released by calcium silicates,[234,237] provided that the curing time is 28 days or more. This result roughly corresponds to a C/S ratio of ~1.10 as found in mixes of C_3S and silica fume.[220]

With lower water/cement ratios, (0.2–0.4), 16 per cent silica fume seems to be sufficient to combine all the free lime contained in pastes cured for 550 days.[199] This difference from the previous result is possibly due to the low water content, which did not allow for a complete hydration of the clinker. In pastes made with a relatively high water/cement ratio (0.6), the $Ca(OH)_2$ content does not change after 91 days of hydration, at least up to 10 years,[208] whereas with a lower water content, it decreases after 90 days. This means that the progress of pozzolanic reaction strongly depends on the water/cement ratio, as does the progress of hydration of plain Portland cement. This dependence can explain the occurrence of portlandite in cement paste containing 15 per cent silica fume cured for 10 years.[208]

After a certain curing time, which depends on many factors such as the type of pozzolana and the temperature, the $Ca(OH)_2$ contained in pozzolanic cement pastes reaches a maximum. In Figure 10.38, the lower two curves represent the average values with cements containing three different natural pozzolanas and three different fly ashes respectively.[111] At later ages, the decreasing branch of the curve can be followed by an increasing one.[236]

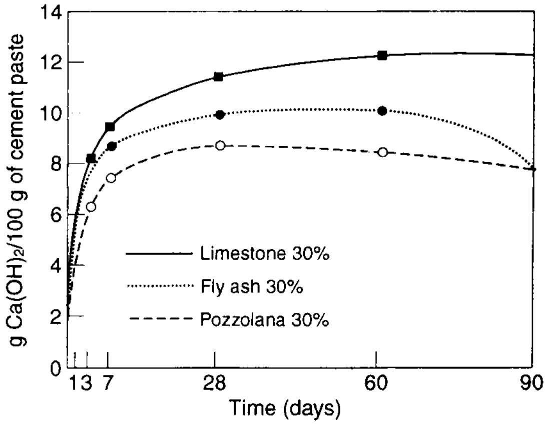


Fig. 10.38 Hydrolysis lime in cement pastes (source: Ref. 111).

This fluctuating trend of $Ca(OH)_2$ has also been demonstrated in cements containing class F fly ashes[196] and high-lime fly ashes[197] as well as with Portland cements.[197,198] The ascending branch of the curve may be due to the prevalence of the hydrolysis of calcium silicates and the descending one to the progress of the pozzolanic reaction. In the case of a cement containing ground limestone, the slope of the descending branch is not so steep; hence, in practice, the decrease should depend on changes occurring in the composition of hydrates rather than to a reaction between limestone and hydrates.

Fluctuations in the portlandite content of pastes are caused by the concurrence of different phenomena:

- acceleration of the hydrolysis of calcium silicates of clinker;
- pozzolanic reaction;
- changes in the composition of the hydrated phases;
- obstacles to the progress of reactions.

The persistence of portlandite also in long-cured pastes must be ascribed to the difficulties encountered by both portlandite crystals and pozzolana particles in reacting. It is most

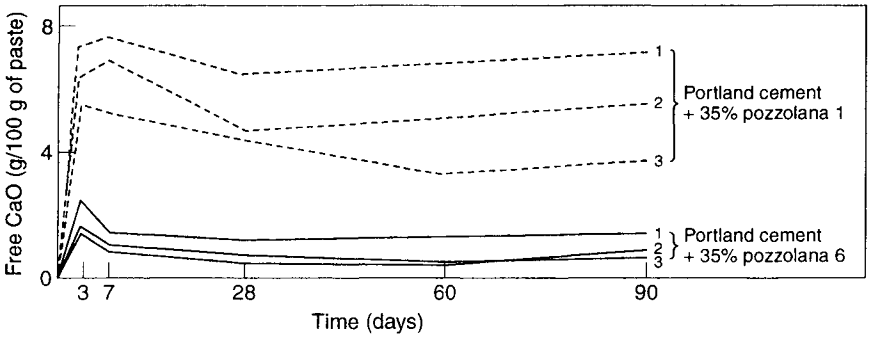


Fig. 10.39 Free portlandite content of (1) paste, (2) mortar (1:3) and (3) concrete (1:6) samples cured at 40°C (w/c = 0.5); 35 per cent of Portland cement replaced by two types of pozzolanas (source: Ref. 236).

likely that the yet-uncombined pozzolana grains will be unable to react with the distant calcium hydroxide crystals as they have been covered and shielded by the products of pozzolanic reaction.

This assumption is supported by the following arguments:

- free lime is progressively less in pastes, mortars and concrete – that is in mixes having increasing w/c ratios and thus greater porosity and permeability (Figure 10.39);[236]
- as Portland cement fineness increases, combined lime first increases, as a consequence of a larger reacting surface, and then decreases owing to the increased difficulty with which dissolved species are able to diffuse (Figure 10.40);[236]
- the combined water content, when it is referred to the Portland cement fraction, is always higher in the blended cement paste than in the control Portland cement paste (Table 10.21);[198]
- in spite of the significant $Ca(OH)_2$ content of pastes, pozzolana has substantially and remarkably reacted after 28 days;[184,203]
- portlandite crystals sometimes occur in contact with fly ash without any sign of reaction.[196]

The difficulties encountered by ionic species when moving through a slightly permeable mass should cause the pozzolanic material to extract lime from the adjacent C-S-H, as in the case of the C_3S–pozzolana mixes.[160]

Mechanisms of reaction in pozzolana-containing cements

The formation of the hydration products, as well as the evolution of the paste microstructure, depend on many factors, such as the nature of the Portland cement and of pozzolana, the fineness of components, the water/cement ratio and temperature. For this reason, it is impossible to describe the processes of clinker hydration and of pozzolana reaction exactly. Nevertheless, the hydration of pozzolana-containing cements follows a general trend common to any individual cement which enables us to draw some general conclusions. Of course these must be completed with other observations obtained on the basis of specific tests and investigations.

The process of hydration of pozzolana-containing cements can be divided into steps of different length, depending on the individual characteristics of materials and environmental

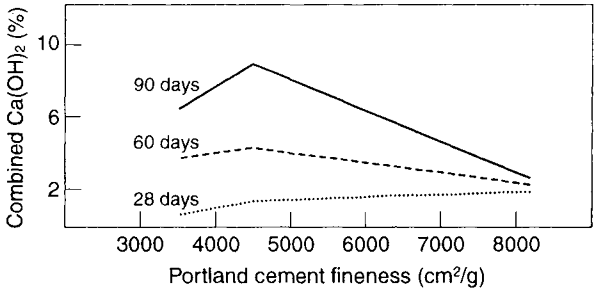


Fig. 10.40 $Ca(OH)_2$ combined by 100 g of fly ash M versus the specific surface area (Blaine) of control Portland cement (source: Ref. 236).

conditions. The steps show that the clinker hydration and the pozzolanic reaction practically overlap throughout the entire reaction time.

- After 1 h of hydration, there are already signs of reaction of clinker grains in the form of needles of ettringite and some poorly defined, small granular products. Fly ash particles appear to have some hydration product on their surface.
- After 4 h, in addition to ettringite, CH appears on the surface of fly ash particles. Some of these show definite signs of pitting, which will be more pronounced in the following hours.
- After 8 h the clinker grains are covered with ettringite, C-S-H and some large CH crystals.
- After 12 h these compounds occur even on fly ash grains/particles.
- After 18 h the paste acquires some cohesion, AFt rods are better crystallised, Haley grains are more numerous, and CH crystals continue to grow.
- After 1 day, AFt crystals appear to be longer and interlocking in some of the void spaces. Some of the fly ash particles appear to have reacted.
- After 3 days some fly ash particles are partially covered with reaction coating. It is assumed that the reacted part is rich in reactive glass, whereas the unreacted one is rich in relatively non-reactive crystalline compounds.
- At up to 14 days the structure becomes denser with continuous infilling from CH and C-S-H.
- At later ages, while the reaction of clinker declines, the pozzolanic reaction goes on gradually until ions in the hardened pastes practically stop moving.
- In long-cured pastes, fly ash particles appear to be
    - encapsulated by the reaction product;
    - etched or reacted according to different patterns;
    - completely dissolved.

Paste microstructure

Morphology of the paste. Apart from the presence of unreacted particles of pozzolana, the morphology of cement pastes containing either natural or artificial pozzolanas is basically similar to that of Portland cements. However, some differences do exist as the structure of hydrated pozzolanic cement pastes seems to be a middle course between the structures of Portland cement pastes and lime–pozzolana mortars.

The first microstructural consequence of hydration of blended cements is the early formation of shells of hydration products around the clinker grains. The shells are typically ~ 1 μm thick and are composed mainly of C-S-H. Ettringite appears as thin needles; locally, monosulfate thin plates and portlandite can also be observed. After a while, C-S-H fibres project outwards, coating the shells and making them appear fuzzy.[239]

After 1 day of hydration, electron microscopic examination of a fly ash-containing cement paste shows that the reaction has involved only clinker. Plenty of ettringite crystals as well as fibrillar C-S-H cover both the clinker grains and fly ash microsphere.[198,239] This microstructure confirms that fly ash particles initially perform as adequate precipitation and nucleation sites for hydrates.[240] In pozzolanic cement pastes, ettringite needles are definitely longer and thinner than those found in Portland cement pastes.[198]

The SEM examination of fly ash-containing cement paste has suggested that, after a day, fly ash particles are covered with a continuous and uniform layer of calcium hydroxide which is in turn covered with a parallel layer of C-S-H.[241] Nevertheless, the occurrence of this duplex film around the fly ash particles has not been confirmed[213] and thus it cannot be considered to be a typical feature of fly ash cement pastes.

In 1 week old samples made with a cement containing 20 per cent fly ash and the parent Portland cement, C-S-H appears in the form of an outer and an inner product around the alite of the clinker. The outer product is very thin while the inner one is 3–4 μm thick.[214] The fly ash particles appear to be covered by shells formed by radial growth of C-S-H and ettringite crystals. These shells were observed on both reacted and unreacted fly ash particles.[240] The morphology of the hydrates and the slowness of the pozzolanic reaction suggest that these shells must have formed according to a process of dissolution (of clinker minerals) and precipitation (on fly ash particles).[240]

The clearance observed between the fly ash particles and the shells of the hydration products has been ascribed to the dissolution of the outer glass layer.[242] The existence of this gap along unhydrated fly ash grain boundaries has been confirmed.[219] It may be due to the relative weakness of the interface between the unaltered fly ash particles and the rim of the hydrates. As a matter of fact, hardened pastes of C_3S blended with silica fume have shown that cracks occur between the inner and outer product when samples are broken during the preparation of the paste surface for SEM examination.[165] However, a small gap at the interface of some particles may be apparent and may possibly be due to the shrinkage of the hydrate gel under the severe drying conditions occurring during specimen preparation.[243] Shrinkage-induced rings were also observed in hardened pastes containing natural pozzolanas.[224] At later ages, some shells appear to be surrounded by portlandite,[240] but this aspect is probably only fortuitous.

The reactivity of fly ash microspheres seems to depend on the surface conditions rather than on the size, since it was noticed that certain small particles had remained unreacted, while some large ones were showing signs of reaction.[240]

After 28 days the fibres of type I and II C-S-H have filled all pore spacings and the grains of the various pozzolanic materials seem to have been attacked and surrounded by a thin layer of newly formed products.[198,224] The structure of pozzolanic cement pastes containing natural pozzolana was examined under the optical microscope, which revealed the formation of a layer of hydrated products around the pozzolana grains.[224]

After 17–21 months of hydration, C-S-H occurs as an inner and outer product around the still-unhydrated clinker particles, both in the fly ash and parent Portland cement pastes, the outer product having a typical fibrillar appearance.[213] In addition, fly ash particles are covered with a radial fibrillar layer of C-S-H formed within the original boundaries of the particle, which results from the pozzolanic reaction.[213] The fly ash particles have a clear outer boundary delineated by fibrillar C-S-H gel and some particles show the presence of reaction products within their boundaries.[213]

In some fly ash cement pastes, well-crystallised hydrogarnet within the boundaries of the fly ash particle occurs.[213]

The addition of silica fume to Portland cement does not change the paste microstructure significantly. Sections of a 7 day old blended cement were prepared by ion-beam thinning and observed under a transmission electron microscope. Microsilica particles appeared to be confined solely to the outer hydration product of clinker. This means that the inner hydration product does not precipitate from the solution; it develops within the boundaries of the clinker particles with the interface travelling forward between hydrated gel and unreacted clinker. At 7 days, the composition of the inner hydrate is not affected by the addition of silica fume.[243]

Porosity of pozzolana-containing pastes. Porosity is an intrinsic property of cement paste which can be limited but not eliminated completely. It influences the strength and permeability of cement pastes, mortars and concretes, i.e. structural properties and durability. However, the connection between porosity and the two properties is different. All aspects of strength are related to the total porosity, whereas permeability depends on the structure and the size distribution of the pores.

The porosity of the paste depends on many factors and typically decreases by decreasing the water ratio and increasing the curing period. Porosity also increases by increasing the curing temperature; the difference mostly concerns the volume of large pores.[244] The type of cement plays a certain role, although it is more important in pastes than in mortars and concretes.[245]

The correct determination of porosity and pore size distribution is an important but difficult target to achieve. Difficulties derive mainly from the structural alteration that the methods of specimen preparation and determination induce on the samples.

The determination of porosity involves the preliminary removal of water from the pores of the paste and then filling the same pores with a suitable fluid. Water removal can be obtained by different procedures, the most widely used one being

- heating for a sufficiently long time period at a temperature >100°C in a CO_2-free oven (oven drying);
- drying under vacuum over a dry ice trap (D-drying);
- drying under vacuum over magnesium perchlorate hydrate (P-drying);
- drying over liquid nitrogen (sublimation);
- replacement by solvent extraction (solvent replacement).

In many cases these procedures have been combined and, to some extent, modified.

The porosity of dried specimens can be determined by

- mercury intrusion under high pressure;
- helium displacement at very low pressure;
- methanol displacement at very low pressure;
- water (or calcium hydroxide saturated solution) intrusion;
- nitrogen sorption.

Backscattered electron imaging of polished cement paste sections has been used to determine porosity, but the method is limited to pores larger than ~500 nm.[246]

The involvement of so many different procedures accounts for the different values obtained in the determination of porosity and the pore size distribution and for the caution required in comparing the results of different types of cement.

In addition to total accessible porosity, mercury intrusion also gives the pore size distribution. Depending on the pressure applied, mercury can intrude pores having diameters ranging between 3.5 nm and 200 μm.[247] The relevant distribution curve allows one to calculate:

- the threshold diameter (TD): the pore diameter at which the continuous mercury intrusion begins;
- the maximum continuous diameter (MCD): the maximum pore diameter corresponding to the main pore frequency;
- the main peak intensity (PI): the frequency of pores corresponding to MCD.

Nitrogen sorption is a suitable technique for determining the radii of pores between 0.5 and 3.75 nm. For this reason the total pore volume of a well-hydrated cement can be measured by combining the results obtained by mercury intrusion porosity and N_2 sorption.

The use of a saturated solution of calcium hydroxide for the determination of porosity with a pycnometer is inadequate as it systematically gives rise to higher results compared with those obtained with helium and methanol pycnometry, the difference becoming very significant at the low porosities.[248]

The influence of the drying procedure on the porosity value and on the pore size distribution is demonstrated by Figure 10.41.[249] Oven drying of saturated paste gives higher porosities than solvent replacement with either mercury intrusion[250] or helium pycnometry.[251] Similarly, specimens dried by liquid nitrogen exhibit a porosity lower than oven-dried specimens.[252]

These results suggest that oven drying could result in a partial disruption of the pore structure, particularly of the pores below ~ 10 nm due to the stresses induced by the receding water meniscuses upon drying.[250] By contrast, the solvent replacement is a milder technique which tends to preserve the original pore structure of the material.[250] The type of solvent has some consequences since, as shown in Table 10.29, methanol and isopropanol give the same total pore volume, but the threshold pore diameter is quite different.[253] This was attributed to a reaction of methanol with hydrates[254,255] or to the difficulties encountered in removing completely the solvents without altering the pore structure.[256] Recent evidence, however, supports the view that the solvent does not react with hydrates at ordinary temperatures.[257]

When Portland cement pastes are prepared with the same drying procedure, the porosity values found by mercury intrusion or helium pycnometry are the same.[197,250,258] It is worth noting that similar agreement has also been obtained with a paste in which 30 per cent Portland cement had been replaced with ground sand,[197] but not with pozzolana-containing cements, as we will see below.

Helium pycnometry gives higher values only when porosity is <21 per cent.[259] Since

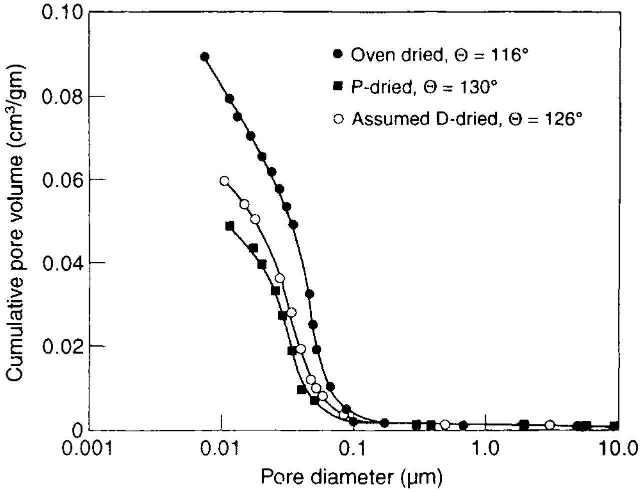


Fig. 10.41 Influence of sample drying procedure on pore distribution measured by MIP (source: Ref. 249). Cement paste with w/c 0.4; cured for 158 days.

Table 10.29 Porosimetric characteristics of paste of CEM I cement dried according to different procedures; w/c ratio = 0.8[253]

Specimen no.	Heat drying with vacuum	Period of preheating vacuum treatment	Solvent replacement	Threshold pore diameter (μm)	Pore volume at 0.1 μm diameter (% v/v)	Pore volume at 0.01 μm diameter (% v/v)	Total pore volume (% v/v)
A	20 h, 100°C	0	Methanol	0.50	16.0	37.5	51.0
B	20 h, 100°C	5	Methanol	0.59	19.0	38.2	52.0
C	20 h, 100°C	16	Methanol	0.59	16.,0	36.0	50.5
D	20 h, 100°C	24	Methanol	0.25	13.6	36.0	49.0
H	20 h, 100°C	0	Isopropanol	0.35	12.0	35.0	49.8
J	20 h, 100°C	5	Isopropanol	0.35	12.0	35.0	49.8
L	20 h, 100°C	16	Isopropanol	0.35	12.0	35.0	49.8
M	20 h, 100°C	24	Isopropanol	0.59	19.0	41.5	49.8

the values of porosity obtained with helium are confirmed by using the methanol saturation method, it is apparent that mercury cannot occupy the entire space accessible to helium and methanol.[259] This is consistent with the diameters of methanol and helium molecules, which are approximately 0.42 and 0.23 nm, respectively, and thus smaller than the ~3 nm diameter pores which can be intruded by mercury at a maximum pressure of ~400 MPa.[197]

Owing to the fact that porosity values depend on the drying and measuring techniques, it would be desirable to use more than one method.[260] Alternatively, the most appropriate procedure should be chosen depending on whether total or accessible porosity is required.

When the total porosity of cement pastes containing pozzolanas is assessed by mercury intrusion, it turns out to be generally higher than that of comparable plain Portland cement pastes.[198,234,240,261-263] This result is true for natural pozzolanas and fly ash-containing cements (Table 10.30).[264] It is also valid for beneficiated fly ashes (Table 10.31)[198] as well as for silica fume-containing cements.[265,266] Whatever the type of pozzolana, porosity decreases with time, but it continues to be higher than in the parent Portland cement paste.[261,262] Porosity increases by increasing the fly ash content, but it decreases when the rice husk ash content is increased.[262]

As was stated earlier, porosity values depend on the drying procedure adopted.[251] Table 10.30[264] shows that more severe drying leads to higher porosities than milder methods do. This conclusion is definitely apparent for the parent Portland cement after 7 months of curing, but for pozzolana cements it becomes clear after 28 days.

Unlike Portland cement, the porosity of blended cement paste depends on the method of determination in the whole range of porosities. As a matter of fact, porosity measured by methanol or helium pycnometry appears to be lower than by mercury intrusion.[197] This is illustrated in Figures 10.42 and 10.43.[251] The few points representing fly ash pastes that lie close to the line of equality correspond to samples which show little or no pozzolanic reaction.[267] The two Figures also show that the mercury porosity/helium porosity ratio is higher for oven-dried than for solvent-replaced specimens, as is the case for Portland cement paste.[251]

The mercury intrusion method also gives higher porosity in the case of cements containing up to 30 per cent silica fume.[267] These findings can be summarised as follows:

Table 10.30 Total porosity (per cent) by mercury intrusion of cement pastes; blending component = 30 per cent, w/c ratio = 0.32[264]

Sample	Portland cement	Blending component	Porosity			
			28 days drying		7 months drying	
			rapid[a]	slow[b]	rapid[a]	slow[b]
CEM 1	100		17.00	14.70	13.10	10.60
Filler	70	30	17.80	21.40	15.30	13.80
Fly ash	70	30	21.80	21.30	17.40	16.40
Vizzini pozzolana	70	30	18.70	21.60	14.30	12.90
Qualiano pozzolana	70	30	20.00	18.80	11.30	10.70
Casteggio pozzolana	70	30	17.80	16.30	13.60	11.60
Barile pozzolana	70	30	17.70	17.90	13.50	12.70
Segni pozzolana	70	30	17.50	19.30	13.40	34.20
Bacoli pozzolana	70	30	17.80	18.70	13.30	11.40

[a] Dried at 70°C for 16 h under vacuum at the residual pressure of 5 mbar.
[b] Dried at 20°C in four successive stages (relative humidity of 55, 33, 10 nd 0.01%).

- mercury porosity is higher than helium porosity;
- helium porosity is higher for samples that are oven dried than for those treated by solvent replacement.

It is reasonable to think that, since the smallest diameter of the pores intruded by mercury is larger than the diameter of the helium molecule and the pressure imposed is definitely higher, the higher mercury porosity is due to the breakdown of the entrances to the larger pores. These entrances are closed by thin deposits of hydrates which are impervious to helium or methanol but which cannot resist a Hg pressure as high as hundreds of MPa.

The damage caused by mercury intrusion in fly ash-containing cements has been demonstrated by subjecting paste specimens to two subsequent intrusions broken up by the distillation of mercury intruded in the first treatment. Repeated intrusion showed that in most samples of plain Portland cement pastes the pore size distribution did not change much, except for an increase in the threshold pore diameter, but major differences occurred in all blended cement pastes. The results of Figure 10.44[268] show that the curve has changed from convex to concave with respect to the pore diameter axes and indicates an intrusion threshold at much higher pore diameters.[268] The difference between the first and the second intrusion increases by increasing the silica fume content.[267]

An explanation for the different results between the first and the second intrusion is that the hydrated blended cement pore structure is made up of relatively large but discontinuous pores. During the first mercury intrusion, the walls of the closed pores were disrupted at high pressure and intruded. Repeated intrusion would result in the filling of these pores at much lower pressure.[268]

The second mercury intrusion reveals the presence of pores that are isolated and not communicating one with another. This means that mercury intrusion gives a picture more resembling the total porosity, and would thus account for the strength better, whereas the less disruptive helium method reveals only interconnected pores which govern permeability and thus durability.[258]

Table 10.31 Porosimetry and permeability data for Portland cement–fly ash pastes[198]

Paste	Age (days)	Total pore area (m^2/g)	Average pore diameter (µm)	Bulk density (g/cm^3)	Skeletal density (g/cm^3)	Porosity (%)	Permeability (cm/s)
Control	1	38.3	0.036	1.37	2.60	47.4	1.2×10^{-7}
	3	53.4	0.022	1.46	2.54	42.5	4.9×10^{-10}
	7	53.9	0.019	1.47	2.39	38.4	6.5×10^{-10}
	28	50.7	0.018	1.51	2.33	35.0	6.2×10^{-12}
4515[a]	1	28.8	0.045	1.43	2.65	46.0	1.1×10^{-7}
	3	48.4	0.026	1.40	2.48	43.6	2.0×10^{-8}
	7	50.4	0.023	1.40	2.32	39.7	1.3×10^{-8}
	28	50.7	0.020	1.50	2.39	37.4	1.3×10^{-11}
4530	1	24.4	0.061	1.32	2.57	48.6	7.1×10^{-7}
	3	43.2	0.031	1.42	2.70	47.5	4.7×10^{-8}
	7	50.7	0.026	1.32	2.30	42.8	5.6×10^{-9}
	28	55.9	0.020	1.43	2.42	40.9	1.0×10^{-12}
1015	1	32.9	0.041	1.37	2.54	46.3	6.0×10^{-8}
	3	43.3	0.028	1.41	2.46	42.7	6.4×10^{-9}
	7	53.9	0.022	1.42	2.43	42.1	6.1×10^{-10}
	28	55.0	0.019	1.47	2.36	37.9	2.9×10^{-12}
1030	1	41.0	0.039	1.29	2.62	50.9	1.6×10^{-7}
	3	49.0	0.030	1.35	2.66	49.3	2.3×10^{-8}
	7	50.0	0.026	1.36	2.43	44.3	1.9×10^{-9}
	28	63.9	0.020	1.35	2.35	42.4	5.3×10^{-13}

[a] Pastes are identified by the shorthand forms 4515, 4530, 1015 and 1030 representing 15% 45 µm ash, 30 45% µm ash, 15% 10 µm ash and 30% 10 µm ash, respectively.

Since the two methods give comparable results with the Portland cement pastes (except for low porosities), it can be assumed that the pore structure of pozzolana cement pastes is different and, in particular, the pore system is more segmented.

The microstructure of the pozzolanic cement pastes also differ from that of Portland cement pastes in the maximum continuous diameter, threshold diameter and main peak intensity (Table 10.32).[269]

The MCD, or critical pore size, represents the group of larger fractions of interconnected pores. After 28 days' curing, the MCD of a pozzolanic cement is lower than that of the parent Portland cement. If curing is prolonged up to 7 months, the critical pore size is further reduced by 10–40 per cent depending on the type of pozzolana present in the cement.[269] The rate of MCD reduction is definitely higher for pozzolanic cement pastes than for the parent Portland cement paste. Between 1 and 28 days of hydration the differential pore size distribution moves to lower values, namely, from ~1.00 to ~0.1 µm.

In pozzolanic cements containing either natural pozzolanas or fly ashes, the rate or frequency of peak intensity, which corresponds to the critical pore size, is generally slightly lower than in Portland cement pastes after 28 days' curing, but definitely lower after 7

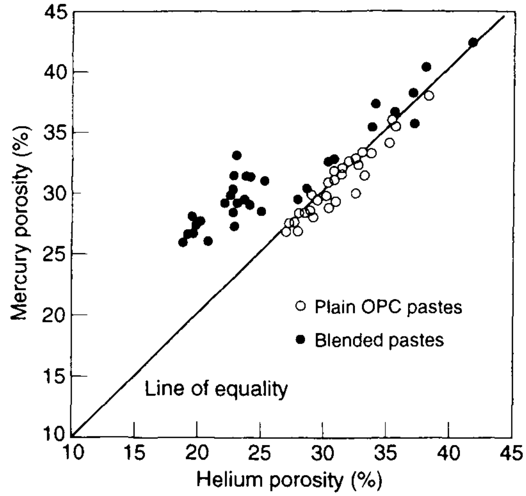


Fig. 10.42 Comparison of mercury and helium porosities; specimens prepared by direct oven drying at 105°C (source: Ref. 251). Samples cured at temperatures from 20 to 80°C and hydrated for periods up to 1 year.

months'.[261] The values of porosity parameters imply that mesoporosity of pozzolanic cement pastes is displaced towards the smaller pores.

10.3.4 PERMEABILITY OF POZZOLANA-CONTAINING CEMENT PASTES

The entry of gases, liquids and solutions into the concrete puts the durability at risk. Typically, sulfate can cause expansion and cracking of concrete, while carbonation and chloride penetration favour and accelerate corrosion of the reinforcement caused by oxygen.

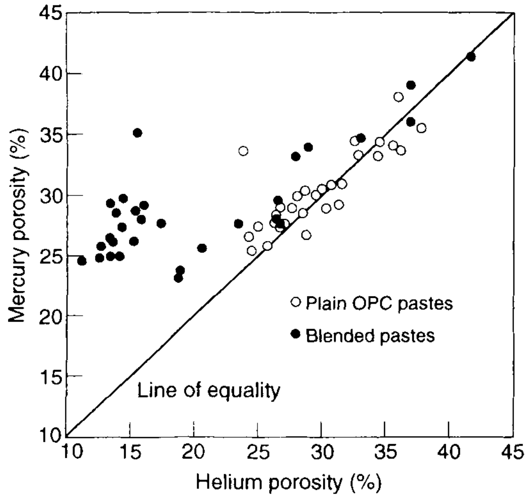


Fig. 10.43 Comparison of mercury and helium porosities; specimens prepared by solvent-replacement method (source: Ref. 251). Samples cured at temperatures from 20 to 80°C and hydrated for periods up to 1 year.

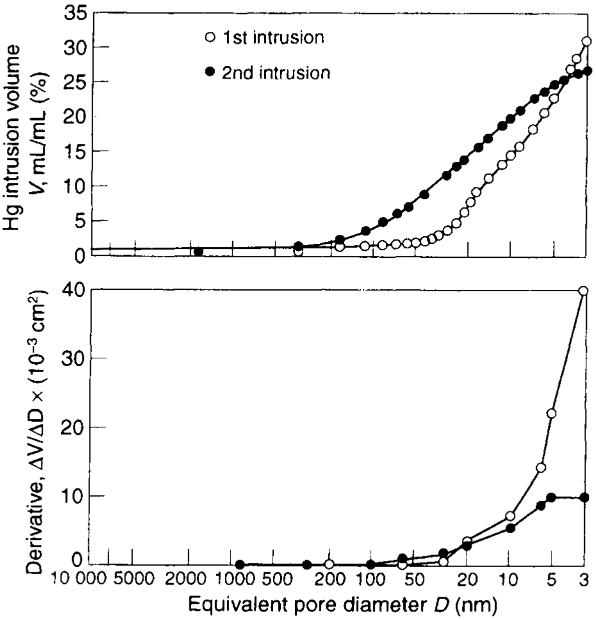


Fig. 10.44 Hg intrusion volume and derivative for fly ash and cement blend hydrated for 2 years at 35°C (source: Ref. 268). Distillation for 360 h, residual Hg = 2.10 per cent.

By assuming that there are no cracks, the entry of fluids into pastes, mortars and concretes depends on the permeability of the cement paste.

Gases and liquids can flow through capillary pores of cement paste by

- permeability (entry of fluids under a differential pressure);
- sorptivity (entry of liquids by capillary suction);
- diffusion (entry of gases or ions dissolved in water).

Permeability, sorptivity and diffusion depend on the interconnected pores; thus when the pores are segmented, penetration of liquid or gases can be very low, in spite of a not negligible porosity.

Permeability

Permeability of pozzolanic cement pastes is initially higher than that of Portland cement ones, but it tends to become lower as the curing time increases. On the contrary, the porosity of pozzolanic cements always remains higher than that of plain ones. This occurs when using both water[234,258] or air[261,270] as the measurement fluid (Table 10.33). Permeability decreases by increasing the pozzolana (natural, fly ash, rice husk ash, etc.) content and the curing time.[28,262] Some occasional deviations,[198] reasonably due to experimental errors, do not invalidate this general rule. Table 10.34 shows some typical permeability values of pastes having different pozzolana contents.[28]

Although permeability and porosity vary with time according to similar equations,[270] there is no general correlation between the two properties, possibly owing to differences in the microstructures of Portland and pozzolanic cement pastes. The apparent contradiction

Table 10.32 Maximum continuous diameter (MCD) and corresponding pore frequency (PI) of hardened cement pastes; blending component = 30 per cent, w/c ratio = 0.32[269]

Sample	Drying[a]	28 days MCD (nm)	28 days PI (%)	7 months MCD (nm)	7 months PI (%)
Portland cement	R	60	20.0	52	18.6
	L	52	19.9	44	27.0
Cement + filler	R	50	25.0	40	26.7
	L	55	18.6	46	23.1
Cement + fly ash	R	50	16.2	30	14.1
	L	54	22.8	32	17.0
Cement + Vizzini tuff	R	40	16.4	24	13.2
	L	40	21.7	24	11.4
Cement + Quagliano pozzolana	R	40	19.5	26	5.7
	L	37	23.4	19	7.3
Cement + Casteggio pozzolana	R	44	15.1	38	12.4
	L	44	28.8	34	19.2
Cement + Barile pozzolana	R	35	19.8	28	9.4
	L	46	22.2	30	13.9
Cement + Segni pozzolana	R	30	17.6	28	8.0
	L	35	16.1	36	10.3
Cement + Bacoli pozzolana	R	35	20.8	24	10.0
	L	40	18.3	24	12.6

[a] R = rapid drying; L = slow drying.

in terms of a higher porosity and a lower permeability of pozzolanic cement pastes as compared to those of the parent Portland cement ones can be explained through the following model.[271]

- In most pozzolanic cements, hydration occurring during the first 7–15 days almost exclusively involves the clinker + gypsum fraction. By that time 70–80 per cent of alite has reacted.[25]
- Part of the hydration products of clinker and gypsum form and develop on site, whereas the remaining part deposits on the pozzolana particles and fills in the pores.
- When the pozzolana starts reacting, its particles are surrounded by a porous but already stiff structure. Only part of the products of the pozzolanic reaction can therefore form on site.
- Since there is no evidence of a growing pressure, part of these products must have been formed elsewhere and later precipitated in the available pores.
- The volume of the precipitating mass is small and is therefore unable to fill the larger pores, but it is sufficient to obstruct the thinner channels connecting the large pores, or at least to reduce their span.
- As a consequence, the porosity of pozzolanic cement paste is still higher, even after the completion of pozzolanic reaction, but permeability is lower compared to the parent Portland cement paste.

Table 10.33 Permeability and porosity of cement pastes hardened for up to 90 days[270]

	Permeability ($\text{m}^2 \times 10^{-17}$)					Porosity (%)				
Curing (days)	1	3	7	28	90	1	3	7	28	90
w/c ratio = 0.32										
OPC paste	5.60	0.30	0.12	0.00	0.00	20.8	19.7	14.4	9.8	5.9
FAC paste	17.40	3.01	0.18	0.07	0.00	34.9	32.5	25.0	20.6	17.4
BPC paste	1.94	0.70	0.12	0.06	0.00	29.5	26.3	21.3	14.7	7.1
w/c ratio = 0.40										
OPC paste	18.70	0.59	0.07	0.07	0.00	33.3	28.6	20.9	16.8	11.1
FAC paste	68.30	8.30	0.91	0.09	0.00	37.7	37.3	31.6	26.2	16.8
BPC paste	14.30	1.80	0.42	0.02	0.00	39.3	29.8	24.7	20.6	10.9
w/c ratio = 0.50										
OPC paste	214.00	14.70	2.35	0.19	0.00	43.6	37.8	32.2	20.8	14.5
FAC paste	284.00	178.00	12.70	0.09	0.00	46.6	40.3	34.0	30.6	24.7
BPC paste	218.00	22.30	3.74	0.06	0.00	44.4	42.4	40.0	24.4	22.4

OPC = ordinary Portland cement; FAC = fly ash cement; BPC = Bacoli pozzolana cement.

This model is supported by the lower porosity values found by helium and methanol pycnometry compared to the value given by mercury intrusion. Since helium and methanol porosimetry indicate only the porosity accessible from the surface of the specimen,[258] the higher porosity and lower permeability of pozzolanic cement paste ceases to be a contradiction.

Sorption

Sorption is due to capillary forces which are active in concretes subjected to natural wetting/drying cycles. Sorption is a more general phenomenon than permeability since it occurs when unsaturated pastes, mortars or concretes come into contact with water or air moisture. Sorptivity, like permeability, decreases by decreasing the water/cement ratio and increasing the curing time.

Sorptivity is remarkably lower in pozzolanic cement pastes than in Portland cement ones.[272,273] These differences are shown in Table 10.35, where cement pastes and mortars made with a pozzolanic and the parent Portland cements are compared. Table 10.35 also shows that after between 28 and 90 days, sorptivity diminishes dramatically while only a slight variation in total porosity occurs.

Table 10.34 Relative depth of penetration of water into hydrated cement pastes (mm). Portland cement blended with Santorin earth[28]

Hydration age	Portland cement	10% pozzolana	20% pozzolana	30% pozzolana
28 days	26	24	25	25
90 days	25	23	23	22
1 year	25	23	18	15

Table 10.35 Porosity by volume P and sorptivity S of pastes and mortars made from pozzolanic cement (CEM IV) and a parent Portland cement (CEM I)

		Curing time (days)								
		28 days			90 days			240 days		
		P (%)^b		S (mm/m$^{0.5}$)	P (%)		S (mm/m$^{0.5}$)	P(%)	S (mm/m$^{0.5}$)	
Sample	Note	A	B		A	B				Ref.
a CEM I paste	1							28.07	0.632	
b CEM IV paste								30.64	0.228	(272)
c CEM I mortar	2							12.34	01, 10	
d CEM IV mortar								14.94	0, 61	
1 CEM I paste	3	21.02	13.69	0.225	21.14	13.13	0.147			
2 CEM IV paste		24.94	13.89	0.153	25.93	14.51	0.104			
3 CEM I mortar	4	14.48	12.32	0.157	14.70	11.31	0.132			
4 CEM IV mortar		14.31	11.43	0.119	14.85	10.64	0.090			(273)
5 CEM I mortar	5	13.21	11.62	0.122	13.11	9.75	0.102			
6 CEM IV mortar		15.51	13.41	0.139	15.74	12.29	0.097			

A = Water-accessible porosity; B = Mercury-accessible porosity.

(1) w/c = 0.5; (2) CEN mortar; (3) w/c = 0.25; (4) 0.5–2 mm sand, s/c = 2.25, w/c = 0.335; (5) CEN sand, s/c = 3, w/c = 0.425.

Gas penetration

Unlike concrete, diffusion of oxygen in the cement paste has not been extensively studied. A possible reason for the paucity of available data are the difficulties encountered in drying the specimens without cracking them before performing the diffusion tests.[270]

By using thin (1–2 mm) hardened paste discs having different humidities, it has been observed that the O_2 coefficient of diffusion strongly depends on the porosity, i.e. on the water/cement ratio but not, at least in the range 50–90 per cent relative humidity, on the equilibrium moisture.[274]

In concrete the effective diffusion coefficient of oxygen decreases dramatically by increasing the cover thickness and the relative humidity (Figure 10.45)[275] since oxygen is poorly soluble in water. Figure 10.45 shows that D_{eff} of O_2 is lower in blended cement concretes since these are less permeable to oxygen diffusion than Portland ones. In any case, all the factors affecting porosity, i.e. water/cement ratio, cement content and degree

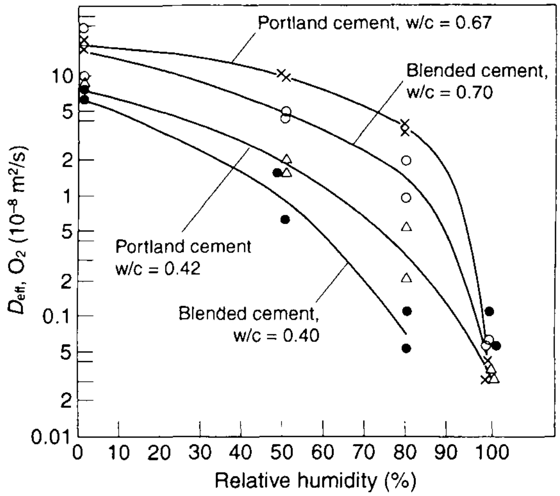


Fig. 10.45 Effective O_2 diffusion coefficient for Slite Portland cement and slag cement (65 per cent/slag + 35 per cent/Portland) concrete (source: Ref. 275). Temperature = 20°C, specimen age = 6–12 months.

of hydration, are more important than the cement type. For this reason, oxygen permeability decreases by increasing concrete strength, irrespective of the cement type.[276]

The carbon dioxide concentration in air is very small. However, CO_2 is able to react with and to decompose all of the hydrates of the cement paste, forming calcium carbonate. The coefficient of diffusion in thin hardened cement paste increases by increasing the water/cement ratio, i.e. as shown in Figure 10.46, by increasing the porosity.[274]

The carbonation rate of concrete is a complex function of many variables such as water/cement ratio, cement content, curing period and so on, but it does not significantly depend on the cement type. The depth of carbonation correlates well with the compressive strength of concrete[277–282] i.e. with its compactness.

The depth of carbonation versus relative humidity attains maximum values at between

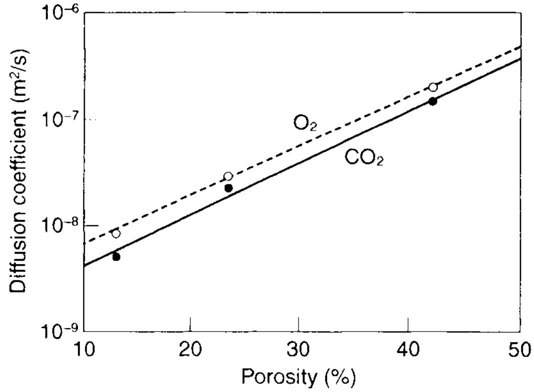


Fig. 10.46 Diffusion coefficients of O_2 and CO_2 as a function of total porosity of hardened OPC paste (source: Ref. 274).

50 and 70 per cent relative humidity. In practice, in the climatic conditions occurring in many countries, the degree of carbonation decreases with increasing relative humidity.[283] The reason is that in saturated or quasi-saturated concrete, carbon dioxide has a low diffusivity and, moreover, it reacts with the calcium ions contained in the pore solution. As a consequence a film of calcium carbonate forms at the meniscus of the solution, thus hindering the diffusion of CO_2.[284]

Entry of ions dissolved in water

Water penetrating into concrete also transports dissolved ions, although the rates are different.

Entry by capillary suction. In cementitious stones, the capillary rise of humidity is faster than that of dissolved ions as though the transport of ions were slowed by the capillary pores of the cement paste. Tests carried out on mortar standard prisms (40 × 40 × 160 mm) dried and placed in contact with a 4 per cent NaCl solution have shown that the height of Cl^- rise was between one-seventh and one-eighth of that of water.[285] Table 10.36 shows also that penetration of Cl^- in slag cement paste is lower than in Portland cement paste.[275] The lower ionic permeability of blended cement mortars can be related to the finer structure of their capillary pores.

Entry by diffusion. In a cement paste the coefficient of effective diffusion of ionic species is smaller by a factor of 1000 than that in water.[286] It decreases by decreasing the water/cement ratio and temperature[286,287] and by increasing the curing period[288] and the thickness of the samples.[287,289,290]

The diffusion coefficient correlates fairly well with the volume of the pores with a radius <2 nm, but not with the total pore volume.[291] As a first approximation, the diffusion coefficient appears to depend on the tortuosity of the capillary pores.[290,292,293] The diffusion coefficient of anions depends on the nature of the cations with which they are associated since, as in the case of Cl^-, the diffusion coefficient decreases from $MgCl_2$ to $CaCl_2$, LiCl, KCl and NaCl. The apparent diffusion coefficient of Cl^- is higher than that of the associated cations and the difference can be as large as one order of magnitude.[294,295] Some data concerning the diffusion rates are given in Figure 10.47.

The differences in D_{eff} between cations and anions have been attributed to the formation of an electronegative semi-permeable membrane in the cement paste, which should retard the movement of the cations,[296] to the reflection of positive ions by the positively charged paste capillaries,[291] as well as to the dissolution of Ca^{2+} from the paste, which should balance the apparently lower diffusivities of alkalis.[297]

Table 10.36 Relation between chloride penetration and water penetration for mortar[275]

	w/c	Cl/H_2O penetration
Portland cement	0.4	1:3
Slag cement[a]	0.6	1:3
Slag cement[a]	0.4	1:6

[a] 30% Portland + 70% slag.

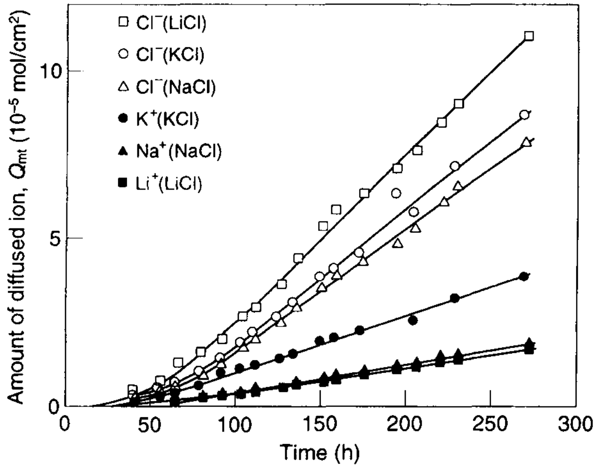


Fig. 10.47 Amount of ion diffused through plate 0.3 cm thick using 0.5 N LiCl, 0.5 N NaCl and 0.5 N KCl solutions (source: Ref. 293).

Diffusion of chloride sometimes dramatically affects the durability of reinforced concrete, and so it has been the object of many studies. Diffusion of chloride depends on the cement type, but within the same type of cement, diffusivity can vary appreciably. Typically, sulfate-resisting Portland cements show higher diffusion coefficients than ordinary Portland cements (Table 10.37).[287,288] Blended cements containing natural or artificial pozzolana give pastes having smaller diffusion coefficients than the parent Portland cement pastes.[286-289,298] This occurrence is exemplified in Table 10.38 and in Figure 10.48.

In pastes with water/binder ratio of 0.60, 40 per cent replacement of fly ash for Portland cement caused a reduction of the Cl^- diffusivity by an order of magnitude. Similar results have been obtained by lower (10 per cent) replacement of silica fume.[289,298] In blended cements, D_{eff} of Cl^- depends on the parent Portland cement as well as on the type of the pozzolana, and decreases with pozzolana content.[300]

The influence of the type of cement on the diffusivity of chloride has not yet been completely explained. As far as Portland cements are concerned, the higher diffusivity in the paste of sulfate-resisting Portland cement as compared to that of ordinary Portland cement,[288] is attributed to its low content of C_3A and thus to a lower capacity to bind the chloride in the form of a complex salt such as calcium monochloroaluminate hydrate

Table 10.37 Effective diffusivity of chloride ions at 25°C in various cement pastes[287]

Type of cement	D (cm²/s × 10^9)
OPC	44.7
OPC + 30% pfa	14.7
OPC + 65% BFS	4.1
SRPC	100.0

Table 10.38 Coefficients for diffusion of chloride ion into cement pastes and concretes[286]

Sample	D (cm^2 s × 10^8)	Temperature (°C)
Portland cement paste	1.23	10
Portland cement paste	2.51	25
Portland cement paste	4.85	40
Pozzolanic cement paste	0.83	10
Pozzolanic cement paste	0.90	25
Pozzolanic cement paste	0.97	40
Portland cement concrete (vibrated)	1.65	25
Portland cement concrete (nonvibrated)	1.05	25
Pozzolanic cement concrete (vibrated)	1.05	25
Pozzolanic cement concrete (nonvibrated)	2.26	25

($C_3A \cdot CaCl_2 \cdot 12H_2O$). However, since the paste made with ordinary Portland cement has also a lower porosity,[287] it is difficult to separate the chemical from the physical effect and to recognise the predominant one. Moreover, pozzolanic cements contain less C_3A than the parent Portland cements; thus they should have a lower binding capacity of chloride and show higher Cl^- diffusivity coefficients than the parent Portland cements, which is in contradiction with experimental evidence.

The lower diffusivity of chloride observed in the pastes of pozzolana-containing cements may be related to their permeability, which is lower than that of the parent Portland cements. As a matter of fact, the chloride diffusion coefficient ratio between Portland cement and pozzolanic cement pastes is between 3 and 10,[287,289,297,300] that is, more or less the same ratio as for the permeability coefficients.[198,261]

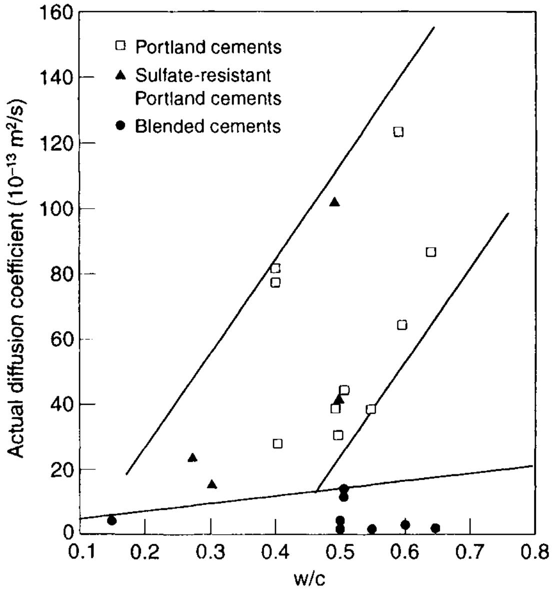


Fig. 10.48 Actual diffusion coefficient of Cl^- ion versus water/cement ratio for cement paste samples exposed to NaCl solution in diffusion cells (source: Ref. 299).

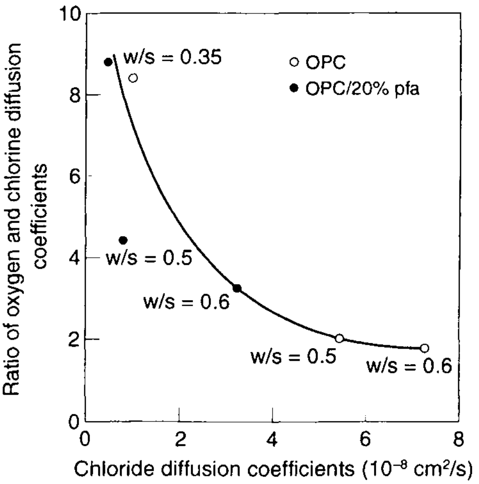


Fig. 10.49 Variation of the ratio of oxygen and chloride diffusion coefficients with chloride diffusion coefficient (source: Ref. 300).

The lower values D_{eff} of Cl^- observed in pozzolana-containing pastes have also been attributed to a certain interaction between Cl^- and the pore walls, which should be stronger in blended cements than in the parent Portland ones.[291,296]

Tortuosity of capillary pores in a cement paste should give rise to the same geometrical hindrance to the movement of all the dissolved species, but Figure 10.49 shows that the ratio of oxygen to chloride diffusion increases with a decrease of the Cl^- diffusion coefficient.[300] This suggests that the ionic diffusion is affected by an electric double layer at the interface between the pore walls and the pore solution. Moreover, since chloride diffusion in a dense paste is more retarded than oxygen diffusion, it seems that the surface charge mainly affects the ionic transport through the micropores.[301]

The activation energy for diffusion of chloride is 17.6 kJ/mol in an electrolyte solution but goes up 40–50 kJ/mol in mature Portland cement pastes with a water/cement ratio of 0.4.[287,296] In contrast, the activation energy of Cl^- through quartzite is only 4–8 kJ/mol.[296] From these results it was inferred that the pore walls of the cement paste interacts with the chloride ions, whereas those of quartzite affect the ion movement only because of geometrical factors.

Measurements of the resistance to the transport of chloride ions through the cement paste under the potential of an electrical field (FHWA test) have demonstrated a proportionality between the charge passed and the water permeability of the paste. At the same water permeability, the electrical charge transported through the Portland cement paste is about three times that passed through fly ash-containing paste.

Silica fume diverges from this behaviour since the electrical charge transported through a 10 per cent silica fume cement paste was more or less the same as that measured through the parent Portland cement paste.[302] This result is inconsistent with diffusion measurements which have shown that the diffusivity of chlorine in silica-containing paste is definitely lower than in Portland and fly ash cement.[298] This apparent discrepancy depends on the changes caused by the presence of silica fume in the composition of the pore solution and of the C-S-H.

By increasing the silica fume content in cement, the C/S ratio of C-S-H decreases, but a lowering of C/S causes a reduction in the amount of so-called chemisorbed Cl^- on

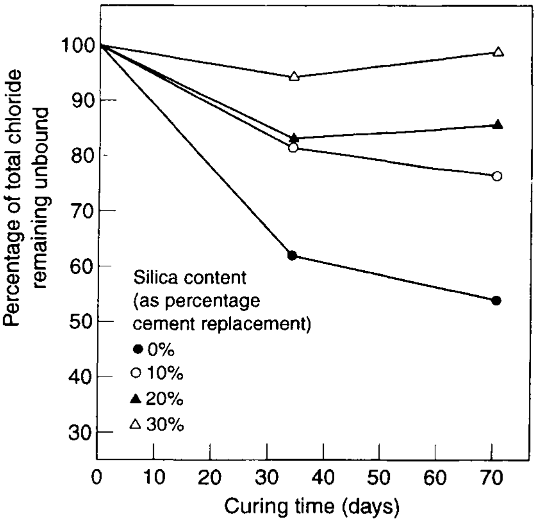


Fig. 10.50 Percentages of total chloride ion content remaining dissolved in capillary pore solution of hydrated cement pastes with total chloride additions of 1.0 per cent by weight of (cement + silica) (source: Ref. 226).

C-S-H.[303] As a consequence the Cl^- content dissolved in the capillary pore solution increases (see Figure 10.50[226]). Thus the lower Cl^- binding capacity of cement causes an increase of the Cl^- concentration in the solution and an improvement in the electrical transport capacity. At the same time, diffusivity remains low since it depends on the pore size distribution and not on the concentration of Cl^-.

Pozzolanic cements also slow down the diffusivity of Cl^- in both mortar[304] and, as shown in Table 10.38, in concrete.[286,305] Of course, the penetration of chloride is faster in concrete than in paste,[275] and depends on the cement content[306] in addition to the parameters acting on cement paste.

The apparent diffusion coefficient of monovalent cations increases with the atomic number (Figure 10.47).[293] The activation energies for the diffusion of Na^+ and Cl^- are similar in an infinitely dilute solution (18.0 and 17.5 kJ/mol, respectively) but are quite different when they are calculated from the diffusion tests through cement paste. In this case the values of D_{eff} are 83.74 and 50.24 kJ/mol for a water/cement ratio of 0.4.[296] These results could mean that Na^+ interacts with the cement paste more strongly than Cl^- does;[296] however, as stated earlier, the discrepancy could be attributed to the co-diffusion of Na^+ and Ca^{2+}. As a matter of fact, in the absence of any calcium ion supply, as in the case of diffusion through a quartzite plate, the diffusion coefficients of both alkalis and chloride are the same.[296]

The migration of Ca^{2+} through the cement paste is not in agreement with the results of chemical analysis of the pore solution derived from the hardened cement pastes. The pore solution is practically free of calcium ions, thus the transported calcium ions must come from the calcium hydrates forming the cement paste. The leaching of Ca^{2+} from cement paste has been evidenced by a decrease in the portlandite content during the diffusion process.[287]

10.4 Mortars containing pozzolanas

10.4.1 MICROSTRUCTURE

Apart from the presence of the aggregate grains, the microstructure of mortars containing pozzolanas differs only slightly from that of the corresponding pastes. SEM observations have shown that the consumption of calcium hydroxide by pozzolana results in a reduction of the number and size of the portlandite crystals at the aggregate–paste interface as well as in the bulk paste. A reduction of free lime is associated with a decrease in the flaws in the mortar and improves the homogeneity of the matrix. At the interface, the *c*-axes of the CH crystals are more or less parallel to the aggregate surface and some fly ash particles appear to be encapsulated by CH.[307]

Condensed silica fume introduces some differences in the microstructure of the interfacial zone of mortars, which becomes dense and uniform, lacking in rims of portlandite or gaps. Practically no border line can be drawn between the bulk cement matrix and the interfacial zone.[308] Compactness has been ascribed to the presence of 15 per cent silica fume in the cement; however, a strong contribution must be attributed to the superplasticiser used at a dosage up to four times that used in the control concrete. Superplasticisers reduce the initial water film around the aggregate grains irrespective of the type of cement[309] and this could account for the high compactness of the interfacial zone observed in silica fume-containing concrete.

Mortars made with pozzolanic cements generally have a higher porosity than those made with the parent Portland cements (Table 10.35).[273] The porosity of mortars gauged with w/(c + sf) ratios of 0.45 and 0.6 increases by increasing the silica fume content. Lower w/(c + sf) ratios require the addition of variable amounts of superplasticiser to maintain a certain workability.[265] The replacement of silica fume for a fraction of Portland cement increases the macroporosity of mortars, i.e. the volume of pores having a diameter > 50 nm.[265,310]

A similar increase is also found by increasing the sand/cement ratio of the mortar.[310] Mercury re-intrusion of mortars containing up to 30 per cent silica fume showed some modification in the pore size distribution caused by the first intrusion, i.e. an increase in the volume of the coarser pores.[310]

10.4.2 PERMEABILITY AND SORPTIVITY

Replacement of Portland cement by pozzolana changes the permeability of mortar. Figure 10.51 shows that, after a 160-day curing, fly ash can reduce the water permeability by more than one order of magnitude.[311] The positive effect of fly ash is more pronounced at low rather than at high water/cement ratios. The same figure shows that the reduction of permeability depends on the type of fly ash and that pozzolana-containing mortars require a prolonged cure to develop the best performance. For this reason, when the wet curing time is too short, the permeability of blended cement mortars remains significantly higher than that of the control Portland cement mortars.[312]

Permeability, determined by water penetration, oxygen or chloride diffusion, gives similar values; thus a significant linear correlation (at the 1 per cent level) is found among the three types of permeability measurements.[311] The importance of the water/cement ratio on the mass transport through mortar is stressed by the coefficient of permeability of the mortars made with a water/cement ratio of 0.5, which was about one-fifth of that made with a water/cement ratio of 0.65.[111]

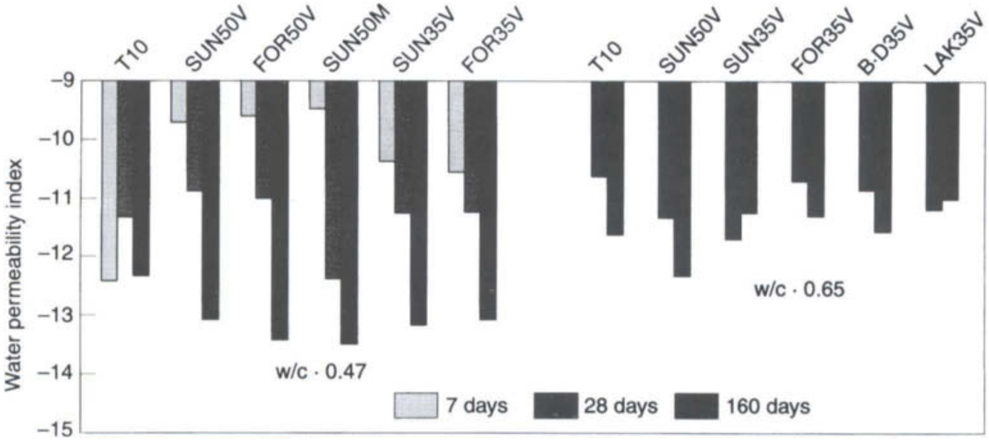


Fig. 10.51 Variation of water permeability with age of mortars; 35 and 50 per cent replacement for T10 Portland cement with SUN and FOR fly ashes (source: Ref. 311). Index is the exponent to base 10 of the permeability coefficient. V = by volume, M = by mass replacement.

In addition to the water/cement ratio and the age of the specimen, the sorptivity of mortars depends on the type of cement used. Table 10.35 shows that pozzolana reduces the sorptivity of both pastes and mortars and increases porosity.

10.4.3 MECHANICAL PROPERTIES

Setting

Setting time of cements containing natural pozzolanas does not differ from the typical values found in Portland cements.[313] On the contrary, fly ash generally delays both the initial and final setting times.[313,314] The different behaviour of fly ashes as compared to that of natural pozzolanas is possibly due to the presence of carbon particles in the fly ash.

Silica fume reportedly prolongs setting times[315] but, since it is generally used together with plasticisers or superplasticisers, it is difficult to differentiate a retarding effect of silica fume from that of the admixture.

Strength

Pozzolana starts reacting somewhat belatedly with the calcium hydroxide produced by clinker hydration and therefore, at least initially, it behaves like an inert material diluting the Portland cement with which it has been mixed. However, as it has been pointed out in section 10.3.3, pozzolana accelerates the early hydration of clinker compounds from ~8 h after mixing with water. As a whole, the partial replacement of pozzolana for Portland cement generally reduces the initial rate of cement hardening, but at greater ages the situation is reversed and pozzolana-containing cements can attain the same or even a higher strength than the corresponding control Portland cements. The initial reduction occurs with natural pozzolanas,[28,190,236,316] high-[317] and low-lime fly ashes[190,198,200,234,317,318] and silica fume.[238,319,320] A typical example of this behaviour is given in Figure 10.52.[236]

The decrease in early strength caused by the partial replacement of common pozzolanas for Portland cement is a general occurrence. Figure 10.53 shows that 30 per cent replacement of fly ash for Portland cement can reduce the early strength of the control cement by 50 per cent, thereby exerting a greater effect than that calculated by a dilution rule.[235] The difference in strength between pozzolanic and Portland cements decreases with age and eventually disappears or changes in sign. The moment of recovery depends on the fineness of both Portland cement,[235] and pozzolana,[237] as well as on the pozzolana activity. For this reason, the curing of pozzolanic concretes and mortars needs more care than that of Portland cements.

The lower hardening rate brought about by the replacement of pozzolana for Portland cement does not create major problems when pozzolanic cements are prepared directly at the cement works, because the cement manufacturer can take all the necessary steps to ensure that blended cements have strength values complying with standard specifications. When pozzolana is added to cement at the building site, where the properties of the pozzolana and the Portland cement cannot be modified further, the only possible corrective measure to optimise the properties of the mix is to increase the cement content.

The effect of pozzolana on strength depends on a number of factors, the most significant of which are

- the pozzolana content of the cement;
- the type of pozzolana;
- grading and specific surface of the pozzolana;
- the individual characteristics of the blending Portland cement.

Type and content of pozzolana. The strength of pastes and mortars is affected by the type and content of pozzolana. Figure 10.52 shows how an optimum replacement level occurs.

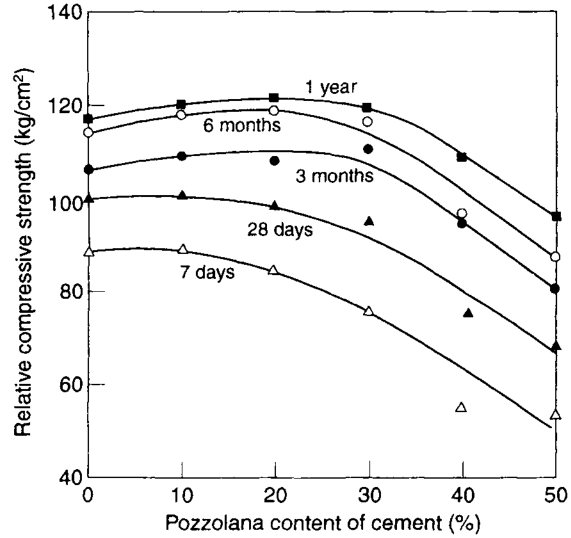
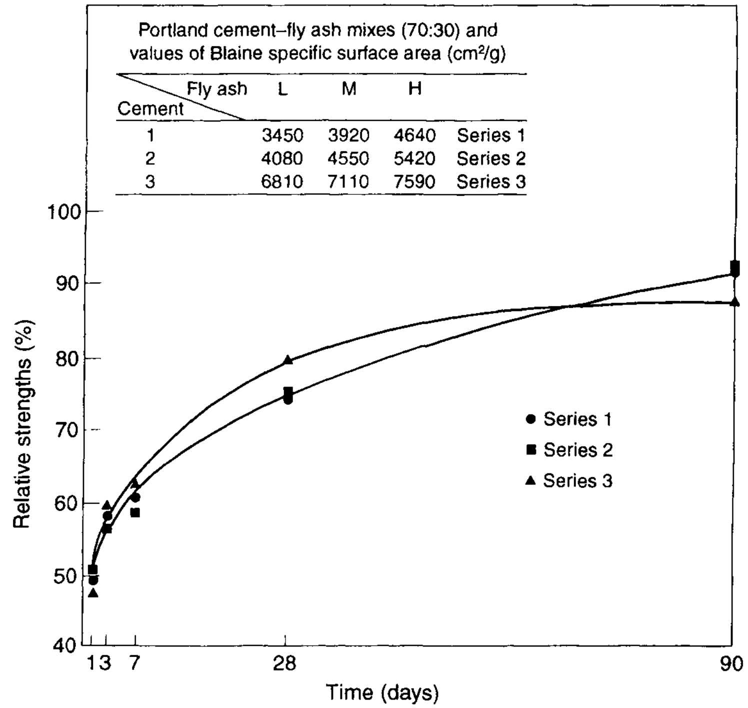


Fig. 10.52 Effect of substituting Portland cement for pozzolana on the compressive strength of ISO mortar (source: Ref. 236). Values expressed as percentage of the 28-day strength of reference cement.



Cement \ Fly ash	L	M	H	
1	3450	3920	4640	Series 1
2	4080	4550	5420	Series 2
3	6810	7110	7590	Series 3

Fig. 10.53 Mean values of relative compressive strength with respect to the control Portland cements (source: Ref. 235). Series 1, 2 and 3 formed by a Portland cement and a fly ash, both of increasing fineness.

It varies depending on the type of pozzolana being used, thus appropriate proportioning of cement is necessary for obtaining high strength. The replacement of fly ashes for 50 per cent Portland cement can give high strength concrete, depending on the binder content and the water/cement ratio.[321]

Common natural pozzolanas and low-lime fly ashes, having a fineness similar to that of Portland cement, give the highest 28-day strength when replacing about one-third of the Portland cement.[111,198] The reduction in 28-day strength following the substitution of pozzolana for Portland cement is lower than that obtained by diluting the control Portland cement with an inert filler.[111,322]

The strength of pozzolanic and pozzolana cements depends on the characteristics of the pozzolana used.[111,318,322,323] This is shown in Figure 10.54, which concerns mixes containing 20 per cent of pozzolana. Owing to the contribution of the pozzolanic reaction, the strength of the mixes is always higher than that of the control sample containing 20 per cent of ground quartz.[322]

The behaviour of Sacrofano pozzolana illustrated in Figure 10.54 is apparently inconsistent with the very high pozzolanic activity due to the high amorphous silica content and high fineness of this material.[111] However, it is similar to that of other materials such as silica fume and ground fly ash. A high specific surface area can possibly slow down the rate of hydration in mixes without water reducers.

The loss in strength caused by pozzolana of common fineness can sooner or later be recovered, depending both on the type[200] and the content of pozzolana. For example, the

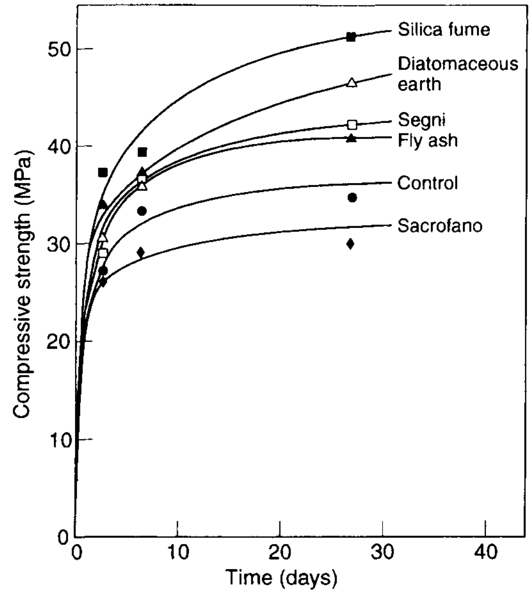


Fig. 10.54 Strength development of different 20 per cent pozzolana–cement mixes. Paste with w/c = 0.5; 40 × 40 × 160 mm specimens cured for 72 h in water and then in 65 per cent relative humidity at 20°C.

strength of a cement containing 15 per cent of rhyolitic glass slightly exceeds that of the control Portland cement after 7 days,[319] but generally strength recovery occurs after 28 days. Conversely, with certain poor-quality pozzolanas the strength of the control Portland cement is always higher than that of the blended cements,[316] at least for 3[324] or 6 months.[312]

After 28 days' curing, the mortar strength of cements containing 5–25 per cent of silica fume proved to be higher than that of plain cement mortar.[320] A maximum strength was recorded at ~15 per cent Portland cement replacement with a behaviour similar to that shown in Figure 10.52, but this result was obtained by adding an increasing amount of a superplasticiser to the mix and by changing the water/cement ratio.

At 28 days the compressive strength of mortars made from cements of varying fineness and containing 10 per cent silica fume can be higher than 30–50 per cent of that of plain cements.[194] The strength of microsilica-containing paste appears to depend on the w/c or w/(c + sf) ratios. The substitution of up to 7 per cent of silica fume for Portland cement increased the 1-day strength but decreased the strengths after 7 and 28 days of pastes made with w/c = 0.45.[238]

A w/(c + sf) = 0.48, strength increased at up to 15 per cent replacement and then decreased slowly up to 25 per cent replacement. At w/(c + sf) = 0.25, strength decreased whatever the silica fume content.[325] When the water content is low, strength is not recovered even after 182 days of curing.[234]

The addition of relatively high amounts of silica fume to Portland cement increases the water demand remarkably; it reduces workability and the strength of the mixes,[326] as shown in Figure 10.54, for the very fine Sacrofano natural pozzolana. The negative influence of very fine silica on strength has also been observed in pastes containing a limited amount of colloidal silica (specific surface area = 390 m^2/g). An improvement of strength was encountered only when the addition did not exceed 3.3 per cent.[238]

The strength loss caused by the high specific surface area of microsilica can be overcome by adding suitable water reducers to the mix.[326] In fact, the addition of 5–10 per cent silica fume to a cement containing 15, 30 and 50 per cent fly ash and of a superplasticiser increased the 28-day strength of standard mortars by 35–80 per cent. The difference in strength decreases with time but remains in the range 15–20 per cent at 90 days.[64]

Particle size distribution of pozzolana. The strength of mortar decreases in a different measure when Portland cement is partially replaced with fly ash fractions of different sizes.[317,318] Figure 10.55 shows that the negative effect increases with the particle size and decreases with time only for the finest fraction.[317] Coarser fractions of high-lime fly ashes behave slightly better than low-lime fly ash, probably because they contain some hydraulic constituents.[317]

Grinding promotes the activity of fly ashes and if the fineness of the fly ash is appropriate, the 90-day strength can be higher than that of the control cement but, if the fineness of fly ashes exceeds certain limits, compressive strength will decrease instead.[317]

The lower strength brought about by too great a fineness of pozzolana corresponds to the decreases in combined lime caused by the increase in Portland cement fineness (Figure 10.40). The fact that both strength and combined lime decrease is possibly due to the decrease in permeability of the paste, which hinders the mobility of the ions.

Properties of the parent Portland cement. The strength of pozzolana-containing mortars also depends on the properties of the individual Portland cement used in the mix. Figure 10.56[318] shows the influence of both eight fly ash types and four Portland cements on the relative compressive strength of standard mortars. The strength of blended cement mortars can be higher or lower than that of the corresponding parent Portland cement mortars. Differences in strength have been attributed to the different content of alkali in the Portland cements[318] but certainly other reasons play a role. As an example, the differences in the rate of strength development caused by fly ashes have been attributed to a higher rate of formation of CH and this, in turn, to the different C_3S contents in the Portland cement.

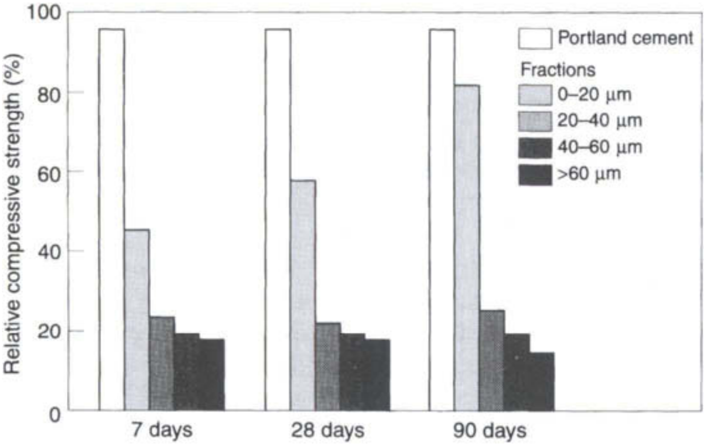


Fig. 10.55 Reduction of the compressive strength of binders containing 30 per cent of low-calcium fly ash, relative to pure cement. (source: Ref. 317).

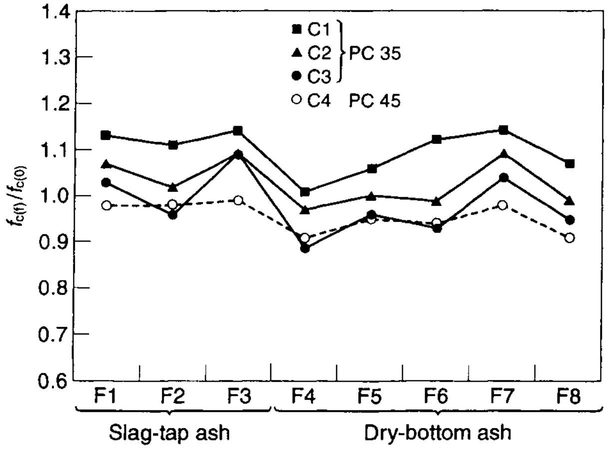


Fig. 10.56 Effect of Portland cement on relative compressive strength $f_{c(f)}/f_{c(0)}$ of mortar with fly ash (source: Ref. 318). Age = 90 days, f/c = 0.25, w/(c + f) = 0.50.

In this case the differences in fineness have been considered to play only a secondary role; however, fineness remains an important factor.

The strength of mortars made with cements containing up to 10 per cent silica fume decreases with decreasing fineness of the parent Portland cement, but it is always higher, at least up to 28 days, than the strength of the plain Portland cement.[194]

The high alkali content of clinker seems to increase the strength and rate of hardening of cements containing 15 per cent silica fume.[327] The partial replacement of fly ash for blastfurnace cements reduces the strength to a greater extent than that which usually happens in Portland cements.[318]

Fly ashes have different effects on mortar strength, depending on the strength class of the Portland cement being used. Eight different fly ashes were blended with a 35 and a 45 class Portland cement made with the same clinker. Replacement of 25 per cent Portland cement caused a general decrease in the strength of the mortars. However, the blended samples from the class 35 Portland cement recovered the strength of the plain mortar after about 90 days, whereas those from class 45 Portland cement were unable to do so.[235] The results obtained suggest that the real behaviour of a pozzolana-containing cement depends both on the individual Portland cement and the pozzolana with which it is blended. For this reason the optimum pozzolana content must be selected on a case-by-case basis, taking into account the properties of the individual component and the properties that have to be improved.

Workability. The use of a pozzolanic material whose fineness is similar to that of the Portland cement does not change the workability of mortars very much. Generally, natural pozzolanas slightly decrease the workability of mortar whereas low-carbon fly ashes improve it.[323] High-carbon fly ash can increase the water demand.

The replacement of pozzolanic materials does not hinder the use of water reducers in mortar and concrete, but the efficacy of superplasticisers in reducing the water demand of mortar can be hindered by the presence of fly ash.[323]

In contrast to the most common pozzolanas, which have a fineness comparable to that of cement, very fine materials such as microsilica and diatomaceous earths increase dramatically the water demand of mortar, thus batches need an appropriate addition of superplasticisers to reach the required workability without adding more water. The dosage of admixtures needed for a certain workability increases proportionally with the quantity of microsilica present.

10.4.4 SHRINKAGE

It is generally agreed that the addition of normal percentages of pozzolanas to cement does not significantly affect the drying shrinkage or the expansion in water of mortar. Table 10.39 shows that shrinkage in air of Portland and pozzolanic cements containing natural pozzolanas do not significantly differ.[328] After a drying for 28 days, replacement of other pozzolanas such as 'opaline breccia' or a fly ash for the same Portland cement gave shrinkage values of 600–800 × 10^{-6}.[329] This range of shrinkage values for pozzolana-containing mortars is comparable to that of Portland cement mortars. Shrinkage values ranging between 640 and 1150 × 10^{-6} have been obtained on mortars made with 40 different Portland cements wet-cured for 24 h before exposure to dry conditions.[330]

Table 10.40 shows that shrinkage of mortars is affected by the fineness of the clinker more than by the fineness of fly ashes[331a] thus it appears to be affected by the fineness rather than the type of cement used.

10.4.5 AUTOGENOUS TEMPERATURE RISE

The rate of temperature rise is a property of concrete that must be accurately checked in mass concrete. Increasing percentages of pozzolanic materials replacing Portland cement decrease the initial temperature rise of Portland concrete.[331b,331c] High volume replacement can halve the early temperature rise[331b] but the temperature maximum is not affected by the source of ASTM Class F fly ash used.[331c]

Table 10.39 Typical shrinkage values for normal mortar (μm/m) for specimens cured for 24 h and then kept in a climatic cabinet at 20°C and 50 per cent relative humidity[328]

Cement		Curing period (days)		
		7	28	90
CEM I	32.5	427	755	890
CEM I	42.5	396	733	873
CEM I	52.5	453	842	1043
CEM I	32.5	329	653	793
CEM I	42.5	381	725	904
CEM I	52.5	434	797	991
CEM I	42.5	430	685	810
CEM I	52.5	461	770	988
CEM IV	32.5	428	784	943
CEM IV	42.5	420	743	915
CEM IV A		393	737	889
CEM IV B	32.5	440	765	900
CEM IV A	42.5	425	706	890

Table 10.40 Influence of cement fineness and fly ash addition on hydraulic shrinkage for 1:3 mortar, 4 × 4 × 16 cm specimens (N/m) (source: Ref. 331[a])

Fineness (cm^2/g)		Fly ash content	Curing period				
Clinker	Fly ash	(%)	7 days	28 days	90 days	1 year	5 years
2540	–	0	430	500	650	750	750
	2880	40	400	460	500	500	550
	8200	40	400	500	560	600	630
3580	–	0	500	650	780	1000	1100
	2880	40	400	530	590	680	720
	8200	40	400	530	620	750	780
5130	–	0	700	870	1060	1340	1450
	2880	40	460	590	720	840	870
	8200	40	440	590	720	840	870

10.5 Concrete containing pozzolanas

10.5.1 MICROSTRUCTURE PERMEABILITY AND SORPTIVITY

Studies on microstructure, porosity, permeability and sorptivity of concrete are numerous, but there are fewer comparisons of these properties between pozzolana-containing cements and the parent Portland cements. Substitution of 10 per cent silica fume for Portland cement modifies the relative content in hydrates as well as the microstructure. The most important changes concern the transition zone between the aggregate and the matrix paste, where the CH content decreases and porosity increases.[332]

Measurements of water permeability are lengthy and need great care while oxygen

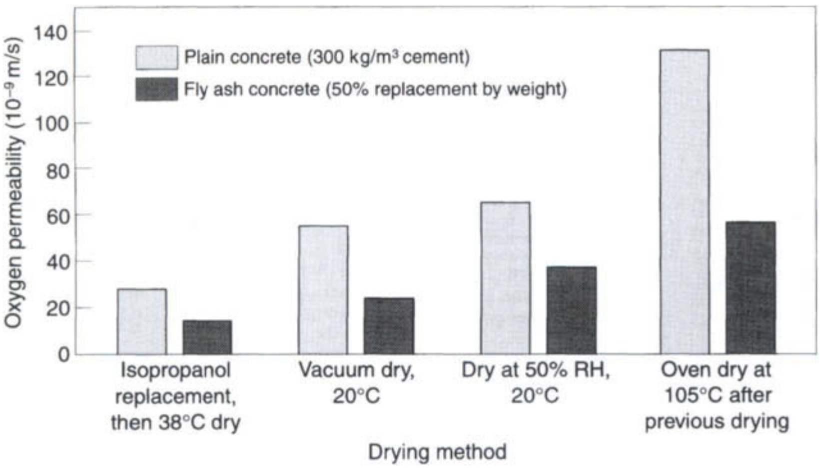


Fig. 10.57 Effect of drying method on oxygen permeability results (source: Ref. 311).

permeability tests are easier to perform and quicker to carry out. However, oxygen flow requires the specimens to be dried first; the drying process can damage the pore systems somewhat, which makes determination doubtful (Section 10.3.3). Figure 10.57 shows that drying by solvent replacement is the recommended technique as it is milder than others.[311]

Air permeability and oxygen diffusion coefficients decrease with time and increase by increasing the water/cement ratio.[277] In concrete, water cured for 28 days, the coefficient of water permeability decreases with strength according to a linear relationship.[333] As far as the influence of pozzolana on the permeability of concrete is concerned, Figure 10.57 shows that, regardless of the drying method, fly ash concrete (50 per cent replacement by weight of cement) has a significantly lower oxygen permeability than a comparable plain concrete of the same age (30 days).[311]

A more general relationship between oxygen permeability, as well as the diffusion coefficient, and compressive strength of concretes has been found which is independent of the type of cement, the water/cement ratio, the cement content and the curing time.[277] The relationships follow the equation:

$$y = Ax^{-B} \tag{10.1}$$

where y = coefficient of permeability or diffusion, x = compressive strength, and A and B are constants.

Figures 10.58 and 10.59 show that both the permeability and diffusion of gases, as well as scattering of results, increase rapidly when the concrete strength drops below about 20 N/mm^2. This means that production of low-permeability concrete requires an effective strength $> 30\,\mathrm{N/mm^2}$.

In addition, water sorptivity decreases remarkably as the strength of concrete decreases.[334] The relationship is given by the following equation:

$$S = S^{\circ} - a\sqrt{F} \tag{10.2}$$

Where S = sorptivity, F = compressive strength and S° and a are constants.

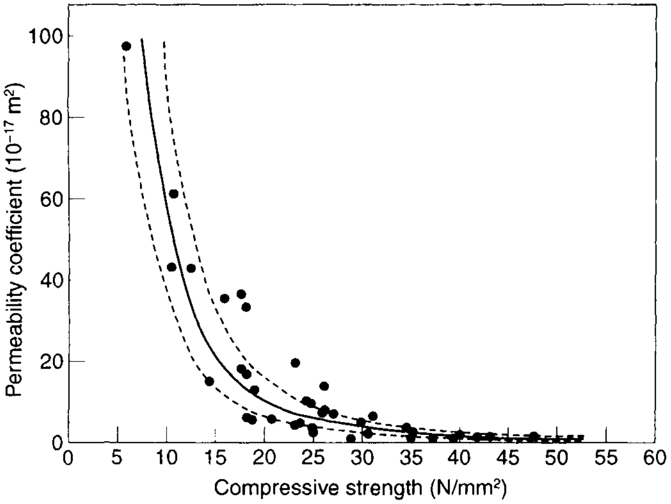


Fig. 10.58 Oxygen permeability coefficient versus compressive strength of concretes (source: Ref. 277). CL = 97.5 per cent; correlation function: $y = 2.576 \times 10^{-13} x^{-2.62}$.

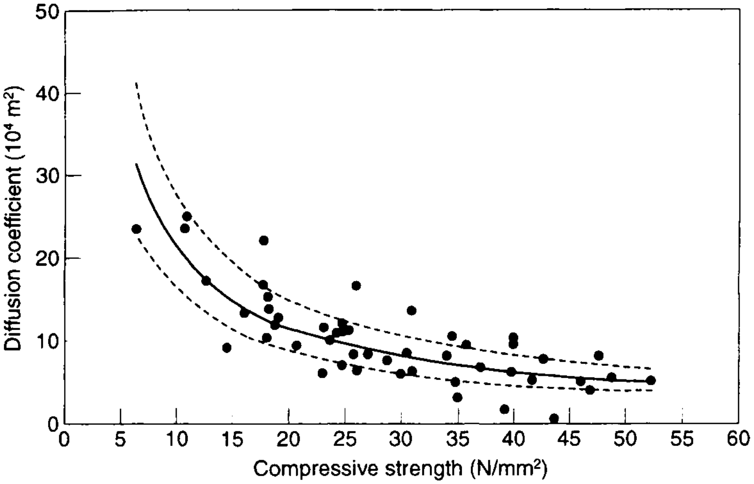


Fig. 10.59 Oxygen diffusion coefficient versus compressive strength of concretes (source: Ref. 277). CL = 97.5 per cent; correlation function: $y = 0.01516x^{-0.858}$.

Equation (10.2) is applicable to concrete cured from 1 to 28 days. $S°$ and a depend on the set of materials used and thus sorptivities form a family of straight lines with correlation coefficients ranging between 0.917 and 0.989.[334]

The replacement of fly ash for 20 or 40 per cent of Portland cement in a given set of materials increases or decreases sorptivity only slightly; thus, by considering that the differences in sorptivity become practically insignificant when compressive strength is > 25 N/mm², the type of cement does not seem to be a very important parameter when

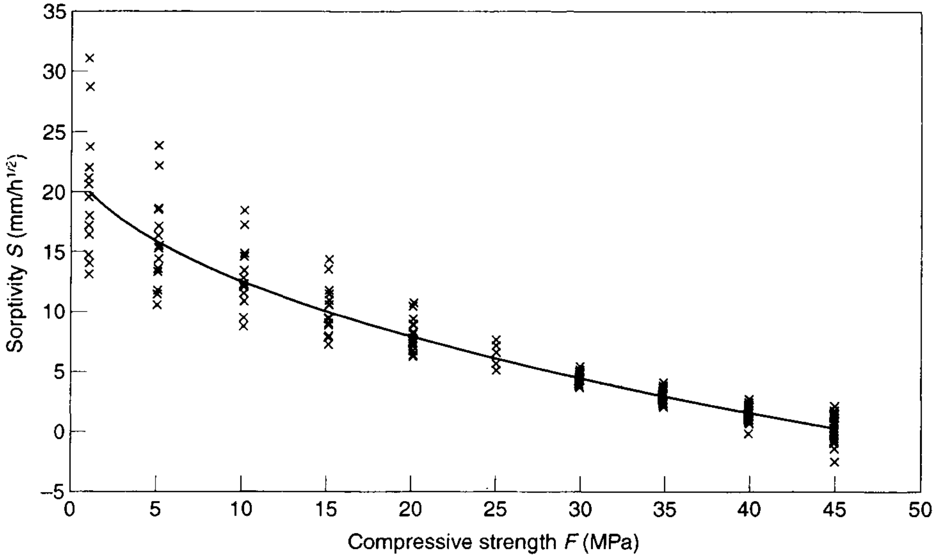


Fig. 10.60 Sorptivity versus compressive strength of concrete made with cements of different type and strength class and cured for different times (data from Ref. 334). $y = 23.19 - 3.43\,x^{1/2}$; $R^2 = 0.86$.

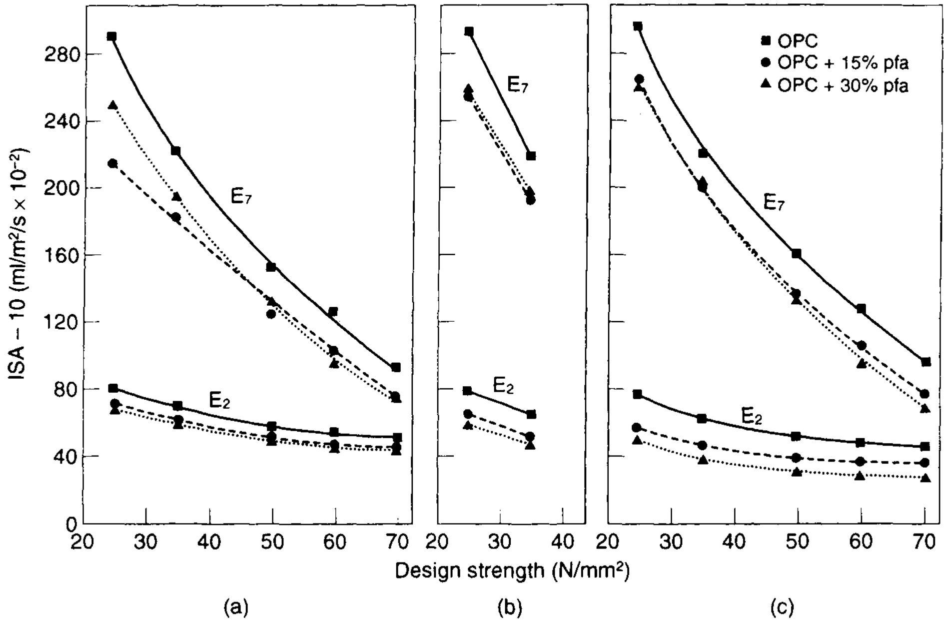


Fig. 10.61 Effect of water curing (E_2) and air curing (E_7) on initial surface absorption at 10 min (ISA-10): (a) 28 days, (b) 90 days, (c) 180 days (source: Ref. 335).

compared to others.[334] The curve of Figure 10.60 was drawn by plotting the sorptivity values, calculated from equation (10.2), versus the corresponding strength of 16 mixes cured for different times; the coefficient of correlation is good and it can be improved by eliminating the results of the samples whose strength is lower than 10–15 MPa.[334]

The initial surface absorption (ISA) of concrete, measured at 10 min for instance, systematically decreases by increasing the fly ash content in cement. However, the differences are not very large.[335] On the other hand, according to Figure 10.61 ISA systematically decreases by increasing the strength of concrete.[335] The decrease, which is small in water-cured concrete, is dramatic in air-cured concretes (55 per cent relative humidity), so that curing appears to be one of the most important parameters in terms of sorptivity of concrete.

On the whole, the results concerning water permeability and sorptivity as well as oxygen diffusion suggest that the type of cement plays only a minor role in the transport properties of concrete, in spite of the differences found among pastes from different types of cement (cf. section 10.3.3). A possible reason is that the fluid flow involves the porosity of the interface between the paste and the aggregate rather than the bulk paste. Figure 10.62 shows how the porosity of concrete dramatically increases as the interface is approached, and this occurs with both pozzolana (silica fume)-containing cements and the parent Portland cement.[332] Electric conductivity measurements carried out on mortar specimens enveloping a stone cylinder proved that the interfacial zone has a higher permeability than the bulk mortar matrix.[336]

10.5.2 STRENGTH

The development of strength in concrete containing pozzolanas is similar but not identical to that observed in mortars and pastes. As a rule, pozzolana reduces the short-term

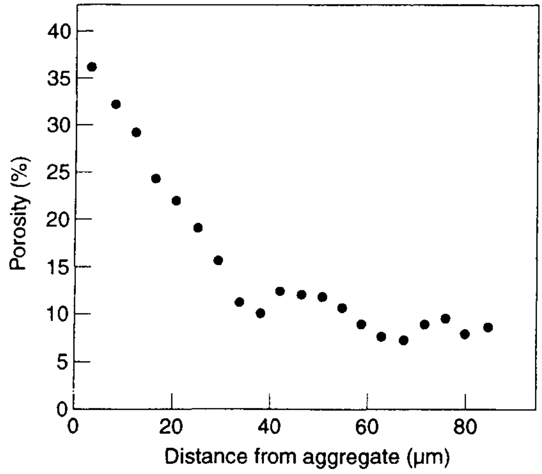


Fig. 10.62 Variation in paste porosity with distance from aggregate (source: Ref. 332).

Table 10.41 Concrete mix proportions (kg/m^3)[338]

Series no.	Free water	Cement	Fly ash	Sand <4 mm	Gravel <4 mm
0	163	181	0	736	1280
1	154	167	146	570	1322
2	154	125	146	604	1331
3	154	107	146	619	1334
4	154	94	146	633	1333
5	154	83	146	644	1333

Table 10.42 Concrete compressive strength as a function of curing time in water at 20°C[338]

	Compressive strength (MPa) after:					
Series no.	2 weeks	4 weeks	16 weeks	181 weeks	362 weeks	R 362/R 4
0	13.4	14.8	20.8	23.8	26.3	1.8
1	19.0	25.4	39.4	55.1	56.1	2.2
2	12.0	17.1	29.2	46.4	45.9	2.7
3	8.8	13.4	25.2	39.8	42.2	3.1
4	6.9	10.5	22.1	36.0	37.9	3.6
5	5.8	8.4	20.6	34.2	33.9	4.0

strength and improves the long-term one. However, depending on the characteristics of the addition, small replacements of fly ashes (~15 per cent) for Portland cement can improve the 3-day strength and the improvement can persist as long as 91 days.[337]

Concrete made with fly ash cement, cured in water for long periods, gains strength beyond 28 days more than the control Portland cement concrete. Table 10.41 lists six concretes of different composition which were tested from 2 weeks up to 362 weeks of curing. Table 10.42 shows that the ratio of compressive strength between 362 and 4 week old samples increases with decreasing Portland cement/fly ash ratios, ranging from 1.8 for the control Portland cement concrete to 4 for the richest fly ash concrete. In other terms, the higher the relative increase in strength, the higher the ratio of fly ash to Portland cement content.[338] The relative strength gain is more marked in lean than in rich mixes.[321]

Silica fume replacement, ranging between 5 and 15 per cent, generally increases the compressive strength of concrete for curing between 1 day and 2 years. However, silica fume reduces the workability of the mixes, thus any positive effect on strength is subordinated to the addition of superplasticisers to the mix.[339] Rheological properties of silica fume concretes strongly depend on the type of silica fume used.[340]

Some workers have found a gradual loss of compressive strength between 90 days and 2 years in 10 per cent silica fume-containing concrete cured in air, while no loss occurred in water-cured samples.[339,341] However, the flexural strength of silica fume concrete started to decrease after ~90 days, as it did in water-cured specimens.[339] Air curing adversely affects the long-term compressive strength of both silica fume and control concretes,[341] but the effect is considerably more marked in silica fume concrete.[342] This phenomenon has been attributed to self-stresses caused by concrete drying.[341]

The addition of silica fume increases a concrete's water demand and, as a consequence, it decreases its strength.[326] However, the addition of water-reducing admixtures copes with this problem and at a given admixture dosage the water demand of a mix containing silica fume may be lower than that of the control mix without silica fume.[326]

The high sensitivity of silica fume to water-reducing admixtures contributes, together with its high pozzolanic activity, to developing high strength in concretes.

Figure 10.63 shows that with a silica fume-containing concrete, strength values of > 110 MPa can be obtained after 28 days' curing and ~ 130 MPa after 91 days'. The figure also shows that similar strength can be achieved by using fly ashes (sample 2), provided that the binder content is high enough and the water/binder ratio is low.[343a]

The strength of high strength concrete (90 MPa) can be increased by about 20 per cent

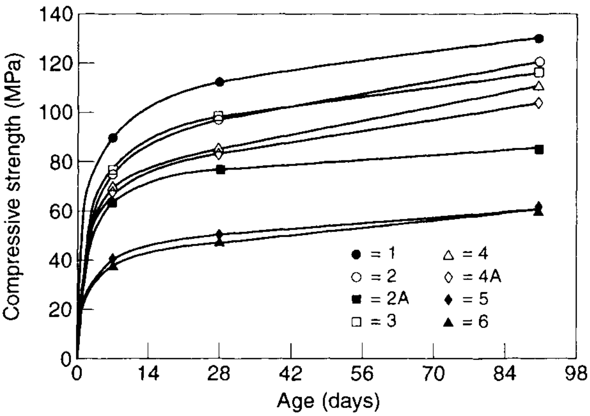


Fig. 10.63 Compressive strength of concrete made with different blends (source: Ref. 343). Samples: 1 = 10 per cent silica fume; 2 and 2A = 25 per cent fly ash; 3, 4 and 4A = ground blastfurnace slag; 5 and 6 are normal strength comparison concretes. Variable water and superplasticiser contents used.

by adding 5–15 per cent of a very fine pozzolanic material such as silica fume, ground fly ash or a blend of the two.[343b]

The mechanical properties of concretes incorporating different product forms of silica fume, i.e. having a silica content ranging from 79 to 95 per cent and specific surface from 20 to 26 m^2/g, do not show any significant difference.[343c]

Replacing 8.5 per cent Portland cement for high reactivity metakaolin (HRM) resulted in a concrete strength increase. After a 90-day water curing, metakaolin-containing concrete reached 112.7 MPa against 83.8 of the control concrete and 105.7 of the silica fume one. Metakaolin had a lower specific surface than silica fume and the corresponding concrete had a lower superplasticizer content.[343d]

10.5.3 SHRINKAGE AND CREEP

Shrinkage of concrete is relatively insensitive to the type of cement since it depends mainly on the percentage by volume of water in the concrete[344] and the type of aggregate.[345] The shrinkage of 12 concretes made with 11 cements containing 11 types of fly ash and with the parent Portland cement was $280–500 \times 10^{-6}$ after 224 days of exposure to a dry environment. They had previously been water-cured for 91 days. The shrinkage of the plain cement sample was 453×10^{-6}. The range was only slightly higher when the specimens were cured in water for 7 days (Table 10.43).[346]

These results are comparable with those obtained with plain Portland cement concretes made with 199 different Portland cements. The mixes, which had a constant water/cement ratio and mix composition, gave shrinkage values ranging from 150×10^{-6} to 420×10^{-6} after 14 days of curing.[347]

Table 10.43 Drying shrinkage of fly ash concretes[346]

		Shrinkage measurements			
		Initially cured for 7 days in water		Initially cured for 91 days in water	
Mixture no.	Duration of drying/ (days)	Moisture loss (%)[a]	Drying shrinkage ($\times 10^{-6}$)	Moisture loss (%)[a]	Drying shrinkage ($\times 10^{-6}$)
Control 2	224	55.0	422	53.7	453
F1	224	57.5	447	47.9	365
F2	224	57.3	364	45.4	280
F3	224	56.9	411	56.2	405
F4	224	54.7	379	49.2	387
F5	224	58.8	404	51.1	403
F6	224	60.6	475	56.4	454
F7	224	64.3	397	54.1	433
F8	224	56.3	400	–	327
F9	224	58.2	390	49.3	361
F10	224	58.4	642	55.2	500
F11	224	49.5	454	48.9	362

[a] As a percentage of total original water.

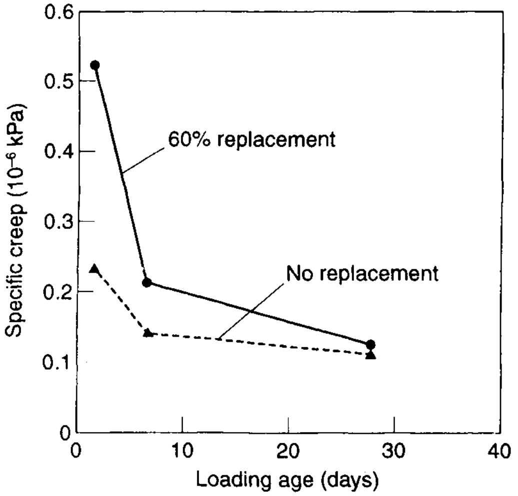


Fig. 10.64 The effects on creep of loading age and replacement of Portland cement by pozzolana (source: Ref. 344).

Shrinkage appears to depend on the type of fly ash used since concretes made with samples coming from different sources and blended with the same cement gave values ranging from 497 to 678 × 10^{-6}. Since the 365-day strength of the three concretes was about the same (68.1, 61.9 and 63.2 MPa) the differences could be attributed to the differences in the amount of admixture added to concrete and in the fineness of the fly ashes.[331c]

Shrinkage is sensitive to the replacement level of fly ashes for Portland cement[348,349] only when initial curing of concrete is limited to 3 days. In that case, it increases with increasing fly ash content. On the contrary, shrinkage is not affected by up to 40 per cent replacement when concrete is cured for 28 days prior to drying.[349]

Creep is strictly related to concrete strength at the time of loading and so, all other conditions being equal, it depends on the strength of cement, the water/cement ratio and the curing period. Since the replacement of pozzolana for Portland cement lowers the early strength of the concrete, the specific creep of a pozzolana-containing cement will be greater than that of the plain concrete if the concrete has been loaded too early (Figure 10.64).[349] The difference, however, tends to fade away as curing proceeds, analogous to that which happens with differences in strength.

For these reasons, creep of blended cement concretes can be lower or higher than that of the control concrete, depending on the strength of concrete and the replacement level. Results of many studies tend to suggest that long-cured fly ash concrete exhibits lower creep than Portland cement concrete.[350]

The higher creep exhibited by pozzolana-containing cement when concrete is loaded early can be a positive effect since it allows massive structures to settle before the concrete becomes too rigid.[345]

10.6 Durability

Durability defines the suitability of concrete to preserve the structural performances, fixed by the designer, over time; hence it plays a fundamental role in determining the service life of the structures. It depends on both the concrete properties and the environmental conditions. The chemical composition of cement and aggregate, the microstructure of hardened pastes, the chemical composition of air, water and soil surrounding the concrete, and temperature variations are the various factors affecting the durability of concrete.

The composition of cement contributes to durability as, in some cases, different types of cement can respond differently to the same attack. In the following sections the behaviour of pozzolana-containing cements is compared with that of Portland cements. In any case it must be remembered that durability depends mainly on the entire set of concrete properties rather than on those of cement.

10.6.1 INFLUENCE OF THE ENVIRONMENT

Carbon dioxide

Carbon dioxide contained in the air is potentially dangerous for concrete durability inasmuch as it can attack all of the hydrates in the hardened cement. In the cement–water–carbon dioxide system the stable phases are calcium carbonate and silica, alumina and ferric oxide hydrates.[351] However, this alarming prospective concerns only low-strength porous concrete, since carbonation of dense and compact concrete improves the structural performance as it reduces the total porosity and specific surface of the cement paste.[274,352] As a consequence, carbonation reduces permeability, increases the strength of concrete and improves the resistance to the attack of sulfate[353] and of other ions.[354]

MAS-NMR studies of partially carbonated Portland cement paste have revealed that the CO_2 picked up from air occurs in the paste mainly as crystalline $CaCO_3$. However, a significant part is also present in a non-crystalline form and is probably incorporated in the C-S-H structure.[355]

Carbonation is a risk for reinforced concrete because it can lower the alkalinity of concrete to such an extent that, when the pH is reduced below certain values, iron may rust and spalling of the cover occurs. To minimise the risk of corrosion of the reinforcement, the concrete must be dense and the cover sufficiently thick.

The depth of carbonation in concrete increases with time and depends on the following parameters:

- partial pressure of CO_2
- temperature
- ambient humidity
- microcracks
- cement content
- water/cement ratio
- curing length

In general, the greater the coefficient of air permeability, the greater the depth of carbonation, this irrespective of the type of cement.[274]

Prolonged curing before exposure to carbon dioxide reduces the depth of carbonation of mortar and concrete. Indoor exposure of concrete results in a depth of carbonation between two and four times greater than that recorded for outdoor exposures.[356] Figure 10.65 shows that carbonation is deeper when samples are sheltered from rain.[357a]

Carbonation is deeper in a concrete exposed to a marine environment, and this irrespective of the type of cement.[357d]

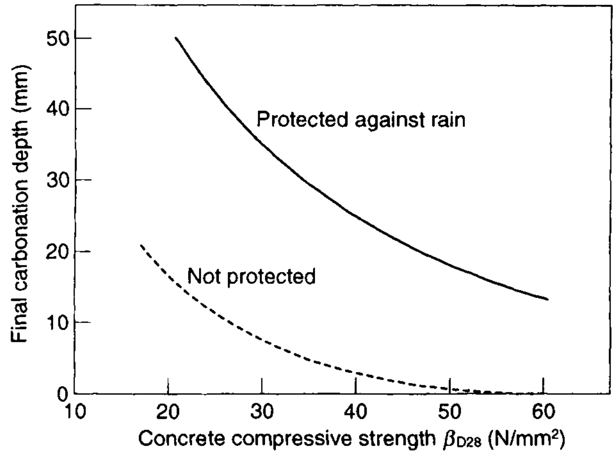


Fig. 10.65 Influence of concrete compressive strength on the expected final carbonation depth (source: Ref. 357). (Outdoor carbonation.)

Pozzolana cements have long been considered to be less capable of resisting carbonation than Portland cements owing to their lower portlandite content. However, many studies have shown that this assumption is rather simplistic. The depth of carbonation is statistically the same in concretes made of Portland or natural pozzolana- and fly ash-containing cements, provided that the comparison is made between concretes having the same 28-day strength.[356,358 360] Figure 10.66 shows an example of this statement: the 1-year carbonation depth of concrete containing Portland and fly ash cements decreases linearly by increasing the 28-day strength.[361] The degree of carbonation in concretes containing 15–30 per cent fly ash as replacement for Portland cement is approximately the same as that found in plain Portland cement concretes;[362] however, the rate of carbonation of concretes containing 50 per cent fly ash carbonates is significantly higher than in the counterpart plain samples of the same strength grade.[363] It should be noticed that, exposure conditions being different, the relationship cannot be expressed with the same straight line.[364]

Carbonation depth appears to be higher in pozzolana-containing mortars and concretes than in Portland ones when compressive strength and carbonation depth tests are performed

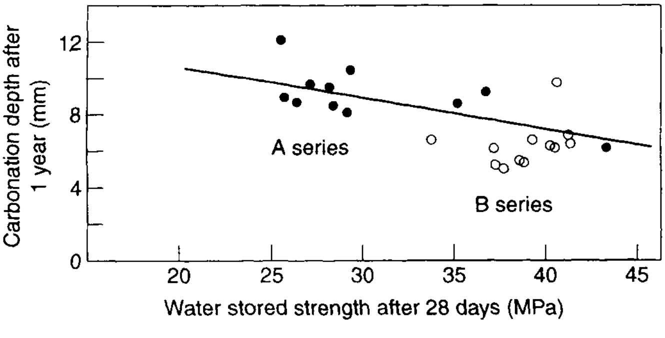


Fig. 10.66 Carbonation depth after 1 year versus 28-day water-stored strength, internal exposure, cure for 3 days (source: Ref. 361). $r = -0.71$ for series A only and for both series combined.

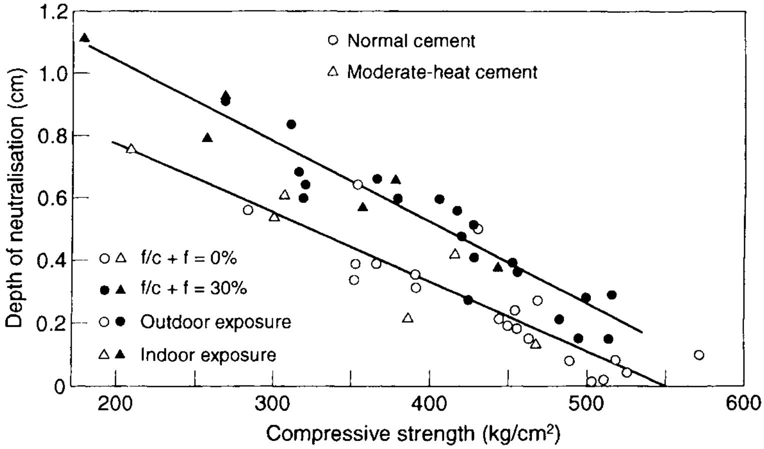


Fig. 10.67 Relation between compressive strength and depth of neutralisation measured on samples having the same age (2 years) (source: Ref. 364).

on samples of the same age.[364] Figure 10.67 shows how in this case the relationship between depth of carbonation and strength is better expressed by two straight lines, the upper one relating to pozzolana-containing cement, the lower one to Portland cements.[364] In any case, the differences shown in Figure 10.67 (1–2 mm) are minor compared to those induced by different exposure conditions (cf. Figure 10.65).

Owing to the slow rate of pozzolanic reaction, carbonation of pozzolana-containing cements is greater when the curing length is short,[365] less than 7 days for example,[312] i.e. when the permeability of pozzolanic cement pastes is significantly higher than that of the parent Portland cement pastes.

The rate and depth of carbonation depend on the fineness of the cement since this affects the degree of hydration and the permeability of the paste. The simultaneous grinding of fly ash and Portland cement proved to be a suitable method for improving the carbonation resistance of mortars and concretes, whereas the addition of fly ash or other pozzolanic materials to the mix at the batch plant did not give such good results.[366]

Carbonation of pozzolana-containing cements is also deeper when accelerated carbonation methods are used instead of long-term exposure on site. A typical accelerated procedure provides for a short moist curing (not more than 7 days), severe drying (21 days at 50 per cent relative humidity) and carbonation of specimens in a CO_2-enriched atmosphere (4 per cent CO_2 and 50 per cent relative humidity).[280] In any case, the scatter of carbonation depth values attributable to different types of cement dramatically decreases when the concrete strength increases.[280]

The depth of carbonation of both mortars and concretes definitely increases with increasing percentage of silica fume replacing up to 20 per cent Portland cement.[367] In addition, the opposite relationship between 28-day compressive strength and carbonation depth observed in concretes containing natural pozzolanas or fly ashes may occur as in the case of silica fume replacement. However, the relationship between 28-day strength and carbonation depth is better expressed by a family of curves, each of them corresponding to a specified silica fume replacement for Portland cement.[367]

The effect of silica fume on the carbonation of concrete also depends on the properties of the concrete. The addition of 10 per cent silica fume to a Portland cement slightly decreased the depth of carbonation of lean mixes and increased that of rich ones.[368] However, when mixing water is reduced by a superplasticiser in order to keep workability constant, an addition of 10–20 per cent silica fume has proved to cause carbonation depth to diminish.[368]

With a microsilica replacement for Portland cement of up to 30 per cent after 91 days of curing, the depth of carbonation and strength increased simultaneously. The workability of mortars and concretes, having the same water/binder ratio, had been kept constant by adding suitable amounts of a superplasticiser to the mixes.[369]

The increase in carbonation depth with the silica fume content is related to decreasing pH of the blends caused by the removal of alkalis from the pore solution (cf. section 10.3.3). Indeed, the increase cannot be attributed to a higher permeability, since chloride diffusion steeply decreases with increasing percentage of silica fume in the cement.[369]

Water

Deterioration of concrete caused by pure or acidic water is a well-known phenomenon. The risk is serious for hydraulic structures such as dams, channels and pipes, but it can also involve those parts of the structure which are in contact with soft or acidic ground waters. Water can decompose any of the hydrated compounds present in the cement and leach lime, leaving a residue made up of $SiO_2 \cdot xH_2O$, $Al_2O_3 \cdot yH_2O$ and $Fe_2O_3 \cdot zH_2O$.[1,370] This residue performs a protective role against leaching on account of the gel-like nature of its compounds. As a matter of fact, if the surface of the specimen is periodically brushed and the protective layer is removed, leaching of lime increases.[371]

The rate of leaching of lime is high when concrete is porous and water is abundant or continuously renewed. It slows down when concrete is compact and strong. Leaching of lime increases both the porosity and permeability of the cement paste and this, in turn, causes a decrease in the strength and durability of the concrete. Thus, the removal of ~50 per cent of the original lime from Portland cement concrete may result in the failure of the specimen.[372] Among the hydrated compounds present in a hardened cement paste, portlandite is the most sensitive to leaching.

The methods for assessing the resistance of cements to the leaching of lime are based on two principles: water percolation through more or less porous mortar or concrete followed by determination of (1) the leached lime or (2) the mass loss of samples.

The amount of lime extracted by means of distilled water from porous pozzolanic cement pastes[373] or mortars[374] is far less than that released by Portland cement, and decreases as the pozzolana/clinker ratio increases (Figure 10.68).[375] Microscopic examination of pastes stored in a distilled water stream for 12 months have shown some microstructural differences between Portland and pozzolanic cement.

When compared to pozzolanic cement, the Portland cement paste showed:

- a thicker corroded layer;
- a diffuse porosity of the altered layer, decreasing from the surface to the inside;
- a deposit on the surface of the gel-like layer crossed by small 'channels'.

On the other hand, the pozzolanic paste was lacking in pores and the small channels were prevailingly oriented parallel to the surface.[373] The channels are possibly cracks formed as a result of the gel drying during specimen preparation.

The mass loss of mortar prisms cured for 28 days, then stored in soft water and brushed fortnightly, increased by substituting 30–40 per cent of fly ash for Portland cement. This

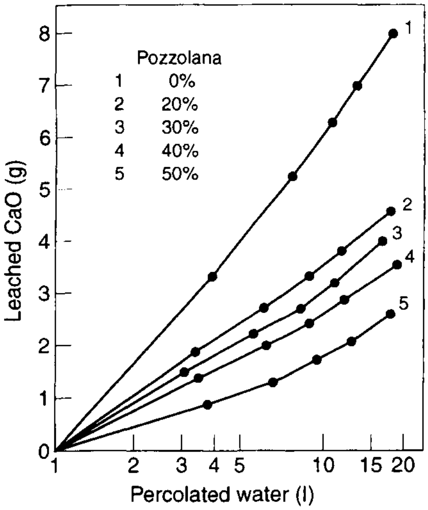


Fig. 10.68 Lime leached from mortars with increasing proportion of pozzolana cement in blended cements (at an age of 21 days) (source: Ref. 375).

loss is related to the decrease in strength caused by the partial replacement of fly ash for Portland cement, since the opposite occurs when the pozzolanic and the parent Portland cement are compared on the basis of the same strength. The opposite happened also, when the previous mortar samples were autoclaved at 1 MPa steam pressure for 10 h and then cured under water for 27 days.[376]

Acid waters containing aggressive CO_2 increase the rate of lime leaching, but pozzolanic cements have shown better resistance than Portland ones.[377,378] Table 10.44 shows that the mass loss of Portland concretes is about 35 per cent higher than that of pozzolanic ones.[379]

Hardened pastes made up of pozzolanic cements are more resistant to lime leaching than Portland cements for closely related reasons:[236]

- they contain only 3–6 per cent of $Ca(OH)_2$[236] compared to the 20–22 per cent of Portland cement pastes;

Table 10.44 Mass loss of concrete samples 110 days old and stored in acid water (pH = 4.1) for 84 days[379]

	Mix composition	
	Mix 105	Mix 109
OPC (kg/m^3)	170	312
Fly ash (kg/m^3)	170	–
water/binder	0.53	0.60
28-day compressive strength	48.4	43.2
Cumulative mass loss (g/kg)		
brushed	5.8	7.8
unbrushed	2.5	3.4

- they contain more calcium silicate hydrates;
- the C/S ratio of C-S-H is lower;
- they have lower permeability.

Of course, the resistance of concrete to pure and acidic waters depends not only on the type of cements but also on the parameters which contribute to the compactness of the structure material.[380] The nature of the aggregate plays an important role too, since it was found that the depth of corrosion of a mortar made with limestone was three times higher than that made with quartz as aggregates.[381]

Chloride

Chloride can harmfully affect the durability of both concrete and reinforcement. Therefore, the Cl^- content of concrete must be kept low and the ionic penetration from outside must be prevented or hindered. Chloride dissolved in waters increases the rate of leaching of portlandite,[285,305,382,383] thus increasing the porosity of mortar and concrete.[384] As a consequence of the attack, concrete swells, loses stiffness and strength and becomes more sensitive to other environmental attacks (sulfate, frost, etc.).

After 100 weeks of exposure to a 4 per cent NaCl or 3.2 per cent NaCl + 0.8 per cent $CaCl_2$ solution, the strength loss of a Portland mortar was about 15 and 20 per cent respectively, while swelling increased by 0.6 per cent.[285] However, Portland cement concrete broke down when placed in a concentrated $CaCl_2$ solution at a temperature of 20°C or lower. The breakdown has been attributed to the formation and crystallisation of complex salts containing $CaCl_2$, $Ca(OH)_2$ and/or $CaCO_3$.[382]

Thirty per cent fly ash, 105 silica fume and 50 per cent GBFS replacements for a Portland cement improve the compressive strength of mortars water-cured for 28 days and then stored in a 30 per cent calcium chloride solution at temperatures of 5, 20 and 40°C for 91 days. Strength increased in all samples except for the fly ash mortar stored at 5°C which showed a decrease in strength, possibly due to the slowness of the pozzolanic reaction at low temperature. This conclusion is supported by the strength recovery observed in the same samples stored in the calcium chloride solution at 40°C.[384b]

Chloride is more dangerous and harmful when, by penetrating into concrete, it reaches the reinforcement. If the Cl^-/OH^- ratio near the steel bars dips below a certain threshold limit, such as 0.6[385] or, more realistically, 0.3,[386] the steel passivation is destroyed and corrosion becomes inevitable, if both water and oxygen are present.

The rate and depth of penetration of chloride into concrete depend on the ionic diffusion coefficient, i.e. on the permeability of concrete, and they decrease by decreasing the water/cement ratio and by increasing the cement content and the length of curing. So, when the risk of chloride attack occurs, concrete must be compact and the cover thickness must be adequate to the environmental conditions.

In addition to these general precautions aimed at improving the compactness of concrete, a contribution to the protection of concrete against chloride attack is provided by certain types of cement. Thus cements containing natural pozzolanas,[305] fly ashes,[306,388] or silica fume[320,369,389] proved to be able to reduce the depth of penetration of chloride. Figure 10.69 shows that the depth of penetration of chloride into pozzolanic cement concrete is about 15 per cent lower than into plain concrete.[386] The difference is smaller than in pastes (~40 per cent)[390] since the interstitial zone between the aggregate and paste is more permeable than the bulk paste.

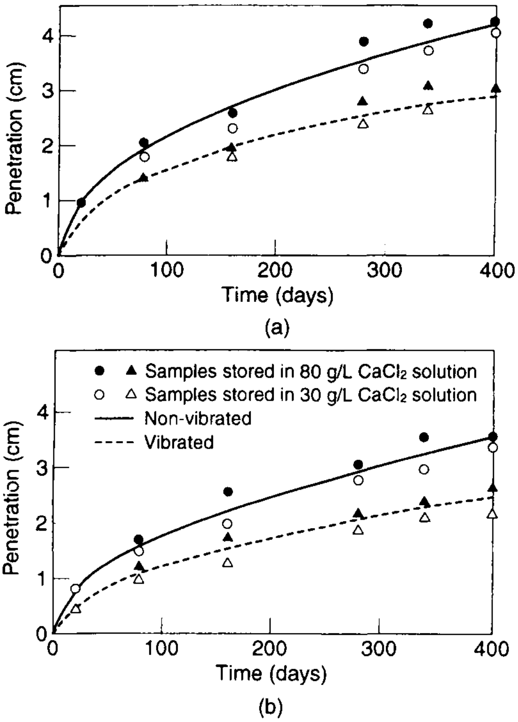


Fig. 10.69 Chloride penetration in Portland (a) and pozzolanic (b) cement concretes (source: Ref. 386).

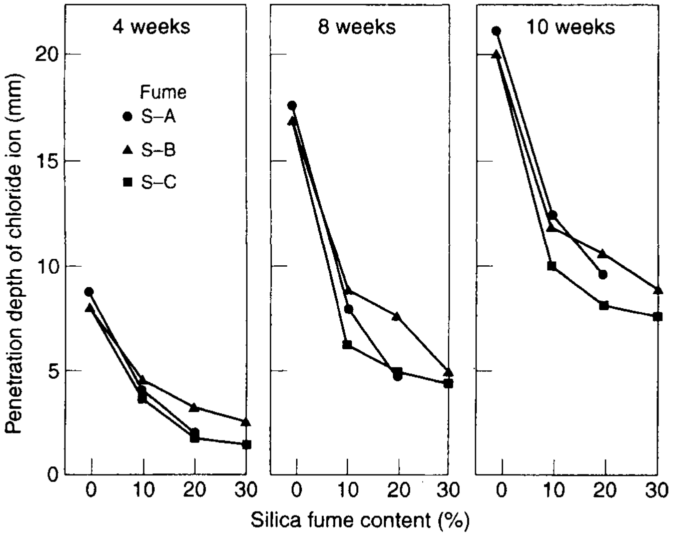


Fig. 10.70 Effect of CSF content in cement on penetration depth of chloride ion in concrete (source: Ref. 369). w/c + sf = 0.55, (c + sf) = 320 kg/m^3.

Portland cement pastes stored for 180 days in a solution containing 300 g/L of $CaCl_2$ lost almost all of their strength, whereas pastes containing 30–40 per cent of metakaolin retained their strength.[383]

The depth of chloride penetration decreases steeply by increasing the substitution of silica fume for Portland cement. Figure 10.70 shows that penetration depth increase with time, but that it is always lower in concrete containing silica fume than in plain cement concrete.[369]

The addition of silica fume reduces the deflection of mortar specimens of a particular shape submitted to flexural load during the exposure to solutions containing different chlorides.[384]

Pozzolanic cement concretes are more resistant to chloride attack than Portland ones because they have a lower coefficient of Cl^- diffusion (Table 10.38)[286] and a very low portlandite content.

Since the D_{eff} coefficient of Cl^- decreases with increasing pozzolana content the use of pozzolanic cements, in which pozzolana amount to ~33 per cent, is recommended instead of pozzolana cements, in which the pozzolana content is lower.

Sulfate

Calcium, sodium, magnesium and ammonium sulfates are, in increasing order of hazard, harmful to concrete[391] as they can cause expansion, loss of strength and eventually transform the material into a musky mass. $CaSO_4$ reacts on calcium aluminate hydrates, thus forming expansive ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$). Na_2SO_4 reacts on calcium hydroxide and forms expansive gypsum ($CaSO_4 \cdot 2H_2O$) which in the presence of aluminates, may in turn give ettringite. $MgSO_4$ reacts on all cement compounds, including C-S-H, forming $Mg(OH)_2$ (brucite) and gypsum which, at a later stage, can give ettringite.

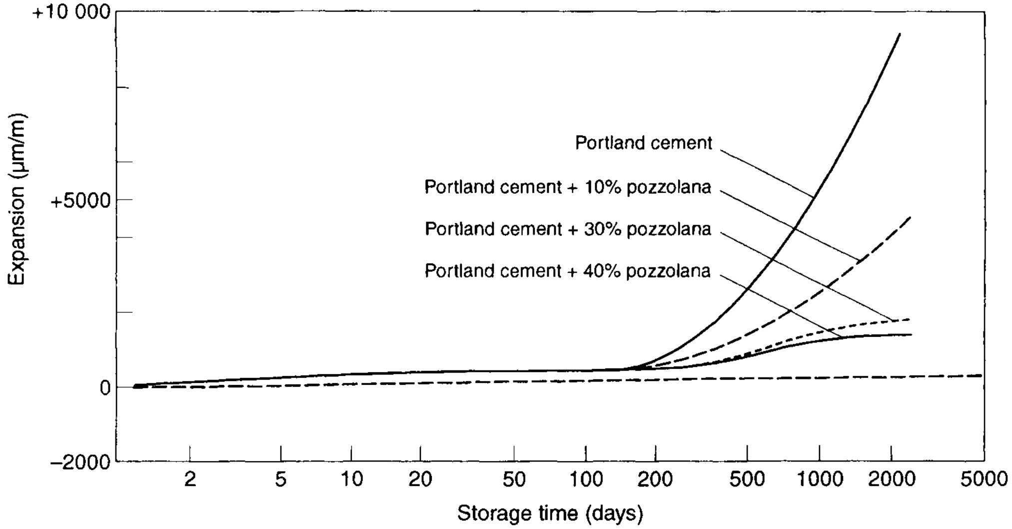


Fig. 10.71 Effect of substituting Portland cement for pozzolana on the expansion of 1:3 mortar (source: Ref. 236). Samples 2 × 4 × 25 cm stored in 1 per cent $MgSO_4$ solution.

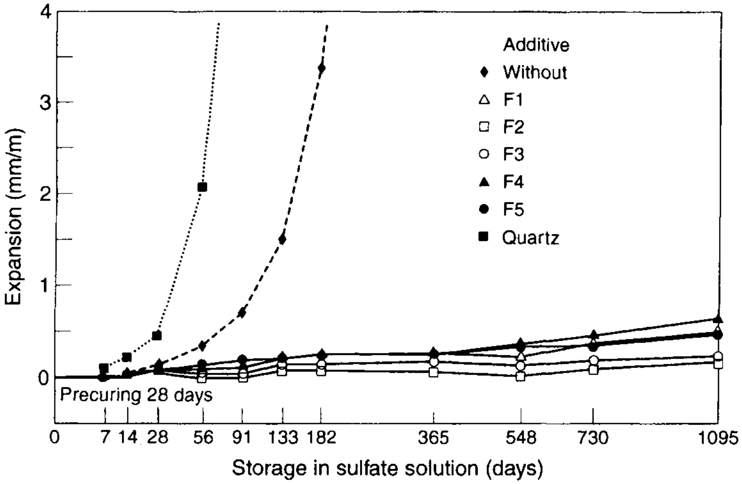


Fig. 10.72 Expansion of mortars stored in 0.31 N sulfate solution, with different types of fly ashes and one quartz powder replacing 40 per cent of Portland cement (source: Ref. 304).

As far as the composition of cement is concerned, the conditions enhancing the formation of expansive compounds are the occurrence of both aluminate hydrates and calcium hydroxide in the paste. As a consequence, cements with low C_3A and low lime contents minimise the risk of sulfate expansion. Partial replacement of pozzolana for Portland cement reduces both the content of C_3A in cement and the portlandite content in the hardened paste. Figures 10.71 and 10.72 illustrate the positive action that natural pozzolanas and fly ashes take in reducing expansion.[236,304]

The depth and rate of the sulfate attack strongly depend also on the characteristics of mortar and concrete, namely their strength, porosity and permeability. Porosity is considered to affect the rate of deterioration to a larger extent than the portlandite and C_3A contents.[392] Figure 10.73 shows that expansion of Portland cement mortars increases by increasing the

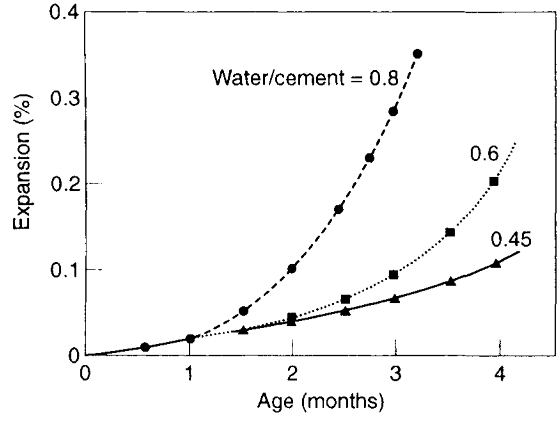
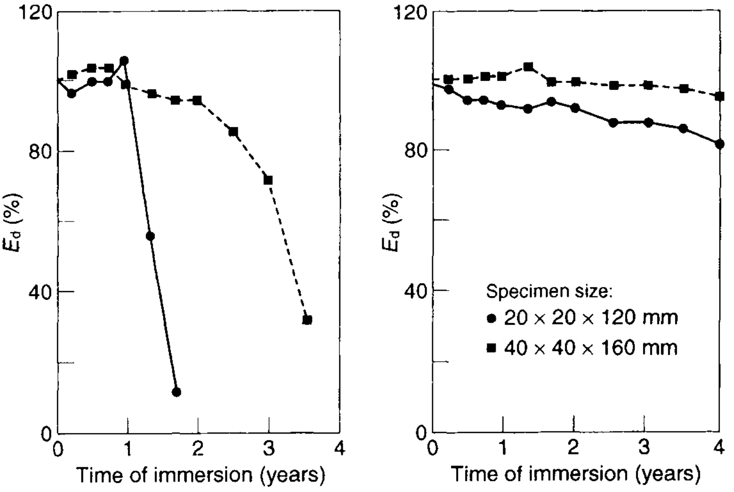


Fig. 10.73 Expansion of Portland cement mortars with different water/cement ratios under external sulfate attack (source: Ref. 393).



(a) (b)

Fig. 10.74 Influence of specimen size on dynamic modulus of elasticity of mortar prisms exposed to 5 per cent Na_2SO_4 solution for (a) plain mortars and (b) with 15 per cent silica fume (source: Ref. 391).

w/c ratio and decreasing the cement content, i.e. by increasing porosity and permeability.[393]

The intensity of the attack depends on the sulfate concentration.[392] Moreover, the higher the pH in the pH range 6–11.5, the less aggressive the environment.[394] It is known that sodium sulfate solutions can increase the pH when mortar prisms are immersed in them, whereas magnesium sulfate solutions may be buffered at a pH near 7 due to the insoluble nature of the $Mg(OH)_2$ produced.[395]

The deterioration of structures also depends on the volume/surface area ratio of the concrete. Figure 10.74 shows that the positive role played by the addition of silica fume in reducing deterioration rate is enhanced by increasing the specimen size.[391]

Na_2SO_4 attack. In countries in which pozzolanic cements have been used for a long time, it is well known that natural pozzolanas increase the sulfate resistance of cement. In a 0.353 M Na_2SO_4 solution, replacement of calcined volcanic glass for 30 per cent of the Portland cement reduced the expansion of three Portland cements having a C_3A content ranging between 9.4 and 14.6 per cent. So the mortars survived 1 year of exposure with <0.1 per cent expansion.[396]

Generally, the strength of natural pozzolana mortars exposed to sodium sulfate (0.15–0.30 per cent) solutions increases in the first week but declines thereafter.[397] Also artificial pozzolanas, such as fly ashes, improve the resistance of paste, mortar and concrete to the attack of Na_2SO_4.[397] The sulfate resistance of fly ash cement pastes increases as the curing length increases, whereas that of the parent Portland cement appears to be relatively insensitive to the length of curing.[398]

The effectiveness of fly ash in reducing sulfate expansion is not the consequence of a mere dilution of the Portland cement, since replacement with sand increases expansion.[392]

Pozzolanic cements, as well as sulfate-resisting Portland cement, delay the decline in the performance of mortar and concrete subjected to sulfate attack but cannot prevent long-term failure. However, they can improve the life expectancy of concrete (Figure 10.75).[399]

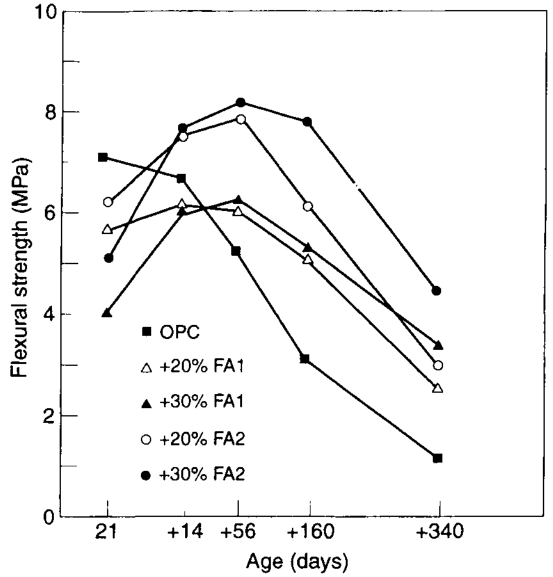


Fig. 10.75 Flexural strength of mortar prisms cured in water for 21 days and then stored in sodium sulfate solution (source: Ref. 399). Ordinary Portland cement with 7.7 per cent C_3A, low-lime fly ash ground to 2800 (FAI) and 4200 (FA2) Blaine finenesses.

The higher resistance of pozzolana-containing concrete against sulfate attack has also been proved statistically by testing several Portland and blended cements.[400] The life of the structure is prolonged when the pozzolana content and the cement dosage are high. Figure 10.76 shows the improvement in resistance to sulfate attack caused by an increase in the cement dosage of concrete.[401]

The sulfate resistance of pastes, mortars and concrete is generally tested by measuring

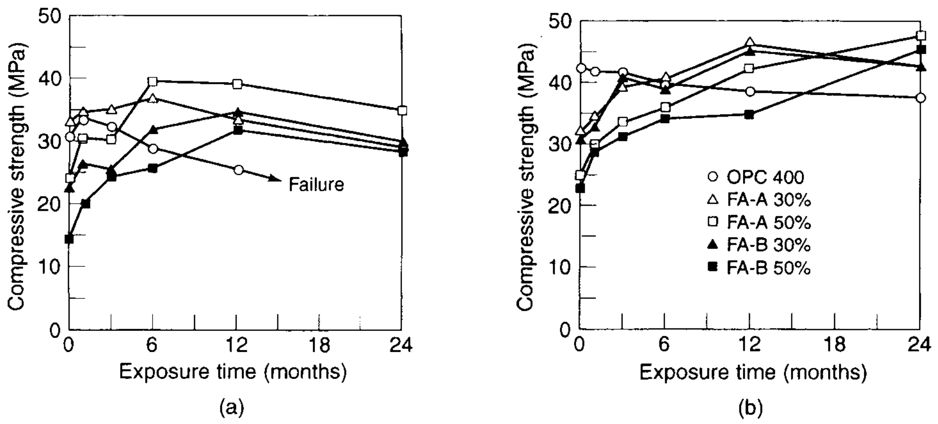


Fig. 10.76 Changes in compressive strength of concretes for binder contents of (a) 300 and (b) 400 kg/m^3 and different levels of fly ash replacement; cylindrical specimens stored for 14 days in sealed condition at 20°C and then immersed in a 10 per cent Na_2SO_4 solution (source: Ref. 401).

Table 10.45 Sulfate resistance and permeability of notched paste beams of ordinary Portland cement (OPC) and cement containing 30 per cent fly ash; specimens stored in 0.7 M Na_2SO_4 solution[398]

	OPC			OPC/fly ash		
Curing (weeks)	1	4	12	1	4	12
T_c (days)	21	17	14	21	58	114
Permeability ($\times 10^{-15}$ m/s)	16.5	6.1	14.0	68.0	8.2	19.0

changes in length, weight and strength occurring in specimens stored in appropriate solutions, but it can also be determined by particular tests.

In a notched paste beam immersed in 0.7 M sodium sulfate solution, a crack appears at the notch tip after a certain time T_c. The appearance of the crack coincides with the onset of rapid expansion and can thus be used as an indicator of the sulfate resistance. Table 10.45 shows that after curing for 12 weeks, the value of T_c of 30 per cent fly ash cement is nearly an order of magnitude greater than that of the control plain cement paste.[398] Moreover, Table 10.45 shows that there is no relationship between permeability and T_c, so that the difference between ordinary Portland cement and fly ash-replaced ordinary Portland cement must be attributed to other reasons.[398] The difference between the two types of cement has been ascribed to the decrease, related to the curing time, of the entry size of the sulfate-susceptible pores contained in the fly ash cement, whilst the entry size in Portland pastes should remain basically the same.[398] However, the reason is in conflict with Table 10.45, which illustrates permeability values that, except at very short curing times, are only slightly influenced by the type of cement. Differences in T_c could be related to the flexural strength/compressive strength ratio, which is higher for pozzolanic cement than for the Portland cements.[34] In any case, the performance of fly ash-containing cements proved better than that of the parent Portland cements.

Replacement of 40 per cent of Portland cement with a low-calcium fly ash also increased the sulfate resistance of concretes when the pH of a 5 per cent sodium sulfate solution was kept constant at 7.[402] The different origin of low-lime fly ashes seems to cause only negligible differences in the expansion values.[304]

Although many high-calcium fly ashes have been found not to improve the sodium sulfate resistance of cement significantly,[403] some high-lime fly ashes proved the contrary.[404]

Silica fume increases the resistance of Portland cement to sodium sulfate attacks; the higher the replacement, the lower the expansion.[396,405a,405b] Low (7 per cent) silica fume replacement could not reduce the expansion of mortars under the required level (0.15 per cent); nevertheless, after 4 months of exposure the appearence of mortar prisms was excellent.[406] Higher degrees of replacement of silica fume (15 per cent) for ordinary Portland cement and sulfate-resisting Portland cement improved the resistance of mortars to sulfate attack, at least up to 4 years of immersion.[391]

The grade of silica plays an important role too, since 10 per cent replacement of a good silica fume was sufficient to keep expansion below 0.1 per cent after 365 days of exposure, but a 15 per cent replacement was required by a poor quality one, having a low silica content (80 per cent) and a relatively low specific surface area (8750 m^2/kg).[407]

Storage for 1 year in water reduced the total porosity of plain and pozzolana containing mortars, but storage in 10 per cent Na_2SO_4 solution increased the pore volume of both Portland and silica fume cements and decreased that of the fly ash cement (Table 10.46).[408]

Table 10.46 Physical and chemical properties of 28 day old fly ash and silica fume mortars. Total pore volume of fly ash and silica fume mortars when immersed in water and in sulfate solutions for 1 year (10^{-3} cm^3/g)[408]

			28 day		1-year total pore volume (10^{-3} cm^3/g)		
		Water/ cement ratio	Compressive strength (MPa)	Total pore volume[a] (10^{-3} cm^3/g)	Water	10% Na_2SO_4	10% $MgSO_4$
Plain mortar		0.55	45.3	39.8 (17.6)	33.8 (11.1)[c]	94.8 (83.3)F^{6}[d]	25.2 (36.1)F^{12}
Fly ash	10%	0.54	37.1	22.4 (23.6)	26.3 (34.6)	– F^{20}	25.8 (32.9)
	30%	0.52	35.8	44.5 (15.1)	33.2 (15.4)	28.7 (20.9)	22.9 (38.4)
	50%	0.50	23.8	42.8 (16.5)	38.6 (13.2)	–	19.9 (42.7)F^{24}
	70%	0.48	11.7	62.2 (34.6)	58.5 (10.6)	–	43.5 (19.5)F^{12}
Silica fume	5%	0.55	44.4	50.7 (13.8)	30.1 (11.6)	–	45.6 (28.9)
	10%	0.54	45.1	36.1 (11.6)	44.7 (22.6)	46.8 (24.6)	22.4 (21.4)
	20%	0.54	46.6	29.0 (20.7)	33.8 (17.8)	–	55.7 (57.6)F^{20}
	30%	0.53	50.2	28.4 (21.1)	17.8 (36.5)	27.2 (31.2)	68.6 (87.5)F^{12}

[a] Measured by MIP, which is expressed as cm^3/g of mortar.
[b] Determined by DSC–TG analysis, which is given by mass of mortar.
[c] Figures in parentheses are ratios of pore volume larger than 0.1 μm to total pore volume (per cent).
[d] F = Failure of sample; time of failure indicated as exponent.

The beneficial effect of silica fume addition also extends to concrete. Linear expansion, weight gain and sulfate consumption of concrete exposed to 5 per cent Na_2SO_4 solution were strongly reduced when silica fume was used to replace 10 per cent of Portland cement.[409] Replacement of silica fume for up to 20 per cent of Portland cement improved the performance of concrete exposed to more concentrated solutions (10 per cent Na_2SO_4).[369] It has been reported that concrete exposed to 10 per cent Na_2SO_4 solution generally expands to a lesser extent when fly ash is interground with clinker and gypsum rather than being added to the cement at the time of batching.[410]

$MgSO_4$ attack. Magnesium sulfate attack is considered to be more severe than that of sodium sulfate. Natural and artificial pozzolanas increase the resistance of mortar and concrete made with ordinary Portland cement but, contrary to what happens in the case of the sodium sulfate attack, they sometimes worsen the performance of sulfate-resisting Portland cements. Moreover, as will be shown below, the performance of cement seems to depend on the type of pozzolana used.

After 180 days' exposure, a 5 per cent $MgSO_4$ solution caused a strength loss of 45 per cent in a Portland cement paste and 5 and 20 per cent in cements containing 30 and 40 per cent of burned kaolin, respectively.[383]

Ordinary Portland cements containing 25 per cent fly ash behaved like sulfate-resisting Portland cements in weak $MgSO_4$ solution (0.75 per cent) but they proved worse in stronger solution (3 per cent).[395]

A 10 per cent replacement of silica fume for ordinary Portland cement improved the resistance of mortars exposed for ~3 years to a solution containing ~3 per cent $MgSO_4$.[395] However, 15 per cent replacement of silica fume for both ordinary Portland cement and

Table 10.47 Compressive strength of mortar cubes 20 × 20 × 20 mm immersed in 4.2 per cent $MgSO_4$ solution[391]

		Compressive strength							
		MPa				Percentage of water-cured samples			
Type of mortar	Type of cement[a]	90	180	1	2	90	180	1	2
		days		years		days		years	
Plain	OPC	37.8	12.8	17.4	7.0	107	61	40	16
	SPC	36.7	20.2	8.5	–	116	61	23	–
	SRPC	40.7	36.6	33.9	32.2	110	93	83	72
15% silica fume	OPC	29.1	22.1	12.0	–	63	46	21	–
	SPC	36.3	20.4	12.5	–	99	48	29	–
	SRPC	46.8	17.7	11.7	–	103	39	23	–

[a] OPC = ordinary Portland cement; SPC = slag cement; SRPC = sulfate-resisting Portland cement.

sulfate-resisting Portland cement reduced dramatically the strength of mortars exposed to a 4.2 per cent $MgSO_4$ solution for 2 years (Table 10.47).[391]

The negative effects caused by silica fume additions have also been observed in 6 mm thick paste beams exposed to 7.67 per cent $MgSO_4$ solution. Figure 10.77 shows that there was not much difference between the extent of damage in ASTM Type I (C_3A = 10.52 per cent) and ASTM Type V (C_3A = 2.26 per cent) Portland cements but, in both cases, the replacement of 15 per cent silica strongly decreased strength and increased mass loss.[411] These results are not consistent with the lower permeability and the smaller portlandite and C_3A contents of the microsilica cement paste. The discrepancies perhaps depend on the decrease in the alkali content of the pore solution (cf. section 10.3.3); in any case, they point out the complexity of the combined attack of sulfate and magnesium ions and account for the difficulty encountered in establishing a satisfactory sulfate resistance test.

As for sodium sulfate attack, a 1-year immersion in a magnesium sulfate solution reduced porosity in plain and fly ash-bearing mortars but increased porosity in silica fume containing mortars (Table 10.46).[408]

Mortars appear to be less resistant to magnesium sulfate attack than their counterpart pastes since they show greater surface deterioration, deeper sulfate penetration, greater gypsum formation and a higher degree of decalcification.[412] Clearly, the greater damage observed in mortars is due to their higher porosity and permeability as compared to pastes.

$(NH_4)_2SO_4$ attack. There is little data available concerning ammonium sulfate attack; however, that shown in Table 10.48[391] indicates that this salt is very dangerous to concrete durability. The improvement in the ammonium sulfate resistance induced by pozzolanic additions does not seem to be effective when the C_3A content of clinker is low. As a matter of fact, a 30 per cent natural pozzolana cement gave a 'resistance coefficient' higher than the plain 5.45 per cent C_3A cement when mortars were immersed in 0.15–0.30 per cent Na_2SO_4 solutions, but it proved to be worse when they had been exposed to 0.14 per cent $(NH_4)_2SO_4$ solution.[397] These results seem to confirm that low-C_3A Portland cements are able to resist ammonium sulfate solutions better than the counterpart silica fume cements

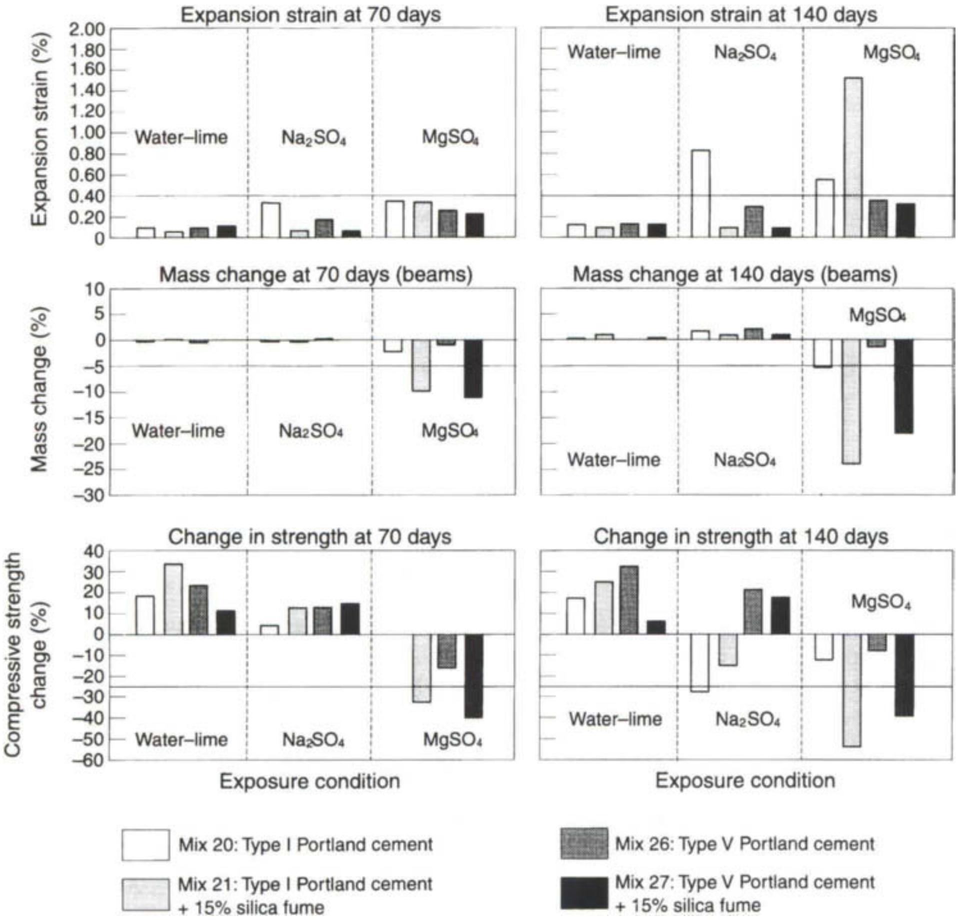


Fig. 10.77 Changes in length, weight and compressive strength of mortar after 70 and 140 days of exposure to 10 per cent sodium and 7.7 per cent magnesium sulfate solutions (source: Ref. 411).

(Table 10.48).[391] Also, the replacement of silica fume for 15 per cent of ordinary Portland cement reduced the strength loss of the plain cement paste very little, since it changed from 88 to 72 per cent.[413]

$MgSO_4$ + Na_2SO_4 attack. Pozzolana improves the resistance of mortars exposed to sodium and magnesium sulfate attacks. As an example 20–40 per cent replacement of low-lime fly ash for 12.0 per cent C_3A Portland cement decreased the expansion of mortars exposed to a solution containing 4.3 per cent magnesium sulfate and 2.5 per cent sodium sulfate. Moreover, the strength of fly ash cement mortars increased with time (at least up to 6 months), whereas that of the parent Portland cement mortar began to decrease after 2 months.[393]

The expansion of mortars was also reduced by replacing a medium-lime (13.3 per cent CaO) fly ash for 35 per cent of a 12.8 per cent C_3A Portland cement. However, it still was significantly higher than that of a highly sulfate-resisting Portland cement (1.3 per cent C_3A).[89] Of course, the initial curing conditions of concrete affect the sulfate resistance of the mixes containing pozzolana as well as plain Portland cements.[414]

Table 10.48 Compressive strength of mortar cubes 20 × 20 × 20 mm immersed in 4.6 per cent $(NH_4)_2SO_4$ solution[391]

Type of mortar	Type of cement[a]	Compressive strength							
		MPa				Percentage of water-cured samples			
		60 days	90 days	150 days	180 days	60 days	90 days	150 days	180 days
Plain	OPC	13.0	10.6	–	–	37	29	–	–
	SPC	17.9	6.6	–	–	57	20	–	–
	SRPC	21.5	15.5	11.1	9.4	59	42	30	28
15% silica fume	OPC	22.4	15.7	10.0	–	49	31	19	–
	SPC	19.3	9.3	–	–	53	24	–	–
	SRPC	16.7	14.4	–	–	43	36	–	–

[a] OPC = ordinary Portland cement; SPC = slag cement; SRPC = sulfate-resisting Portland cement.

Composition and microstructure changes. The addition of pozzolanic material to Portland cement changes the reaction rate, the mineral composition and the microstructure of mortars exposed to sodium or magnesium sulfate solutions. Table 10.49[401] shows that by increasing the replacement of pozzolanic material for Portland cement, ettringite, gypsum and calcium hydroxide contents decrease when mortars are exposed to sodium sulfate solution, while portlandite decreases and gypsum and brucite contents increase when mortars are immersed in magnesium sulfate solution.

In the presence of fly ashes, ettringite, gypsum and crack formation is delayed since pozzolanic reaction reduces the portlandite content and permeability of the paste.[399] SEM examination of fly ash cement mortars stored in a sodium sulfate solution revealed that

Table 10.49 Reaction products identified by DSC–TG and XRD analysis in fly ash and silica fume mortars when immersed in sulfuric acid and sulfate solutions for 1 year[401]

		10% Na_2SO_4				10% $MgSO_4$			
		Et	Gp	Ch	Mh	Et	Gp	Ch	Mh
Plain mortar		+	+	+ +	–	+	+	+ +	+
Fly ash	10%	–	+	+ +	–	–	+	+ +	–
	30%	–	+	+	–	+	+	+	–
	50%	–	–	+	–	+	+ +	+	+
	70%	–	–	–	–	–	+ +	–	–
Silica fume	5%	–	+	+ +	–	–	+	+ +	–
	10%	–	–	+	–	–	+	+	–
	20%	–	–	–	–	–	+ +	–	+
	30%	–	–	–	–	–	+ + +	–	+

Et = ettringite; Gp = gypsum; Ch = calcium hydroxide; Mh = magnesium hydroxide. Intensity of peak: + + + = very strong; + + = strong; + = weak, – = not detected.

ettringite crystals develop in the voids and that the initial filling is accompanied by an increase in the flexural strength of the mortars. Ettringite crystals continue to grow and cause cracking and strength loss in the specimen.

After exposure for 1 year, the samples were destroyed and under SEM the ettringite crystals filling the voids appeared to have sizes 15–25 μm by 2–3 μm. Gypsum crystals were localised in cracks where they had formed blocks of 30–150 μm.[399]

In hardened concretes exposed to the attack of a 5 per cent Na_2SO_4 solution, the depth of the sample into which ettringite crystals were observed to fill the air voids was found to decrease with increasing content of fly ash up to 50 per cent.[415] Unlike plain cement mortars, mortars made with 15 per cent silica fume cement and stored in 5 per cent Na_2SO_4 solution did not show any corrosion product in the pores such as that observed in the fracture surface.

Magnesium sulfate attack in medium (5.3 per cent) C_3A Portland cement resulted in the surface deposition of a double layer composed of brucite (40–120 μm) and gypsum (20–70 μm) and several internal layers of gypsum.

The microstructure of the paste of cement containing 10 per cent silica fume was significantly different since the surface double layer was followed by an adjacent M-S-H (or high-Mg C-S-H) layer, whereas the internal gypsum layers were replaced by dispersed gypsum crystals. The silica fume-containing pastes appeared to be less permeable than the parent Portland cement ones, since the depth at which gypsum occurred was lower (800 μm) than that of Portland cement paste (1200 μm).[416]

The surface layer of silica fume-bearing mortars exhibits a lower secondary mineralisation than that of parent Portland cement mortars. In silica fume mortar exposed to magnesium sulfate attack:

- brucite and gypsum form a thinner surface double layer;
- the amount of precipitated gypsum is smaller;
- gypsum is generally not observed around the aggregate grains;
- the surface of the specimen is crossed by intensive microscopic polygonal cracking.

However, despite the lower secondary mineralisation, the overall degree of surface deterioration in silica fume mortars is higher than that of plain cement mortars.[412]

Certain experimental results could explain the differences between plain and silica fume mortars as follows. In the former mortars, the thinner double layer formed by brucite and gypsum accounts for the lower penetration depth of the sulfate and the lower expansion, while the intensive network of polygonal cracks which characterises the deteriorated layer reveals a general weakening of the bond among the particles and thus a higher mass loss.[412]

Sea water

The high salt content in sea water is dangerous to the durability of both ordinary and reinforced concretes. By simplifying a complex series of chemical reactions and physical changes which occur between structure and salt contained in the sea water, it can be said that Mg^{2+} and SO_4^{2-} affect the durability of concrete whereas Cl^- affects that of reinforcement.

Deterioration of concrete caused by sea water is revealed by expansion, followed by cracking and scaling, and a progressive decrease in the mass and volume of concrete. All these phenomena cause mechanical properties to drop. Sea water-induced deterioration is less intense than one would assume from sea composition and, particularly, from the SO_4^{2-} and Mg^{2+} contents.[417,418] The reason why the sea water attack is less intense is that HCO_3^- and Mg^{2+} contained in the sea water react with the cement hydrates forming aragonite ($CaCO_3$) and brucite [$Mg(OH)_2$]. These compounds, which are practically insoluble, fill the pores of the paste and thus slow down the penetration of sulfate and chloride into the concrete.[419] Aragonite seems to play an important role, since when HCO_3^- is absent, the same amount of brucite precipitates but its protective effect is definitely reduced.[420] Moreover, ettringite and gypsum, whose formation causes mechanical stresses, are more soluble in chloride-bearing solutions[421] and less stable in an environment in which the pH is lower than in the bulk cement paste as a consequence of the formation of brucite.

As in other chemical attacks, the initial protection of the structure against the sea water is given by the compactness of concrete which reduces both the rate and depth of penetration of aggressive ions. Storage in sea water causes a reduction in the permeability of concrete.[422] This reduction, evidenced by a marked increase in the electrical resistivity of concrete, occurs in spite of the ingress of ions, and particularly of chloride, into the concrete. When the sample surface exposed to the sea water is cut away (1 mm thick layer), the resistivity of the sample returns to the original value, thus indicating that a protective surface layer has been removed.[423]

The compactness of concrete reduces both the rate and depth of attack of aggressive ions. Nevertheless, an important contribution to concrete protection comes from certain types of cement. Since expansion of cement is due to the formation of ettringite and gypsum, it is generally believed that Portland cements with a C_3A content of <8–9 per cent can resist seawater attack well.[355,424]

Several investigators, quoted in Ref. 418 have also found excellent long-term durability

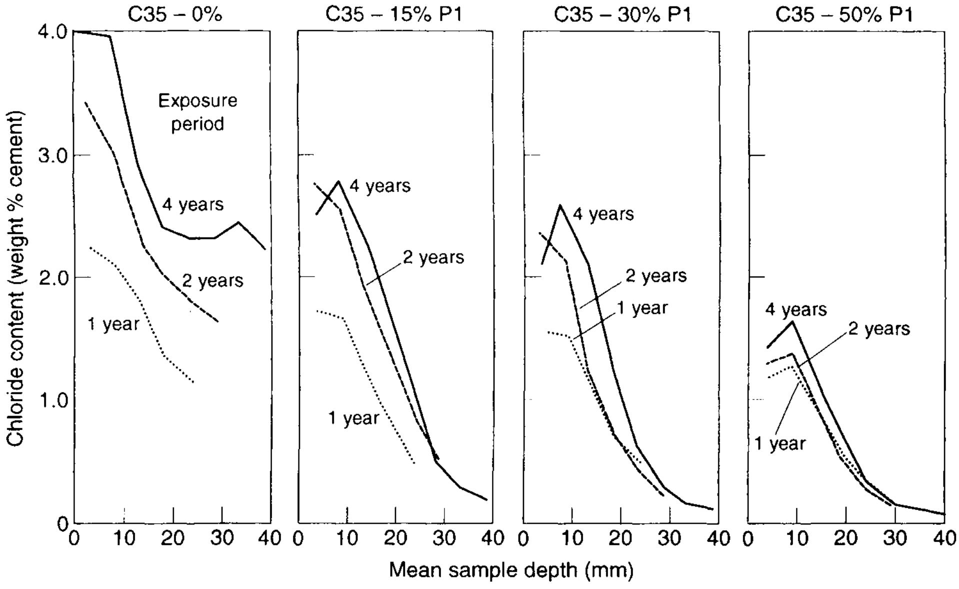


Fig. 10.78 Chloride profiles in marine-exposed concretes made with cements containing 0–50 per cent P1 fly ash (source: Ref. 429).

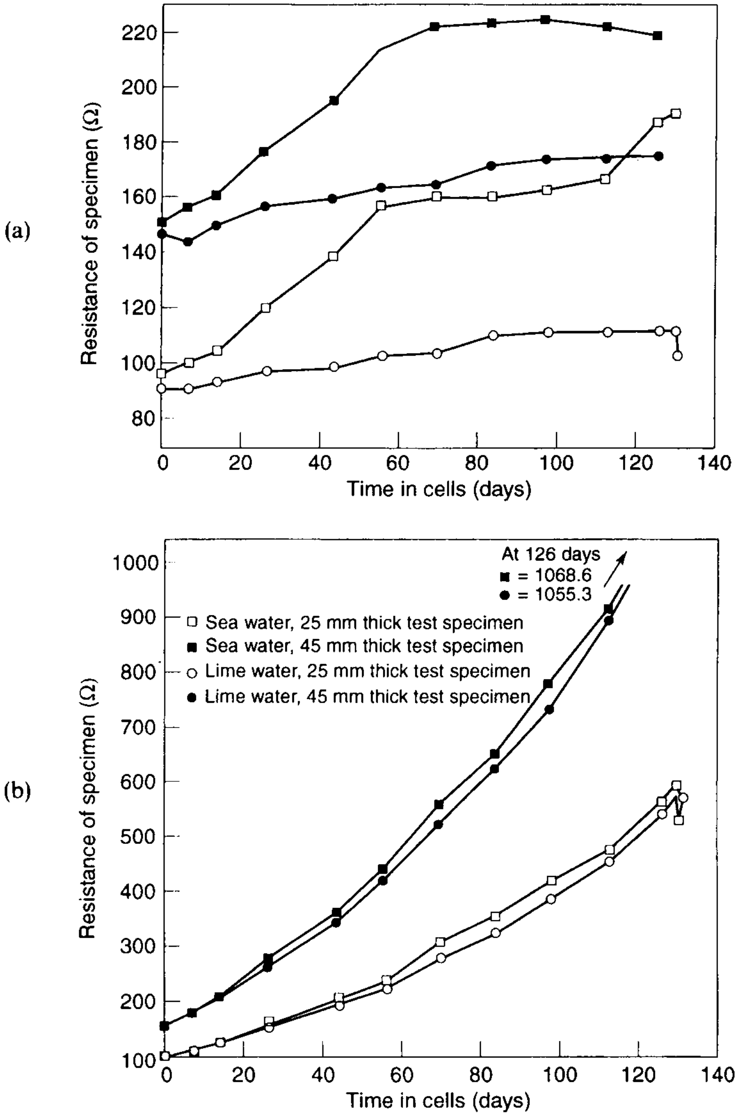


Fig. 10.79 Effect of sea water upon mortar electric resistance for (a) OPC and (b) OPC + 35 per cent fly ash (source: Ref. 422).

in concretes made with Portland cements containing 12–17 per cent C_3A. These results have been obtained with relatively rich mixes and low water/cement ratios, so the great influence of compactness of concrete in determining the resistance of Portland cements to seawater attack is eventually confirmed.

Partial substitution of pozzolanic material for Portland cement reduces swelling of mortars stored in artificial sea water, provided that the replacement level is sufficiently high. For this reason a 20 per cent replacement of Portland cement by natural pozzolanas and fly ashes had only slight influence on mortar expansion[425] and silica fume proved to be effective only when replacement was > 10 per cent.[426] Mortars incorporating pozzolanic materials such as fly ash proved to swell less than plain Portland cement ones having similar strength.[427]

Chloride penetration in mortars does not seem to depend on the C_3A content of Portland cement since little difference has been found between cements containing zero and 8.6 per cent C_3A. On the contrary, penetration in Portland cement mortars was five times higher than in trass cement mortars.[424]

It has been suggested that the compactness of concrete, i.e. to water/cement ratio, is more crucial than the pozzolana content,[428] but both parameters are important and play a complementary role. From Figure 10.78, it is evident that, by increasing the fly ash content, the chloride profile of concrete exposed to sea water changes.[489] The overall result is that the depth of chloride penetration and the total chloride content of the concrete decreases by increasing the pozzolana content in the cement.

Figure 10.79 shows that the increase in the electrical resistance of mortar caused by exposure to sea water is smaller in plain cement mortars than in fly ash-containing mortars and that the overall resistance given by fly ash cement is five times greater than that given by plain Portland cement.[422]

The influence of the water/cement ratio, i.e. the compactness of mortar, on chloride penetration is limited to the portion of mortar near the surface (i.e. < 15 mm) but it is negligible in the bulk mortar (depth > 20 mm; Figure 10.80).[427] Thus it appears that chloride penetration in the mortar portion near the surface depends mainly on the porosity and permeability, while in the bulk mortar it is controlled by other factors, such as chloride binding or ion exchange, which depend on the type of cement.[428]

The positive role played by pozzolanic cements in slowing down the deterioration of concrete exposed to sea water was stressed in 1951 during a survey of maritime structures

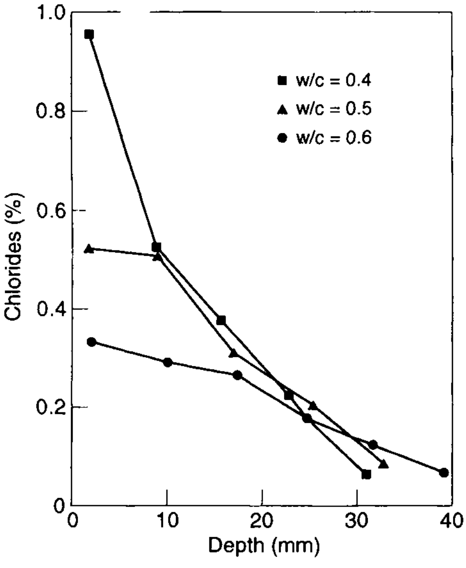


Fig. 10.80 Effect of water/cement ratio on chloride penetration into mortars after 2 years of exposure to sea water (source: Ref. 427).

built at several Italian harbours with pozzolanic mortars,[430] and has been repeatedly confirmed since then.[431]

In many countries, the partial replacement of Portland cement by pozzolanic materials is a well-established practice for producing seawater-resisting cements. Compared to the parent Portland cements, blended ones have a lower C_3A content, while mortar and concrete have lower portlandite content, more C-S-H together with a lower C/S ratio and lower permeability.

10.6.2 INFLUENCE OF THE AGGREGATE

Alkali–silica reaction

Preventing expansion induced by alkali–aggregate reaction is one of the most recent and fruitful applications of pozzolanas. Over the past 50–60 years, several harmful chemical reactions between aggregates and Portland cements have been demonstrated. The most common reaction is that occurring between certain types of silica (opal, chalcedony and tridymite) and cement alkalis. This reaction forms a more or less viscous gel made up of alkali and alkaline-earth silicates which should tend to absorb water from the environment and to expand. As a consequence, cracks develop in concrete. Concrete deterioration manifests itself at the surface as extensive map cracking, gel exuding from cracks, pop-outs and spalling. A short summary of the different mechanisms suggested for explaining causes and effects of alkali–silica reaction is found in Ref. 432.

Three conditions seem to be essential to start and sustain alkali–aggregate reaction:

- the alkali content of cement must be high;
- only part of the aggregate must be reactive;
- the humidity of the environment must be high.

Moreover expansion increases by increasing the cement content[433] and the water/cement ratio.[434] A number of methods have been proposed to evaluate the effectiveness of the different types of cement in preventing damage caused by alkali–aggregate reaction[435] but, owing to their more or less empirical nature,[436] they do not always agree with or reproduce the field behaviour of concrete.[437,438]

The expansive reaction does not occur with Portland cements containing <0.6 per cent of Na_2O alkali equivalent.[439] However, modern cement technology and pollution-preventive regulations in force in many countries make this target too expensive.[440] Again, for economic reasons, the problem cannot always be solved by changing the aggregates. Alkalis can come from external sources (sea water or de-icing salts), and in these cases the use of a low-alkali cement cannot prevent delayed deterioration of concrete occurring.[65,441]

Soon after the discovery of alkali–silica reaction, it was found that the addition of a finely ground reactive material, such as natural or artificial pozzolanas, to Portland cement could prevent the expansion of mortar and concrete caused by the presence of reactive minerals in the aggregate.[442] The effectiveness of pozzolanas in reducing expansion induced by alkali–aggregate reaction has been examined in many publications and at several conferences devoted to this particular phenomenon.[443–449] Expansion reduction has been observed when replacing natural pozzolanas and volcanic tuffs,[450,451] both in the raw state and after thermal activation,[452] fly ash, calcined shale, silica fume, kieselguhr, moler,[453,454] as well as burned clay.[455]

The addition of pozzolana might seem a contradiction because natural pozzolanas can contain up to 11 per cent alkalis and up to 5 per cent fly ashes. However, when certain conditions are met, expansion is actually reduced and brought back within acceptable levels.[453,456,457]

Low-alkali cement mortars cured in an NaCl solution exhibited expansion in the same way as high-alkali cements.[458] In this case, 30 per cent substitution of fly ash for Portland cement prevented mortar expansion.[458] Pozzolana is more effective in reducing expansion when it is used as Portland cement replacement instead of as a cement additive.[459] In Italy, despite the presence of reactive aggregates in some districts and their use in marine environments, only a few examples of alkali–aggregate reactions have been found. This condition could partly be due to the widespread use of pozzolanic cements in that country.

Influence of Pozzolana on alkali–silica expansion

There are cases in the literature in which the fly ash and natural pozzolana were not effective in preventing cracking and expansion due to alkali–silica reaction[460] and cases in which they even increased.[461 464] Both cases can be ascribed to an insufficient quantity or of a poor quality of pozzolana.

It is well known that the expansion of mortar bars containing reactive aggregates varies with the proportion of reactive aggregate and that it reaches a maximum at a certain content of the reactive mineral (the 'pessimum' effect).[433,441] The addition of pozzolana

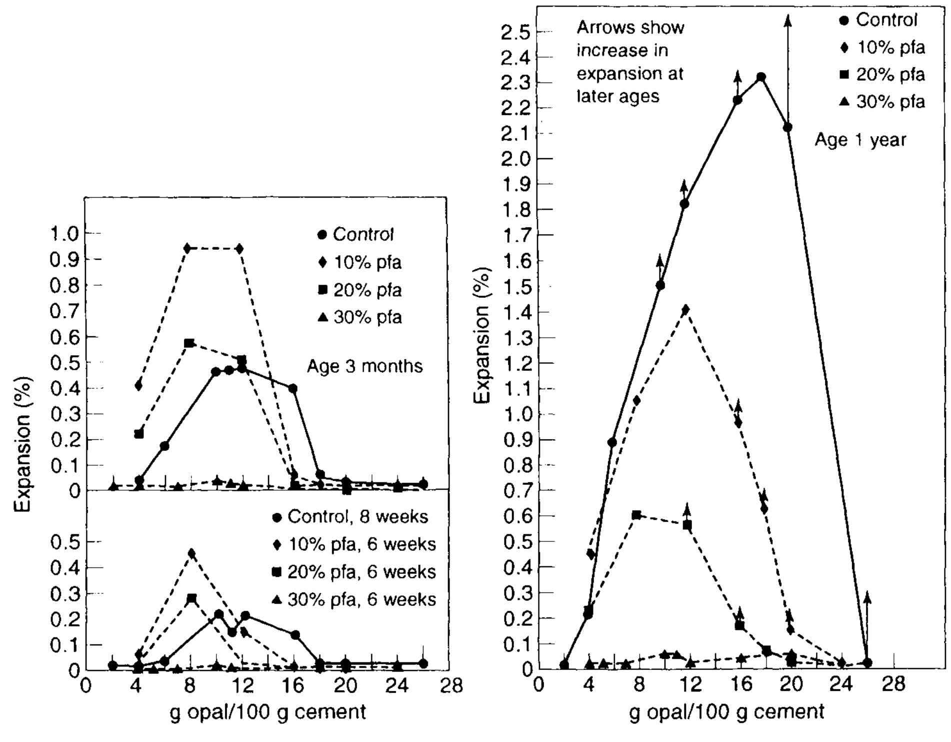


Fig. 10.81 Mortar bars containing high-alkali OPC/high-alkali fly ash with Beltane opal aggregate at 20°C (source: Ref. 466).

reduces this effect;[465] however, pozzolanas can also cause a similar 'pessimum' effect. Figure 10.81 shows that 10–20 per cent replacement of a high-alkali fly ash for Portland cement increased expansion caused by sand containing very reactive Beltane opal, whereas a 30 per cent replacement caused a levelling of the peak corresponding to the pessimum effect, thus preventing deleterious expansion.[466] When using low-alkali fly ash, a smaller replacement level (20 per cent) can be sufficient to suppress dangerous expansion.[467]

Generally, the partial replacement of high-alkali cement with pozzolanas produces a significant reduction in the expansion of mortar bars. However, with some fly ashes, a pessimum effect occurs, i.e. up to a certain fly ash content, expansion increases instead of decreasing (Figure 10.82).[451,463] This effect is not a general rule since with other fly ashes, blended with the same Portland cement, the peak does not occur (Figure 10.83).[463] In addition, certain natural pozzolanas, such as trass, caused an increase in expansion.[461] Italian natural pozzolanas brought about a continuous decrease of expansion of a Portland cement containing 1.8 per cent Na_2O_{eq}.[452]

Owing to the high reactivity of silica fume, the amount of microsilica necessary to prevent expansion is lower than that required by other pozzolanas.[65] The pessimum effect of silica fume addition appears with certain types of reactive aggregate but not with others.[436] Also, less common pozzolanas, such as moler, prevent expansion on condition that the content is not less than 15–20 per cent of the binder mass.[454]

The possible existence of a pessimum effect, which depends on the replacement level of pozzolana, indicates that the total alkali content of the binder (Portland cement + pozzolana) cannot be used as general criteria to distinguish expansive from non-expansive mixes.

Figure 10.84 shows that the critical Na_2O/SiO_2 mole ratio of the binder changes depending on the fly ash–Portland cement combination.[462] As a practical consequence, replacement of class C fly ash for high (0.85 per cent Na_2O_{eq}) or low (0.4 per cent Na_2O_{eq}) alkali Portland cement may be dangerous for concrete if fly ash is used arbitrarily.[462]

The importance of pozzolana content in preventing expansion has also been experienced in the field: the expansion of mortar bars made from eight highly reactive sands become

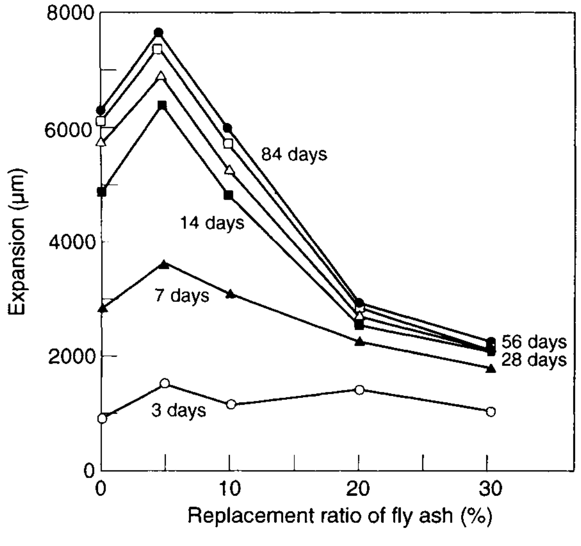


Fig. 10.82 Effect of replacement ratio of B fly ash on expansion of mortar (source: Ref. 463).

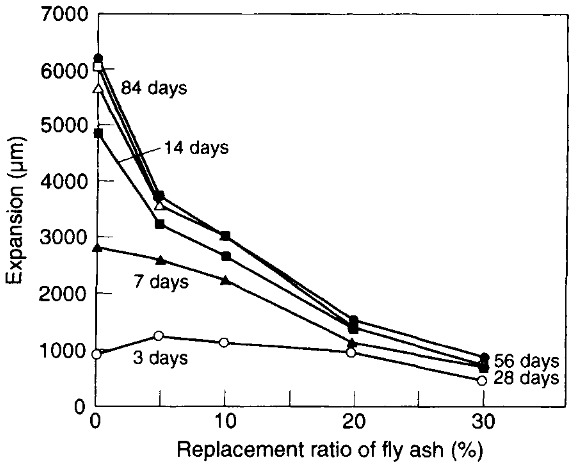


Fig. 10.83 Effect of replacement ratio of F fly ash on expansion of mortar (source: Ref. 463).

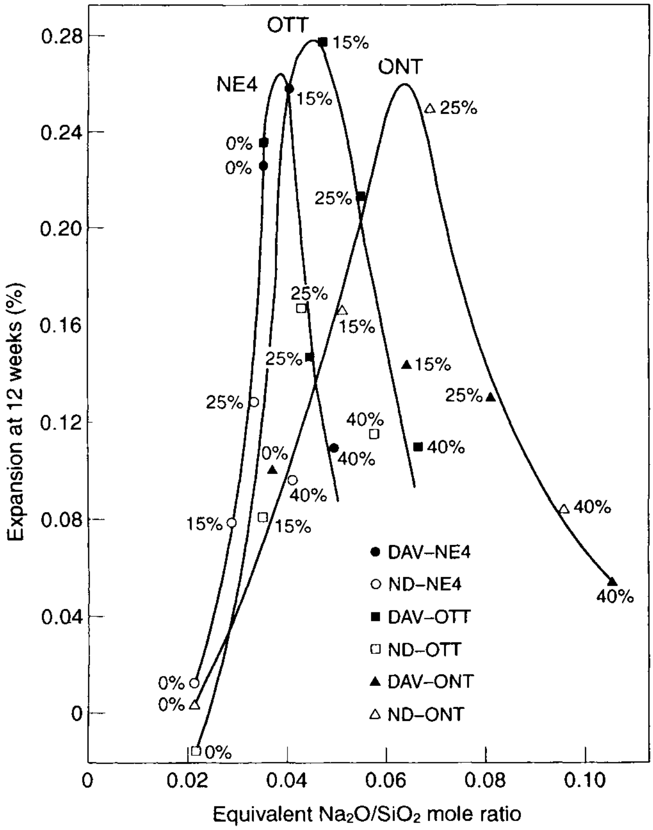


Fig. 10.84 Effects of N/S mole ratio on mortar bar expansion (source: Ref. 462). DAV, Portland cement with 0.85 per cent Na_2O_{eq}; ND, Portland cement with 0.49 per cent Na_2O_{eq}; ONT, fly ash with 7.35 per cent Na_2O_{eq}; OTT, fly ash with 3.39 per cent Na_2O_{eq}; NEA, fly ash with 2.26 per cent Na_2O_{eq}.

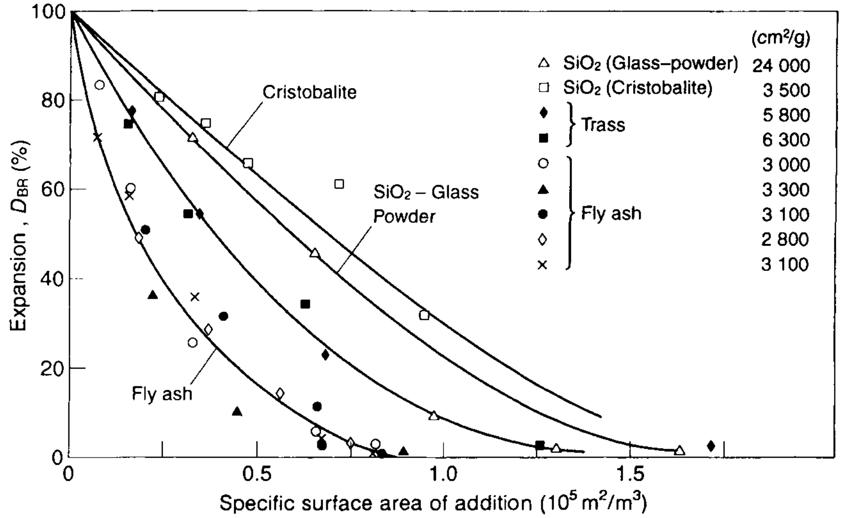


Fig. 10.85 Decrease of expansion by several kinds of additions according to their specific surface area (Blaine) and quantity in concrete (source: Ref. 468).

insignificant when cements incorporating a high percentage (40–70 per cent by volume) of fly ash were used.[467] The higher the fineness of pozzolana, the lower the expansion due to the alkali–silica reaction.[468,469] As shown by Figure 10.85, the effect also depends on the added material.[468]

The addition of pozzolana generally increases the total alkali content of mortar and concrete. However, the availability of alkalis depends on the progress of pozzolanic reaction and particularly of the alkaline attack of glass forming the active part of volcanic pozzolanas and fly ashes (see Figure 10.24).[184] For this reason, it has been suggested that fly ash acts like a Portland cement with an alkali content of ~0.2 per cent by weight.[470] This assumption means that the addition of fly ash, or of other pozzolanas, should reduce the available alkali fraction of the binder and thus expansion, but it does not explain the pessimum effect related to the replacement.

Figure 10.86 shows that the expansion reduction due to the alkali–silica reaction depends on the source of the pozzolana.[470] It could depend on the alkali content of pozzolana, but it has been found that the partial replacement of two fly ashes having 3.35 and 1.32 per cent Na_2O_{eq}, respectively, for a Portland cement resulted in almost the same expansion.[456] Other factors, such as the fineness of pozzolana, the available alkali content and the rate of the pozzolanic reaction, certainly play an important role.

The reduction in the intensity of attack due to pozzolana addition has been observed directly in reactive silica glass tubes plunged in the cement paste. Stereoscopic microscope observations and EDS analysis showed that after 28 days curing at 40°C, quartz glass was strongly corroded with the formation of a calcium potassium silicate hydrate, whereas it was not attacked by the paste containing 50 per cent fly ash. An intermediate degree of corrosion was observed with a 30 per cent fly ash cement.[471] Replacement of 30–60 per cent Portland cement by fly ash reduces the reaction rim observed on the glass particles used as reactive aggregate, as well as expansion in mortar samples.[472]

In conclusion, all the laboratory tests and field experience have shown that pozzolana

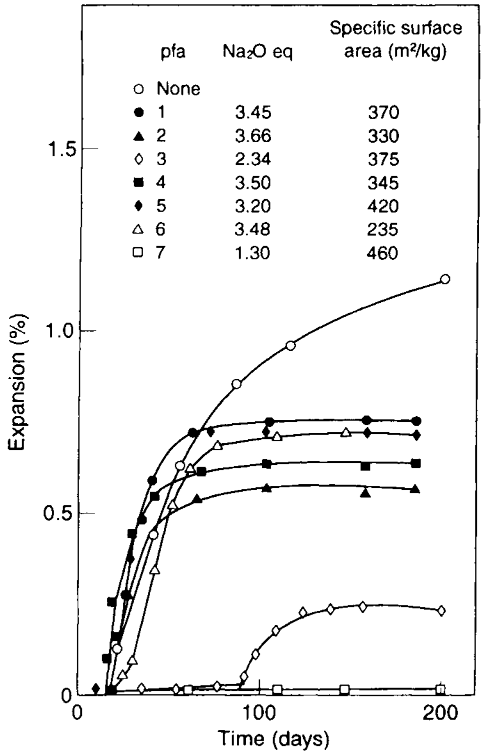


Fig. 10.86 Variation of expansion of mortar with age (source: Ref. 470). w/(c + pfa) = 0.53; a/(c + pfa) = 3.5; pfa/(c + pfa) = 0.3 Portland cement A containing 1.04 per cent Na_2O_{eq} blended with 7 fly ashes having different specific surfaces.

significantly reduces expansion provided that replacement of Portland cement is sufficient, i.e. it is proportional to the reactive aggregate content and to the active alkali content of Portland cement.

Factors reducing expansion

Some typical properties of pozzolana-containing cement have been associated with the reduction of expansion of mortars and concretes:

- lower permeability and consequent lower ion mobility;
- lower alkalinity and pH of the pore solution;
- higher alkali content of hydrates;
- lower portlandite content;
- lower C/S ratio of C-S-H.

Permeability. The lower permeability of pozzolana-containing mortars and concrete, as compared to that of plain Portland cement ones, can contribute to slowing down the alkali–silica reaction, but can hardly prevent it. This factor could play an important role, as in the case of alkali ions entering from outside the mortar or the concrete.

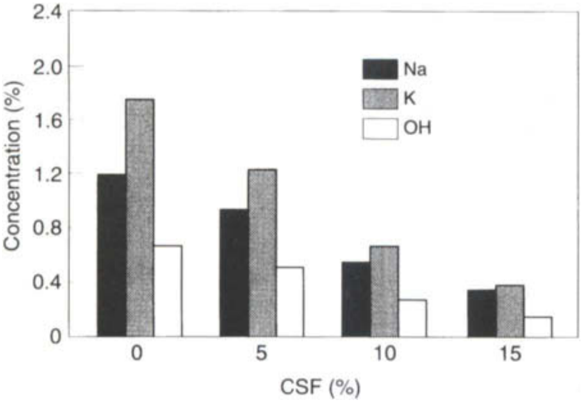


Fig. 10.87 Ion concentrations in pore solution at 6 months with 0, 5, 10 and 15 per cent CSF (source: Ref. 476).

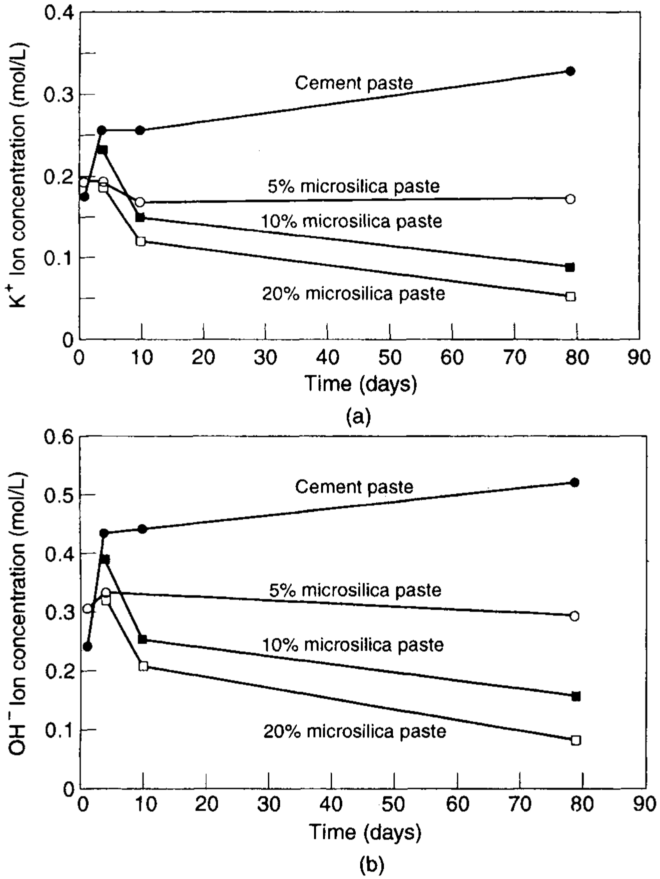


Fig. 10.88 Concentration of (a) K^+ and (b) OH^- in pore solutions expressed at times indicated from cement paste and microsilica-bearing pastes, all at water/solid ratio of 0.50 (source: Ref. 284).

Alkalinity. Alkalinity of the pore solution of Portland cement pastes is mainly given by sodium and potassium hydroxide,[473] since the Ca^{2+} concentration is very low (~0.001 N).[474] Replacement of Portland cement by pozzolanic materials generally reduces the alkali and OH^- concentration in the pore solution.[229,473,475,476,477] Table 10.26[198] shows the effect of fly ashes on the composition of the pore solution, while Figure 10.87 shows that of silica fume.[476]

In some cases, high calcium and high sodium sulfate fly ashes[474] and high-alkali natural pozzolanas[477] blended with low-alkali cement have been reported to increase alkalinity of the pore solution. However, high-alkali fly ashes have been found to reduce the alkalinity of the pore solution of concrete made with slowly reacting aggregate when they are blended with high-alkali Portland cement, while they increased alkalinity when blended with low-alkali Portland cement.[478] Chemical equilibrium effects related to the pore solution and solid phases could account for the different influence of the same pozzolana on pH.

The reduction of alkali concentration in the pore solution is accompanied by a reduction of expansion,[473,474,476] and if the alkali concentration falls below a certain safe level, deleterious expansion does not occur. The threshold of alkali or hydroxide concentration which is suitable for preventing deleterious expansion due to reactive aggregate is not yet well established. It ranges from 0.25[476] or 0.3[479] to 0.65 N.[473] In the pore solution of concrete the concentrations of Na^+, K^+ and OH^- decrease to a lesser extent than in mortar.[476]

Silica fume possesses a remarkable ability to remove alkali hydroxides from the cement paste pore solution. As an example, the OH^- concentration, which was 0.5 N in plain paste solution after 76 days of hydration, dropped to 0.3, 0.15 and 0.075 N when silica fume replaced 5, 10 and 20 per cent of Portland cement, respectively.[284] In the presence of silica fume, the concentration of Na^+ and K^+ reaches a maximum after ~4 days, then decreases[284,476] and possibly stabilises at certain levels (Figure 10.88).

The amount of alkalis removed from solution depends on the alkali content of microsilica. A 5 per cent substitution of a low-alkali (0.77 per cent Na_2O_{eq}) silica fume reduced alkali concentration in the pore solution whereas the same amount of a high-alkali (3.63 per cent) silica fume increased it. With low-alkali silica fume, the reduction of the alkali and OH^- concentration of the pore solution is proportional to the microsilica content in the cement (Figure 10.89).[476] In general, the reduction in the alkali concentration in the pore

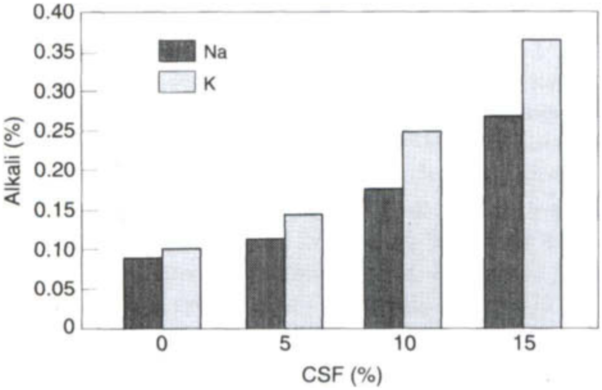


Fig. 10.89 Alkali content at 6 months in solid phases of pastes with 0, 5, 10 and 15 per cent CSF (source: Ref. 476).

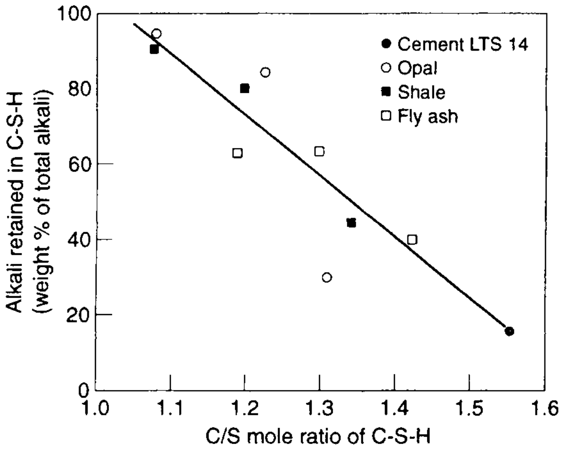


Fig. 10.90 Alkali retained in C-S-H formed in Portland cement and blended cement pastes (source: Ref. 480). Three levels of pozzolana replacement.

solution caused by pozzolana replacement is small if compared with the large decrease in mortar expansion.[475,479]

Alkalis in the solid hydrates. The decrease in the alkali content of the pore solution is parallel with the increase in the alkali content of the solid phases (Figure 10.89).[476] Pozzolana reduces the C/S ratio of C-S-H and this allows more alkalis to be incorporated in calcium silicate hydrates (Figure 10.90).[480] About 95 per cent of the total alkali content can be retained by blended cement pastes, where only ~ 15 per cent is blocked in Portland cement ones.[480] In solid phases, potassium prevails over sodium.

The replacement of pozzolanic material for Portland cement reduces the lime content and increases the silica content of the blend. Thus the expansion caused by alkali–silica reaction appears to depend on the basicity of the blend, i.e. on the (CaO)/(SiO_2 + Al_2O_3 + Fe_2O_3) ratio.[471,481]

Portlandite content. Both alkalis and $Ca(OH)_2$ take part in alkali–silica reaction, but the presence of crystalline portlandite is considered to be a necessary condition for the breakdown of Portland cement concrete when an alkali–aggregate reaction occurs.[454,482] This condition is consistent with the increasing reduction of expansion which occurs when the replacement of pozzolana for Portland cement increases, i.e. when the free lime content decreases as a consequence of the pozzolanic reaction, but it does not account for the pessimum effect.

Replacement of 25 per cent fly ash or 45 per cent calcined clay in a 1.22 per cent Na_2O_{eq} Portland cement prevented the expansion of mortar containing opal, but the addition to the mix of 10 per cent finely ground lime (calcined at low temperature) caused dangerous expansion (Figure 10.91).[481,483] Similarly, the addition of 9 per cent $Ca(OH)_2$ to mixes containing reactive aggregate and high-alkali (1 per cent Na_2O_{eq}) cement increased expansion of mortar bars by about 30 per cent. The 20 per cent replacement of silica fume in the same Portland cement prevented expansion, but when 9 per cent $Ca(OH)_2$ was added to the blend, silica fume no longer was able to control the expansion.[432] These results have been confirmed by field observations: in spite of the presence of a reactive

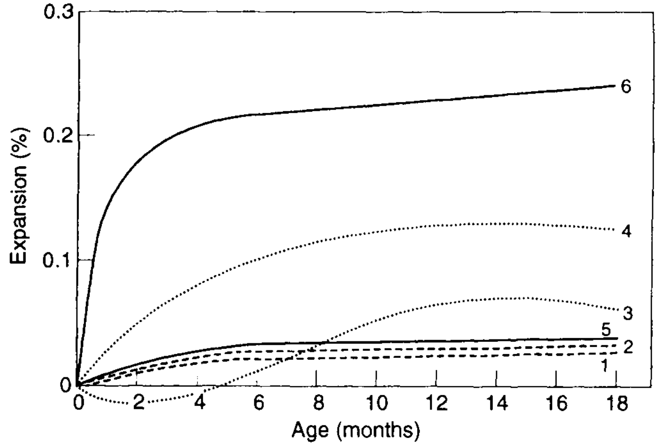


Fig. 10.91 Expansion of mortar bars made from cement with supplementary materials, with aggregate containing 6 per cent by weight of opal (source: Ref. 481). 1–3–5: 30 per cent tuff, 30 per cent slag and 30 per cent fly ash, respectively. 2–4–6 is the same as 1–3–5, but with 10 per cent CaO added.

aggregate, concrete lacking in free lime had not suffered destructive expansion when a de-icing salt (NaCl) penetrated into the slabs.[482] Laboratory tests confirmed this occurrence because, by removing free lime from mortar by either combining it with a highly active pozzolana (moler) or leaching it with 30 per cent $CaCl_2$ solution, expansion was prevented.[482]

For a given reactive aggregate and a Portland cement, the higher the pozzolana replacement, the lower the portlandite content in the paste and the lower the concrete expansion. This inverse relationship between pozzolana content and expansion has often been found.[65,469,484] However, when considering all results recorded on several pozzolanas, no significant global relationship was observed between concrete expansion and portlandite content.[485] The lack of such a general relationship is possibly due to the occurrence of other factors. Among these, the available content does not correspond to the total portlandite content since a variable proposition is embedded and shielded by the hydrates and cannot take part in the pozzolanic or in the alkali–silica reactions. In this case the permeability of mortar or concrete can play a certain role in expansion since it can affect the Ca^{2+} migration.

Specific surface. The Blaine specific surface of pozzolanic constituents affects expansion induced by the alkali-silica reaction. Figure 10.92 shows that expansion of mortars bars decreases with increasing fineness of the fly ash. The Na_2O content of the fly ash samples ranged between 1.29–1.47 and the replacement level for Portland cement was 30 per cent.[485b]

Competition between alkali–pozzolana and alkali–aggregate reaction

Many experiments have demonstrated that there exist many similarities between pozzolanic reaction and alkali–silica reaction. As a typical example, a 10 per cent replacement of

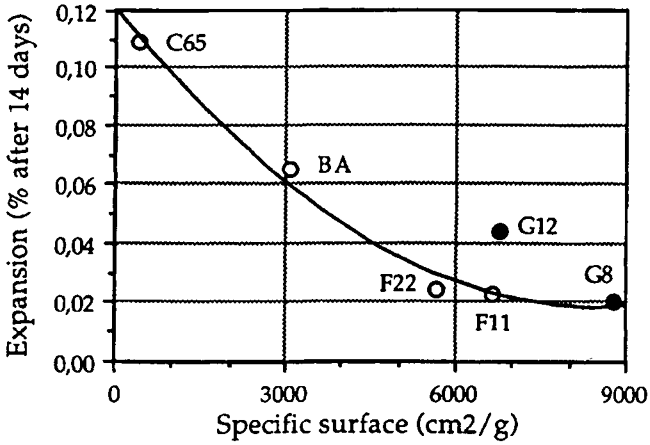


Fig. 10.92 Fourteen-day expansion results in accelerated mortar-bar tests as function of fly ash fineness (Blaine specific surface).[485b]

Table 10.50 Pozzolana needed for complete $Ca(OH)_2$ reaction[480]

	Amount needed (wt.%)	
Pozzolana	LTS #14	LTS #18
Opal	26	26
Shale	39	40
Fly ash	38	34

Na_2O equivalent in LTS #14 cement = 0.92.
Na_2O equivalent in LTS #18 cement = 0.21.

finely dispersed silica fume in high-alkali Portland cement prevented expansion of a 28 day old mortar immersed for 2 months in a saturated $Ca(OH)_2$ + 1 M NaCl solution. On the contrary, mortars containing the same amount of granulated silica fume exhibited the typical map cracking of alkali-silica reaction.[486] On the other hand, a typical reactive aggregate such as opal was transformed into a very active pozzolana by finely grinding it before blending with Portland cement. Table 10.50 shows that, owing to the high silica content of the mineral, the percentage of opal needed for complete $Ca(OH)_2$ removal from the paste was far lower than that necessary for shale and fly ashes.[486]

Opal and silica fume pastes behave similarly in terms of expansivity and chemical reactivity when mixed with $Ca(OH)_2$ and/or NaOH solutions.[487] However, in a mortar bar test, dispersed silica fume prevented expansion caused by a high-alkali cement whereas the agglomerate opal caused expansion.[488] Moreover, silica fume is effective in preventing expansion; however, it has been found that very high silica fume replacement (45 per cent) can cause expansion with non-reactive aggregate, provided that Portland cement contains a high percentage of alkalis (0.66 per cent).[488]

These results suggest that pozzolanas reduce the risk of alkali–silica expansion, primarily by their ability to react with the alkalis in the pore solution more rapidly than the sand sized or coarse aggregate-sized reactive minerals do.[474] This ability depends on the fineness and the dispered form of pozzolanas, otherwise they can contribute to the expansion due to alkali–silica reaction.

Mechanisms of expansion reduction by pozzolana

In spite of many experimental results, the role played by pozzolanas in preventing the deleterious expansion caused by alkali–silica reaction is not yet fully understood. Silica in pozzolanas can react both with Ca^{2+} and $Na^+ + K^+$ giving silicate hydrates but, since calcium silicate hydrates are more stable than alkali silicate hydrates, calcium prevails in solid C-S-H and Na^+ and K^+ in the pore solution. Pozzolana combines free lime and decreases the pH of the pore solution, so the reduction of expansion could be referred to the decrease of pH. Moreover, owing to its low C/S ratio, C-S-H occurring in pozzolana-containing pastes removes part of the dissolved alkalis and combines them. The combination of both portlandite and alkalis reduces pH. This could account for the inhibiting effect on expansion also shown by high-alkali pozzolanas.

This model requires pozzolana to combine all of the portlandite, or at least that available for the pozzolanic reaction, i.e. the portlandite that is not embedded and shielded by hydrates. This means that the cement must have a high pozzolana content and, practically, must comply with the pozzolacinity test.

The decrease in free portlandite and alkali concentration reduces the pH of the pore solution. In this condition the rim of the silicate hydrate covering the reactive aggregate which is suspected to give expansion is thinner[472] or, depending on the pozzolana content of cement, does not form.[471] Many results suggest that pozzolanas as well as reactive silica give rise to pozzolanic reaction or deleterious expansive reaction, depending on the fineness of the particles. This assumption is supported by the similar composition of the products of the two reactions. Incidentally, accurate TEM analyses showed that the rim of silicate hydrate formed on the reactive aggregate particles has a C/S ratio of ~1[472] and the rim formed on silica fume particles varies from 1.7 to 0.8 in moving from the bulk cement paste to the core of the particles.[223]

If C-S-H is formed by the reaction of siliceous reactive aggregate, and pozzolana belongs to the same family, both would be expected to expand, whereas no sign of expansion appears when they are finely dispersed in the cement paste.[223] Thus, if the siliceous material is finely dispersed in the paste, the reaction rim which forms around the grains is very thin and uniformly distributed in the paste and thus a possible expansion could not be detected. On the contrary, if the particles of the reactive materials have the same size distribution as sand, the depth of the rim would be higher and expansion would no longer be negligible. As an alternative, the lower pH resulting from the pozzolanic reaction could account for the non-expansivity of the calcium alkali hydrate or could prevent alkali enrichment of C-S-H, which is expected to be the cause of expansion.

The pessimum effect caused by a low pozzolana replacement could be due to a more rapid rise of alkali concentration and pH of the pore solution caused by the addition associated with a delayed beginning of the pozzolanic reaction.

If the reactive siliceous material is coarse and has a low specific surface area, portlandite and alkali cannot be removed. So the pore solution alkalinity remains locally high and the reaction of the siliceous materials produces expansive compounds.

These observations do not take into account the kinetics of the reaction and in particular the rate of the alkali dissolution. As far as this aspect is concerned, we have to consider that expansion increases by increasing the water/cement ratio and the fineness of cement[434] and decreases with increasing fineness of the pozzolana.[468,469]

10.6.3 FROST ACTION

As a rule, concrete does not have good frost resistance due to the presence of water-filled capillary pores. If water freezes, concrete increases in volume and tends to expand. The opposite happens when the temperature rises above 0°C. Repeated freeze–thaw cycles accelerate the material's decay. The frost resistance of concrete decreases by increasing the water/cement ratio and by shortening the wet curing before exposure to freezing. As a consequence, frost resistance increases by increasing the strength of concrete, but the best protection is obtained by introducing microscopic air bubbles into concrete. Bubbles are able to accommodate water being pushed forward by the ice in the process of being formed. For this reason, natural pozzolanas,[489] fly ashes[490,491] and silica fume[491] contained in blended cements do not worsen frost resistance, provided that concretes have a suitable entrained-air content and similar strengths.

According to some authors, fly ashes and silica fume reduce the frost resistance of non-air-entrained concretes but improve that of air-entrained ones.[491] The influence of pozzolanic material on the frost resistance of concrete depends on the replacement level. Figure 10.93 suggests that only high percentages of replacement Portland cement by fly ash ultimately decrease frost resistance.[348] The presence of pozzolanas such as fly ash has no significant effect on the freezing and thawing resistance of concrete within 15–40 per cent replacement limits.[492,493]

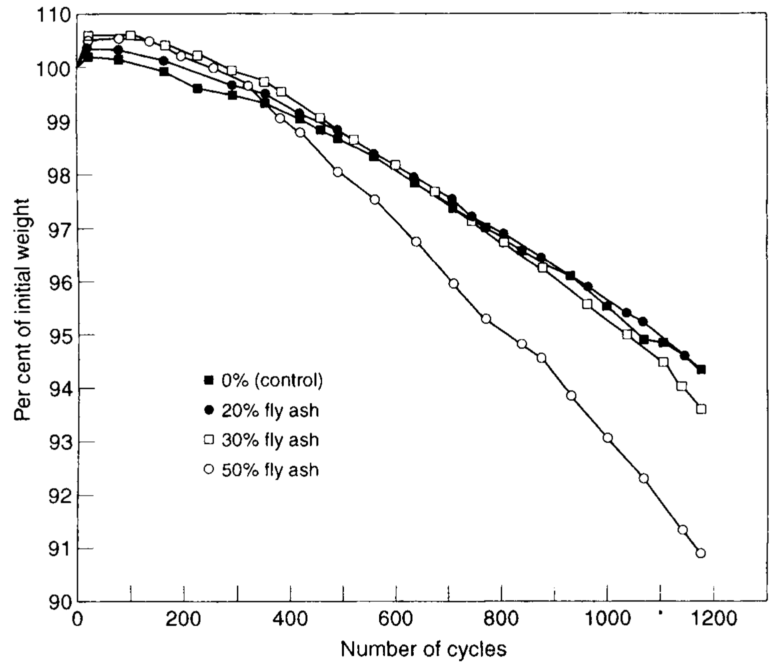


Fig. 10.93 Weight loss versus number of freeze–thaw cycles for air-entrained concrete with indicated percentage of cement replacement with fly ash after 14 days of curing (source: Ref. 348).

In some cases the use of a pozzolanic material requires special care. Owing to its high surface area, the carbon remaining in the fly ash from incomplete combustion requires an additional amount of air-entraining admixture to obtain a specified air content in concrete.[494] Replacement of silica fume for Portland cement at percentages exceeding 15 per cent, for example 20–30 per cent, also causes the freeze–thaw resistance to decrease in the presence of entrained air.[495-497] The reason perhaps lies in the changes occurring in the specific surface area, as well as the spacing of air voids in concretes.[496]

Field applications have confirmed laboratory test results. In the Alpine regions of Italy, many dams built with pozzolanic cements are in an excellent state of preservation after decades of service despite the large number of freeze–thaw cycles they are annually subjected to.[498] Owing to the slow initial hardening of pozzolanic cements, the frost exposure of pozzolana-containing concretes should be somewhat delayed compared to that of Portland cements. Insufficient curing is the reason why several standard methods for measuring the freeze–thaw resistance of Portland cement concretes often give inferior results when applied to blended cement ones.[499]

Freeze–thaw tests carried out after long curing periods have shown that blended cements develop equivalent or higher resistance than that of Portland cements, provided that the concretes have the same strength.[500] The replacement of fly ash[501] or limited amounts of silica fume[502] in Portland cement has not resulted in a clear increase of scaling caused by de-icing agents. However, in spite of the fact that no particular benefits occur when pozzolana cements are used in the presence of freezing conditions and de-icing salts, they reduce the risk of penetration of chloride into concretes and thus of reinforcement corrosion.

In conclusion, the freeze–thaw resistance of ordinary concretes mainly depends on the concrete properties (strength, water/cement ratio, entrained air content, etc.) and only indirectly on the type of cement.

10.6.4 CONCLUDING REMARKS

Pozzolana cannot remove all durability problems, but it can contribute to solving most of them provided that it is appropriately used. The main conclusion of the effect of pozzolanic materials on the durability of concrete can be summarised as follows.

As a whole, pozzolanas increase the resistance of concrete against environmental attack since they reduce permeability, absorption and ion diffusivity. Pozzolana does not affect the carbonation depth adversely provided that concretes are compared on the basis of the same strength. The resistance of concrete against pure and acid waters is definitely increased by the substitution of pozzolanic materials for Portland cement. The diffusion of aggressive ions such as chloride into concrete is lowered by pozzolana. The effect is proportional to the replacement level.

No cement can save concrete from a prolonged sulfate attack. The depth and rate of attack depend on the type of cation associated with the sulfate ion and on the concentration of the salt solution. Typically, exposure to sodium sulfate solution initially causes an increase in strength but, after a certain time, a loss of strength occurs.[391] Nevertheless, some types of cement can slow down the process of deterioration, especially if the concrete is a high performance one.

Natural pozzolana, fly ash and silica fume reduce expansion, mass change and strength loss in both ordinary Portland cement and sulfate-resisting Portland cement when samples are stored in a sodium sulfate solution. Typical results are reported in Figure 10.73.[411]

Table 10.51 Summary of the main effects on concrete durability of the addition of pulverised-fuel ash[365]

Durability	Effects of PFA
1. Permeation	Reduced, the extent depends on the property and the test method. Effect more marked with age for the water-cured concrete
2. Sulfate attack	Resistance increased. OPC/PFA blends recommended up to class 4 sulfate exposure
3. Chloride ingress	Coefficient D reduced significantly, depending on the curing of concrete
4. Carbonation	Slightly increased for low strength mixes and at the initial stages of carbonation. Ultimate values essentially similar to OPC concrete
5. Corrosion:	
Chloride induced	Slightly reduced
Carbonation induced	No significant difference
6. ASR resistance	Generally improved. Question of contribution of PFA alkalis remains unresolved
7. Freeze–thaw resistance	No significant effect. Requires suitable air-entraining admixture
8. Abrasion	Resistance generally improved. Extent depends on the curing of concrete and its age

The importance of the cation associated with the sulfate ion is evident in the case of magnesium sulfate attack. The loss of strength of mortar exposed to magnesium sulfate solutions is slowed down if a pozzolanic material replaces ordinary Portland cement, but it is accelerated if the pozzolana replaces sulfate-resisting Portland cement. As an example, after 18 months of exposure to a 3 per cent $MgSO_4$ solution, fly ash cement mortars retained 55–84 per cent of their strength whereas sulfate-resisting Portland cement retained 82–94 per cent of their strength.[395] Thus, in a magnesium sulfate environment, sulfate-resisting Portland cements on the whole behave better than pozzolana-containing cements. However, the fact that some results overlap suggests that selected blended cements could perform as well as sulfate-resisting Portland cement. As for the alkali–silica reaction, pozzolanas proved to reduce expansion provided that the pozzolana content in the blend is rather high.

When concretes undergo repeated freeze–thaw cycles, the risk of deterioration appears to be independent of the type of cement and therefore of the presence of pozzolana. Table 10.51[365] summarises the main effects on concrete durability of the addition of fly ash to Portland cement.[365] These effects have also been ascertained with natural pozzolanas, burned clays and silica fume, so the validity of Table 10.51 can be extended at least to the more common pozzolanic materials.

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11

Cements Made From Blastfurnace Slag

Micheline Moranville-Regourd

Blastfurnace slag, BFS, applied to iron blastfurnace slag is a non-metallic product which consists essentially of silicates and aluminosilicates of calcium.[1] Slag has found a considerable use in the road and building industries, in the production of cementing materials, as an aggregate in concrete and tarmacadam, in the production of lightweight aggregate, and in the manufacture of slag wool for thermal insulation. In the UK its major use has been as a roadstone, the other uses representing only a relatively small proportion of total slag production. The use of slag as a concrete aggregate is discussed in Chapter 16.

11.1 Processing of blastfurnace slag

In the operation of a blastfurnace the iron oxide ore is reduced by means of coke to metallic ion, while the silica and alumina constituents combine with the lime and magnesia to form a molten slag which collects on top of the molten iron at the bottom of the furnace. The iron itself dissolves some of the constituents in a reduced form, notably silicon, manganese and sulfur. The partition of sulfur between iron and slag is important. In order to favour solution of sulfur in the slag, either the temperature or the lime content of the slag is increased; the latter in any event necessitates an increase in temperature in order to retain fluidity. An increase within certain limits in magnesia content also lowers the slag viscosity and tends to be favoured in modern practice with low slag volumes. Dolomite or magnesian limestones are also used in some countries for economic reasons.

Blastfurnace slag issues from the blastfurnace as a molten stream at a temperature of 1400–1500°C. Its conversion into products suitable for various uses depends on the subsequent processing; widely different products are obtained according to the kind of process used in cooling the molten slag.

- Aggregate.
  When the slag is allowed to cool slowly, it solidifies into a grey, crystalline, stony material, known as 'air-cooled', 'lump', or 'dense' slag. This forms the material used in a roadstone and as a concrete aggregate. The various cooling procedures and the properties of a slag as an aggregate are discussed in chapter 16. More rapid chilling with a limited amount of water, applied in such a way as to trap steam in the mass, produces porous, honeycombed material which resembles pumice. This lightweight material is called 'foamed' slag and after crushing and grading is used as a lightweight aggregate.

- Wool.
  Slag wool is normally made by reheating old slag from a slag bank, sometimes with added silicious or other materials. The process is carried out in a cupola from which the remelted slag is tapped in a thin stream. As it issues from the tap hole it is chilled quickly by means of a jet of air, or air and steam, causing the slag to form vitreous threads which felt together into a lightweight mass. The product is an excellent thermal insulator.
- Slag for cements.
  The slag is cooled very rapidly and solidifies as a glass. The granulated slag is poured into a large excess of water ($100\,m^3/t$ of slag) or subjected to spraying jets under 0.6 MPa pressure (water, $3\,m^3/t$ of slag). After the treatment, the water content of slag ($\leqslant 30$ per cent) is largely eliminated in dryer mills or filter basins.

A newer granulation process, the pelletiser, has been developed in Canada. In this semi-dry process, the molten slag is first cooled with water, then in air by a rotary drum (300 rpm). The water consumption is $1\,m^3/t$ of slag and the residual moisture of about 10 per cent. Several fractions are obtained. The layer pellets (4–15 mm) occur as nodules with a porous structure which is partly crystalline. This expanded slag is suitable as lightweight aggregate. The smaller fraction, <4 mm, is mostly in a glassy state and is used as hydraulic constituent of blended cements.

Table 11.1 gives the world slag production and utilisation rates in 1984.[1] Traditionally, a considerable amount of the slag is air cooled. The slag utilisation rates reflect mostly the quantity of slag that is available in the granulated or pelletised form.

The extent to which slag is used in cements varies greatly between different countries. It is particularly well developed in several Western European countries and several different types of cement are produced.

- Ground slag, mixed with a suitable proportion of limestone, is used as a raw material for the manufacture of Portland cement.

Table 11.1 Annual production and utilisation of blastfurnace slag (10^6 t)[1]

Country	Production	Utilisation
Australia	4.7	0.12
Canada	2.9	0.2
China	22	16
Denmark	None	None
France	7.5	1.9
Germany	15	2.8
India	7.8	2.8
Japan	24	8.2
Netherlands	1.1	1
Norway	0.1	None
South Africa	1.5	0.6
Sweden	0.1	0.03
UK	1.5	0.25
USA	13	1

- Granulated blastfurnace slag is ground with Portland cement clinker in various proportions. Such cements form the UK and US Portland blastfurnace cements, the UK low-heat slag cement, the German Eisenportland and Hochofen cements, the French 'ciment Portland composé', 'ciment de haut fourneau', 'ciment de laitier au clinker', 'ciment au laitier et aux cendres', and analogous cements in other countries. In a Belgian development, known as the Trief process, the granulated slag is ground wet and added either as a slurry, or after drying, to the cement and aggregate in the concrete mixer.
- Granulated slag is ground with a small proportion of dead-burned gypsum or anhydrite together with a smaller addition of cement or lime. Such products are known as supersulfated cements. This type of cement is made mainly in Belgium, but also in Germany and England.
- Ground granulated slag is mixed with hydrated lime. The French and Belgian 'ciments de laitier à la chaux' and the American slag cement are of this type; it was also formerly made in Germany and in the UK, when it was sometimes known as cold-process slag cement.
- Minor quantities of granulated slags are sold for glass making, as abrasive or as sand for concrete.

11.2 Composition of blastfurnace slag

The chemical composition of slag[1 4] can vary over a wide range depending on the nature of the ore, the composition of the limestone flux, the coke consumption and the kind of iron being made. It can also change over the years with alterations in the sources and types of ore being smelted. These variations affect the relative content of the four major constituents, lime, silica, alumina and magnesia, and also the amounts of the minor components, sulfur in the form of sulfide, and ferrous and manganese oxides. Some analyses of blasfurnace slags are given in Table 11.2. In general the lime content may be in the range 30–50 per cent, silica 28–38 per cent, alumina 8–24 per cent, magnesia 1–18 per cent, sulfur 1–2.5 per cent, and ferrous and manganese oxides 1–3 per cent, except in the special case of ferromanganese production when the manganese oxide content of the slag may be considerably higher. Other minor components are TiO_2 (<4 per cent and $Na_2O + K_2O$ <2 per cent).

The chemical composition of granulated slags can be represented in the quaternary

Table 11.2 Chemical composition (per cent) of blastfurnace slags

Source	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	MnO	S
UK	40	35	16	6	0.8	0.6	1.7
Canada	40	37	8	10	1.2	0.7	2.0
France	43	35	12	8	2.0	0.5	0.9
Germany	42	35	12	7	0.3	0.8	1.6
Japan	43	34	16	5	0.5	0.6	0.9
Russia	39	34	14	9	1.3	1.1	1.1
South Africa	34	33	16	14	1.7	0.5	1.0
USA	41	34	10	11	0.8	0.5	1.3

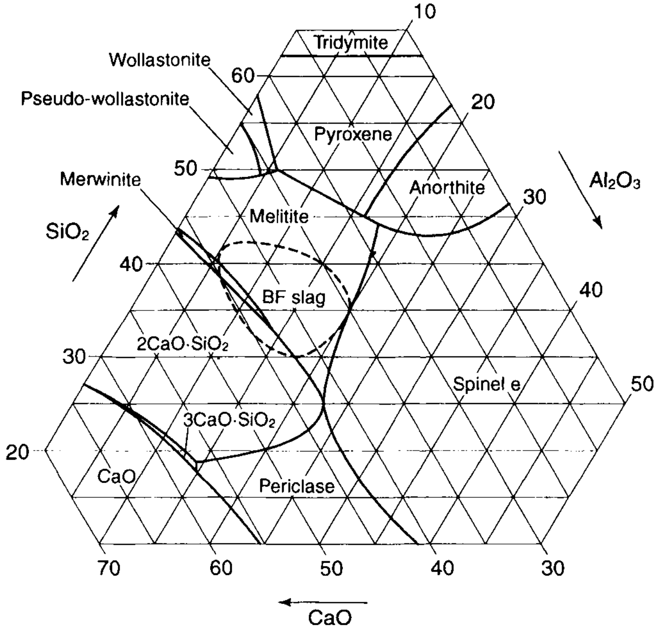

Fig. 11.1 Chemical composition of blastfurnace slags in the ternary diagram $CaO-SiO_2-Al_2O_3$ for MgO = 10% (source: Ref. 4).

diagram C-S-A-M or more easily in the ternary system C-S-A with a constant amount of MgO (Figure 11.1).[4]

11.2.1 MINERAL COMPOSITION OF AIR-COOLED SLAGS

Crystallised slags contain melilite as the main constituent (Table 11.3). Melilite is the name of an isomorphous series of solid solutions of which the two end members are gehlenite (C_2AS) and akermanite (C_2MS_2). Other minerals that may occur are C_2S (α, α', β, γ), pseudo-wollastonite (CS), rankinite (C_3S_2), merwinite (C_3MS_2), monticellite (CMS) and oldhamite (CaS). Seldom observed minor components are anorthite (CAS), forsterite (M_2S), enstatite (MS), perovskite (CaO), TiO_2 and spinel (MA).

11.2.2 CONSTITUTION OF GLASSY SLAGS

Granulated and pelletised slags can be regarded as supercooled liquid silicates. The structure of a silicate glass is approached by considering the vitreous silica in which some Si–O–Si bonds are broken and neutralised by metal cations called structure modifiers.[2-6] Silica tetrahedra are isolated or polymerised with bridging oxygen atoms (Figure 11.2).[6] Negative charges of these anionic condensed groups are neutralised by cations such as Ca^{2+} or Mg^{2+} in the cavities of the network. Calcium atoms are octahedrally coordinated to the oxygen atoms. The coordination of magnesium atoms is considered as either octahedral[6] or both octahedral and tetrahedral.[2,8] Aluminium also appears as Al^{3+}, AlO^+,[6] or AlO_4^{5-}.[2,3,7,9] Tetrahedral atoms are network formers and octahedral atoms are network

Table 11.3 Some possible assemblages of minerals from the four components CaO, Al_2O_3, SiO_2 and MgO in slags

No. of slags of 21 examined	C_2AS/C_2MS_2 solid solution	C_2MS_2	C_2S	CS	C_3S_2	C_3MS_2	MA	CMS_2	CMS	CAS_2	M_2S	MgO
5	×		×		×							
5	×			×						×		
4	×			×	×							
3	×					×	×					
2	×						×			×		
1		×					×			×	×	
1		×				×	×		×			
Other possible assemblages not observed in the 21 slags	×		×			×						
		×		×				×		×		
		×						×		×	×	
		×					×		×		×	
			×			×	×					×
						×	×		×			×

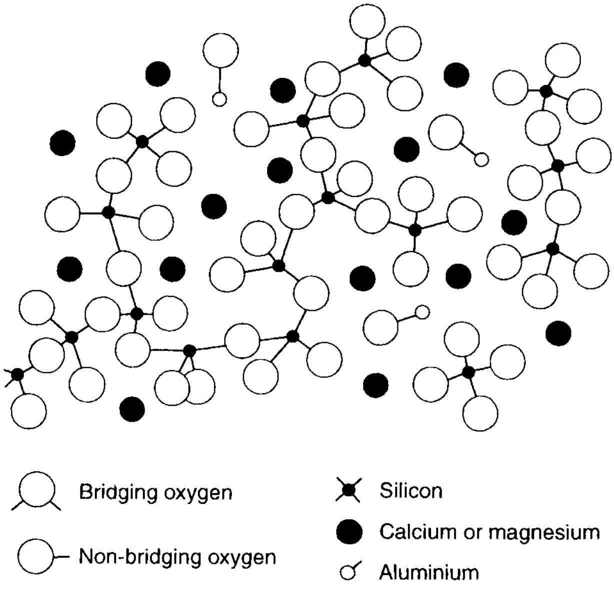

Fig. 11.2 Schematic structure of a glassy slag (source: Ref. 6).

modifiers.[4,7] As Mg is an element of the glass network, it does not appear as periclase in granulated blastfurnace slags even with high MgO contents (10–20 weight per cent).[4]

Manganese is in sixfold coordination in slags with up to 7.5 per cent MnO by weight.[10] Titanium is in sixfold coordination at up to 4 per cent TiO_2, when it becomes a network former with fourfold coordination.[7] Sulfur is incorporated homogeneously as S^{2-}. At contents of $S > 3.3$ weight per cent, sulfides start to precipitate.

The glassy part of a slag can be characterised as a large halo in the X-ray diffraction pattern peaking at 0.3 nm (Figure 11.3). The crystalline phases present are merwinite, melilite, calcite and quartz. The crystallisation of merwinite and melilite is very often dendritic (Figure 11.4). In this dendritic crystallisation the thin edges represent an initial stage of crystal formation from seeding points in the melt which has been stopped by rapid quenching.[11] Inside each dendrite and between dendrites themselves there is a glassy phase which, in the case of merwinite crystallisation is enriched in alumina[12,13] (Table 11.4). Microheterogeneities as 30–100 nm particles have been identified by small angle X-ray scattering.[14]

11.2.3 COMPOSITION REQUIREMENTS

Ordinary air-cooled slag has no, or very little, cementing properties. Granulated slag alone similarly has a negligible cementing action but, if some suitable activator is present, all except the more silicious granulated slags show marked cementitious properties. The activator may be lime, Portland cement, alkalis such as caustic soda or sodium carbonate, or the sulfates of the alkalis, calcium or magnesium. It is, of course, this property which has led to the use of the material in various forms of cement.

In general, the more basic the slag, the greater its hydraulic activity in the presence of

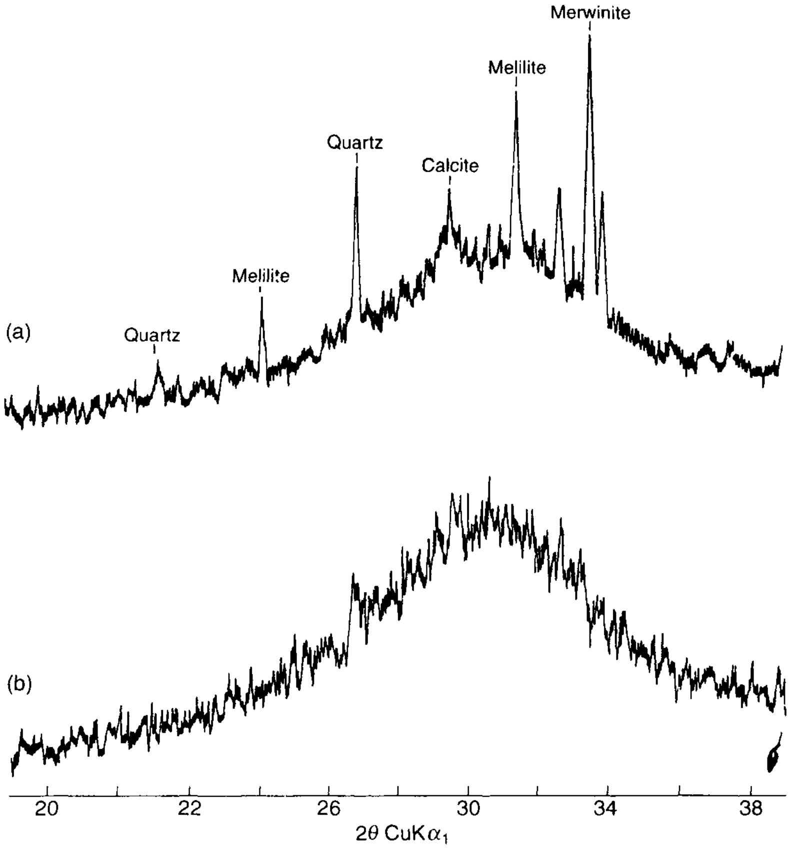

Fig. 11.3 X-ray diffraction patterns of two slags. (a) glass: halo, (b) glass + crystals: halo + peaks (source: Ref. 11).

alkaline activators. When sulfate activators are used, the basicity of the slag is not the only criterion; the slag also needs to contain at least an average or moderately high alumina content. The cause of this hydraulic activity and its relation to the chemical composition and physical state of a slag have been studied extensively, without reaching finality as yet. The glass content is a prime factor and an increase in the temperature of the molten slag when granulated promotes the hydraulicity of the product. Thus for a series of hematite slags quenched to give varying glass contents, Schwiete and Dolbor[15] obtained a roughly linear relation between strength and glass content. Increasing contents of crystalline components reduce the cementing properties though some of them may make some contribution to strength. This would be expected for α'- or β-dicalcium silicate but there is also evidence that gehlenite and akermanite may not be inert. In merwinitic slags, dendritic crystals of C_3MS_2 coexist with a more reactive glass.[12,13]

Acid–base considerations have been used to correlate the chemical composition with reactivity. Chemical indices or hydraulic moduli are numerous and have been extensively reviewed by Schröder.[2] The more common moduli used in the prediction of hydraulic reactivity of slags or compressive strengths of blended cements mortars include the main oxides of the slag C, S, A and M (Table 11.5). The best known in many countries is (C + M + A)/S. It is included in regulations, i.e. it must be $\geqslant 1.0$ in Germany or $\geqslant 1.4$ in

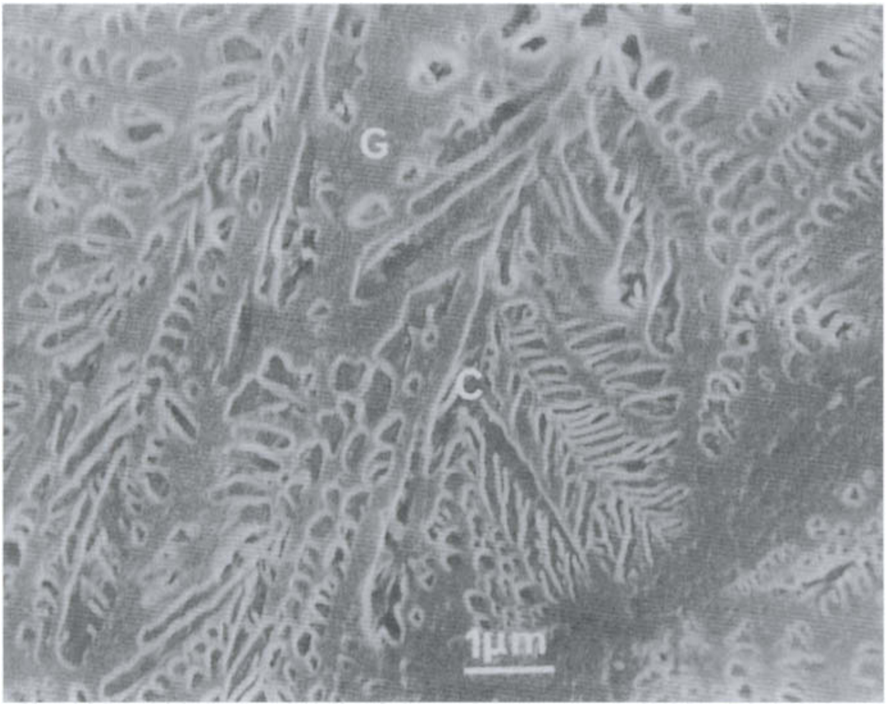

Fig. 11.4 SEM image of a polished section of slag (b) in figure 11.3: dentritic crystals C of merwinite and glass G (source: Ref. 11).

Japan. MgO has been found efficient up to 18 per cent. It has the same influence as CaO in the range up to 11 weight per cent.

Low values of moduli correspond to low hydraulic reactivity but there is not always a good correlation between the hydraulic and the mechanical strength at different ages (Figure 11.5). Some new moduli presented at the 7th International Congress on the Chemistry of Cement in Paris take into account the whole chemical analysis including minor elements, and the degree of crystallinity that corresponds to a more complicated analysis.[12]

The prediction of mechanical strength at different ages has been tried by many workers using hydraulic moduli, glass content and mineralogical composition. Kameshima and Takemura,[16] using multiple regression analysis and the ratio (Y) of measured 28-day strengths between slags cement and corresponding Portland cement, found the following relationship:

Table 11.4 Bulk chemical composition of a slag containing 35 per cent merwinite and EPMA elementary analysis of the glassy fraction[12]

	SiO_2	Al_2O_3	FeO	MnO	TiO_2	CaO	MgO	Na_2O	K_2O	S^{2-}	F^-
Slag	33.6	11.1	0.89	0.64	0.55	42.1	8.7	0.38	0.81	1.10	0.09
Glass	32.0	17.0	1.37	0.98	0.85	37.2	6.7	0.58	1.25	1.69	0.14

Table 11.5 Some hydraulic moduli of granulated slags derived from chemical analyses

Slag	1	2	3	4	5	6	7
C/S	1.31	1.26	1.22	0.95	0.93	1.30	1.34
$\frac{C+M+A}{S}$	1.88	1.88	1.79	1.63	1.39	1.98	1.92
$\frac{C+M+\frac{1}{3}A}{S+\frac{2}{3}A}$	1.52	1.57	1.51	1.32	1.15	1.55	1.41
A/S	0.43	0.36	0.34	0.41	0.34	0.51	0.45

$$Y = -73.33 + 74.06x_1 + 0.48x_2 - 2.41x_3 \tag{11.1}$$

where x_1 = basicity, x_2 = glass content and x_3 = picric acid–methanol residue after the dissolution of anhydrous compounds.

Hooton and Emery[17] determined hydraulic indices at 7, 28 and 91 days, using both glass content and chemical analysis as follows:

$$\mathrm{HI}(7) = 0.688(\mathrm{glass}) + 3.03(\mathrm{CaO}) - 7.97(\mathrm{SiO_2}) - 14.24(\mathrm{Mn}) \pm 177.1 \tag{11.2}$$

with coefficient of correlation $r = 0.943$ and standard error ± 7.4.

$$\mathrm{HI}(7) = 0.580(\mathrm{glass}) + 153.8\,\frac{C+M+A}{S} - 243.0 \tag{11.3}$$

with $r = 0.919$ and SE = ± 8.7. Performance indicators obtained at 28 and 91 days were not very suitable for predicting strengths ($r = 0.811 - 0.771 - 0.795$).

Various rapid qualitative tests have also been proposed. The refractive index of slag glasses varies from about 1.635 to 1.67, but lime-rich slags usually have an index above 1.65. There is no close correlation between activity and the heat of crystallisation of vitreous slags of differing composition. For one composition activity is related to heat of crystallisation insofar as this is a measure of the efficiency of the initial granulation. Studies

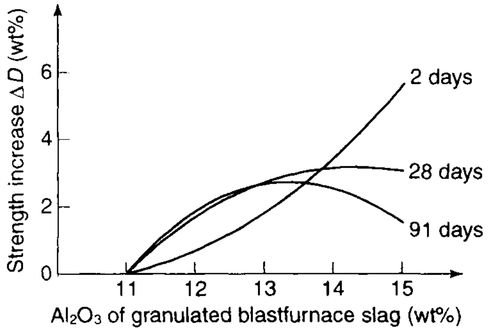

Fig. 11.5 Influence of Al_2O_3 on the development of strength for a hydraulic modulus (C + M)/S = 1.4 (source: Ref. 4).

by DTA methods on granulated slags have also failed to show any relation between the exothermic peaks observed and the hydraulic properties.[18]

Considerable use is made in Germany of a fluorescence test[19,20] as a rapid method for assessing granulated slags, though experience with UK slags indicates that it is only useful for slags produced by one particular process or even by a single furnace. In this test the sample is examined under ultraviolet light. Vitreous slag particles are claimed to emit red and pink colours whereas highly crystalline particles emit blue and violet colours. The product of the percentage of red fluorescing particles in a granulate multiplied by the CaO/SiO_2 ratio of the slag is considered to be a reliable index of hydraulic value. The fluorescence test is claimed to distinguish between glasses of different hydraulic value and therefore to be preferable to the estimation of glass, microscopically. It is evident from this test, and that used by Parker and Nurse,[117] that neither a composition modulus nor a glass content alone are sufficient to characterise the hydraulic properties of a slag and that some product of the two is required.

A chemical method for assessing the activity of granulated slags has been described by Lieber.[21] Five grams of the slag ground to a specific surface area of 3200 cm^2/g are shaken for 3 h at 80°C with 50 mL of 5 per cent NaOH solution, filtered, washed four times with 40 mL methanol and twice with 25 mL diethylether. The residue is then dried for 30 min at 60°C and the loss or ignition at 600°C was determined as a measure of the bound water. A fair relation was found between the amount of bound water and the strength developed in a 50:50 Portland cement–slag cement tested in German standard mortars (DIN 1164).

Kondo and Oshawa[22] determined the rate of hydration of slag in cement by an extraction method: 0.5 g sample is mixed in a beaker with 2.5 g of salicyclic acid, 35 cm^3 of acetone and 15 cm^3 of methanol for 1 day at room temperature. Then it is filtered and the residue is washed with methanol, dried and heated at 850°C for 10 min. The original slag sample has to be treated in the same way as a standard. Mironov *et al.*[23] and Regourd *et al.*[24] have used this method with success.

Composition moduli are convenient for the rapid control of slag quality, since regular chemical analysis of the slag is necessary in any event in the control of pig-iron production, but the only final guide is the strength developed in cements. For the purpose of assessing the contribution to strength made by the slag a 'hydraulic index' is recommended by Keil.[25] This is based on a comparison of the compressive strength at 28 days of mortars containing (I) the Portland–slag cement, (II) the same Portland cement alone, and (III) a Portland–ground quartz sand cement (sand ground to a specific surface area of 4000 cm^2/g by the air permeability method). If the strengths developed in mortars I, II and III are a, b and c respectively, and the amount by weight of slag, or ground quartz, in cements I and III is 30 per cent, then

$$\text{hydraulic index } 70{:}30 = \frac{a-c}{b-c} \times 100 \tag{11.4}$$

If the slag is non-hydraulic, its effect should be similar to the inert ground sand and the hydraulic index should be zero. If it is as cementitious as the Portland cement itself, the index should be 100. In practice the index is found to vary with the proportion of slag present in the cement and it is not necessarily the same in a 50:50 or 30:70 Portland cement–slag mix as in the 70:30 mix.

To conclude, the basicity, glass content and hydraulic moduli are not always adequate criteria.[26,27] The determination of compressive strengths of the blended cements for quality control purposes is highly recommended.[17,24,27] Such a performance test is used in the

ASTM C 989 method.[1] The Canadian Standard CAN 3-A 23.5 on slag does not require the basicity ratio.

11.3 Lime–slag cements

Cements made of mixtures of hydrated lime and ground granulated slag were the earliest of the cementitious products made from slag. They were first produced in Germany but their use spread to many other countries. In the UK production never attained large dimensions and ceased many years ago. The use of the cement has, in fact, now practically died out in most countries although some, notably France and Belgium, still retain standard specifications for the material which is used as a masonry cement. In the UK the cement was known as slag cement, or 'cold-process' cement; in the United States in the early years of the twentieth century it was sometimes known by the confusing name of pozzolan cement. It is now known there as 'slag cement' and is covered by ASTM specification C 595-68, which defines it as a mix consisting essentially of granulated slag and hydrated lime containing $\geqslant 60$ per cent slag. It is intended for use as a blend with Portland cement in concrete or with hydrated lime in masonry mortars. In Germany the term 'zement' may only be used for materials that attain the lowest grade of Portland cement; otherwise they are known as 'mischbinder' or 'schlackenbinder'. The French nomenclature is 'ciments de laitier à la chaux', while in Belgium the material is known as 'ciment de laitier'; it was also sometimes called 'tilleur' cement.

With the normal granulated slag of high lime content, ~ 10 per cent of high-calcium lime is required to give optimum results[28,29] although this figure varies somewhat according to the test criteria adopted, e.g. bending or compressive strength, or suitability for use in sulfate-bearing waters. Hydraulic lime may be used instead of high-calcium lime without affecting the strength, but a higher content of lime is needed. In practice, higher lime contents, up to 30 per cent, are used to offset the deleterious effects of carbonation during storage, which can render the cement inactive. As the slag–lime mix sets rather slowly, an addition of sodium sulfate to the extent of 1 per cent or less was sometimes made, but it had the disadvantage of producing efflorescence. A gypsum addition can be made with advantage instead of sodium sulfate. After storing in water, slag cement specimens show a strong greenish tint when fractured, and the odour of hydrogen sulfide can often be detected.

The Belgian specification (NBN 49) recognises three types of ciment de laitier called, in terms of increasing strength requirements, normal (LN), special (LS) and special 400 (LS 400). The cements must contain not less than 75 per cent of granulated slag. The French specification (P 15-306) requires a mix containing not less than 70 per cent granulated slag and a maximum SO_3 content of 5 per cent; the cement is designated as CLX 160.

Lime–slag cements have been specially used for seawater and underground foundation works because of their resistance to attack by sulfates and because of their good plasticity. Feret[28] cited as an example a breakwater at Calais which was removed after 16 years when the concrete was found to be in good condition. De Langavant[30] quotes their satisfactory use in the construction of the underground Métropolitan railway in Paris in 1900 because of their resistance to sulfate ground waters. A lime–slag cement was also probably used in the seawater jetty at Skinningrove (Yorkshire, UK) which was built about 100 years ago and is still in good condition.

The abandonment in most countries of production of this form of cement must be ascribed to its sensitivity to deterioration in storage and its low strength in comparison with modern Portland cements.

11.4 Slag as a raw material for the manufacture of Portland cement clinker

The use of slag in place of clay or shale as a raw material for Portland cement manufacture falls strictly into the chapters dealing with Portland cement, since the product obtained is a true Portland cement; it is convenient, however, to discuss it briefly here.

A slag containing 35–50 per cent lime, 30–40 per cent silica, 10–18 per cent alumina and small amounts of magnesia, and of manganese and iron oxides, is, except for its lower lime content, similar in composition to Portland cement. If mixed with the necessary quantity of limestone, its composition can be brought to that required in a Portland cement raw mix. Blastfurnace slag forms therefore a very useful raw material for the manufacture of Portland cement.

The method of manufacture is similar to that used when clay or shale are the raw materials. The slag and limestone are finely ground and mixed in the requisite proportions and burned in a rotary kiln in the usual manner. The resultant clinker often has a somewhat brownish colour, owing to the manganese oxide present, but does not differ in any other respect from the clinker obtained from a clay or shale raw mix. High-lime slags are usually preferred, since a smaller addition of lime is required in preparing the raw mix. The fuel consumption is somewhat reduced by the use of a slag–limestone mix, since a smaller amount of calcium carbonate has to be dissociated during burning. In ordinary Portland cement manufacture the heat necessary to dissociate the calcium carbonate corresponds to an expenditure of ~ 7 per cent standard coal (defined as $29\,260\,\mathrm{J.g^{-1}}$) on the mass of clinker produced.

Air-cooled lump slag is sometimes used, but it is more usual to granulate the slag. The water–granulated slag contains 10–40 per cent water and is dried in rotary driers. It is then ground and mixed with the ground limestone. Both the drying and grinding of granulated slag are relatively expensive operations. The dry process of cement manufacture is most often used, but some plants utilise the wet process, which avoids the necessity of drying the slag. In Germany the slag is used both in the manufacture of the Portland cement clinker by the dry process and for grinding subsequently with the clinker to form the Portland blastfurnace cement.

One difficulty which is peculiar to this raw material is encountered in the manufacture of Portland cement by the wet process from blastfurnace slag. A slurry containing a ground high-lime blastfurnace slag has a definite tendency to thicken and gradually set into a cake. This is due to the latent cementitious properties of the slag which thus exhibit themselves to a slight degree without the presence of any accelerator. Cases have occurred where a whole silo of a ground slag cement slurry has set into a solid mass which had to be dug out. The tendency to setting of the slurry is more marked with granulated slag than with the air-cooled form. The setting action increases rapidly with temperature and above about 36°C may become very rapid.[31] This trouble has been surmounted by the addition of a small amount of sugar which inhibits the setting of the slurry and by storing the slurry for as short a time as possible before use.

11.5 Portland blastfurnace cement

Portland blastfurnace cement is a mixture of Portland cement and granulated slag containing not more than 65 per cent of granulated slag according to BS 146:1958. In the USA, where the cement is called Portland blastfurnace slag cement, the granulated slag content is 25–65 per cent (ASTM C 595-68). In Germany two varieties are specified (DIN 1164) namely, Eisenportland cement, containing not more than 40 per cent CEM III/A, and Hochofen cement, 41–85 per cent granulated slag CEM III/B. In France (NF P15-301), ciment Portland composé can contain 6–20 per cent granulated slag (CEM II/A), 21–35 per cent CEM II/B, ciment de haut fourneau 36–65 per cent (CEM III/A), 66–80 per cent (CEM III/B) and 81–95 per cent (CEM III/C). Various grades, according to the rate of strength development, are specified in France, Germany and other European countries. In the UK and USA there is one grade corresponding to ordinary Portland cement together with a low-heat cement (BS 4246: 1974) in the UK and moderate heat and moderate sulfate-resistant cements in the USA.

The Portland cement clinker is manufactured as usual or may be made from slag and limestone and burned in the usual manner in a rotary kiln. The resulting clinker is then fed, together with the required proportion of dry granulated slag and added gypsum to control the set, to the grinding mill. The ground cement is then stored in silos and bagged in the usual way.

Though it has been usual to grind the Portland cement clinker and the slag together, they may be ground separately and subsequently mixed.[2] When ground together it is the softer material which will be preferentially ground and this is usually the clinker. With slag contents up to about 50–60 per cent, the early strength is mainly determined by the fineness of the clinker fraction and later strengths by that of the slag fraction. With cements of higher slag content the fineness of the slag is of major importance at all ages, as shown in Figure 11.6 for tests on German standard mortars (DIN 1164). In cements of lower slag content, the influence of slag fineness is to be expected to be rather less, and that of the clinker fineness more pronounced at early ages. For the same fineness of the components there seems to be little difference in strength development between interground or separately

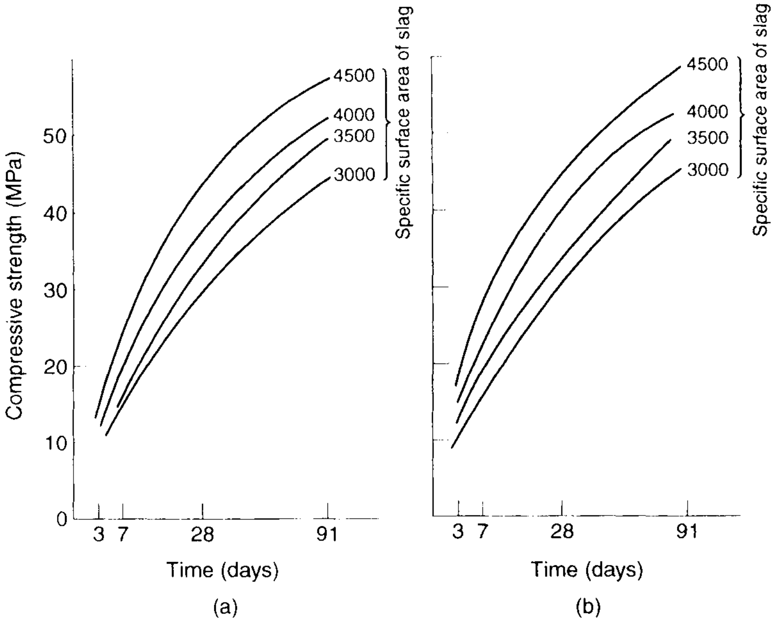

Fig. 11.6 Compressive strength of mortars: cements CEM III/B with 75 per cent slag of specific surface areas (a) 3000 and (b) 4000 cm^2/g (source: Ref. 3).

Table 11.6 Composition (per cent) of Portland blastfurnace cements

	Scotland				USA[a]		
CaO	60.90	56.83	57.34	58.15	54.97	56.32	59.36
SiO_2	23.90	24.70	24.50	24.12	26.29	25.94	24.12
Al_2O_3	8.16	9.48	8.40	8.23	8.25	7.64	6.55
Fe_2O_3	2.34	1.89	2.48	2.65	2.22	2.00	2.52
Mn_2O_3	–	–	0.44	0.25	0.33	0.40	0.10
TiO_2	0.25	0.28	0.44	0.40	–	–	–
MgO	1.50	3.22	2.55	1.85	3.76	3.69	2.31
Na_2O	0.28	0.32	0.26	0.31	0.07	0.21	0.06
K_2O	0.56	0.54	0.71	0.55	0.19	0.76	0.63
SO_3	1.32	1.36	1.41	1.97	2.39	1.67	2.07
Loss on ignition	0.73	0.82	1.62	0.15	0.48	0.94	1.97

[a] Source: Ref. 33.

ground materials or, in the latter case, between slag ground dry or wet. Separate grinding is used as an easy means of varying the slag–clinker proportion in the finished cement to meet market demands. Separate grinding of the slag is also beneficial in improving the strength developed by slags of below optimum activity (see Table 11.4).

Portland blastfurnace cement has been manufactured in the Glasgow area of the UK for over 50 years. Originally a high-lime slag was used,[32] but changes in the iron production have led to lowerlime slags being granulated. Such changes, which would normally result in a reduced strength, can be compensated by increasing the ratio of Portland cement clinker to granulated slag. Some analyses of Scottish and US Portland blastfurnace cement are given in Table 11.6.

The range of compositions of German Eisenportland and Hochofenzement is shown in Table 11.7, with the corresponding range for German Portland cements.

Portland blastfurnace cement is similar in physical properties to ordinary Portland cement and the British Standards for the two are identical in respect of fineness, setting time and soundness. The strengths required are somewhat lower than for Portland cement and are shown in Table 11.8.[3]

The cement clinker used in the manufacture of Portland blastfurnace cement is required to conform to the same composition limits as are laid down for Portland cement. The

Table 11.7 Composition range (per cent) of German Portland cement, Eisenportlandzement and Hochofenzement

Type	CaO	SiO_2	Al_2O_3	MgO	FeO[a] Fe_2O_3	MnO[a] Mn_2O_3	SO_3	S
Portland	61–68	19–24	3–7	0.7–3	1.5–7.2	0–0.2	1.3–3.0	0.0–0.1
Eisenportland	56–61	22–26	7–8	1.7–4	1.3–3.3	0.1–0.5	2.0–3.0	0.3–0.7
Hochofen	45–58	24–30	7–12	1–7	0.9–2.9	0.4–1.1	1.5–3.9	0.4–1.6

Source: F. Schröder, personal communication.

[a] FeO and MnO in Hochofenzement, Fe_2O_3 and Mn_2O_3 in Portland cement and Eisenportlandzement.

finished cement, which may not contain more than 65 per cent of slag, is required to conform to the maximum values given in Table 11.8.

The ASTM specification (C 989) places no limit on the MgO content and limits the SO_3 content to 3.0 per cent and the sulfur to 2.0 per cent. For the moderate sulfate resistant

Table 11.8 Comparison of British Standard requirements for Portland cement and ground granulated blastfurnace slag (ggbs)[34]

Requirement	OPC BS 12 CEM I	PBFC BS 146 CEM II/A,B CEM III/A	LH PBFC BS 4246 CEM III/A, B, C	ggbs BS 6699	
Slag content (%)	None	Up to 65	50–90	100	
Minimum fineness (m^2/kg)	225	225	275	275	
Minimum glass content	n/a[a]	n/a	n/a	Pure glass 40%: glassy particles 85%	
Minimum concrete compressive strength: mean of 3 cubes (N/mm^2)				CEM III/B	
Age (days) 3	13	8	3	3	70% ggbs combined with 30% OPC
Age (days) 7	-	14	7	-	
Age (days) 28	29	22	14	22	
Setting time:					
Initial (not less than) (min)	45	45	160	45	70% ggbs combined with 30% OPC
Final (not greater than) (h)	10	10	15	10	
Soundness: maximum expansion (mm)	10	10	10	10	70% ggbs combined with 30% OPC
Maximum insoluble residue (%)	1.5	1.5	1.5	1.5	
Maximum magnesia (%)	4.0	7.0	9.0	14.0	
Sulfur:					
maximum present as sulfide (%)	n/a	1.5	2.0	2.0	
Maximum present as SO_3 (%)	3.0	3.0	3.0	n/a	
Maximum loss on ignition:					
Temperate climates (%)	3.0	3.0	n/a	3.0	
Tropical climates (%)	4.0	4.0	n/a	4.0	
Chemical modulus (%): $\frac{CaO + MgO + Al_2O_3}{SiO_2}$, not less than	n/a	n/a	n/a	1.0	
CaO/SiO_2 ratio, not more than	n/a	n/a	n/a	1.4	
Maximum moisture content (%)	n/a	n/a	n/a	1.0	
Maximum heat of hydration (J/kg):					
7 days	n/a	n/a	250	n/a	
28 days	n/a	n/a	290	n/a	

[a] n/a = not applicable.

cement the C_3A content of the Portland cement used must not exceed 8.0 per cent. The strength requirements for the ordinary cement are the same as for Type I Portland cement.

The general standards require that the slag shall conform to the formula

$$\frac{CaO + MgO + Al_2O_3}{SiO_2} \geqslant 1 \tag{11.5}$$

The SO_3 content of the cement is limited to 3.5 per cent for Eisenportland cement with a specific surface not above 4000 cm^2/g and 4.5 per cent for higher specific surfaces. For Hochofen cement the corresponding limits are 4 and 4.5 per cent with the additional provision that when the slag content is above 70 per cent the limit is 4.5 per cent for any specific surface area. There is no limit to the MgO content of the cements but the Portland cement clinker used must not contain >5 per cent.

It is generally recognised that the rate of hardening of Portland blastfurnace cement in mortar or concrete is somewhat lower than that of Portland cement during the first 28 days, but thereafter increases so that at 12 months the strengths become close to, or even exceed, those of Portland cement. Table 11.9 is derived from data given by Keil[25] on the relation of compressive strength to age for German Portland, Eisenportland and Hochofen cements. These are average values for a large number of cements and have been calculated in terms of the strength of Portland cement at 28 days expressed as 100.

Portland blastfurnace cement is rather lighter in colour than Portland cement and has a slightly lower average specific surface gravity, about 3.0–3.05 as compared with 3.1–3.15. The setting time is affected by the addition of salts in a manner similar to that of Portland cement. Thus gypsum acts as a retarder while chlorides act as accelerating agents and may also increase the initial rate of hardening. Slag which has been granulated with salty water, as from tidal river water, may show this effect. The moisture movement, drying shrinkage and creep of blastfurnace cement are very similar to those of Portland cements, as is also the bond to steel reinforcement.

The heat evolution during the setting and hardening of Portland blastfurnace cement varies with the composition of the Portland cement clinker and of the granulated slag, as well as with their relative proportions. Some comparative values for Portland and Portland blastfurnace cements are shown in Table 11.10 and Figure 11.7.

Table 11.9 Relative compressive strengths of Portland cement, Eisenportlandzement and Hochofenzement

Age	7 days	28 days	3 months	1 year
Portland cement	66	100	119	135
Eisenportlandzement	61	101	–	–
Hochofenzement	50	90	114	144

Table 11.10 Total heat liberated at 108 h by five blastfurnace slag cements (CEM III/B) made with 70 per cent slag and 30 per cent ordinary Portland cement (CEM I) (see calorimetric curves in Figure 11.7)

Cement	BFC_1	BFC_2	BFC_3	BFC_4	BFC_5	OPC
$J.g^{-1}$	241	242	223	174	180	341

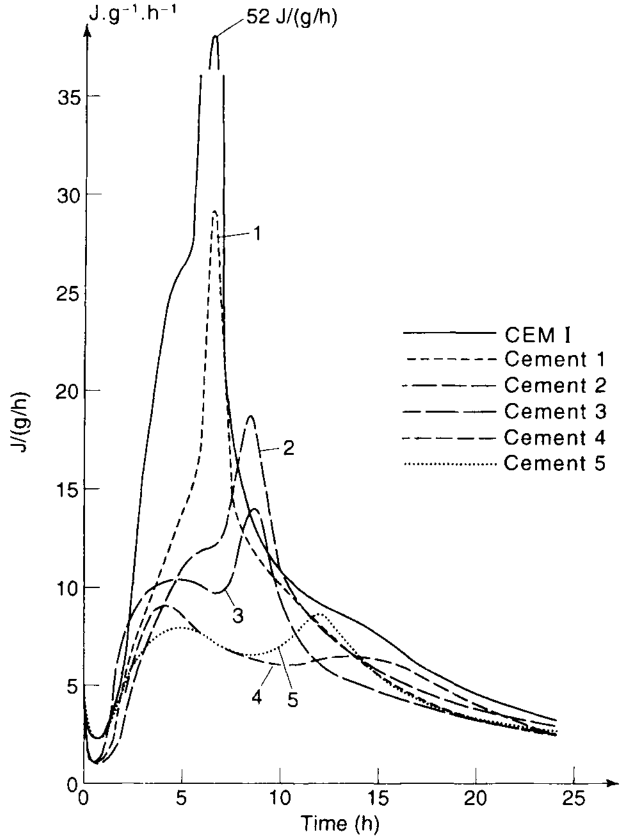

Fig. 11.7 Calorimetric curves of five blastfurnace cements CEM III/B containing 70 per cent slag and 30 per cent Portland cement CEM I (source: Ref. 24). Slag 1 is more reactive than slag 2 and reacts as early as CEM I but slag cement 1 is a low-heat cement compared to CEM I.

The British Standard for low-heat Portland blastfurnace cement (BS 4246: 1974) requires that the heat of hydration at 7 and 28 days shall not exceed 60 and 70 cal/g (251 and 293 J/g), respectively. It is determined by a modified heat of solution method. The strength requirements are shown in Table 11.8. The proportion of granulated slag must lie between 50 and 90 per cent by weight of the cement. The maximum permitted content of MgO is 9 per cent and of sulfide sulfur 2 per cent. These limits are both higher than in BS146: 1958 for ordinary Portland blastfurnace cement, reflecting the increase in knowledge. The SO_3 content is limited to 3 per cent and the insoluble residue to 1.5 per cent.

The lower heat of hydration is used to advantage in mass concrete structures to reduce the temperature rise, but it is a disadvantage in cold weather when the rate of hardening may become slow.

The effect of low temperatures in retarding strength development of Portland blastfurnace cement seems to be comparable to that of Portland cement when the water/cement ratio of the concrete is low (0.4). At water/cement ratios of 0.5 and upwards the blastfurnace cement is the more affected as is shown by the data in Table 11.11.[35] The loss in strength at low temperatures is also more pronounced in cements with slag contents approaching or above 70 per cent.

Table 11.11 Compressive strengths of 1:1.75:3.5 by volume concrete, w/c = 0.515, expressed as percentages of the values at the same age for samples stored at 17°C

Age	Portland				Portland blastfurnace				Supersulfate			
	8°C	6°C	4°C	2°C	8°C	6°C	4°C	2°C	8°C	6°C	4°C	2°C
3 days	86.7	66.7	40.3	18.6	37.4	21.5	12.1	10.3	35.9	25.7	24.3	23.3
7 days	83.2	74.5	58.5	49.7	54.7	52.3	39.0	30.8	67.5	48.2	36.6	34.2
28 days	85.5	79.0	76.1	68.2	62.5	61.8	60.0	53.2	75.9	76.0	63.3	60.5
1 year	95.5	92.5	85.8	82.4	76.5	74.5	73.6	69.4	100.0	90.0	84.5	78.9

Since Portland blastfurnace cement often shows a somewhat lower strength at early ages at normal temperatures than Portland cement, the reduction in rate of strength development at low temperatures can be correspondingly more troublesome.

Steam curing can be used to accelerate the development of early strength of Portland blastfurnace cements, as with Portland cements. Some data[36] obtained on Belgian rapid-hardening blastfurnace and Portland cements and on supersulfated cement concretes are given in Table 11.12. The immediate gain in strength of Portland blastfurnace cement is somewhat greater than with Portland cement and the loss in strength at 28 days is lower.

Table 11.12 Effect of steam curing on strength of Portland blastfurnace cement, Portland cement and supersulfated cement

Pre-steaming period hours	Period of steam curing at 80°C	Portland blastfurnace cement		Portland cement		Supersulfated cement	
		w/c 0.40	0.45	0.40	0.45	0.40	0.45
		Compressive strength as percentage of strength after 48 h normal curing					
0	4	65	48	49	67	41	38
	6	95	76	72	80	50	41
	12	145	131	75	92	54	46
8	4	113	87	81	87	51	39
		Compressive strength at 28 days as percentage of strength after 28 days normal curing					
0	4	78	86	70	64	60	52
	6	82	92	70	75	53	49
	12	98	94	80	77	48	43
8	4	104	101	84	84	56	43
Normal curing		*Compressive strength (MPa)*					
	24 h	11.5	14.2	24.1	17.7	10.0	10.3
	48 h	33.6	34.1	41.1	35.4	22.5	27.7
	28 days	54.9	56.6	63.1	59.8	38.5	45.1

Concrete 1:1.75:3.5.

Table 11.13 Effect of steam curing on strength of US Portland blastfurnace cement and Portland cement

		Compressive strength (MPa)			
Curing	Cement	1 day	3 days	7 days	28 days
4 h at 23°C 16 h in steam at 71°C Then at 23°C	Portland blastfurnace cement	27.6	30.7	32.4	42.7
	Portland cement	25.5	27.9	30.7	39.3
23°C	Portland blastfurnace cement	9.0	18.6	28.6	44.8
	Portland cement	10.0	23.1	32.4	44.8

Concrete w/c = 0.42.

Supersulfated cement is adversely affected by curing in steam at atmospheric pressure above 50°C. Tests on US Portland blastfurnace cements shown in Table 11.13, give a broadly similar pattern.

11.5.1 TRIEF PROCESS

A modification of the usual process for making blastfurnace cement was introduced in Belgium by V. Trief[37] and has become known as the Trief process. In this process the slag, after granulating, is ground wet and stored as a wet slurry. It is kept as a separate constituent until the concrete is being mixed in the concrete mixer, where the Portland cement, slag slurry and aggregate are added together. The advantages claimed are a saving in fuel for drying the slag and a greater efficiency of grinding in the wet state, so that a ground granulated slag of much higher specific surface area than would be the case with dry grinding may be obtained for the same power consumption in the mills. With the finer slag, good strengths can still be obtained with low proportions of Portland cement and in the application of the Trief process only 30 per cent or less of Portland cement is commonly used. In a further modification the slag is ground wet to a high fineness and then dried and bagged so as to adapt the process to conditions which do not permit the grinding of the slag at, or near to, the place of use.

It is clearly essential that the slurry should remain inactive during the period of grinding and storage. Experience has shown that this is so, providing the temperature of the slurry does not rise too high. Slurry temperatures of 40°C do not cause the slurry to begin setting and hardening, but at 70°C the slurry is unstable.[38] Badly granulated high-lime slags may also act as activators and cause the slurry to set. Difficulties can also arise from sedimentation of the slurry, which contains about 30 per cent water, leading to the formation of a stiff paste.

The Trief process has been used for the manufacture of concrete products in Belgium and also for the construction of dams, for example at Bort-les-Orgues[39,40] in France and the Cluanie[41] and Avon dams[42] in the UK.

An increase in the fineness of a granulated slag increases its activity as is indicated by the data[43] in Table 11.14. This shows the compressive strengths of 1:2:4 concrete made with cements composed of 30 per cent Portland cement and 70 per cent granulated slag, somewhat low in lime (hydraulic modulus I = 1.0), the latter being ground to various finenesses.

The strength at 1 or 3 days of Portland cement–granulated slag mixes with Portland cement contents of 30 per cent or less is often very low and very fine grinding does not

Table 11.14 Effect of slag fineness on strength of concrete

Specific surface area (air permeability) of slag (cm^2/g)	Compressive strength (MPa)				
	1 day	3 days	7 days	28 days	90 days
3095	0.72	2.48	5.90	16.96	27.23
3930	0.88	2.88	8.41	21.79	32.34
4850	1.05	3.60	10.58	24.82	36.34
6140	1.19	4.87	12.48	27.06	39.09
100 per cent Portland cement	6.31	16.65	24.20	34.13	43.92

30:70 Portland cement:slag in 1:2:4 (vol.) gravel concrete, w/c = 0.55, water stored.

compensate for this. Accelerators such as NaCl or $CaCl_2$ give some improvement. The former was used at the Bort dam and the latter at the Cluanie and Avon dams. Parker and Ryder[43] have observed that a much greater increase in strength can be obtained by using air-cooled slag aggregate in the concrete with this type of cement, as shown in Table 11.15.

11.5.2 TERNARY CEMENTS

Cements composed of Portland cement, granulated slag and pulverised-fuel ash (called 'ciment au laitier et aux cendres') are manufactured in France.[44,45] They contain 18–30 per cent slag and fly ash (CEM V/A) and 31–50 per cent slag and fly ash (CEM V/B). They are stated to meet the strength requirements for ordinary Portland cement and to offer particular advantages in workability and chemical resistance.

11.6 Estimation of granulated slag in cement

The presence of slag in a cement can be detected by moistening a sample with HCl and noting the evolution of H_2S, recognisable by its smell. Under the microscope, granulated slag grains can be differentiated from Portland cement by differences in the refractive index, that of the slag being about 1.65–1.66 while the Portland cement particles have indices of ~ 1.70. If a small amount of a Portland blastfurnace cement on a microscope slide is moistened

Table 11.15 Early strength of Trief concrete

Aggregate	Slag fineness (cm^2/g)	Compressive strength (MPa)		
		1 day	3 days	7 days
Gravel	3930[a]	0.88	2.88	8.41
Slag	3930	3.52	9.65	16.89
Gravel	4930[a]	1.01	7.58	18.00
Slag	4930	3.79	12.55	23.79
Gravel	Portland cement[b]	6.31	16.65	24.20

30:70 Portland cement/slag in 1:2:4 (vol.) concrete, w/c = 0.55, water stored.

[a] The granulated slags ground to 3930 and 4930 cm^2/g fineness are different slags.

[b] Same Portland cement as used for the Trief concrete.

with a lead acetate solution acidified with acetic acid (the reagent is made up by mixing 2 parts of a 5 per cent lead acetate solution with 1 part of a 50 per cent acetic acid solution) and examined under the microscope, the slag grains are found to exhibit a rapid progressive brown to black coloration. The Portland cement grains do not show this change in coloration but, as some of them are brownish originally, the differentiation is not absolutely clear.

A rapid control method in manufacture when the compositions of the separate constituents are known is based on a determination of the reducing power by means of titration with $KMnO_4$. Rapid polarographic methods are also available, making use of a suitable reference component.[46,47]

Quantitative estimation when the composition of the constituents is unknown is less easy. Simple separation by sedimentation in heavy liquids, making use of the density difference between granulated slag and Portland cement, is not practicable because the finest particles do not separate owing to coagulation effects. A preliminary separation on a very fine sieve is necessary to prepare a coarse fraction. The slag content of the latter is then determined either by flotation in heavy liquids (usually assisted by centrifuging) or by planimetric measurements under the microscope.[48-50] Since the coarse fraction may differ in Portland cement/slag ratio from that of the whole sample, a check is advisable by analysis of a reference component in the original and in the coarse fraction. For this purpose sulfide sulfur[51,52] is the most obvious, being present in all slags but absent, or only present in negligible quantities in clinker. Alternatively MnO may be estimated.[53] When the separation of slag and Portland cement is not sufficiently complete the proportion of cement in the slag fraction and of slag in the cement fraction is measured microscopically. If the Portland cement/slag ratio in the coarse fraction examined is not the same as in the whole cement, a correction can be applied by estimating the content of the reference component in the slag and Portland cement fractions and in the original cement. In any event the estimation is not a precise one, but it is not usually necessary to know the slag content of the cement to within more than a few per cent to identify its type.

The coarse fraction of grain size 0.06–0.09 mm is prepared by washing with alcohol between two appropriate sieves. The prepared fraction is dried and heated in a covered crucible for 5 min at 700–800°C. For sedimentation analysis, mixtures of methylene iodide and benzene (density range 3.3–0.9), methylene iodide and acetylene tetrabromide (3.3–3.0) or acetylene tetrabromide and benzene (3.0–0.9) may be used. The density of clinker is taken as 3.2; that of slag as 2.9. In the planimetric work, the same grain size fraction is used, setting the sample for examination in Canada balsam on a microscope slide. Three slides are prepared and the measurements carried out with the aid of an integrating table or planimeter ocular on the microscope. The values obtained correspond to volume ratios and need correction to weight ratios using the approximate densities given above.

The relative accuracy of these methods has been examined by Grade,[54] who recommends that for arbitration purposes both microscopic counting of particles in a 30–40 μm sample and heavy liquid separation combined with analysis of a reference component should be used.

Other physical methods have also been recommended. Thus, when granulated slag is subjected to differential thermal analysis, an exotherm is found corresponding to the heat of crystallisation of the slag. Kruger[55] has used this effect to estimate the slag content of cements. An X-ray method for determining the proportion of crystalline material in the cement has also been described.[56] It is based on the assumption that the slag is all vitreous and the Portland cement fraction all crystalline.

All these methods have been discussed recently by Glasser.[57] For example, Luke and Glasser[58] reviewed selective dissolution methods and concluded that considerable care in execution is required and also that systematic error can occur in the presence of hydrotalcite (an hydration product containing Mg). A correction has to be applied too if the Mn content of the slag is known. Heavy-liquid separations are not always effective because minor slag and cement particles are able to agglomerate. The optical microscopy appears as the most accurate method. For the fine particles, scanning electron microscopy and backscattered electron images are very useful since grains are easily distinguished from unhydrated clinker and paste matrix.

11.7 Hydration of Portland blastfurnace cement

The hydration of Portland cement–granulated slag mixes is more complex than that of Portland cement, since both constituents react with the water. There seems little doubt that the Portland cement grains hydrate in the manner described in previous chapters. It is, therefore, necessary to consider the hydration of the slag as influenced by the calcium hydroxide liberated from the Portland cement. No hydration products can be observed when ground granulated slag is placed in water (in the absence of hydraulic C_2S). However, surface analysis by X-ray photoelectron spectrometry (XPS) showed that the slag surface was modified as soon as it came into contact with water.[59] The initial slag hydration appeared to be an incongruent dissolution and a precipitation of the hydrated silicate C-S-H.

Slag activators can be either alkaline activators, such as sodium hydroxide, lime, sodium carbonate and sodium silicate, or sulfate activators like calcium sulfates or phosphogypsum.[30] Two kinds of activators can coexist, as in Portland slag cement. The nature of the activator influences the nature of the hydrates formed. As an example, soda or sodium carbonate favours the production of brucite as the Mg-containing phase. However, brucite is not observed in the presence of Portland cement. Instead a hydrotalcite-like phase, Al–Mg silicate, is formed. Table 11.16 summarises the hydrates produced with different activators.[57]

Tanaka *et al.*[60] gave a schematic hydrated microstructure of a glassy slag in Portland cement (Figure 11.8). Glassy discs were zebra-coated with gold. After hydration, the Au-coated surface gave the position of the original slag–solution interface. These discs were embedded in Portland cement paste. The cross-section of glassy discs was then observed under scanning microsocope. The slag surface is first covered by Portland cement hydrates, then attacked by Ca^{2+} ions from the supersaturated solution, producing the 'inner' hydrate. The dissolution of Ca^{2+} and Al^{3+} ions from slag leaves a skeleton hydrated layer, which

Table 11.16 Slag reaction products in the presence of different activators[57]

Nature of activator	Crystalline phases	Comments
NaOH, Na_2CO_3, Na silicate	C-S-H, C_4AH_{13}, C_2AH_8, $Mg(OH)_2$	Some Si in C_3AH_{13}, C/S in C-S-H less than in OPC
$Ca(OH)_2$	C-S-H, C_4AH_{13}	C_2AH_8 absent
Sulfate, e.g. gypsum, hemihydrate, phosphogypsum	C-S-H, AFt, $Al(OH)_3$	S in slag acts to some extent as an autoactivator
Cement	Various: C-S-H, AFm, AFt, hydrogarnet, hydrotalcite-like phase; also, vicatite, ($C_3S_2H_3$)	Not all these phases are likely to be encountered in the same paste

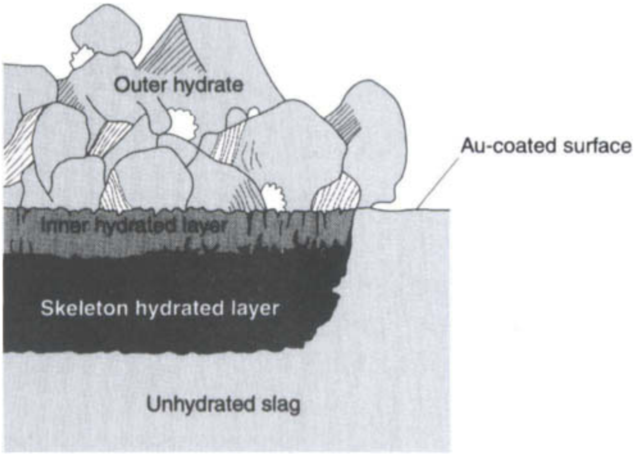

Fig. 11.8 Distribution of slag hydrates in a cement paste (source: Ref. 60). The original surface of the slag disc is Au-coated.

transforms gradually into inner hydrate by the supply of Ca^{2+}. Under the microscope, the inner hydrate appears crystallised and dense. The skeleton hydrate is a porous solid containing equant grains of type III C-S-H. The elemental distribution shows that the Ca/Si ratio increases and Al decreases from the skeleton to the outer hydrate. There is a restricted mobility of Mg^{2+} ions which are found at higher concentrations in the skeleton hydrate than in anhydrous slag and inner hydrate.

A zonation was also observed by Rajaokarivony-Andriambololona *et al.*[61] on a synthetic glass similar to blastfurnace slag (SiO_2 = 33.5 per cent, Al_2O_3 = 12.5 per cent, CaO = 42.1 per cent, MgO = 10.0 per cent). Experiments were carried out at 40°C from 4h to 150 days in an alkaline solution of 0.1 N KOH (pH = 12.9). After reaction the glass surface was studied by XPS and then observed by SEM and TEM on ultrathin sections (50 nm thick) cut perpendicularly to the superficial hydrated layer developed on the glass surface. At 150 days, three distinct zones are observed in the hydrated layer (Figure 11.9): (1) an internal fibrous layer corresponding to the residual glass coexisting with some lamellae, (2) a lamellar layer of hydrotalcite-like composition marking the initial glass–solution interface, and (3) an outer layer composed of granular C-S-H (C/S = 0.5–1.4) covered by aluminosiliceous lamellae and carbonates. Two main processes appear to be involved: (1) nucleation growth which concerns calcium silicates, C-S-H and carbonates, and (2) restructuring of a residual Si–Al hydrated glass by fixation of Ca and Mg.

The same type of zonation was noted by Barker[62] in cements blends with Portland cement as activator and at room temperature. Electron microscopy and EDAX have identified intimately mixed C-S-H and AFm, and hydrotalcite.

Feng *et al.*[63] studied slag cements with 40 and 50 per cent slag. They observed the formation of a gel-like layer around slag grains, which is more dense than the Portland hydrates and with a higher silica content. It was called inner slag hydrate (ISH). The composition and microstructure are modified with time. Mg is more concentrated than in the slag, while Ca, Si and Al are lower. Incipient crystals of a hydrotalcite-like phase appear in the outer hydrated zone, which is decorated by a precipitate rich in Fe, Ti and Mn. At the anhydrous slag interface, the ISH is less structured and in constant exchanges with the glass. In large grains, the glassy slag is replaced after 885 days' hydration by a 'rhythmically

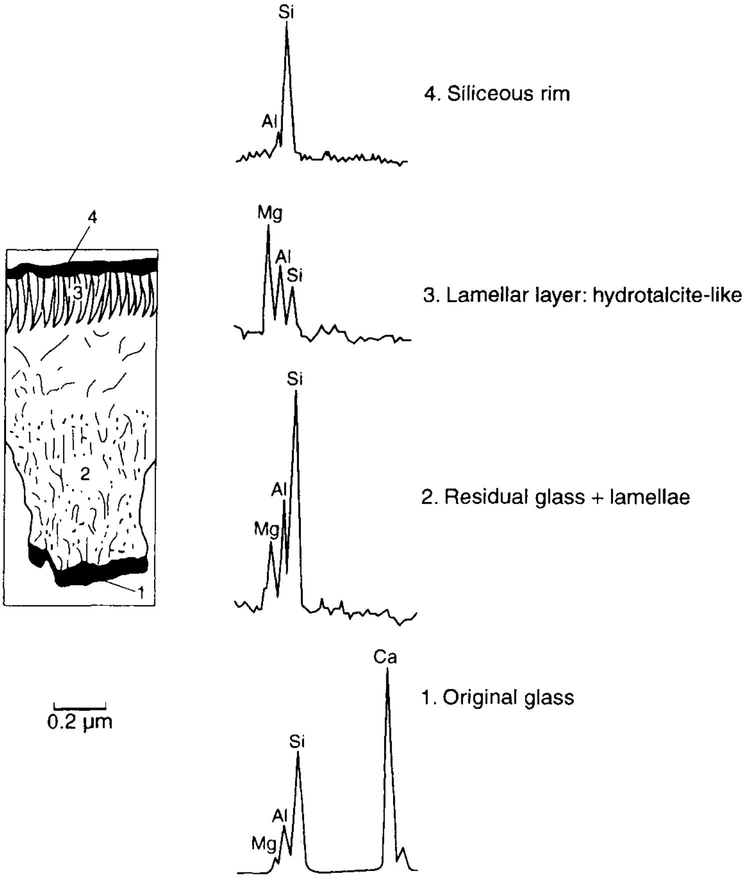

Fig. 11.9 TEM-EDS traces of an ultrathin section of a blastfurnace slag after 30 days in KOH solution (source: Ref. 61).

repeating pattern of zones'. Glasser[57] interprets this periodic structure as Liesegang rings formed when an aqueous solution is in contact with a gel. This theory can be applied to the slag in contact with the hydrated Portland cement paste. From the early hydration, slag grains are surrounded by an impermeable membrane. In the gel there occur ionic diffusion and precipitation of crystalline phases in a zonal structure.

Compared to Portland cements, blastfurnace slag cements show differences in total porosity and pore size distribution. As reported by Uchikawa,[64] at early ages a slag cement exhibits the same porosity as that of Portland cement. At later ages, when the slag has reacted, the volume of pores in the 3–5 nm size range becomes larger. From porosity measurements using the mercury intrusion process and after repeated intrusions following mercury removal by distillation, Feldman[65] concluded that in blended cements the pore structure is characterised by relatively large but discontinuous and thin-walled pores. As this characteristic was the same for slag and fly ash cements, Feldman related the pore structure to the CH content. Continuous capillary pores in Portland cements pastes should be due to deficient CH/C-S-H interfaces. In cement blends the amount of CH is lower; when it is < 7 per cent, the same pore size distribution is obtained for slag and fly ash cements.

Table 11.17 Chemical analyses of pore solutions extracted from high-alkali cement mortars[67]

	Concentration equivalents/L (N)				
Age (days)	Ca^{2+}	Na^{+}	K^{+}	$Na^{+} + K^{+}$	OH
15	0.001	0.22	0.55	0.77	0.73
49	0.002	0.24	0.59	0.83	0.77
70	0.000	0.22	0.57	0.79	0.75
149	0.002	0.23	0.60	0.83	0.80
585	0.000	0.24	0.58	0.82	0.78

The particularly low permeability of slag blends has been related to chemical migrations by Feng *et al.*[63] By analysing the initial slag and cement, and the hydration products, these workers calculated the changing mass balances. Chemical imaging for Mg, which is rather immobile compared to Al, Ca or Si, was used as an analytical marker. Chemical transport from the slag results in a higher porosity in the residual glass. In hydrates, the pores are concentrated on isolated sites distributed homogeneously in the densified paste. If the total porosity does not change, the redistribution of pore space results in a lower permeability.

Blended cements behave differently regarding the pore solution. Longuet *et al.*[66] were the first to analyse pore solutions derived from hardened cement pastes up to two years old. At 1 day hydration an ordinary Portland cement (CEM I) pore solution can be considered as an alkali hydroxide solution (Na^{+}, K^{+}, OH^{-}) containing traces of calcium, sulfate and silica ions. Table 11.17 gives the composition of pore solutions extracted at long times by Barneyback[67] from mortars prepared with a CEM I containing 0.9 per cent Na_2O equivalent, with about two-thirds of the total being K_2O, and a water/cement ratio of 0.5. The pore solution remains an alkali hydroxide solution. Diamond[68] showed that at the state of equilibrium, the concentration of alkali hydroxide is a linear function of the total alkali content of the Portland cement used. The slope is almost exactly 0.7 mol/L of OH^{-} ion concentration per cent of Na_2O_{eq} in the cement. A slag cement CEM III/A containing 50 per cent slag and a CEM I, both with the same amount of Na_2O_{eq} liberate respectively 36 per cent and 70 per cent of their alkalis in the pore solution (Table 11.18).[69] Similar results were published by Silsbee *et al.*[70] who found a drop from 0.78 to 0.25 N at 28 days for a 65 per cent slag replacement of a high-alkali OPC (1.02 per cent). Canham *et al.*[71] determined the hydroxyl ion content in pore fluids of blastfurnace slag cements and found that the reduction in alkalinity at high slag replacement was not very large, i.e. 650 mmol/L for CEM I, 300–500 mmol/L CEM III/A with 40 per cent slag and 200–350 mmol/L CEM III/A with 60 per cent slag. The alkalinity was related to the Na and K content of the slag. A slag cement CEM III/B containing 80 per cent slag and produced with a CEM I at 0.99 per cent Na_2O_{eq} reduced the solubility of alkalis at 30 per

Table 11.18 Pore solutions of an OPC and a blastfurnace/slag cement (BFSC) (with a different clinker) extracted from cement pastes with w/c = 0.5 after 28 days[69]

Cement	(Na_2O_{eq}) total	(Na_2O_{eq}) soluble	(Na_2O_{eq}) rate of dissolution (%)
CEM I	1.13	0.81	70
CEM III/A, 50% slag	1.12	0.40	36

Table 11.19 Pore solutions of a Portland cement CEM I and a slag cement CEM III/B (with the same clinker) extracted from cement pastes with w/c = 0.5, stored in sealed batches at 25°C for 6 months[72]

		Pore solution		
Cement	Na_2O, K_2O (wt %)	$Na^+ + K^+$ (eq/L)	OH^- (eq/L)	pH
CEM I	$Na_2O = 0.23$ $K_2O = 1.16$ $Na_2O_{eq} = 0.99$	0.69	0.65	13.9
Slag cement CEM III/B (80% slag)	$Na_2O = 0.20$ $K_2O = 0.39$ $Na_2O_{eq} = 0.46$	0.14	0.13	13.1

cent (Table 11.19) but the pH was still high, 13.1 compared to 13.9 for OPC.[72] Longuet[33] also observed the maintenance of high pH at long periods. Table 11.20[57] from Longuet's results moreover shows a variation of Ca solubility versus alkali solubility, the enhanced solubility of Al and Si, and the presence of sulfur as S^{2-} and SO_4^{2-}.

In OPC, sulfur appears as sulfate SO_4^{2-}. The redox potential is maintained between +100 to +200 mV. Values of between −150 and −410 mV (Table 11.20) and of −400 mV[74] were obtained for blends with >70 per cent slag in which sulfur appears as chemically reduced species such as S^{2-}, S_2^{2-} and SO_4^{2-}. Vernet[75] found in hydrated slag cements the disulfur aluminate $C_3A \cdot 2CaS \cdot 10H_2O$. This definite compound consumed S^{2-} ions and decreased sulfur ions in the pore solution. Electrochemical measurements (pH, conductance, redox potential, corrosion potential and potentiometric curves) taken by Longuet[73] have shown that slag cements containing >80 per cent slag still protected the steel reinforcement as well as the Portland cements.

Slags react more slowly with water. They are more sensitive to temperature. The Arrhenius law can be applied to the hydration reactions and more particularly to the evolution of the heat of hydration.[76] For a given degree of hydration, at two temperatures T_1 and T_2, the time of hydration, t, can be related to an Arrhenius-type law as follows:

$$\frac{t_1}{t_2} = \exp \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{11.6}$$

The calculated activation energy for slag cements is higher than that of their corresponding Portland cement, i.e. 50 and 46 J.mol^{-1}, respectively (Table 11.21). Thus thermal treatment is favourable to slag cements as an effective supplier of activation energy to the hydration of slag, which can be considered as a latent cementitious material. However, all blastfurnace slags do not react in the same way. Active slags rich in alumina do not need a long period of treatment due to the excessively rapid formation of hydrated aluminate crystals.[77] This is another example of the role of alumina content, already shown in Figure 11.5, in the development of mechanical resistance.

Autoclaved treatment of elevated temperature (180°C) and pressure (2 MPa) increases mechanical strength, i.e. the chemistry is changed: tobermorite and hydrogarnet are observed in a material the denseness of which is related to the decrease of mesopores (2–4 nm).[79] Once more, there is an optimum alumina content which was found to be 9 per cent for a slag in a blended cement at 60 per cent slag, treated for 6 h.[80]

Table 11.20 Pore fluid composition of slag blends[57] CEM III/B

	Blend proportions (%)			Cure duration (months)	Pore fluid analysis (mg/kg), pH and E_h								
No.	Clinker[a]	Gypsum	Slag		Na_2O	K_2O	CaO	Al_2O_3	SiO_2	S[b]	SO_3	pH	E_h (mV)
1	19.1	4.5	76.4	11	1600	3900	Nil	16		25	70	12.9	−350
2	18.3	8.6	73.1	12	1600	3800	90	12	35	40		13.2	−150
3	19.1	4.5	76.4	24	2660	7410	0	37	45	201	470	13.8	+78[c]
4	18.3	8.6	73.1	12	2520	7160	0	40	33	158	260	13.3	−320
5	19.1	4.5	76.4	24	3990	6140	0	56	63	112	716	13.4	−318
6	18.3	8.6	73.1	24	2800	6000	20	24	32	638	Nil	13.5	−295
7	19.1	4.5	76.4	24	3890	6740	0	53	96	294	353	13.6	−293
8	18.3	8.6	73.1	24	3540	6320	0	n.d.	40	540	333	12.9	−410

[a] Paste alkali Na_2O and K_2O, respectively, weight per cent; 1: 0.20, 0.41; 2: 0.20, 0.39; 3: 0.27, 0.87; 4: 0.28, 0.79; 5: 0.50, 1.10; 6: 0.49, 1.06; 7: 0.60, 1.06; 8: 0.58, 1.02.

[b] Chemically reduced S: S^{2-}, S^0, $S_2O_3^{2-}$, etc.

[c] At 12 months, E_h was −370 mV.

Nil = below detection limits, n.d. = not determined.

Table 11.21 Activation energy of blastfurnace slag cements compared to their Portland cement equivalents

Cement	Activation energy (kJ/mol)	Ref.
OPC + 50% slag (US)	49.1	7
OPC	44.3	
OPC + 70% slag (French) CEM III/B	56.0	
OPC	42	28
OPC + 80% slag (French) CEM III/B	50	77
OPC	46	

11.8 Supersulfated cement

Cement made from granulated blastfurnace slag activated by means of calcium sulfate is known in the UK as supersulfated cement (BS 4248: 1968). In Belgium, which has been one of the main sources of commercial production, the name given is 'ciment métallurgique sursulfaté' (Belgium specification NBN 132). In Germany the material is known as 'sulfathüttenzement' (DIN 4210).

The cement is made by grinding a mixture of 80–85 per cent granulated slag, 10–15 per cent anhydrite or hard-burned gypsum, and ~5 per cent Portland cement; the product is ground more finely than is characteristic of Portland cement. The British Standard requires the content of granulated blastfurnace slag to be not less than 75 per cent, MgO not greater than 9 per cent, SO_3 not less than 4.5 per cent, sulfur other than that present as SO_3 not

Table 11.22 Compositions of supersulfated cements (per cent)

	Belgian			German	UK				
No.	305	558	586	550	335	585	613	628	629
CaO	45.41	44.71	44.45	41.40	45.23	41.52	41.01	41.67	42.26
SiO_2	27.00	25.88	28.56	25.47	24.40	30.52	28.89	30.39	29.74
Al_2O_3	11.93	11.86	12.38	13.30	13.04	13.79	13.85	14.04	13.74
Fe_2O_3	1.07	0.80	0.95	0.54	0.64	1.18	0.93	0.81	0.83
Mn_2O_3	1.18	0.76	0.81	0.73	0.75	1.18	0.95	1.01	1.08
TiO_2	0.50	0.48	0.60	0.83	0.57	0.56	0.52	0.48	0.51
MgO	2.61	3.63	3.69	6.75	3.34	3.75	3.64	3.56	3.38
Na_2O	0.34	0.29	0.42	0.63	0.47	0.27	0.28	0.33	0.34
K_2O	0.75	0.54	0.52	0.65	0.79	1.03	1.14	1.06	1.08
SO_3	6.72	7.80	5.65	8.53	7.57	5.29	5.76	5.04	5.37
S (sulfides)	0.84	0.96	0.98	1.41	1.07	0.98	0.98	1.01	1.00
P_2O_5	–	0.25	0.32	0.10	–	0.09	–	–	–
Loss on ignition	1.00	0.22	0.14	0.49	2.35	0.17	0.85 (gain)	1.36 (gain)	1.23 (gain)
Total[a]	98.93	97.70	98.98	100.13	99.69	99.84	98.95	100.40	99.33

[a] Totals less O for S. Ignition gains excluded from totals.

more than 1.5 per cent and insoluble residue not greater than 3 per cent. The specific surface area must be not less than 4000 cm^2/g. The German Standard requires a minimum content of 75 per cent slag and 3 per cent SO_3, and a maximum content of 5 per cent Portland cement or other alkaline activator. The slag must contain at least 13 per cent Al_2O_3 and conform in composition to the formula

$$\frac{CaO + MgO + Al_2O_3}{SiO_2} \geqslant 1.6 \tag{11.7}$$

A moderately high alumina content is usually preferred in the slag used. Keil gives values of 15–20 per cent but cements are made satisfactorily with slags of rather lower alumina content. Blondiau[81] has suggested that the CaO/SiO_2 ratio should be between about 1.45 and 1.54 and the SiO_2/Al_2O_3 ratio between 1.8 and 1.9. Keil and Gille[82] recommended a modulus of at least 1.8 and preferably 1.9 or higher as calculated by modulus III:

$$\frac{CaO + CaS + \frac{1}{2}MgO + Al_2O_3}{SiO_2 + MnO} \geqslant 1.5 \tag{11.8}$$

Some typical cement compositions are shown in Table 11.22.

The standard strength requirements for supersulfated cement required by the British Standard are (MPa):

	3 days	7 days	28 days
Method 1 (vibrated mortar cubes), w/c = 0.4	13.8	23.4	34.5
Method 2 (concrete cubes), w/c = 0.55	6.9	16.6	25.5

The expansion in a modified le Chatelier test for soundness in which the test specimen is immersed in cold water (19°C) for 24 h must not exceed 5 mm. When a low-heat cement is specified, the heat of hydration determined by a modified heat of solution method must not exceed 60 and 70 cal/g (251 and 293 J/g) at 7 and 28 days, respectively. The initial setting time must not be less than 45 min and the final setting time must not exceed 10 h, the same as for Portland cement. Some typical physical properties of supersulfated cement are shown in Table 11.23.

Table 11.23 Physical properties of supersulfated cements

		British			Belgian		German
Specific surface area (cm^2/g)		5055	4930	–	4980	4150	3340
Compressive strength of vibrated mortar cubes (MPa)	1 day	2.4	2.0	3.9	6.7	6.4	12.2
	3 days	16.4	16.8	17.3	30.5	32.9	15.7
	7 days	28.3	27.6	36.1	48.5	44.8	43.9
	28 days	45.8	45.4	55.4	65.7	63.7	59.0
Compressive strength of concrete, 1:2:4, w/c = 0.6, water stored (MPa)	1 day	4.0	3.0	2.8	4.9	0.6	2.4
	3 days	9.5	10.0	7.0	17.1	4.7	10.3
	7 days	18.1	16.8	15.6	28.9	16.5	23.7
	28 days	31.0	30.2	35.4	36.5	38.1	41.4

Supersulfated cement, like high-alumina cement, combines with more water on hydration than does Portland cement. The curve for strength versus water/cement ratio has been reported to be unusually flat. The strength falls off more rapidly than with other cements as the aggregate content of the mix is increased, so that it is not desirable to use mixes much leaner than 1:2:4. The cement is rather more sensitive to deterioration during storage than Portland cement, owing to the effects of carbonation; the setting time is lengthened and the early strength is very seriously affected. Cement that has deteriorated in this way can be restored by the addition of 1 per cent hydrated lime.[83] Supersulfated cement has a low heat of hydration, about 166–188 $J.g^{-1}$ at 7 days and 188–209 at 28 days. The rate of hardening increases with temperature up to about 40°C and the cement has been used in tropical climates. At higher temperatures its strength drops seriously and a similar effect is found on curing in high-pressure steam or in steam above 50°C. This fall in strength is ascribed to the dehydration, or decomposition, of calcium sulfoaluminate. Because of its high sulfate resistance, the cement has been particularly used below ground, although it is also used for structures above ground. In the latter case, care needs to be taken in the initial curing stages to keep the surface damp, otherwise there is a tendency for it to become friable or dusty. Alternatively, the shuttering should be left in place as long as possible or a curing compound applied. The depth of this friable layer does not increase progressively with time. According to Keil,[83] the chances of it occurring can be reduced by increasing the Portland cement content of the cement.

Supersulfated cement is resistant to a variety of aggressive agents, although there may be some variation with the slag composition. Blondiau[84] found a satisfactory behaviour during test periods of up to 3 years in contact with saturated gypsum solution; natural ground waters, strongly sulfated, of the Liège area; $MgSO_4$ solution (20 g/L); $Al_2(SO_4)_3$ (20 g/L); $(NH_4)_2SO_4$ (5 g/L); humic acid (2 g/L) in the presence of $MgSO_4$ (20 g/L) and NaCl (30 g/L); and artificial and natural sea water. Good resistance was also shown against HCl (5 g/L) and also to linseed oil, an agent which damages both Portland cement and Portland blastfurnace cement.

Other tests[85,86] have shown the cement to be resistant to calcium and sodium sulfates, and to be slightly affected by magnesium sulfate, at a concentration of 350 parts SO_3 per 100000, but to be more severely attacked by ammonium sulfate of this concentration. The resistance to sodium and calcium sulfates can be attributed to the absence of calcium hydroxide and the fact that part of the alumina is already combined in ettringite in the set cement. Magnesium sulfate has a more severe action because it also attacks the C-S-H hydrate and decomposes ettringite. There is evidence that supersulfated cement concrete of good quality will resist acid conditions with or without the presence of SO_4^{2-} ions down to a pH of about 3.5. It has also proved serviceable in some conditions of use, e.g. floors, when exposed to mineral acids of lower pH values. Both in practice and in laboratory tests, the results obtained under these more acid conditions will depend on the extent to which the strength of the acid in contact with the concrete is maintained and on how long coatings of reaction products can give some protection. Thus in laboratory tests with stagnant solution, the concrete showed a good resistance to 0.25 per cent sulfuric acid up to 2 years and then lost strength.

The cement is also resistant to weak concentrations of organic acids (e.g. <0.5 per cent), such as lactic, acetic, citric and tartaric acids, and phenols and cresols. Stronger solutions, such as 1 per cent, cause damage.[87] Chlorides and alkali hydroxides and carbonates seem to have no action.

Supersulfated cement has been used in harbour and breakwater construction on the

Belgian coast, and it was also included in the Belgian seawater trials showing a generally good performance.

11.8.1 HYDRATION

The initial setting and hardening of supersulfated cement is associated with the formation of calcium sulfoaluminate from the slag constituents and the added calcium sulfate.

The formation of the high-sulfate form of calcium sulfoaluminate (ettringite) does not take place readily in saturated lime solution and the monosulfate tends to be formed as an unstable phase; neither can ettringite be formed in water when no calcium hydroxide is present. The addition of Portland cement to the cement is required to give the correct alkalinity to enable the ettringite to be formed. Blondiau found the most favourable concentration to be ~0.2 g CaO/L in the liquid and later workers[88,89] indicate a range from 0.15 to 0.5 g CaO/L. Combination of lime by carbonation leads to a CaO concentration in the solution which is too low and this accounts for its deleterious effect. An excessive addition of Portland cement, giving a saturated lime solution, results in low strengths. In manufacture hydrated lime can be used, in a smaller proportion, in place of Portland cement, but the latter is rather less sensitive to carbonation and is therefore preferred.

Examination of the set cement by X-ray and DTA methods has shown that the main hydration products are ettringite and a tobermorite-like phase.[90-92] The ettringite has been detected after a few hours hydration and the tobermorite-like phase after 1 day. The ettringite phase develops rapidly and seems to reach a maximum within 3–7 days. The early strength seems, therefore, to be largely attributable to ettringite formation, but the development of strength from about 3 days onwards must come from the increasing formation of the C-S-H. There is less certainty about the extent to which, and at what stage, the monosulfate form of calcium sulfoaluminate is produced. Blondiau and Blondiau[93] had earlier suggested that it was formed during the first few hours when the CaO concentration in the solution was high, and that as the lime in solution became depleted by this reaction, the reserves being small, the formation of ettringite set in. It has not been detected at this stage, but Smolczyk[90] was able to identify it in the set cement at 7 days. Whether it is formed directly or by decomposition of ettringite, as D'Ans and Eick[94] suggested, is still not clear, though it may be questioned if a change between two compounds of such different molecular volume could occur without some marked effect on strength. The amount of sulfur trioxide in a supersulfated cement is sufficient only for conversion of about a quarter of the alumina to ettringite, so the excess must be present in other forms, either hydrated or unhydrated. Even formation of the monosulfate still leaves substantial excess alumina. From consideration of the phase equilibrium in the system $CaO-Al_2O_3-CaSO_4-H_2O$, D'Ans and Eick[94] deduced that hydrated alumina must be a product of the hydration and considered that the final product is a mixture of the two forms of calcium sulfoaluminate and hydrated alumina together with a hydrated calcium silicate. The hydrated alumina has not been detected by X-ray diffraction but it would be expected to be amorphous. Some of this missing alumina is probably present in the C-S-H phase. The ettringite formed is probably not the pure compound. First, ferric oxide may substitute for alumina and, second, Nurse[95] has advanced evidence that the phase in supersulfated cement contains some $Ca(OH)_2$ substituting for $CaSO_4$.

11.9 Utilisation of slag cements

When cements of the Portland blastfurnace type were first introduced, they met with considerable suspicion and opposition and the literature of 100 years ago contains many articles condemning them. The suspicion was not without foundation, since some manufacturers had ground air-cooled or even dusted slag with Portland cement, and such additions were correctly regarded as a valueless adulteration. The same opinion was advanced in regard to granulated slags and it was only gradually, as experience was gained and it became understood that only glassy granulated material could be used, that their cementing qualities became generally accepted. The fear was also expressed that the sulfide sulfur present in granulated slag would oxidise, causing expansion of a concrete and corrosion of any reinforcement. It was only after years of use and the results of many tests that these suspicions were shown to be groundless.

The addition of granulated slag to Portland cement was first introduced in Germany in 1892, but despite the advocacy of Michaelis and Passow, its industrial development was delayed. By 1901, however, the manufacture had sufficiently developed for Eisenportland cement to become an accepted name and for the German Association of Eisenportland Cement Manufacturers to be formed. Hochofen cement was first made in 1907. By 1930 Eisenportland cement production had reached 550000 t per annum and Hochofen cement 460000 t. By 1961 these figures had risen to 4.2 and 3.2 million tonnes respectively, together with 8000 t of supersulfated cement. By 1984 the production of slag was 15 million tonnes and the utilisation 2.8 million tonnes.

The history of cements of these types in other countries followed much the same course as in Germany. The extent of their manufacture now depends primarily on economic factors and the availability of suitable slags in sufficient proximity to sources of Portland cement clinker. In the UK manufacture is limited to the Glasgow and Lincolnshire areas, but it is much more widespread in Belgium, France and other European countries including the former USSR. There is a large production in Japan and a significant one in the USA.

For many years after the first introduction of the Portland blastfurnace type of cement in Germany, their use was restricted to seawater work, foundations, and other structures in which the concrete was not in contact with air. It was considered that while blastfurnace cement hardened excellently under water or in damp conditions, it was uncertain that in air the strength development would be so satisfactory. In 1915–16, however, an official decree was issued in Germany placing blastfurnace cement on the same footing as Portland cement. This decree followed as a result of a series of tests which showed that the blastfurnace cement developed strengths either in air or water, and in rich or lean mixes, which were equal to those given by Portland cement, and after it had also been established by extensive investigations by the German Reinforced Concrete Committee that reinforcement in concrete made with blastfurnace cement did not behave any differently from that in Portland cement concrete.[96] Tests carried out at the Berlin Material-prüfungsamt showed that the protection against corrosion afforded to embedded steel by blastfurnace cement was as good as that given by Portland cement and that there was no objection to its use for reinforced concrete structures. This conclusion has been confirmed by many subsequent investigations and observations on the conditions of concrete structures made from slag-containing cements. It has also been found[97] that no difference in the susceptibility to corrosion of prestressing wires in Portland or Portland–slag concretes could be detected. Much of the earlier opposition to slag cements was based on the supposition that instability might be caused by the presence of sulfides in the slag. Gutt and Hinkins[98] showed that most of the sulfide in slag cement concrete disappeared after 1 year without causing any expansion or instability. Cements containing more sulfide than is permitted in the British Standard were stable in the ASTM autoclave soundness test. A recent structure made with blastfurnace slag cement (65 per cent) is the prestressed post-tensioned concrete bridge over the river Rhine at Cologne in Germany.[5]

Blastfurnace type cements have now long been used in many countries for general building work, including reinforced concrete, for water-retaining structures and for precast products such as concrete pipes. They develop strengths comparable to Portland cement but require more careful handling at low temperatures when the rate of strength development is depressed rather more than that of Portland cements unless the water/cement ratio is low. As in Portland cement concretes, the air content has the greatest influence on freeze–thaw resistance. An increase in critical factor spacing of the air void system with high slag content has been observed by Fagerlund[99] and Pigeon and Regourd.[100] For mixes with <65 per cent, the behaviour of mortars and concretes was found to be good. Further, the reduced diffusivity for chlorine ions (Figure 11.10), already shown by Smolczyk,[4] increases the salt resistance of concrete.[100] The expansion with alkali-reactive aggregates is considerably lower than that with Portland cement of similar alkali content.[33,101,102] Tests conducted by Smolczyk,[103] Bakker,[104] Oberholster and Westra[105] and Nixon and Gaze[106] show that the expansion due to alkali–silica reaction decreases in relation to the slag content. Using a slag containing 0.45 per cent Na_2O_{eq} but 0.12 per cent Na_2O_{eq} as water-soluble alkalis, Spellman[107] found with a Portland cement at 1.15 per cent Na_2O_{eq} a beneficial effect of slag on the expansion of mortar bars (ASTM C 227 test and pyrex glass). The expansion was <0.1 per cent in blends with 50 per cent slag (Figure 11.11). The German regulation regarding the permitted amount of alkalis in cement when the aggregates used in concrete are potentially reactive increases the limit of Na_2O_{eq} from 0.6 per cent for Portland cement to 2 per cent for blastfurnace cement with an addition of 70 per cent slag (Table 11.24).

The claim has always been made for Portland blastfurnace cement that it is more resistant

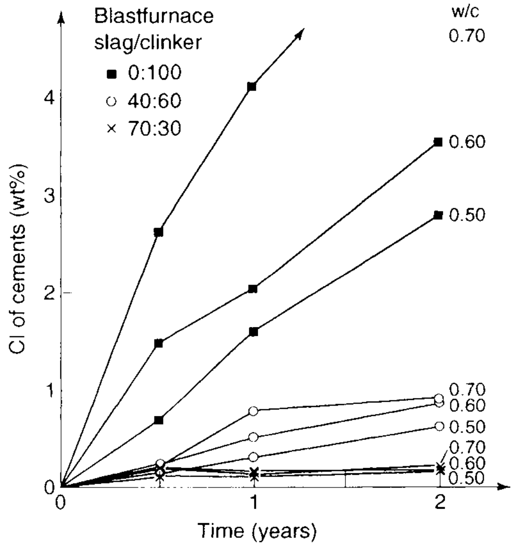

Fig. 11.10 Chloride diffusion into concrete bars (source: Ref. 4). NaCl solution: 3 mol/L; test layer: 2–4 cm.

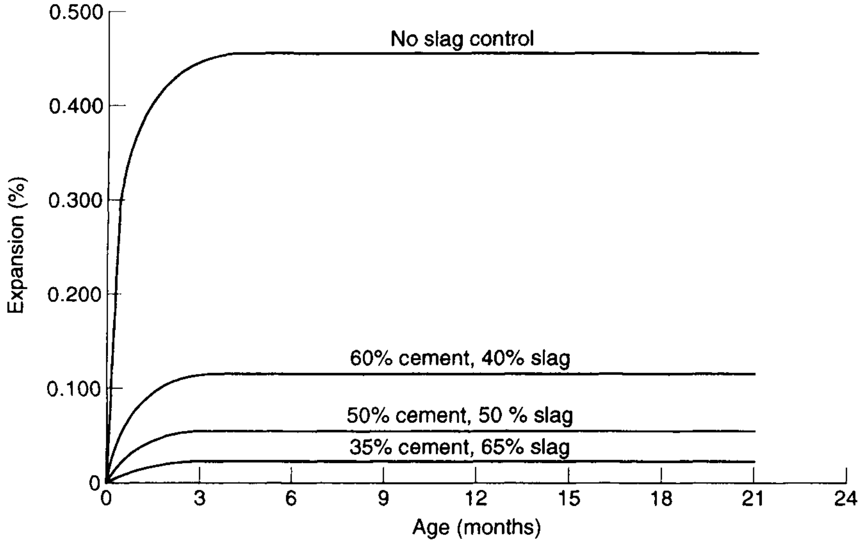

Fig. 11.11 Linear expansion of mortars bars with pyrex glass, showing the influence of the amount of slag as Portland cement replacement (source: Ref. 106). Total alkalis as Na_2O of cement = 1.15 per cent; total water-soluble alkalis as Na_2O of cement = 0.12 per cent; for Atlantic NewCem granulated blastfurnace slag.

to attack by sea water and other chemical agencies than Portland cement. The sulfate resistance of slag-type cements is dependent on the C_3A content of the Portland cement fraction and the alumina content of the slag. Increasing the alumina content in the slag can have an unfavourable influence. From tests on mortar in 4.4 per cent Na_2SO_4 solution Locher[108] found that for cements with at least 65 per cent slag content the sulfate resistance was always greater than that of the parent Portland cement, though the improvement was much more marked with Portland cements of 8 and 11 per cent C_3A content than with one of zero content. When, however, the slag content was between 20 and 50 per cent the use of a high-alumina (17.7 per cent) slag decreased the sulfate resistance, whereas that of a low-alumina (11 per cent) slag increased it independently of the C_3A content of the cement in both cases. Other tests[109] have confirmed these influences of the Al_2O_3 content of the slag and the C_3A content of the Portland cement and shown that they also apply to exposure in 5 per cent $MgSO_4$ solution. There is, however, still a need for more tests using larger concrete specimens rather than small mortar specimens, since the results from the latter are the more dependent on the specific test conditions.

Table 11.24 German regulation for the amount of alkalis in cement in the presence of potentially reactive aggregates

Cement	Na_2O_{eq} (wt%)	Blastfurnace slag (wt%)
Portland cement	$\leqslant 0.60$	–
Slag cement	$\leqslant 1.10$	$\geqslant 50$
Slag cement	$\leqslant 2.00$	$\geqslant 65$

The increased resistance of blastfurnace cements to attack by sulfates is generally associated with the lower content of free calcium hydroxide present in the set cement and the less basic nature of the hydrated calcium silicates. Obviously the amount of alumina from C_3A available for conversion to ettringite is reduced because of the smaller Portland cement content. No balance sheet for the hydration products of the alumina in the slag can be drawn up, but part of it is taken up in the C-S-H where it is less readily open to sulfate attack.

Frearson[110] found that the sulfate resistance of blended cements increased as the slag increased and that mortars with a 70 per cent slag content showed a superior resistance to sulfate-resisting Portland cements (SRPC). At lower slag contents (<30 per cent), slag cements were more resistant than OPC but less resistant than SRPC.

Slag cements are resistant to sea water only with an addition of >60 per cent slag if the OPC is a non-marine cement.[111,112] The compressive strength of cements after 6 months, 1 year and 3 years in sea water were measured by Miyairi *et al.*[112] and compared to their strength at 6 months. They were were found to increase over a long period of time for blends with >60 per cent slag (Table 11.25). Loss of strength and expansion are mainly due to the lime leaching and the formation of expansive ettringite. The attack is both chemical and physical in tidal zones. The degradation of some slag cements containing >65 per cent slag which had insufficiently resisted the combined action of sea water, waves, sand, wind, sun and freezing has been related to the superficial drying of concrete and the slow hydration of slag grains. Some precautions are therefore necessary in marine environments: surface protection, a longer hydration period than that for OPC before immersion in sea water, and dense concretes. Blastfurnace cements have been widely used in Germany and Holland and elsewhere for seawater work. Having tested different types of cement for 7 years, l'Electricité de France selected a blastfurnace cement CEM III/B for the construction of the Rance tidal power station which began in 1966. The total surface area exposed to sea water is 90000 m^2. Slag cements have also been used as injection grouts in marine environments.

The carbonation of slag cements is not greater than that of Portland cement if the concrete is compact and stored in an atmosphere which is sufficiently humid.[4] Litvan and Meyer[113] analysed concrete cores after 20 years of exposure and compared an OPC to a slag cement with 65 per cent slag. The rate of carbonation was higher in the slag cement concrete. Very little lime was left in the slag cement concrete. In a dry atmosphere, Osborne[112] observed a deeper carbonation in cements with a high slag content (70 per cent) than in either OPC or cements with a lower slag content ($\leqslant 50$ per cent). In highly carbonated samples Bier *et al.*[115] identified a porous silica gel as the product of C-S-H decomposition. The increase in larger pores resulted in a higher permeability. However, this silica gel was able to react with alkalis forming C-S-H with a fine structure (pore size <10 nm). The compressive strength at 28 days has been found to be a good specification for all types of cement and more particularly for those which react slowly with water.[116]

Supersulfated cement is still more resistant than Portland blastfurnace cement to attack by sea water, sulfates and other aggressive agencies. It has been used successfully in a variety of aggressive conditions, for example in Belgium for sea water work and for reinforced concrete pipes in ground waters that had proved very destructive to Portland and Portland blastfurnace cements. It has also found some use in general building construction, a notable example being the Palais de Chaillot in Paris built in 1937. As noted earlier, care is required in moist curing to avoid the formation of a friable or dusty surface layer. In the UK, it has been used in chemical works under conditions involving exposure to high concentrations

Table 11.25 Influence of slag content on the compressive strength of 4 × 4 × 16 cm mortar samples immersed in sea water compared to the resistance in fresh water, given by the following:

$$\frac{R_c \text{ compression in sea water at time } t}{R_c \text{ compression at 6 months in fresh water}} \%$$

Portland cements			Slag cement type A, $S < 30\%$[a]			Slag cement type B, $30\% < S < 60\%$			Slag cement type C, $S > 60\%$		
6 months	1 year	3 years	6 months	1 year	3 years	6 months	1 year	3 years	6 months	1 year	3 years
*[c]73	57	×[b]	66	51	33	68	86	118	99	124	191
**64	33	×	59	41	×	63	63	52	95	140	193
***58	24	×	53	25	×	68	63	×	108	133	160

[a] S = slag.

[b] Destruction of the sample.

[c] Asterisks refer to the following potential compositions of Portland cement (per cent by weight):

	C_3S	C_2S	C_4A	C_4AF
*	46	32	6	16
**	55	22	10	13
***	60	17	10	13

of sulfates and for the underside of bridges over railways to resist the action of locomotive flue gases.

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12

Microsilica as an Addition

Per Fidjestøl and Robert Lewis

12.1 Introduction

Mircosilica is a very fine powder mostly composed of amorphous silicon dioxide. (The terms 'condensed silica fume' or only 'silica fume' are also used. These can however be said to designate any powder coming out of the smelting industry, while 'microsilica' is material that has property and quality good enough for use in concrete.) The material is a product of the silicon and ferrosilicon smelting industries. Microsilica in concrete was first tested in Norway in the early 1950s.[1,2] Good strength results were obtained in concrete, and later it was established that sulfate exposure tests begun in those early days[3] documented microsilica concrete to be as durable as concrete made with sulfate-resisting cement. However, at that time industrial production was impossible: no method of retaining the large quantities of the ultrafine particles was available. Thus, these favourable results only ended up as an incident, and might have been forgotten.

Then, in the early 1970s the Norwegian government announced strict environmental requirements for the smelting industry. This made necessary huge improvements in filtering technology, thus, within a few years, substantial quantities were made available. These consequences of regulatory action temporarily turned microsilica into a waste product, a stigma which is still noticeable today.

In order to accommodate and use the large volumes of material, large-scale and intensive research efforts were undertaken by the principal Norwegian smelting companies. These efforts, based upon the early work in Trondheim, form a large part of the basis of microsilica technology and are essential to the large and increasing use of microsilica worldwide.

12.2 The material

12.2.1 APPEARANCE

Microsilica (also known as **silica fume** or **condensed silica fume**[4]) in its basic form is a grey (nearly white to nearly black) powder. As discussed later, it is available in several forms, depending on the application and facilities for handling.

12.2.2 PHYSICAL CHARACTERISTICS

The primary microsilica particle is spherical and has a mean diameter of about 0.15 μm. Figure 12.1 shows a collection of particles in a transmission electron micrograph. Figure 12.2 shows typical grain size distributions of microsilica.

The small particle size of the material gives a specific surface area of 15000–25000 m^2/kg. The primary particles will often group and form agglomerations of loosely bonded particles.

12.2.3 CHEMICAL CHARACTERISTICS

Microsilica is commonly considered to contain >85 per cent silicon dioxide. If the origin is a ferrosilicon furnace, fairly large quantities of iron may be present, other elements are only present in small amounts (1 per cent and less).

12.3 Effects on fresh concrete

12.3.1 MECHANISM

The small size of the microsilica particle means that the material has a large specific surface area. This has significant effects on the properties of fresh concrete mixes with microsilica. At a dosage of 10 per cent microsilica by cement weight, between 50000 and 100000 microspheres are added for each grain of cement (Figure 12.3). Thus the mix will be suffused with fine material and this addition causes an increase in internal surface close to an order of magnitude. For example, in a typical mix:

350 kg of cement (Blaine = 3000) contribute $350 \times 1000 \times 0.3 = 105000\,m^2$
8 per cent microsilica, 28 kg, provides $28 \times 1000 \times 20 = 560000\,m^2$

12.3.2 WORKABILITY

The large increase in surface area gives a corresponding increase in internal surface forces which means an increase in the cohesiveness of the concrete. This effect is mostly advantageous, but it also means that the concrete seems to be slightly stiffer in placing, which means that an increase in slump is required to maintain ‘apparent’ workability. This is one important reason why microsilica should be used with plasticisers or superplasticisers.

The term ‘apparent’ workability refers to the effect of microsilica on the slump cone measurement of a concrete and on how the slump compares with the workability of the mix: a fresh microsilica concrete will have a lower slump than a similar ordinary concrete due to the cohesiveness of the mix. When energy is applied to the mix, as in pumping, vibration or tamping, the microsilica particles, being spherical, will act as ball bearings and lubricate the mix giving it a greater mobility than ordinary concrete of similar slump. The effect is thoroughly described by Wallevik and Gjørv.[5] In the (Tattersall) two-point tester, the addition of microsilica will cause a decrease in the viscosity of the material while slightly increasing the shear strength of the fresh mix (Figure 12.4).

The effect on workability will vary between microsilicas from different sources. In addition, the type of product (dry, wet, etc.) that is used will influence the water demand of the material.[6] The high specific surface area of microsilica (typically 15–30 m^2/g) means that there will be an increased water demand. This may be partly offset by additional modifications to the mix design, such as reducing the content of other fines.

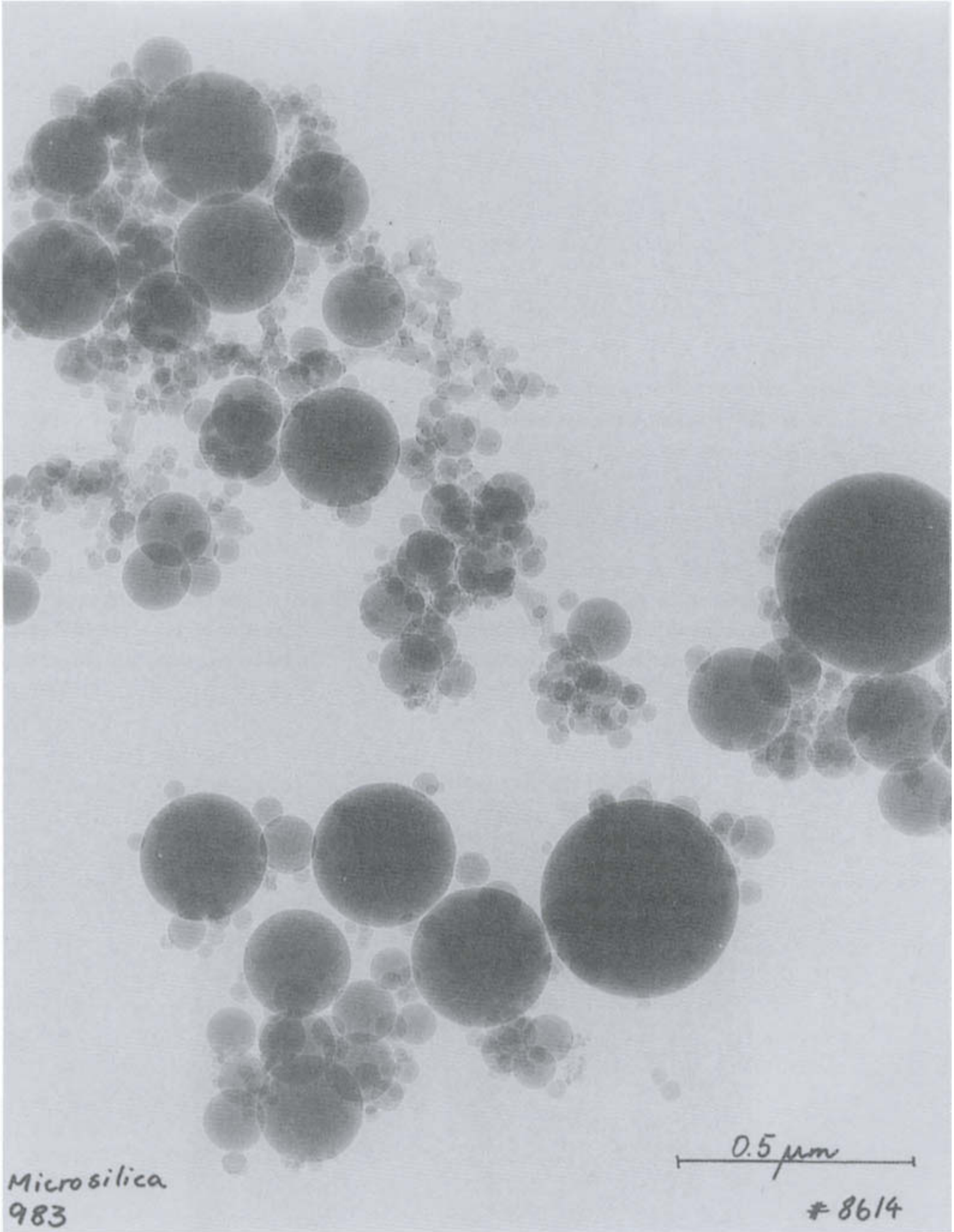

Fig. 12.1 Transmission electron microscopy photograph showing individual particles of microsilica.

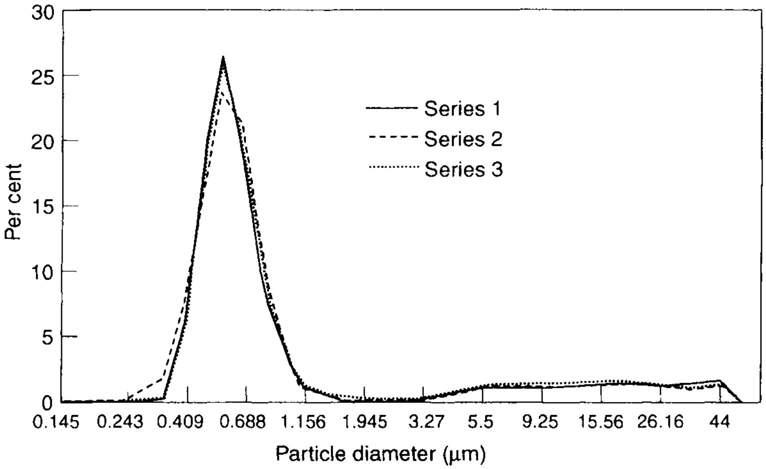

Fig. 12.2 Grain size distribution of various microsilicas, measured with MicroTrac (courtesy of Elkem Materials). The particle sizes indicated represent the size of the primary agglomerates, not the primary microsilica particles.

12.3.3 STABILITY (Figure 12.5)

Since microsilica concrete is more cohesive, it is therefore less susceptible to segregation than regular concrete, even in flowing concretes. The reduced tendency to segregation is also useful for high-fluidity grouts and pumped concrete mixes. The addition of small amounts of microsilica to a mixture designed for pumping will act as a pumping aid, giving very good pumping characteristics.[7,8]

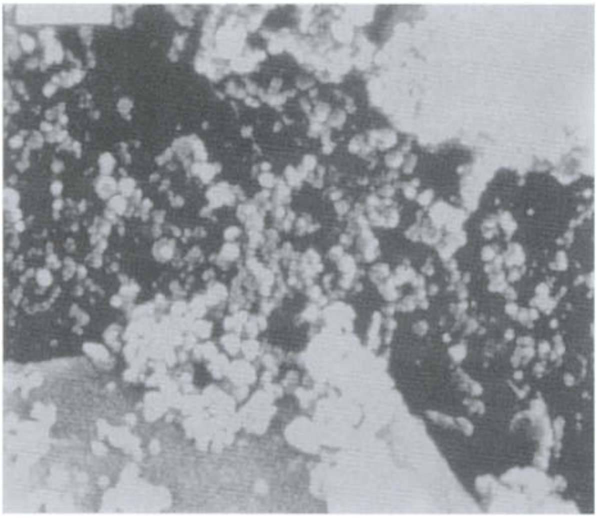

Fig. 12.3 Micrograph of fresh concrete with microsilica (source: *CtO Arbejdsmark*, 13 October 1980, published by CtO, Aalborg, 1980).

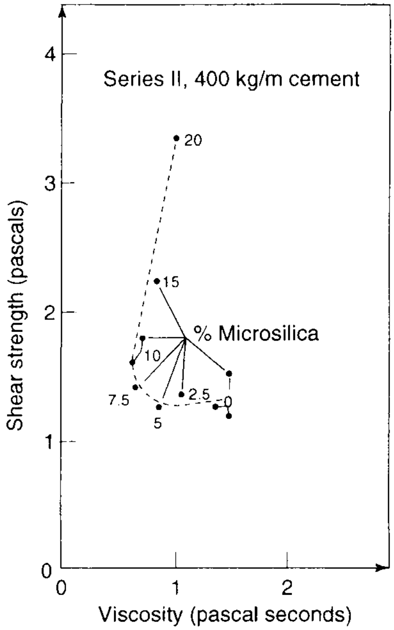

Fig. 12.4 Effect of microsilica on viscosity and shear strength in fresh concrete (source: Ref. 5).

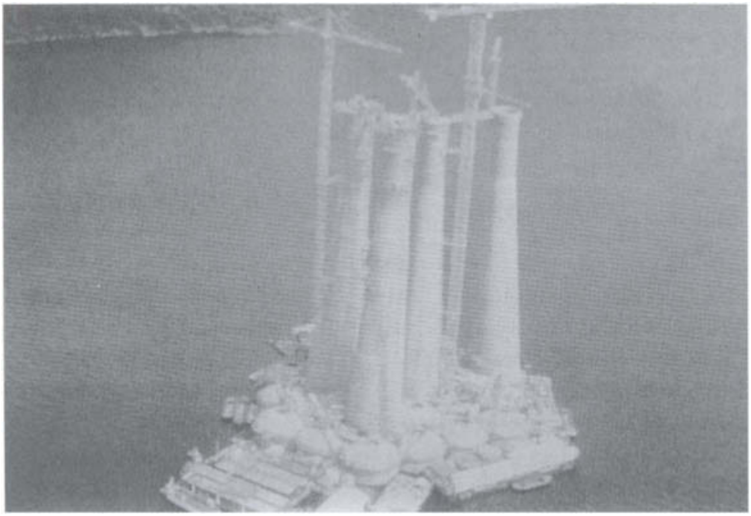

Fig. 12.5 Gullfaks C. Marine durability/pumped.

Another consequence of the cohesiveness is that a microsilica concrete will produce virtually no bleed water. The concrete must therefore be cured in accordance with good site practice. The lack of bleed water also means that finishing of flatwork, such as powerfloating, can start much earlier than with ordinary concretes.

The lack of bleed water, increased shear resistance and a tendency to gelling (stiffening when not agitated) have been taken to indicate that the addition of microsilica means a more rapid set. The microsilica, however, is a pozzolan and requires calcium hydroxide to start the pozzolanic reaction. The necessary calcium hydroxide is produced by the hydration of cement and thus the pozzolanic reaction is only possible after the cement has started reacting. The setting times for microsilica concretes are similar to those of ordinary concretes.

12.4 Setting and hardening of concrete

12.4.1 MECHANISM

As the concrete hardens, the chemical action of the microsilica takes over from the physical effects.[9] Microsilica reacts with calcium hydroxide to produce calcium silicate hydrates (C-S-H). Thus the amount of binder is increased, which both increases the strength and reduces the permeability by densifying the matrix of the concrete.

Since microsilica has a very high surface area and a high content of reactive silicon dioxide, it is more reactive than other supplementary materials, such as pulverised fuel ash (pfa) and ground granulated blastfurnace slag (ggbs).[10,11] Some investigators have found that the increased reactivity appears to push the hydration of the C_3S fraction of the cement initially,[12,13] thus creating more calcium hydroxide, and that the reaction rate settles down to more normal rates beyond 2 days.

As the microsilica reacts and produces the calcium silicate hydrates, voids and pores within the concrete are filled as the hydrates that are formed bridge the gaps between cement grains and aggregate particles. The combination of chemical and physical effects means that a microsilica concrete will be very homogeneous and dense. This gives greatly improved strength and impermeability.[14] It has been found that the relatively porous interface, rich in portlandite, which surrounds aggregate particles in normal concrete is virtually absent in microsilica concrete.[15,16]

12.4.2 HEAT OF HYDRATION

For a given 28-day strength, microsilica concrete will normally develop less heat than a regular Portland cement concrete. The reason is that the amount of cement is reduced, which means that the total heat evolved early on is also reduced. The microsilica, added at one-third of the amount of cement that can be removed, starts reacting a little later after calcium hydroxide is released, and does not contribute as much heat as does cement.

Microsilica concrete is very sensitive to temperature variations while hardening. The rate of hydration, and with it a gain in strength, will be reduced with low and dramatically accelerated with increased temperatures.[17]

12.5 Mechanical properties of hardened concrete

12.5.1 COMPRESSIVE STRENGTH

Many reports are available[18 20] which show that microsilica, when added to a concrete mix, will increase the strength of that mix significantly. The actual amount and percentage of strength increase will depend upon numerous factors, some of which are: the type of mix, type of cement, amount of microsilica, use of water reducing admixtures, aggregate properties and curing regimes.

Concrete with microsilica appears to follow the conventional relation between strength and water/cement (w/c) ratio. However, the curves are shifted when microsilica is added (Figure 12.6).

As with other supplementary materials, microsilica concretes are somewhat sensitive to early drying; one consequence can be reduced final strength.[21] Some combinations of microsilica and fly ash appear more resistant to this effect.[22]

With proper mix design, concretes of very high strengths can be produced using normal ready-mix facilities. In the USA concretes of 100–130 MPa are used in tall buildings; microsilica concrete was recently used in the construction of the world's tallest concrete building, Petronas Towers in Kuala Lumpur.

12.5.2 TENSILE AND FLEXURAL STRENGTH

The relationships between tensile, flexural and compressive strengths in microsilica concrete are similar to those of ordinary concrete. Thus an increase in the compressive strength using microsilica will result in a proportional increase in the tensile and flexural strengths the same as in concrete without microsilica.

12.5.3 BRITTLENESS AND YOUNG'S MODULUS

High-strength concrete often exhibits a brittle behaviour,[23] and microsilica concrete is no exception to this rule. In general, the higher the strength, the more brittle the material.[13,24] The modulus of elasticity is not proportional to the compressive strength, so that a high compressive strength does not mean a similar increase in modulus.[25] The final strain before failure in uniaxial compression increases with increasing strength, but the stress–strain curve is often close to linear before such failure. The brittle behaviour of the concrete is

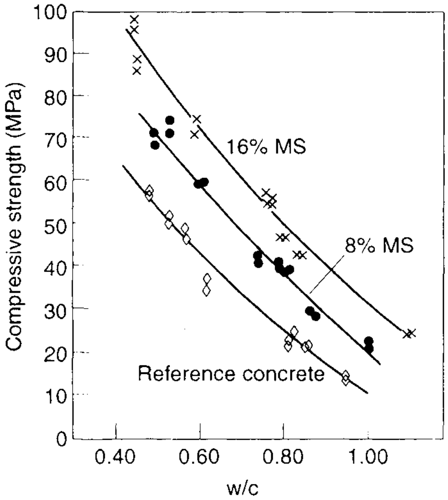

Fig. 12.6 Typical results for strength improvement (source: Ref. 18).

not necessarily imparting brittleness to the structure as such, the ductility of the whole structure will rely as much on reinforcement and detailing as on the ductility of the component material concrete.

12.5.4 BONDING

The improved packing contributed by the very small size of the particles of microsilica will improve the contact surface, and thus the bond, between the fresh microsilica concrete and the substrate such as reinforcement, old concrete, fibres and aggregates. Investigation has shown[26] that the aggregate cement interface is altered when microsilica is present, and pull-out tests[27,28] show improved strength. Bonding to fibres is greatly improved.[29] [31] This is particularly beneficial in the steel fibre/microsilica-modified shotcrete such as is widely used in Scandinavia.

12.5.5 SHRINKAGE

The shrinkage of microsilica concrete is similar to that of normal concrete. However, due to the reduced rate of drying, shrinkage takes place at a slower rate in the microsilica concrete. In standard tests this means that observed shrinkage will be less in microsilica concrete than in normal concrete, as shown in Figure 12.7.[32-34]

12.5.6 CREEP

Most work on the creep of microsilica concrete is related to high-strength concretes. Ost and Burg[35] found significant reduction in creep with the addition of microsilica, while Hansen[36] reports scant effect of microsilica on creep, providing the modulus of elasticity was constant. Persson[37] and Tomaszewicz[38] report reduced specific creep for high-strength concrete with microsilica compared to conventional normal-strength concrete.

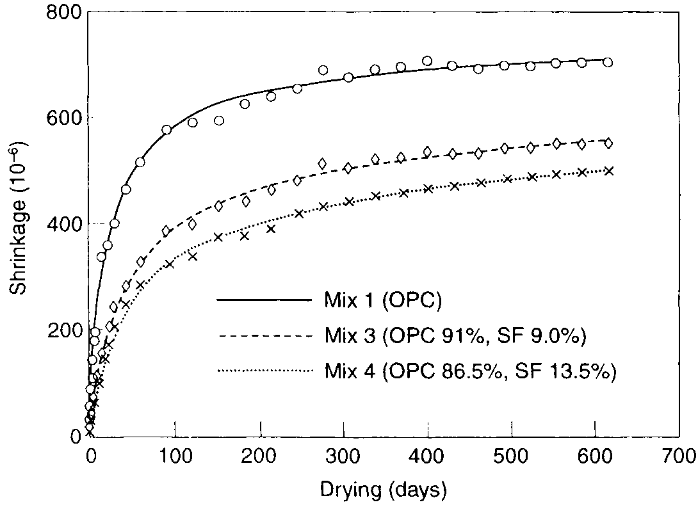

Fig. 12.7 Drying shrinkage of prisms (source: Ref. 32). Specimens were moist-cured for 28 days prior to testing.

12.5.7 FIRE RESISTANCE

Based on some early tests,[39] a concern formed that high-strength microsilica concretes could explode when exposed to fire. However, several tests[40–42] have shown that under normal fire conditions microsilica concretes do not behave any differently to normal concretes. The mechanism involved is probably one of high resistance to steam movement.[43] If soaked concrete is tested in very intensive fire tests, where the low permeability of the microsilica concrete means that steam cannot escape, spalling occurs due to steam pressure. Well-cured and conditioned concretes like those above have not shown spalling; however, there are indications that for all high-strength concretes, regardless of microsilica content, there is a water/cement ratio below which spalling due to fire may be a concern. Some investigators[44] put this limit at about 0.33. Below this limit, special care should be taken, and plastic fibres are suggested.

It should be noted that the type of fire is of great importance. The concerns above are much more valid for fires with very rapid rise, while for the typical ISO fire,[45] the concern and associated risks of spalling are much less, perhaps even absent.

12.5.8 ABRASION AND EROSION

High-strength microsilica concretes show greatly improved resistance to abrasion and erosion. Though not extensively reported and publicised, abrasion resistance has become an important application area for microsilica concrete. A large repair project on the Kinzua Dam, USA, has been studied[46] and subsequent inspection still, after 10 years,[47] showed good performance of the microsilica concrete (Figures 12.8–12.11).

The Norwegian practice of using studded tyres on cars during winter means extreme wear of the road surface. In recent years high-strength microsilica concrete has become the paving material of choice for high wear resistance. One example is a 95 MPa concrete on a 10 km stretch of highway north of Oslo. It has been found that the use of such paving reduces the wear by a factor of 5–10 compared to high-quality black-top.[48]

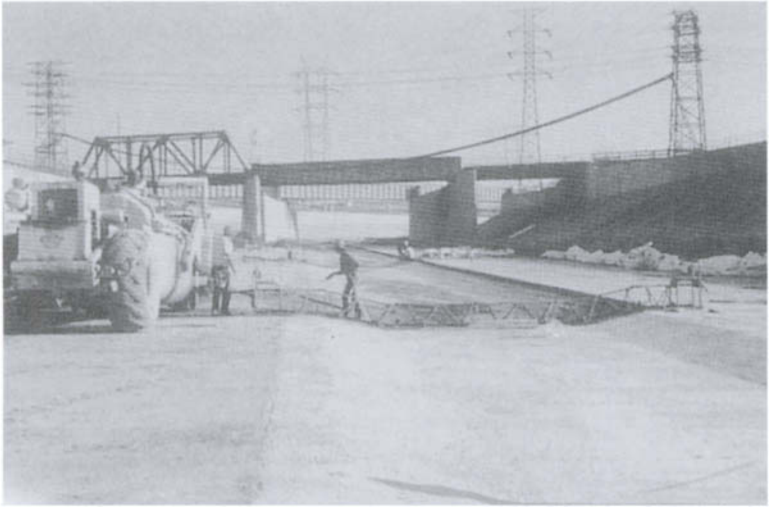

Fig. 12.8 Los Angeles river channel showing abrasion resistance.

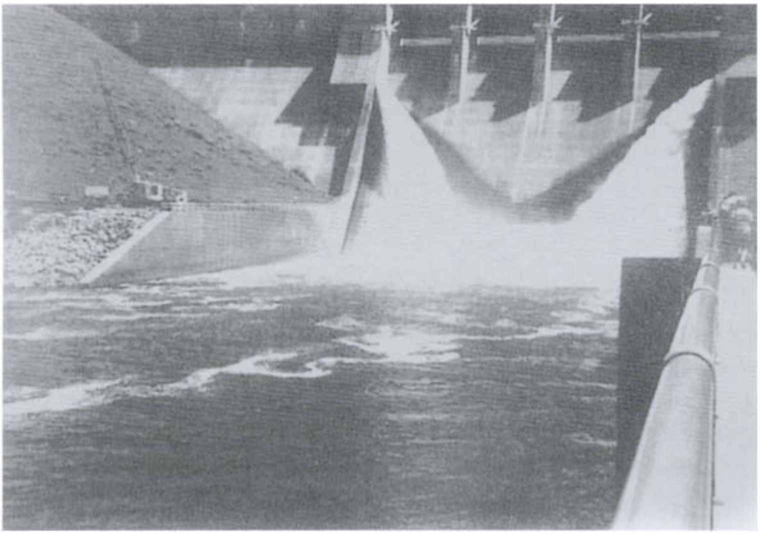

Fig. 12.9 Kinzua Dam in operation.

Fig. 12.10 Kinzua Dam, showing damage to high-strength fibre-reinforced concrete.

12.5.9 SUMMARY OF EFFECTS ON MECHANICAL PROPERTIES

- High-strength (80 MPa) and very high-strength (120+ MPa) concretes can be produced on a routine basis with microsilica.
- Tensile and flexural strengths are as in normal concretes, and increase proportionally with the compressive strength.
- In fire testing, very high-strength, low water/cementitious ratio concrete, may be susceptible to spalling on exposure to a very rapid temperature rise.

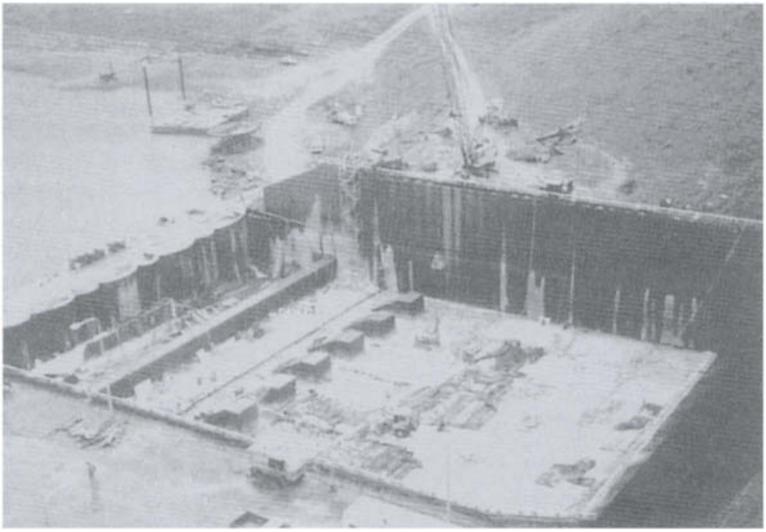

Fig. 12.11 Kinzua Dam stilling basin, under repair with microsilica concrete.

- High-strength microsilica concrete has excellent potential for abrasion and erosion resistance.

12.6 Durability of hardened concrete

12.6.1 GENERAL

The main chemical and physical effects of microsilica addition to concrete are a reduction in the content of calcium, potassium and sodium hydroxides and a refined pore structure in the hardened concrete.

12.6.2 ALKALINITY OF MICROSILICA CONCRETE

A high pH is important for the durability of reinforced concrete because steel passivation is ensured by a high pH (greater than about 8.5 according to the Pourbaix diagram). In an alkaline environment, a passive oxide layer forms on the surface of the reinforcing steel and prevents corrosion attack. Even if alkalis are leached from the concrete or consumed by chemical reactions with weak acids, such as SiO_2 (silicic acid), concrete normally has a large buffer of undissolved calcium hydroxide to replenish this loss and renew the supply of OH^- in the pore water. The consumption of free lime by microsilica has caused concern about the pH levels in the pore water of microsilica concrete. Additionally it is feared that the reduced content of $Ca(OH)_2$ can cause reduced resistance to carbonation because $Ca(OH)_2$ acts as a buffer on the total carbonation reaction.

Hydrated cement paste consists of 20–25 per cent $Ca(OH)_2$, which means that the pore water is saturated calcium hydroxide solution. Such a solution has a pH of 12.4. Thus sufficient alkalinity of concrete is ensured by calcium hydroxide alone. However, since several measurements show pH up to 14, calcium hydroxide is only one factor.

Furthermore, measurements of alkalinity of concrete with up to 20 per cent microsilica (which should mean virtually no remaining lime), has shown alkalinity of about 12.5 in such mixes, with a linear reduction of pH from 13.5 to 12.5 with microsilica content increasing from 0 to 20 per cent (e.g. Gautefall and Vennesland[49]).

The main question concerning alkalinity is what determines the pH of the pore water. This has been determined by squeezing pore water and analysing the concentration of different ions (e.g. Page and Havdahl[50]). It was found that in young concrete sodium hydroxide and potassium hydroxide have even greater influence on the alkalinity than calcium hydroxide. Thus, the alkali hydroxides in the pore water protect the reinforcement against corrosion, but do not carry any reserve alkalinity, such as would be provided by undissolved calcium hydroxide.

In concrete where some of the alkalis have reacted with weak acids, the reaction products are of great interest. Alkali hydroxides are soluble and they can be partly neutralized by weak acids, such as CO_2 or SiO_2 in water. The salts produced by the reaction give a high pH in solution.[51]

Standard pH values for solutions of these reaction products are:

0.1 M Sodium hydroxide	$NaOH$	pH = 13.0
0.1 M Sodium carbonate	Na_2CO_3	pH = 11.6
0.1 M Sodium metasilicate	Na_2SiO_3	pH = 12.6

Thus a cement paste with a very high content of microsilica and thus without free lime, still can have a high and passivating pH. Note that the reduction in alkalinity described above, and the corresponding binding of the K^+ and Na^+ ions in the pore solution[52] is one of the ways in which the addition of microsilica is assumed to decrease the risk of alkali–silica reaction (ASR) in concrete. Based on literature, Parker[53] suggests that it is possible to use microsilica to compensate for high alkali contents of cements.

12.6.3 POROSITY

The main physical effect of microsilica on the microstructure of hardened concrete is a refinement of the pore structure. The total pore volume is not necessarily changed, but

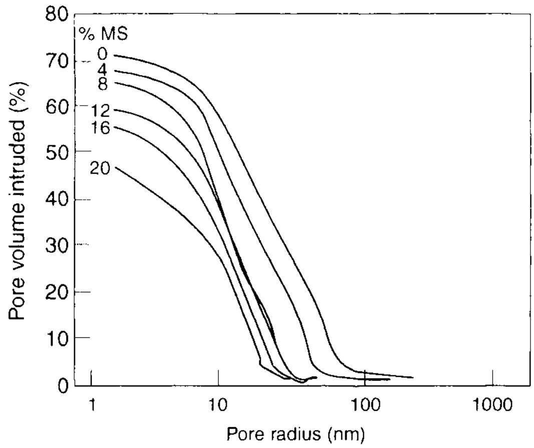

Fig. 12.12 Effect of microsilica on pore structure (source: Ref. 54). The method does not work for pore radii below 1 nm.

large pores appear to be subdivided into smaller pores.[54] The effect is shown in Figure 12.12. This improvement in pore structure is reflected in the higher strength, but it is also of great importance to the permeability of the material.

Another important factor is the improvement in quality of the transition zone between aggregate particles and cement paste. Studies[55–57] have shown the significant improvement in structure and composition. The improvement in interface structure is shown in Figure 12.13. Apart from the improved bond between aggregate particles and paste, the porosity and transport capacity of the interface region is reduced.

12.6.4 PERMEABILITY

Permeability is a measure of the ease of passage of liquids or gases or specific chemicals through the material. Permeability is determined by applying a head and determining the depth of penetration or the amount of liquid or gas passing through the sample. Measurements using heads of pressure can be supplemented by capillarity and porosity studies. Similar information can be obtained (for water) by measuring rate of weight loss when drying out. Figure 12.14 shows the effect of microsilica on the permeability of drilled cores,[58] while Figure 12.15 shows the effect of microsilica and ggbs on water penetration.

Permeability is important for two reasons: the parameter describes how rapidly deleterious substances may enter the concrete and how easily material can be leached from the concrete.

12.6.5 SULFATE RESISTANCE

A major study was started in Oslo during the first years of testing of microsilica in concrete. This involved submerging specimens, of various mixes, in acidic sulfate-rich groundwater leached from the alum shale in Oslo. (Alum shale contains high amounts of unstable iron sulfides. On contact with air, the sulfur is oxidised into sulfur dioxide, which will give a

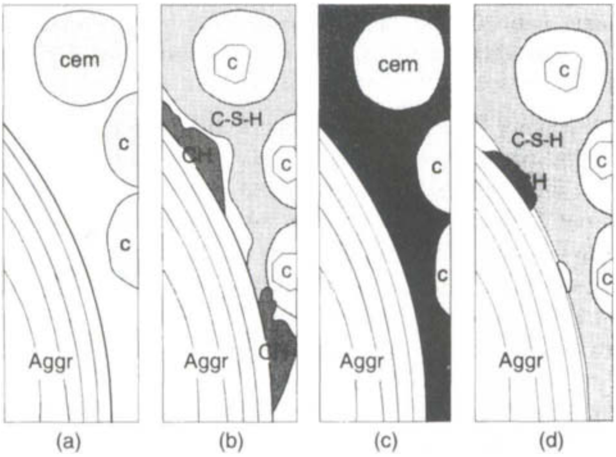

Fig. 12.13 Effect of microsilica on interface structure (source: Ref. 16). (a), (b) Fresh and hardened concrete without microsilica; (c), (d) fresh and hardened concrete with microsilica. Note the reduced amount of calcium hydroxide in, and the general improvement of, the interfacial zone between binder and aggregate.

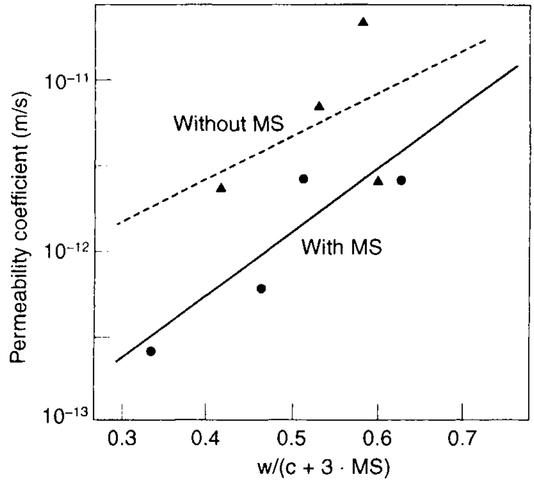

Fig. 12.14 Permeability of drilled cores for different water/(cement + microsilica) ratios (approximately equal 28-day strength)(source: Ref. 58).

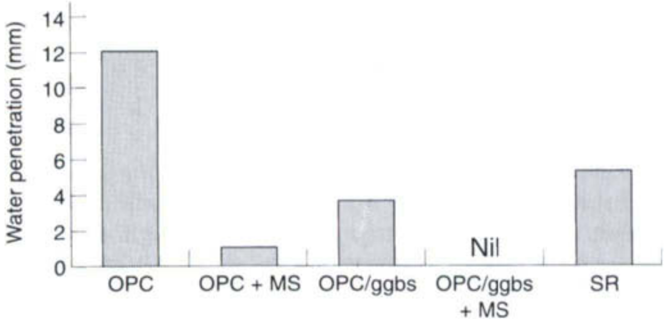

Fig. 12.15 Permeability with different binder compositions at water/cementitious ratio ~0.42, measured according to DIN 1048 (source: Ref. 64).

low pH dissolved in water.) The 12- and 20-year results are available from this trial.[59,60] These results show that the microsilica concretes (15 per cent MS, w/c = 0.6) performed as well as the mixes with sulfate-resisting cement (w/c = 0.45). This is confirmed in the unpublished data from 30 years of reports and by laboratory tests.[61,62]

When used with ggbs or pfa,[63,64] microsilica mixes have been found to be more resistant to sulfate attack than special sulfate-resisting cements. This experience has caused microsilica to be required for concrete in the Arabian Gulf to combat the severe deterioration of the concrete there. Here the mechanisms of attack are both sulfate attack and chloride initiated corrosion.[65]

The good performance of the microsilica mixes in a sulfate environment can be attributed to several factors,[66] of which the most important are likely to be:

- the refined pore structure and thus the reduced passage of harmful ions;[67]
- the lower calcium hydroxide content, which leads to reduced formation of gypsum (and consequently of ettringite).

12.6.6 CARBONATION

The results of tests on carbonation and carbonation rates are somewhat contradictory. One study[68] of the effect of microsilica on carbonation and transport of oxygen, adding up to 20 per cent microsilica caused a slight reduction of both processes in water-saturated concrete. Normally, however, the rate of carbonation can be related to the water/cement ratio of the concrete, as illustrated in Figure 12.16 based upon data from Johansen.[69]

In essence the conclusions shown by those reports which are available[68,70] are that for a given strength of concrete below 40 MPa, carbonation is higher in microsilica concrete than in ordinary concretes, corresponding to the increase in water/cement ratio. Concretes above 40 MPa, corresponding to a low water/cement ratio, show little change in carbonation rate.

Microsilica concrete will normally be intended for special use and have a low water/cement ratio. Thus concerns over changes in carbonation rate due to microsilica are not normally warranted. Proper curing procedures are essential to optimum performance of the microsilica concrete.

12.6.7 CHLORIDE RESISTANCE

Chloride resistance is normally considered in terms of chloride entering from the surface of the concrete. Occasionally, however, chloride can be introduced into concrete at the time of mixing. A common source used to be chloride-based accelerators and poorly cleaned marine aggregates. Thus the ability of the concrete to bind chlorides chemically is of interest, in addition to the ability to withstand chloride penetration, from sea water or de-icing salts.

A number of studies have been made[71 73] which consider the combined effects of reduced permeability and the reduction of pH in the pore water and how these factors interact regarding the passivity of embedded steel.

The slight reduction in pH caused by the introduction of microsilica, as decribed in section 12.6.2, will cause a reduction in the threshold chloride concentration, i.e. the amount of chlorides necessary to destroy the passive layer and initiate corrosion. This effect is counterbalanced by the reduced rate of chloride diffusion due to the addition of microsilica.[74]

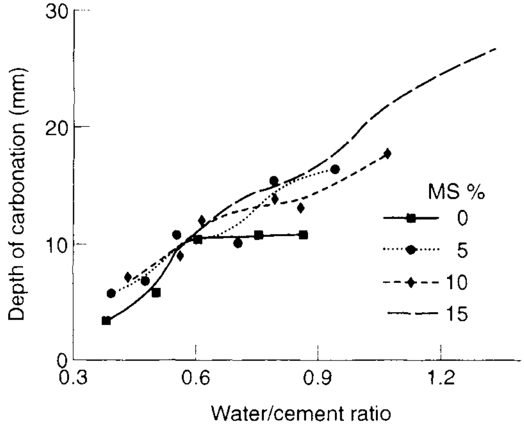

Fig. 12.16 Carbonation depth versus water/cement ratio (data from Ref. 21).

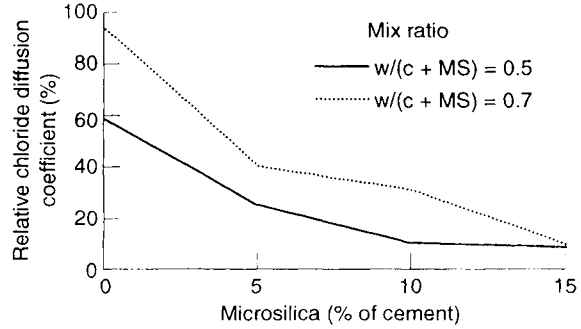

Fig. 12.17 Chloride diffusion versus microsilica content (data from Ref. 74).

Figure 12.17 shows the result of tests on chloride ingress into cement pastes of varying compositions. There is a very significant effect from the replacement of cement by microsilica, especially at high water/cement ratios, but also at the low values.

The rapid chloride permeability test[75] is routinely used to describe the resistance of concrete to chloride ingress. Typically, microsilica concrete achieved a very low (good) rating in this test.

Microsilica works in several ways to reduce the risk of corrosion. The improved permeability properties of microsilica concrete mean greatly reduced rates of chloride penetration in marine structures and structures exposed to de-icing salts. These concretes also have very high electrical resistivity, thereby greatly diminishing the rate of corrosion, should it be initiated.[76] [85]

12.6.8 ELECTRICAL RESISTANCE

It is essential to measure the electrical resistance of concrete in order to determine the rate of any initiated corrosion. A high resistance of the concrete means that little current will flow, and the corrosion rate will be small. If the resistance is high enough, the rate of corrosion will be similar to the leakage current from passive steel, i.e. insignificant. Microsilica provides a large increase in the electrical resistance of concrete. Figure 12.18 shows the effect of microsilica addition on the electrical resistance of concrete. It is assumed[86] that a limiting resistance of the order of 300–600 Ω m is sufficient to prevent corrosion

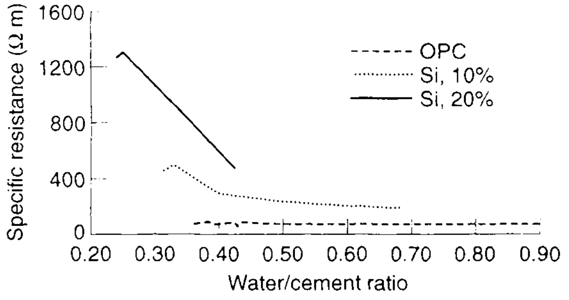

Fig. 12.18 Electrical resistance and microsilica (data from Ref. 49).

from progressing. As seen from the figure, such resistances are approached by microsilica concrete, even in very wet conditions.

12.6.9 LEACHING AND LIME BLOOM

This problem mainly occurs where one surface of the concrete is subjected to continuous water contact or to wetting and drying. Calcium hydroxide leaches through the concrete to the surface where it carbonates, giving the white powdery deposit that can often be seen on new buildings. Although mainly a problem of aesthetic appearance, excessive leaching will result in increased porosity and permeability and a weaker concrete. The addition of microsilica will reduce leaching.[87] This is due to:

- the refined pore structure, causing less opportunity for moisture movement;
- consumption of the calcium hydroxide by microsilica.

The results indicate that the more efficient the curing and the longer that curing took place before exposure, the more resistant the concrete became.

12.6.10 FROST RESISTANCE

For a more general discussion of frost resistance of concrete, see section 7.1. Frost resistance of microsilica concrete has been extensively investigated. Investigations have included the individual and combined effects of construction variables, such as:

- microsilica
- superplasticisers
- varying dosages of air entrainers
- different aggregates
- various curing sequences.

Air entrainment

The purpose of entraining air into concrete is to achieve a proper air void system (the correct amount of air and the correct size and spacing of the air bubbles) in the hardened concrete. In the fresh concrete this requires a stable air system, which is able to withstand transport, placing and compaction.

Many different concretes have been compared[88,89] to determine the effect on frost resistance of microsilica addition to the concrete. It was found to be difficult to entrain air in a microsilica mix without a plasticiser, but by increasing the dosage of air entrainer and adding a plasticiser it was easy to achieve the desired levels of air in the mix. In hardened concrete it was found that the spacing factor and the stability of the bubbles improved. Variations in air content, occasionally experienced with pfa, were not noticed in the microsilica concretes. Curing method and duration had a marked effect on these tests.

Frost resistance testing

There are now various methods that can be used for frost resistance testing. It is unfortunate that these different test methods evaluate the frost resistance according to different procedures and are to some extent incompatible. Hence a large amount of the information now available[90-94] is conflicting and the effect on frost resistance of microsilica is unclear.[95,96] The differences that have been observed in the response of different (national) test methods to the addition of microsilica are likely to be as much due to the lack of experience in applying the material as in any inherent lack of frost resistance of microsilica concrete.

The combined use of microsilica and air entrainment is probably a very good option, the microsilica giving low permeability, while maintaining good stability of the air in fresh concrete, with a uniform bubble spacing of the air providing the best frost protection. Very long-term tests[97] show salt scaling resistance of air-entrained microsilica concrete to be similar to that of ordinary concrete.

12.6.11 ALKALI–SILICA REACTION

Consideration of the effect of microsilica on this form of chemical attack requires attention to the three main factors that are required for possible reaction to take place:

1. high alkali content in the mix (normally supplied by the cement);
2. reactive aggregates, containing reactive silica;
3. available water.

Well-dispersed microsilica reacts with the available alkalis in the fresh concrete, forming alkali silicates. This binds the alkalis, and should prevent attack on reactive siliceous aggregates. This mechanism reduces the risk of ASR through combating factor 1 above. Since microsilica contributes to a reduced permeability, the amount of available water is less. These two factors combine to reduce the susceptibility of microsilica concrete to ASR.

This aspect of microsilica concrete was one of the first to be commercially exploited on a large scale. Since 1979 all concrete in Iceland has been made with ~7 per cent microsilica, a remedy which, together with other improvements in construction procedures, has put an end to the previously severe ASR problems[98,99] (Figure 12.19).

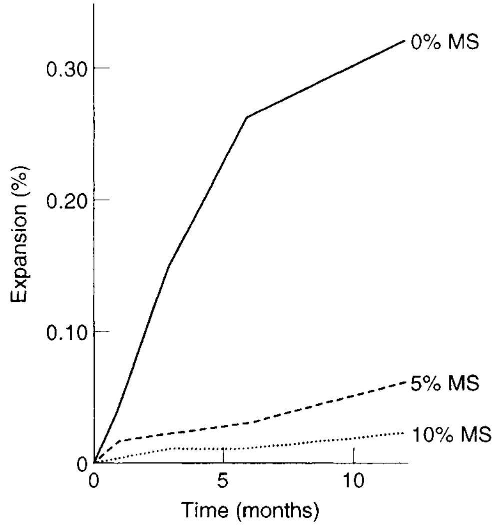

Fig. 12.19 Effect of microsilica on ASR (source: Ref. 99).

The minute size and the pozzolanic reactivity of the microsilica greatly refines the pore structure of the concrete, increasing the impermeability, and this means less water is able to pass into and through the concrete. In the alkali–silica reaction it is the absorption of water by the hygroscopic gel that causes the damaging expansion in the concrete.

Thus a normal dosage of microsilica can negate the main factors that could lead to alkali–silica reaction in a concrete or mortar. Several reports are available, e.g. Refs 100–102, on this property of microsilica.

12.6.12 SUMMARY OF DURABILITY PROPERTIES

The major influence of the microsilica on the chemical and physicochemical durability of concrete is through the large change in the permeability. For water the reduction in permeability can be by a factor of between 10 and 100 times compared to a control concrete.

The deterioration of microsilica concrete is demonstrably slower than comparable normal concretes for most chemical and physicochemical attacks. The actual increase in resistance depends on the mix design, quality control and curing of the concrete. Neglect in the execution of any of these may result in a weaker and less durable concrete than normal.

12.7 Practical use of microsilica in concrete

12.7.1 SHOTCRETE

Microsilica gives a cohesive fresh concrete and strongly improved bonding. This has been utilised in both dry and wet shotcrete to reduce rebound by a factor of between three and five and to increase the efficiency of fibres in wet shotcrete. The high reactivity and extreme cohesiveness of the microsilica shotcrete also reduces the need for an accelerator to speed the set of the concrete. The use of microsilica in this fashion has resulted in rebound of <5 per cent.

For wet shotcrete, microsilica is introduced in the usual manner at the mixer. In dry shotcrete, several approaches are used in practice, including:

- microsilica, cement and sand delivered to site in a premix;
- microsilica added to the hopper, either as dry or slurry;
- microsilica added at the nozzle, as slurry;
- microsilica slurry added to the water system.

12.7.2 HIGH-STRENGTH CONCRETE

High-strength concrete is used in various applications, and as the achievable strength increases with developing technology, the advantages of concrete as opposed to other building materials becomes more clear. Typically, high strength refers to concretes of 80 MPa and above, but with the advent of highly efficient superplasticisers and microsilica, strengths can be as high as 130 MPa or more for casting *in situ*. As an example, UK production concrete has reached values in excess of 155 MPa. Such high strengths allow improvements in design, such as a reduction in the cross-section of a compressive member and increased spans of flexural members. Thus large savings can be made on materials and construction and the rent-generating area of a building can be increased. A Brite Euram study[103] into the ready mix production and use of concretes over 100 MPa has been led by Taylor Woodrow. Full reports have yet (1997) to be released but the mechanical properties of the 120 MPa concretes easily met the anticipated performance levels with respect to handling and mechanical properties.[104,105]

High strength can be considered in two settings: either for high early strength or for high ultimate (design) strength. High early strength is utilised in the precast industry for faster turnaround of moulds and then increased strength for early age handling. High early strength ready-mixed microsilica concretes can be delivered, placed, finished, cured and gain a strength of more than 40 MPa in just 24 h. This allows fast construction with high turnaround on formwork and short downtime for projects which require suspension of other activities during construction (e.g. motorway work).

Concretes with high ultimate strength have similar mix design parameters, such as a low water/cement ratio. High ultimate strengths can also be obtained with blended cement, pfa or ggbs,[106] where a lower heat of hydration and slower pozzolanic action reduces problems in massive sections, while still giving sufficient early age strength values for construction purposes. A major example of such use was the slipform construction of the twin towers of the Tsing Ma bridge in Hong Kong. Seventy per cent ggbs was used to reduce thermal effects and 6 per cent microsilica was added to give improved rheology to the mix and better strength gain at early ages (in addition to improved durability).

High-strength lightweight concretes can also be produced using the pozzolanic action of microsilica. In this way a wide variation of strengths and densities can be achieved, from 100 MPa at 2000 kg/m^3 to 5 MPa at 500 kg/m^3.

An example of the use of high-strength microsilica concrete is one of the world's tallest reinforced concrete buildings, 311 South Wacker Drive, Chicago. This construction used microsilica concretes of varying strengths. This allowed the same formwork to be used on the columns from the first to the top floor. Nearly 84000 m^3 of concrete was used; starting at 83 MPa for the first 14 floors and ranging from 69 through to 52 MPa at the top. By using high-strength concrete to give a uniform column size a saving was achieved, in comparison to the conventional design quantities, of 3000 tonnes of reinforcing steel and 7650 m^3 of concrete. The saving in concrete volume is directly equivalent to increased space within the building and hence increased return for the client.

The improved tensile and flexural strengths are important to the use of microsilica concretes in flooring, bridging or roadway projects. The increased tensile strength allows for a possible reduction in the slab thickness while maintaining high compressive strengths, thus reducing overall slab weight and cost. Combinations of high-performance microsilica concretes, both normal and lightweight, are being considered for the possible construction of the Millennium Tower in London, in order to achieve maximum strength with minimum unit volume. Another facet of the very high strength, 100–120 MPa, microsilica concrete is the utilisation of the high modulus, 45–50 GPa. Buildings can be designed to resist fatigue effects which can cause structural failure with normal concretes.

12.7.3 SPECIFYING FOR DURABILITY

The use of microsilica concrete for its durability is being specified with an increasing frequency. Some examples are given.

Storebælt, Denmark (Figure 12.20)

This giant infrastructure project linking the two major Islands of Denmark has a very detailed concrete specification, including the use of between 4 and 8 per cent microsilica,

Fig. 12.20 Storebælt Western Bridge, Denmark.

in slurry form. The philosophy is that microsilica protects against ASR and chloride induced corrosion.[107]

Norwegian bridges

The new bridge code of the Norwegian Road and Bridge Authority has standard requirements for the use of microsilica in concrete:[108]

No chloride exposure	0–2 per cent
Moderate chloride exposure	3–5 per cent
Severe chloride exposure	8–10 per cent

The purpose is to ensure adequate durability with respect to chlorides and salt frost scaling and to improve fresh concrete properties.

Concrete in the Middle East

In a proposal for the requirements for construction in the Gulf area, Rasheduzzafar *et al.*[109] have proposed that the use of microsilica is to be one of the options for preventing chloride and sulfate attacks on concrete. High-performance microsilica concrete has been used on the Baynunah Tower in Abu Dhabi, the offshore Chicago Beach Hotel, which will be the world's tallest hotel at 321 m, the Aluminium Bahrain Potline no. 4 (for high electrical and abrasion resistance), Dubai Airport extension and a number of power and desalination plants throughout Saudi Arabia.

Tsing Ma Bridge, Hong Kong

One of the world's longest single-span bridges, the centre span is 1377 m, constructed using 400000 m^3 of high-performance concrete including the use of two triple-blend mixes.

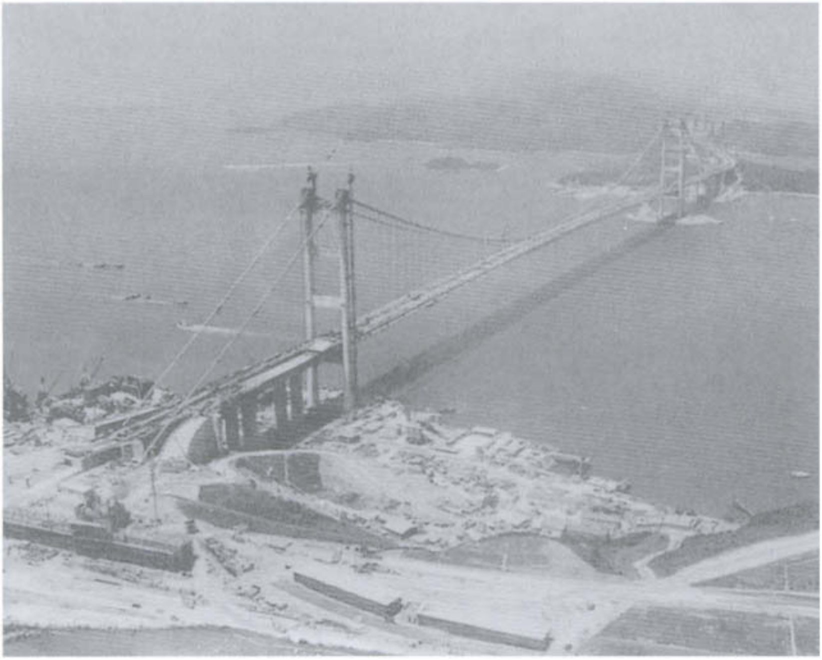

Fig. 12.21 Two views of the Tsing Ma Bridge, Hong Kong.

OPC–ggbs (70 per cent) – microsilica concrete was used for the slipformed towers[110] and an OPC–PFA–microsilica mix was used for the roadway support towers and other stuctures. A very narrow specification led to the design of some of the most durable concrete ever produced in the region.

Northumberland Bridge (Nova Scotia–Prince Edward Island, Canada)

The bridge links the island province of Prince Edward Island to mainland Canada. The length of the bridge will be 12.9 km and the design life is 100 years. Durability of the concrete with respect to chloride ingress, sulfate attack, freezing and thawing, abrasion resistance and alkali–aggregate reactivity are addressed in the proportioning of concrete mixtures where extensive use is made of microsilica and fly ash.[111]

12.8 Production of microsilica

12.8.1 GENERAL

Microsilica is produced during the high-temperature reduction of quartz in electric arc furnaces (Figures 12.22–12.24) where the main products are silicon or ferrosilicon alloys. The high-purity quartz is heated to 2000°C in an electric arc furnace with coal, coke or wood chips added to remove the oxygen. The alloy is collected at the bottom of the furnace (A). As the quartz is reduced to alloy, it releases silicon oxide vapour. In the upper parts of the furnace this fume oxidises and condenses into microspheres of amorphous silica (B).

The fumes are drawn from the furnace by powerful fans, often through a precollector and cyclone (C) which removes the larger coarse particles of unburned wood or carbon, and then blown into a series of special filter bags (D).

The chemistry of the process is composed of temperature-dependent steps. The SiC formed initially plays an important intermediate role, as does the unstable SiO gas which eventually forms the microsilica:

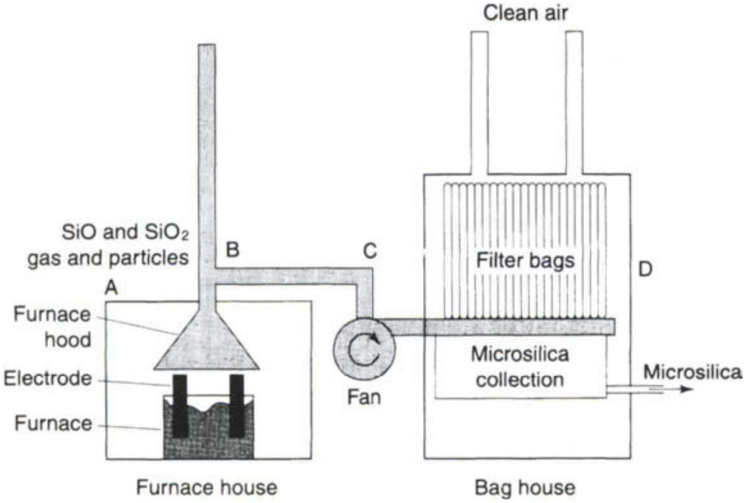

Fig. 12.22 Diagrammatic outline of the production process for microsilica.

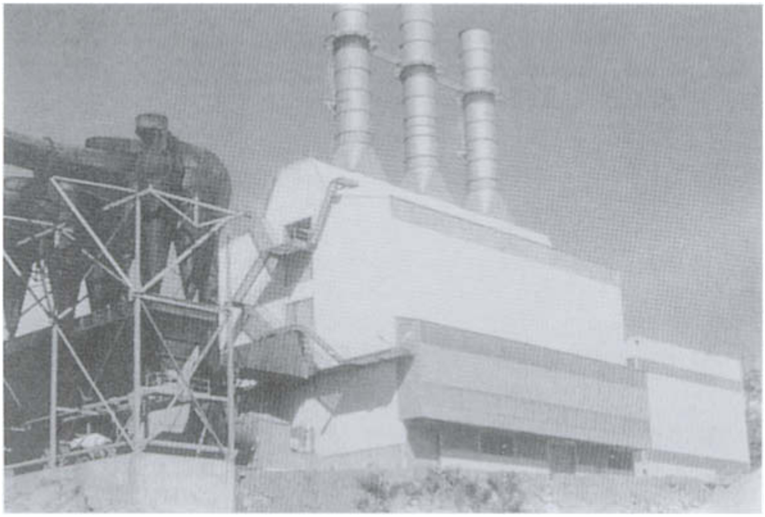

Fig. 12.23 Bag house.

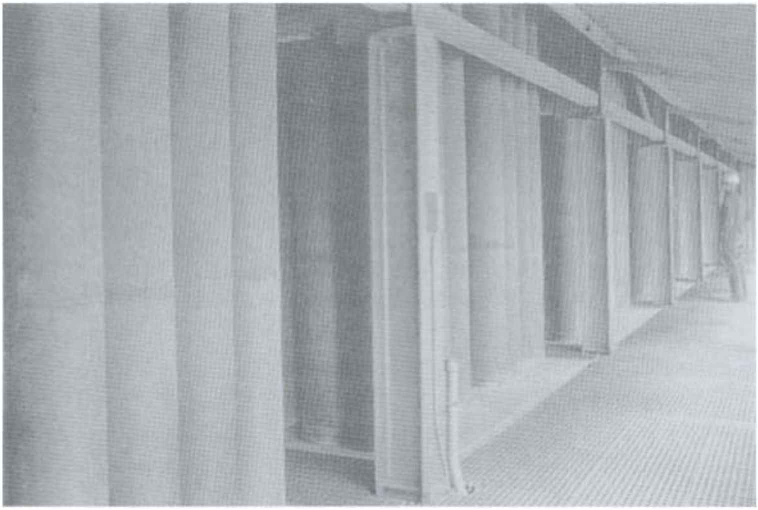

Fig. 12.24 Filter bags.

$T > 1520°\mathrm{C}$: $SiO_2 + 3C = SiC + 2CO$

$T > 1800°\mathrm{C}$: $3SiO_2 + 2SiC = Si + 4SiO + 2CO$

The unstable gas travels up the furnace where it reacts with oxygen to give the silicon dioxide: $4SiO + 2O_2 = 4SiO_2$

As the temperature drops in the smokestack, the SiO_2 condenses into small droplets of microsilica. These small spherical particles have an average diameter of 0.1–0.2 μm. However, while they are in the molten state, a common occurrence is that some of these primary particles fuse where they come into contact into primary agglomerates, typically with a circumscribed diameter of 0.5–0.8 μm.

12.8.2 CHARACTERISTICS

Microsilica is initially produced as an ultrafine, grey powder and has the following typical properties:

- at least 85 per cent SiO_2 content;
- mean primary particle size of 0.1–0.2 μm;
- specific surface area $> 15000\,m^2/kg$;
- spherical particle shape;
- low carbon content.

An element of processing microsilica is the removal of coarse particles. Such particles can be wood chips, pieces of coke and other components of the charge for the furnace. These have been pulled by the furnace draught into the stream of silicon dioxide.

12.8.3 AVAILABLE FORMS OF MICROSILICA

As the powder is 100 times finer than ordinary cement, there are certain transportation, storage and dispensing considerations to be taken into account. To accommodate some of these difficulties, microsilica is available in various forms. The differences between these forms are related to the shape and size of the particles and do not affect the chemical make-up of the material. (These differences have an influence on the areas of use and careful thought should be given to the type of microsilica chosen for a specific application).

The main forms of microsilica are as follows.

- **Undensified** (bulk density 200–300 kg/m^3) Due to the very low bulk density and subsequent problems in handling, undensified microsilica is often considered impractical for use in normal concrete production. Areas where it is used successfully are in refractory products and formulated bagged materials such as grouts, mortars, concrete repair systems and protective coatings.
- **Densified** (bulk density $> 500\,kg/m^3$) In the densification process the ultrafine particles become loosely agglomerated, making the particulate size larger. This makes the powder easier to handle and cheaper to transport than the undensified form. Areas where this material is successfully used are in those processes that utilise high-shear mixing facilities, such as precast works, concrete roof tile works or ready-mixed concrete plants with 'wet' mixing units, and in the refractory industry. If the bulk density is taken too high during the densification process, the user will experience problems with obtaining proper dispersion of the material.[6] Additionally, material that has been densified beyond 700 kg/m^3, has shown a tendency, given pessimal combinations of microsilica dosage and cement alkalinity, towards deleterious performance, closely resembling ASR if the large (> 100 μm) agglomerates are not broken up.[112,113]
- **Pelletised** (bulk density $> 600\,kg/m^3$) Pelletising involves forming the microsilica into pellets about 0.5–1 mm in diameter on a pelletising table using water and a little cement to bind the pellets. Material in this form is not suitable for use in concrete since it is virtually impossible to disperse properly in concrete mixing.

Pelletising is a form of treatment most commonly used at times of excess or out-of-specification production to prepare the material for use in landfilling.

- **Slurry** (specific gravity 1400 kg/m^3) This material is produced by mixing the undensified powder and water in equal proportions by weight to produce a stable slurry. The production of a stable slurry is a complex process, requiring very efficient, high-shear mixers and special microsilica qualities. In this form the material is easily dispersed into the concrete mix.

12.9 Health and safety

Microsilica is classified by CAS (Chemical Abstracts Service) number 69012-64-2. The corresponding EINECS (European Index of Existing Chemical Substances) number is 273-761-1. Other forms of silicon dioxide, including fumed silica, colloidal silica, diatomaceous earth and quartz have other classification numbers.

Papers presented at a symposium entitled the Health Effects of Synthetic Silica Particulates[114] indicated that there is little health hazard potential from the inhalation of amorphous microsilica due to the non-crystalline structure. Jahr[115] stated that experience in Norwegian ferrosilicon manufacturing plants indicated that if the limits (TLV) given in ACGIH (The American Conference of Governmental Industrial Hygienists) are not exceeded, then there is only a very small risk of silicosis from exposure to this type of amorphous silica since the silicon dioxide that causes this lung disease appears to be of the crystalline form. ACGIH specifies as Threshold Limit Value (TLV) a time-weighted average (TWA) of 2 mg/m^3 for the respirable portion of the dust.

The author is not aware of any reported health-related problems associated with the use of microsilica in concrete. There are no references to the use of microsilica in the concrete industry in the publications of either OSHA (the Occupational Safety and Health Administration of USA) or ACGIH. It is recommended that workers handling microsilica use appropriate protective equipment and procedures which minimise the generation of dust.

Spillages of the powder or slurry should be treated as a 'common mess' i.e. non-hazardous and dealt with accordingly. (An exception here is when hydrofluoric acid is present because the reaction product would be silicon tetrafluoride, which is toxic.) There are no special requirements for the disposal of the waste material.

Flash inflammation of the material is not a hazard since the powder is completely non-flammable and will act as an extinguishing medium. The use of the slurry material will reduce any nuisance value to a minimal level.

12.10 Standards and specifications

Various national standards, codes of practice and recommendations relating to microsilica and its use have become available over the past few years. Some of the material standards are:

USA	ASTM C1240 covers microsilica for use in concrete
Canada	CAN/CSA-A23.5-M86. *Supplementary cementing materials.* The standard has been in place since 1986 and is (1996) under revision
Norway	NS 3045 covers microsilica for use in concrete
France	NF P 18-502, 1992. *Additions pour Beton Hydraulique – Fumées de Silice.* Also available in English

Japan	Draft standards available, e.g. Japan Society of Civil Engineering: JSCE-D 106-1995. *Quality Standards for Silica Fume Concrete (Draft)*
Australia	AS 3582. *Supplementary cementing materials* (1992)
Europe (CEN)	The proposed European standard for microsilica will be voted on in 1997
UK	British Board of Agrément Certificate 85/1568

In addition, a large number of national and project guidelines/specifications for microsilica/silica fume exist.

Concerning the use of microsilica in concrete, a number of documents are available. A very comprehensive guide has been published by American Concrete Institute Committee 234.[116]

12.11 Mix design criteria

There are dosage ranges depending on application that can serve as guidelines for initial trial mixes. It should, however, be stressed that even with the precedent of past work contained herein, trial mixes should always be conducted before acceptance of a mixture.

The following are often used as starting points (per cent of cement by weight)

Normal concretes	5–10
High strength	8–15
High chemical resistance	12–15
Underwater concretes	10–15
Pumping aid	2–5

Because of the high surface area of the microsilica, in nearly all ready-mix production a plasticiser is used to give optimum dispersion while maintaining the water/cement ratio, although this is not always necessary. Occasionally minor adjustments can be made to the total fines or to the coarse/fine ratio to accommodate the microsilica, reducing the need for a plasticiser. Such a mix design relies on the microsilica filling the bottom end in the fine fines percentage and producing a workable mix.

Mixing times will need to be adjusted to allow for maximum dispersion of the microsilica. This is most important when using any of the powder forms to prevent any agglomerates within the mix. The slurry form should not need increased mixing times.

Like most cementitious materials, the microsilica will function more efficiently with some types of chemical admixtures than with others and here again the need for comprehensive trial work is emphasised. No specific incompatibilities with concrete additives are known to the author, neither are generic preferences in, say, the type of superplasticiser.

12.12 Other mineral additions and calcium aluminate cements

Microsilica is very compatible with calcium aluminate cements, and published literature[117] indicates that the use of microsilica will prevent the conversion of high-alumina cement. The combined use of calcium aluminate cement and microsilica is an important part of modern refractory technology.[118]

Microsilica is compatible with both pfa and ggbs. When high replacement levels of pfa or ggbs are used, microsilica can be added to improve the early age strength, as it reacts faster in the first 3 days, or to improve the consistency of the fresh concrete. High replacement levels of ggbs can cause problems with bleed water, not only on the surface of the concrete but also within the matrix itself. The microsilica will virtually eliminate this bleed effect and hence maintain the integrity of the concrete.

With more standard replacement levels, microsilica is added to improve the concrete. In such cases the minor reduction in strength gain is offset by the microsilica and high early and ultimate strengths can be achieved without an excessive increase in the cost of the concrete.

When microsilica is used in forming a triple blend cement, improvements in both fresh concrete consistency and hardened concrete durability are gained. The beneficial characteristics of both pozzolanic materials combine in producing an optimally durable concrete. This type of concrete is being specified for the areas of major construction throughout the world where concrete structures are expected to last for upwards of 100 years, such as the Storebælt in Denmark, Northumberland Bridge in Canada and Tsing Ma Bridge in Hong Kong.

12.13 Concluding summary

The addition of microsilica to concrete, mortar or grout will produce significant changes in the structure and properties of the matrix. These include a densified refined pore system and greater strength through both a filler action and a pozzolanic reaction.

These improved properties help to design concretes that comply with onerous requirements or give improved durability in hostile environments. Microsilica should be considered as an addition to a mix rather than a replacement for cementitious content. Thus sensible mix design is essential, as discussed in section 12.11.

Microsilica concretes, mortars and grouts are susceptible to poor curing. The detrimental effects are more pronounced than in ordinary concretes. Close attention to the curing methods and times required by existing codes of practice is therefore important to ensure optimum performance of the finished product.

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13

Calcium Aluminate Cements

Karen L. Scrivener and Alain Capmas

13.1 Introduction

The term 'high-alumina cement' (HAC) came into use when this type of cement, containing 32–45 per cent Al_2O_3 was introduced in the UK after World War I, to distinguish it from Portland-type cements which contain much less alumina. Subsequently many other aluminous cements have been developed with alumina contents between 50 and 90 per cent, intended mainly for refractory purposes.

The common characteristic of all these types of cement is that the reactive phases and hydrates formed are calcium aluminates and they are therefore best referred to collectively as calcium aluminate cements (CACs). The term 'aluminous cements' is also commonly used, particularly in other European languages (e.g. French, 'ciment alumineux', and Spanish, 'cemento aluminoso').

Calcium aluminate cements are obtained by fusing or sintering a mixture, of suitable proportions, of aluminous and calcareous materials and grinding the resultant product to a fine powder.

In comparison with Portland cements, the annual production of calcium aluminate cements is very small; they are also considerably more expensive. Therefore they do not compete directly with Portland cement in everyday applications. However, they have several unique properties which make them the materials of choice in specialist applications where the performance of Portland cement is insufficient. When used in conventional concrete, these properties include

- rapid strength development, even at low temperatures;
- high temperature resistance/refractory performance;
- resistance to a wide range of chemically aggressive conditions.

CAC is also widely used in combination with other minerals and admixtures, including Portland cement and calcium sulfate. In such formations CACs contribute to a wide range of properties including rapid setting and drying and controlled expansion or shrinkage compensation.

The largest single use of CACs today is in refractory concretes (section 13.10.10), followed by their use as a reactive component of complex formulations used in construction (section 13.10.7). However, since this book mainly concerns the use of cements in concrete for construction, it is this aspect of calcium aluminate cements which is the main focus for this chapter.

Following some building collapses in the UK in the early 1970s (section 13.6.5), calcium aluminate cement concrete is not presently recommended there for general structural purposes. However, in the UK many structures containing this material continue to exist and perform satisfactorily, including some 50000 buildings containing precast CAC concrete beams. In addition, CAC concrete has continued to be used in niche applications justified by its unique properties.

The role of CAC concrete in construction has recently been reassessed by the UK Concrete Society.[1] The principal conclusion of this report is that 'Specifiers, users and clients should be encouraged to consider applications where calcium aluminate cements would have technical and commercial benefits either in conventional concrete form or as specialist proprietary products.'

This chapter summarises the present state of knowledge on the chemistry and performance of CACs and in the main refers to the 'standard' type of calcium aluminate cement (e.g. Ciment Fondu), which is the type mostly used in construction.

13.2 Origins of calcium aluminate cement

Reports from the mid-nineteenth century indicate that several investigators realised that alumina-rich calcium aluminates had excellent cementing properties[2-4] and the first patent for a limestone–bauxite cement appeared in 1888.[5] However, the industrial development of calcium aluminate cement is mainly associated with the work of Bied in the laboratories of the J. & A. Pavin de Lafarge company at Le Teil, France.[6] This work arose out of problems in France with the rapid degradation of mortars and concretes in ground containing large quantities of sulfates, notably gypsum and anhydrite.

Studies in the 1840s by Vicat led to him to suggest that a cement with a ratio of silica + alumina to lime + magnesia greater than unity would be resistant to sulfate action.[7] Starting from this hypothesis Bied considered pozzolanic additions, but knowing that the less basic calcium aluminate silicates had little cementing value, concentrated on the development of cements with a high alumina content. In 1908 this work resulted in the patenting of a manufacturing process in which bauxite, or other aluminous and ferruginous material of low silica content, was fused together with limestone.[8] The resulting cement proved not only to have the desired properties of sulfate resistance, but also to harden considerably more rapidly than the Portland cements then manufactured. It took several more years to develop a satisfactory method of manufacture on an industrial scale, and then 5 years of trials by the Lafarge Company and the French government, before the cement was put on the market in 1918 under the trade name Ciment Fondu Lafarge (CFL). However, the first uses of the cement took place during World War I for the construction of gun replacements, exploiting its rapid hardening potential; and, for its sulfate resistance, by the Paris–Lyon–Marseille (P.L.M.) Railway for reconstruction work of a tunnel passing through a solid mass of anhydrite.[9]

Contemporaneously with the work of Bied, patents were taken out by Spackman in the United States.[10-12] Spackman's aluminate compounds were intended for use as mineral additives (similar to pozzolanic materials) and were marketed for a time under the name of Alca natural cements, but their manufacture was later abandoned. A study of calcium aluminate cements was also carried out by Bates at the US Bureau of Standards in the early 1920s.[13]

13.3 Manufacture

13.3.1 RAW MATERIALS

The basic raw materials for the manufacture of calcium aluminate cement are limestone and bauxite. Although alumina is widely distributed in nature, bauxite is the only suitable material available commercially, on a scale adequate for cement production. The standard grades of CAC (38–40 per cent Al_2O_3) are made with ferruginous bauxites and contain up to 20 per cent Fe_2O_3. The silica content must be fairly low (<6 per cent), but several per cent TiO_2 is not a problem. During World War II, when bauxite was short, use was made of aluminium dross and the red mud from the Bayer process for the production of alumina.[14] For the grades of calcium alumina cements with higher alumina contents, purer raw materials are used, e.g. low-iron bauxites, alumina, lime, etc. Further details on raw materials can be found in Ref. 15.

13.3.2 METHODS OF MANUFACTURE

A variety of processes have been used for the manufacture of calcium aluminate cements. Originally they were made in a water-cooled vertical furnace, lined with refractory material, rather similar to, but much smaller than, a blastfurnace. For the production of the standard grades this type of furnace has been superseded by reverberatory open-hearth furnaces,[16] which is the most common method of manufacture today (Figure 13.1). This open-hearth

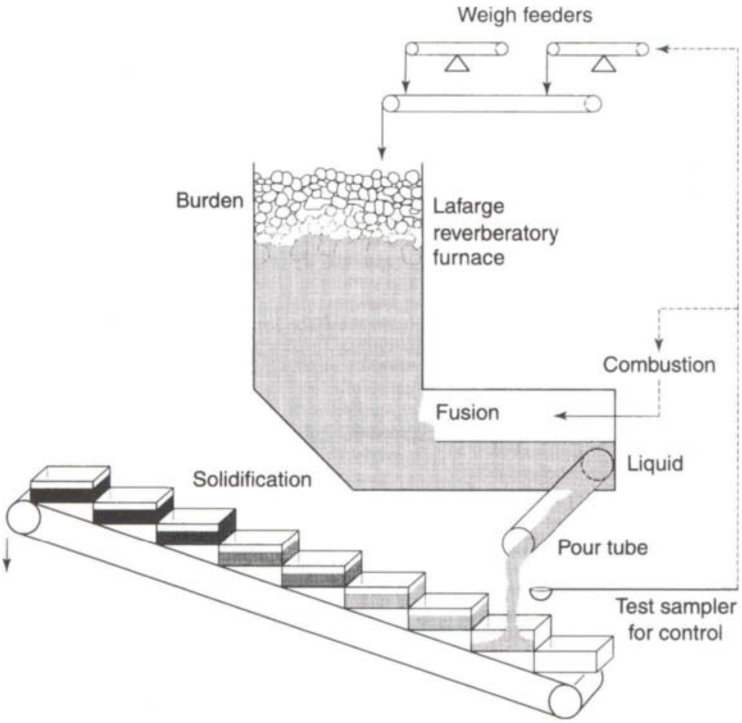


Fig. 13.1 Schematic diagram of a reverberatory furnace.

furnace is arranged with a long vertical stack into which the bauxite and limestone, or chalk, are charged. It is fired with pulverised coal or oil with a hot-air blast. The furnace gases pass through the charge of raw materials, driving off water and carbon dioxide. Melting occurs at the point where the charge drops from the vertical stack into the hearth of the furnace. The cement is maintained in a liquid state in the hearth by heat radiated from the arched roof. The molten cement pours out continuously from a tap hole, and is run into moulds and cooled. The temperature reached is above 1450°C. Electric arc furnaces are also used in some plants. These furnaces are tapped intermittently and so have a fairly low output.

After cooling, the fused cement clinker resembles a dark, fine-grained compact rock such as basalt. The clinker ingots are crushed and then ground in ball mills. The cement is very hard to grind, resulting in high power consumption and heavy wear on the grinding equipment. In contrast to Portland cements, where gypsum is added to regulate setting, no additions are made during grinding, the setting time being controlled primarily by the composition.

Grades of higher aluminate content (60–80 per cent Al_2O_3) are usually made by sintering in rotary kilns. As alumina is used instead of bauxite, they contain practically no silica or iron oxide and are white in colour. These grades are predominantly used as binding agents in castable refractories (section 13.10.10), although they are also used in some building chemistry formulations (section 13.10.7).

Calcium aluminate cements are manufactured in France, UK, Spain, USA, Japan, Croatia, China, Poland, Brazil, India, and on a small scale in many countries of the former USSR.

13.3.3 PHYSICAL CHARACTERISTICS OF CALCIUM ALUMINATE CEMENTS

The specific gravity of calcium aluminate cement rises with iron content. For the standard grades it is around 3200–3250 kg/m^3, which is somewhat higher than those of Portland cements. The loose bulk density depends on packing, but is typically around 1100–1400 kg/m^3, rising to 1850–1950 kg/m^3 on consolidation.

The standard grades of calcium aluminate cement on the market have a specific surface area (Blaine) of 250–400 m^2/kg, with a typical residue of 5 per cent on a 100 μm sieve. CACs with higher finenesses are available, especially for grades with a higher Al_2O_3 content, which may have a fineness up to 1000 m^2/kg.

Since CACs contain no free lime, calcium sulfate or periclase, tests for soundness are not really relevant. Expansions in the autoclave test are below 1 mm.

13.4 Composition and constitution of CACs

13.4.1 CHEMICAL COMPOSITION

Table 13.1 gives a summary of the approximate composition ranges of the various grades of calcium aluminate cement presently manufactured. The 'standard' grades (usually made by fusion), which are the main subject of this chapter, contain roughly equal amounts of calcium and aluminium oxides (36–42 weight%), up to 20 per cent of iron oxides (in both ferrous and ferric forms) and a few per cent of silica. Of the minor constituents, titania is present up to about 2 per cent, the content of magnesia is usually 1 per cent or less, and that of sulfate or sulfide less than 0.5 per cent. The content of alkalis is usually less than 0.5 weight%; too high an alkali content may produce undesirable quick setting. Insoluble

Table 13.1 Composition ranges for calcium aluminate cements

Grade	Colour	Al_2O_3	CaO	SiO_2	$Fe_2O_3 + FeO$	TiO_2	MgO	Na_2O	K_2O	Countries of manufacture
'Standard' low alumina	Grey or buff to black	36–42	36–42	3–8	12–20	<2	~ 1	~ 0.1	~ 0.15	France, Spain, Croatia, USA, India, Eastern Europe
Low alumina, low iron	Light buff or grey to white	48–60	36–42	3–8	1–3	<2	~ 0.1	~ 0.1	~ 0.05	France, USA, India, Korea, Brazil
Medium alumina	White	65–75	25–35	<0.5	<0.5	<0.05	~ 0.1	<0.3	~ 0.05	France, UK, USA, Japan, China, India, Korea, Brazil
High alumina	White	$\geqslant 80$	<20	<0.2	<0.2	<0.05	<0.1	<0.2	~ 0.05	USA, France, Japan, Brazil, Korea

matter is around 2 per cent. The cements usually show a gain on ignition owing to the oxidation of the ferrous oxide.

13.4.2 PHASE COMPOSITION

All CACs contain monocalcium aluminate ($CaAl_2O_4$ or CA) as the principal hydraulic phase in amounts from 40 per cent upwards. The white CACs contain very low concentrations of iron oxides, SiO_2 and other minor components and essentially lie in the two-component system $CaO-Al_2O_3$ (Figure 13.2). The higher-alumina grades, made by sintering, are not equilibrium products. These may contain CA_2 in addition to CA and $C_{12}A_7$ and may also have α-Al_2O_3 added after sintering. Tricalcium aluminate, C_3A, is not a normal constituent of CACs. CA_6 is rarely present.

Understanding of the phase composition of the standard-grade CACs is complicated by the presence of silica and of iron oxide in both the ferric (Fe_2O_3 or F) and ferrous (FeO or f) forms (the relative amounts depending on the extent to which an oxidising atmosphere is maintained in the furnace during production). Several studies of the equilibria within this six-component system have been made.[17-24] The regions of CACs in the two three-component systems $CaO-Al_2O_3-SiO_2$ (C-A-S) and $CaO-Al_2O_3-Fe_2O_3$ (C-A-F) are shown in Figure 13.3.

The possible five phase equilibrium assemblages relevant to standard-grade CACs, which always include CA and ferrite solid solution (F_{ss}), are:

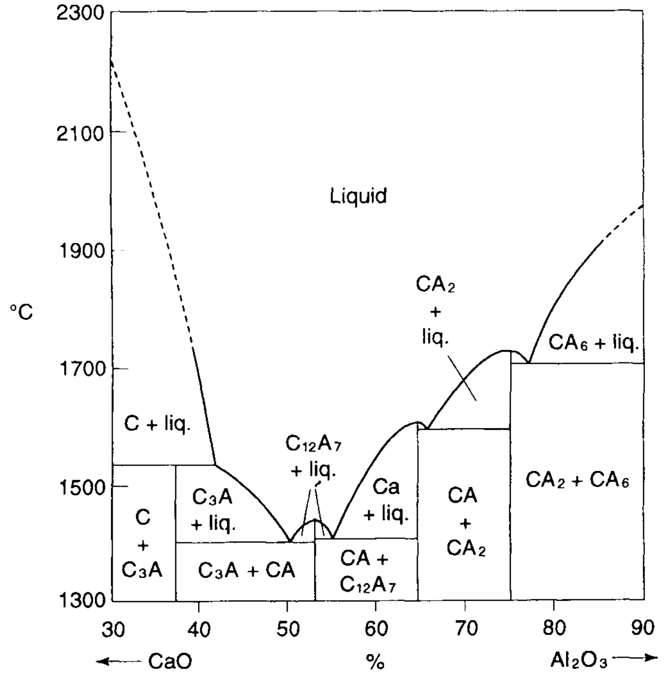


Fig. 13.2 $CaO-Al_2O_3$ phase diagram.

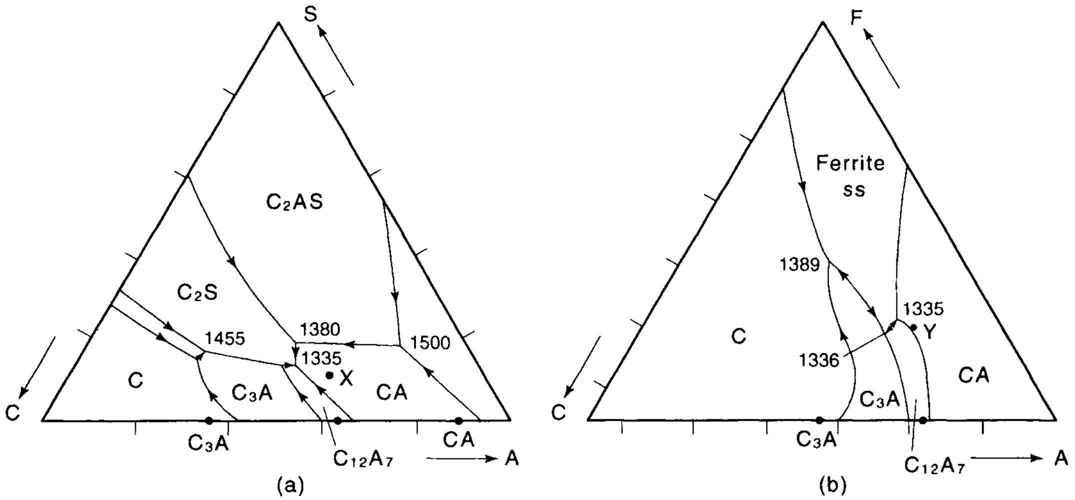


Fig. 13.3 (a) Part of the $CaO-Al_2O_3-SiO_2$ phase diagram. Point X represents the composition of Ciment Fondu excluding iron oxide. (b) Part of the $CaO-Al_2O_3-Fe_2O_3$ phase diagram. Point Y represents the composition of Ciment Fondu excluding silica.

- CA–F_{ss}–$C_{12}A_7$–FeO–pleochroite
- CA–F_{ss}–$C_{12}A_7$–C_2S–pleochroite
- CA–F_{ss}–C_2S–C_2AS–pleochroite
- CA–F_{ss}–C_2S–FeO–pleochroite
- CA–F_{ss}–C_2AS–FeO–spinel

Silica is usually present as C_2S, C_2AS (gehlenite) or both. A relatively low silica content is important to minimise the formation of the low-reactivity C_2AS which combines alumina at the expense of the reactive phase, CA. Most of the iron oxide usually exists as ferrite solid solutions in the series C_6A_2F–C_2F with substantial incorporation of TiO_2, SiO_2 and MgO. The presence of ferrous oxide leads to the formation of one or a combination of a spinel phase, wüstite (FeO) and pleochroite. In cements containing pleochroite the content of CA is much reduced and the strength is usually lowered. Other minor oxides are usually present in solid solution.

During solidification the melt is cooled rapidly at the edge of the ingot and more slowly in the interior, resulting in a wide range of crystalline assemblages which may depart from equilibrium. A small quantity of glass is also generally present. The ground cement contains polymineralic grains containing up to four or five phases (Figure 13.4).

Some characteristics of the more important phases are described below.

Monocalcium aluminate

Monocalcium aluminate ($CaAl_2O_4$ or CA) is monoclinic, pseudohexagonal, with a density of 2945 kg/m^3. The CA present in industrial cement is a solid solution, which usually has a higher refractive index than the pure compound due to the presence of iron. Jeanne found up to 4.5 weight% Fe^{3+} in CA.[25] Sorrentino proposed an average composition $Ca_xAl_yFe_zSi_tO_{x+3/2(y+z)+2t}$ with x varying from 4.4 to 4.8, y from 4.7 to 5, z from 0 to 1.3 and t from 0 to 0.1.[23]

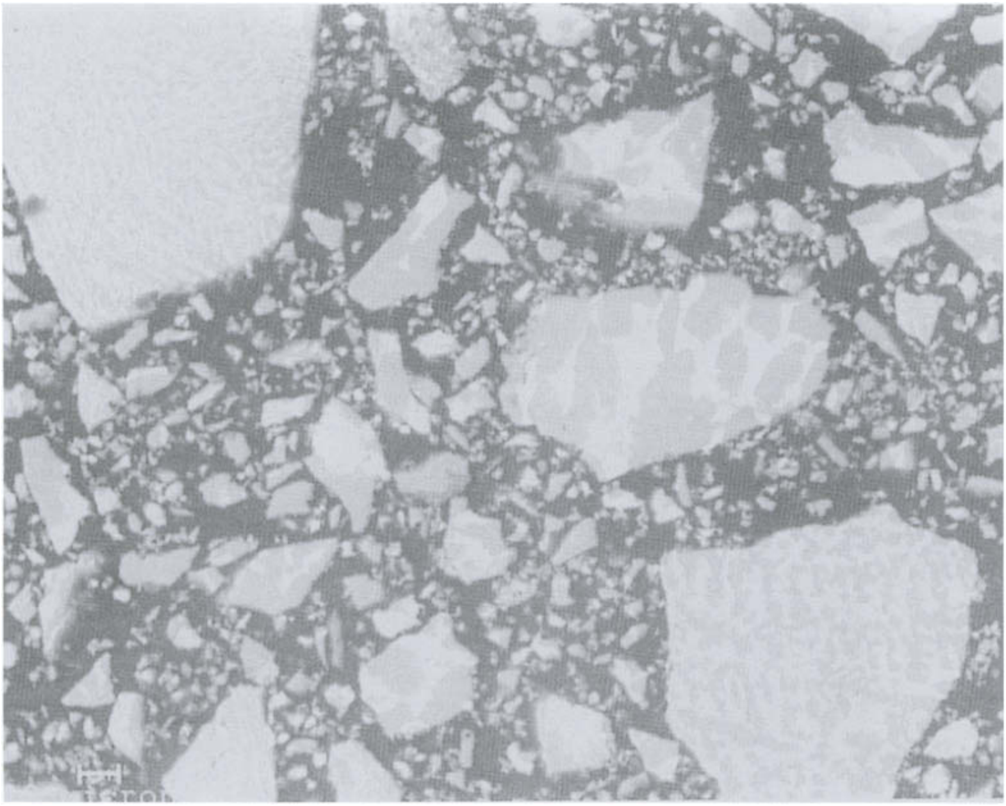


Fig. 13.4 Backscattered electron (BSE) micrograph of a polished section of standard grade CAC in the scanning electron microscope (SEM). Grains of various sizes can be seen dispersed in resin. The size of the crystals within the grains also varies due to the variation in cooling rate through the clinker. Within the most coarsely crystalline grains four phases can be distinguished: the most prevalent (darkest) phase is monocalcium aluminate, CA; the lighter grey phase is dicalcium silicate; the bright phase is ferrite solid solution; and the small amounts of white phase are wüstite or spinel high in iron.

$C_{12}A_7$

Dodecacalcium heptaaluminate ($C_{12}A_7$) is nearly always present in calcium aluminate cements. $C_{12}A_7$ was for a long time misidentified as 'stable' C_5A_3. This phase is cubic and often has a triangular morphology in microscopic sections. $C_{12}A_7$ is obtained under oxidising conditions, and can have a water uptake of up to 1.4 per cent at normal humidity at 950/1350°C; the formula $Ca_{12}A_{14}O_{32}(OH)_2$ was proposed by Jeetvaratnam *et al.*[26] and later by Sing and Glasser.[27]

Pleochroite

The phase now referred to as pleochroite or fibres (due to its morphology in section; Figure 13.5), was for a long time thought to be an unstable form of C_5A_3. In the past it was the subject of considerable investigation.[23,28 31] This phase is now generally accepted to form when there is some reduction of the iron in the melt from Fe^{3+} to Fe^{2+}. The pleochroite

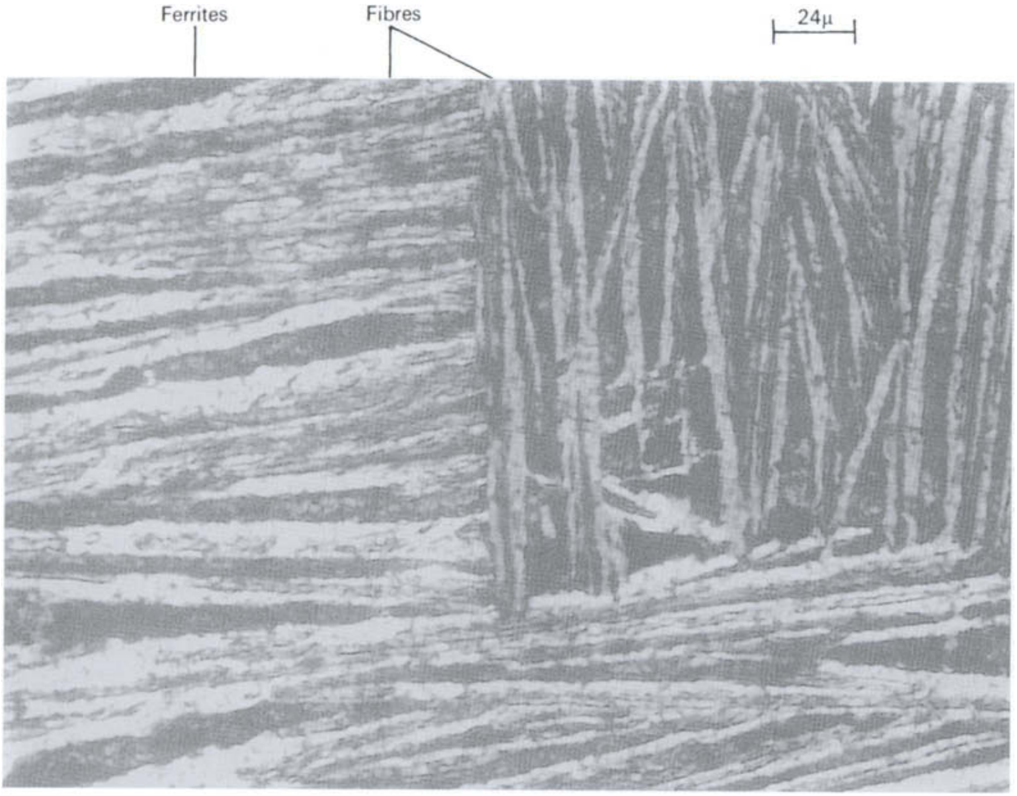


Fig. 13.5 Optical micrograph of pleochroite.

in industrial cements is a complex solid solution containing ferric and ferrous iron, silica and magnesia. Hanic *et al.*[32] showed the unsubstituted compound to have the composition $Ca_{20}Al_{32-2n}Mg_nSi_nO_{68}$. The formula suggested from microprobe analyses by Conjeaud[33] is $Ca_{20}Al_{22.6}Fe^{3+}_{2.4}Mg_{3.2}Fe^{2+}_{0.3}Si_{3.5}O_{68}$.

Ferrite solid solution

This phase was first identified in calcium aluminate cements by Tavasci.[34] The composition, sometimes quoted as C_4AF is in fact variable both in terms of its A/F ratio and also in the amounts of SiO_2, TiO_2, MgO and smaller quantities of other elements in solid solution. Microanalyses of this phase are made difficult by the fact that the crystal size is often below 1 μm. However, it appears that the A/F ratio is generally less than 1 and that the composition of this phase may vary from grain to grain in a single cement.

Gehlenite

Gehlenite belongs to the melilite family. The stoichiometric formula is $Ca_2Al_2SiO_7$, but the compound in CAC is found to be high in Al_2O_3 and low in SiO_2, possibly due to solid solution or random interlaying with C_5A_3,[35] or pleochroite.[36] The gehlenite in iron containing CACs typically contains about 9 per cent Fe_2O_3.[37] Pure C_2AS has little or no hydraulic activity, but the impure compound found in CACs may not be so unreactive.[32,38]

13.4.3 DETERMINATION OF PHASE COMPOSITION AND PETROGRAPHIC EXAMINATION

Due to the complexity and variability of the phase assemblages, there is no generally accepted equivalent of the 'Bogue' calculation, used for Portland cements, to calculate the potential phase composition of calcium aluminate cements. Parker suggested some approximate methods based on analytical data from the cement and on the insoluble residue after solution in 0.5 N HCl.[29] More recently Calleja[39] and Sorrentino and Glasser[40] have proposed calculation procedures to estimate the phase compositions of fused cements from the chemical compositions. These models give reasonable agreement with experimental determinations of CA and ferrite contents providing that $(FeO + MgO) < 3.7$ per cent, but some discrepancies remain in the calculation of the contents of the minor phases C_2S, C_2AS, $C_{12}A_7$ and pleochroite. This might be explained by departures from equilibrium during crystallisation in industrial production.

X-ray diffraction has been widely used to estimate the phase composition of CACs, e.g. Refs 41–43. However, as with Portland cements there is extensive overlap of the peaks from the different phases and variation of the peak positions due to solid solution, such that quantitative analysis is difficult. Small quantities of minor phases such as C_2S and wüstite may not be detected.

The petrographic examination of polished and thin sections of calcium aluminate cement is used, although the structure of the clinker is such that identification of the phases may not be easy. In addition, there is much more variability from one clinker to another, or even between different parts of the same clinker, than is common with Portland cement clinker. Due to the different cooling rates, the crystal size may vary considerably from fine grained to coarse. In fine-grained samples the general appearance is of transparent prismatic, lath and fibre-shaped crystals set in a brown to opaque groundmass. The larger transparent crystals are CA, gehlenite and $C_{12}A_7$, although not all of them may occur together in the same section. It is often difficult to distinguish between CA and gehlenite. Pleochroite is easily recognised by its characteristic fibrous form in sections and strong violet pleochroism. Very occasionally, samples can be obtained in which this compound predominates, and crystals may then be very large in size. The other phases cannot be identified with certainty in thin sections by optical microscopy, although ferrites are usually assumed to be one of the constituents.

Backscattered electron (BSE) imaging in the scanning electron microscope (SEM) is a very useful technique for studying the phase distribution (Figure 13.4), and compositions of the individual phases may also be determined by X-ray microanalysis,[35,44] although this may be only approximate for phases below 1 μm in size.

13.5 Hydration of CACs

13.5.1 CALCIUM ALUMINATE HYDRATES

In contrast to the hydration of calcium silicate compounds, in which the hydrates formed remain broadly similar with time and temperatures up to about 100°C, the process of hydration in calcium aluminate cements is strongly dependent on temperature. The stable hydrates at all temperatures from 5°C (and possibly lower) are C_3AH_6 (a form of hydrogarnet) and γ-AH_3 (gibbsite). However, the nucleation of these stable hydrates is usually preceded by the formation of metastable hydrates, CAH_{10}, C_2AH_8 and amorphous phases. The reaction of the metastable phases to the stable phases is known as 'conversion'. At ambient temperatures the metastable hydrates may persist for many years, but there is an inevitable thermodynamic force for conversion to the stable hydrates. Some physical properties of the calcium aluminate hydrates are given in Table 13.2.

Figure 13.6 shows the characteristic morphology of CAH_{10} (fine needles) and C_2AH_8 (hexagonal plates) seen on fracture surfaces; C_3AH_6 (not illustrated in Figure 13.6) is characterised by equidimensional crystals. Figure 13.7 shows the appearance of these phases in backscattered electron images of polished surfaces. CAH_{10} often forms relatively massive areas with no distinct morphology, C_2AH_8 still forms in plates, while crystals of C_3AH_6 may be very small and may occur in granular aggregates.

Poorly crystalline or amorphous hydrates may also form in CAC pastes. These have not been well characterised. They are often assumed to be based on hydrous alumina and the term 'AH_3 gel' is often used. However, several authors report that at early ages they may have compositions closer to CAH_{10}.[48,49] NMR studies by Cong and Kirkpatrick[50] also indicated the presence of amorphous material, possibly containing aluminium in fivefold coordination.

13.5.2 *HYDRATION REACTIONS OF CALCIUM ALUMINATES (CA AND $C_{12}A_7$)*

$$CA + 10H \rightarrow CAH_{10} \tag{13.1}$$

$$2CA + 11H \rightarrow C_2AH_8 + AH_3 \tag{13.2}$$

$$3CA + 12H \rightarrow C_3AH_6 + 2AH_3 \tag{13.3}$$

$$2CAH_{10} \rightarrow C_2AH_8 + AH_3 + 9H \tag{13.4}$$

$$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H \tag{13.5}$$

Equations (13.1)–(13.5) show the possible reactions during the hydration of monocalcium aluminate (CA) and analogous reactions may be written for $C_{12}A_7$.

For CA, at temperatures below 10°C the formation of CAH_{10} [equation (13.1)] predominates, this phase continues to form up to about 27°C. Between 10 and 27°C CAH_{10} and C_2AH_8 are formed together [equations (13.1) and (13.2)]. At higher temperatures

Table 13.2 Cell parameters and densities of calcium aluminate hydrates (adapted from Refs. 45 and 46)

	CAH_{10}[47]	C_2AH_8[a]	C_3AH_6	C_4AH_{13}[a]	C_2ASH_8[a]	γ-AH_3 gibbsite
Crystal system	Hexagonal	Hexagonal	Cubic	Hexagonal	Hexagonal	Monoclinic
Unit cell or structural element (nm)	$a = 1.6381$ $c = 0.8317$	$a = 0.574$ $c = 1.07$	$a = 1.257$	$a = 0.5752$ $c = 0.794$	$a = 0.5747$ $c = 3.764$	$a = 0.864$ $b = 0.507$ $c = 0.972$ $\beta = 94.57°$
Density (kg/m^3)	1720	1950	2520	2046	1936	2400

[a] Structural element.

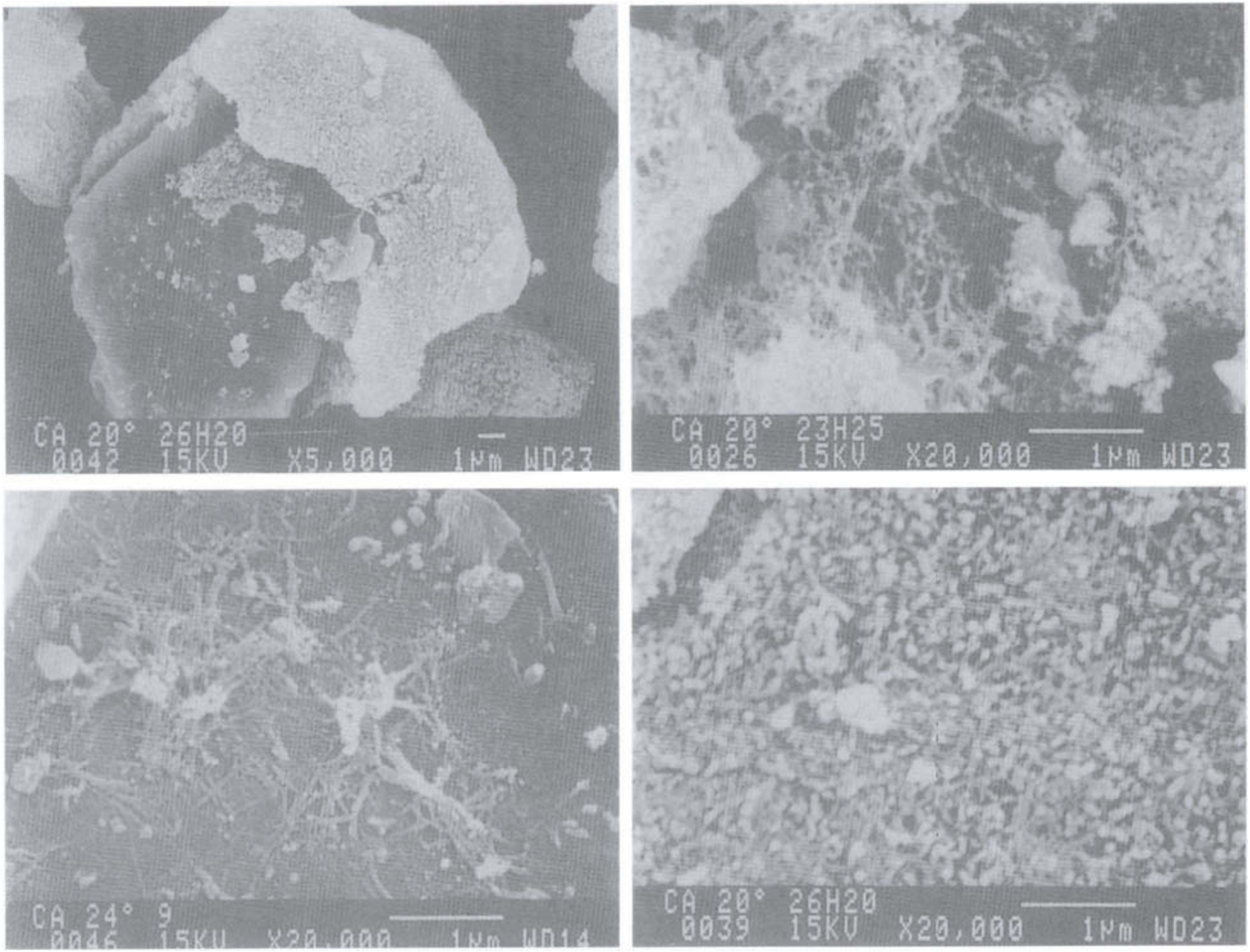


Fig. 13.6(a) SEM micrographs showing well-formed CAH_{10} (courtesy of D. Sorrentino).

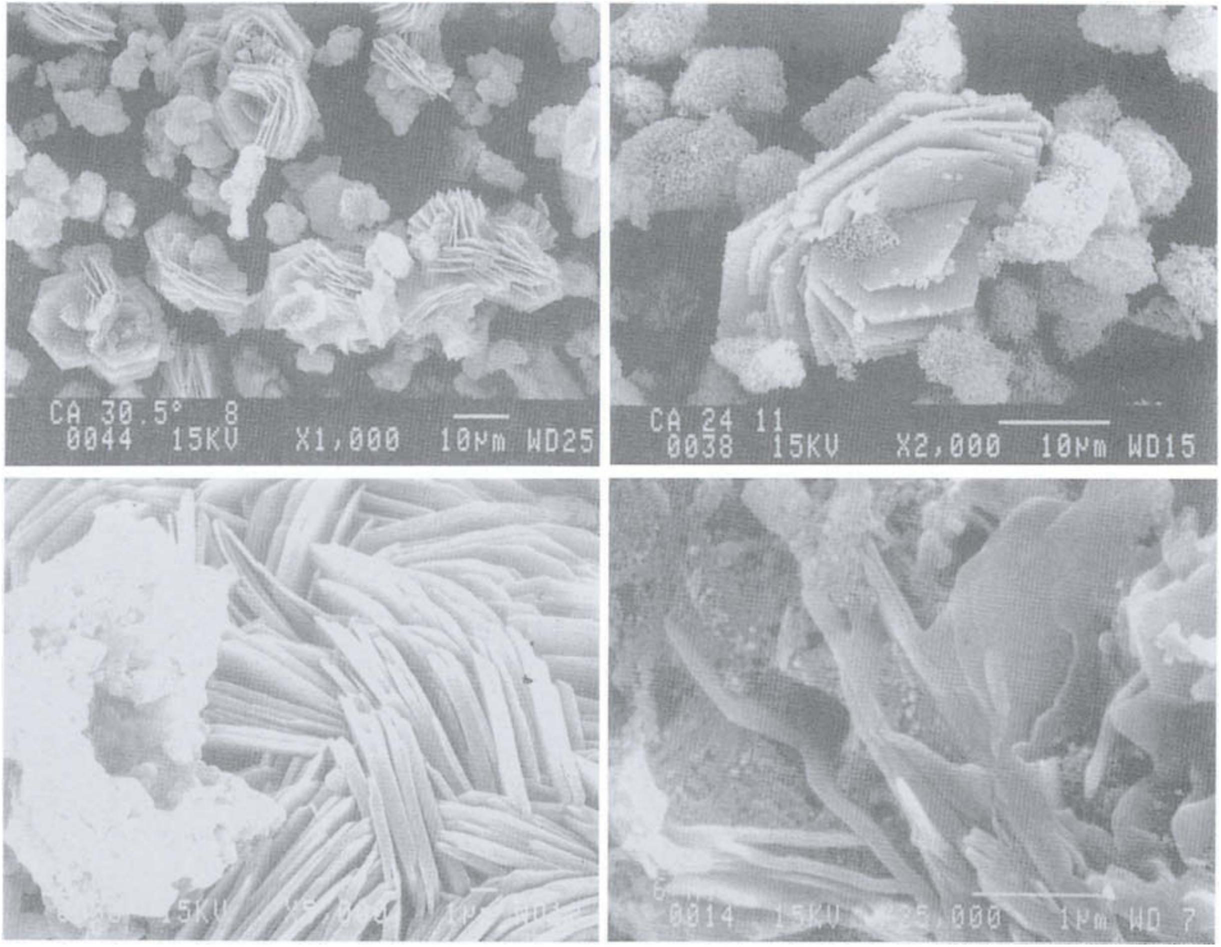
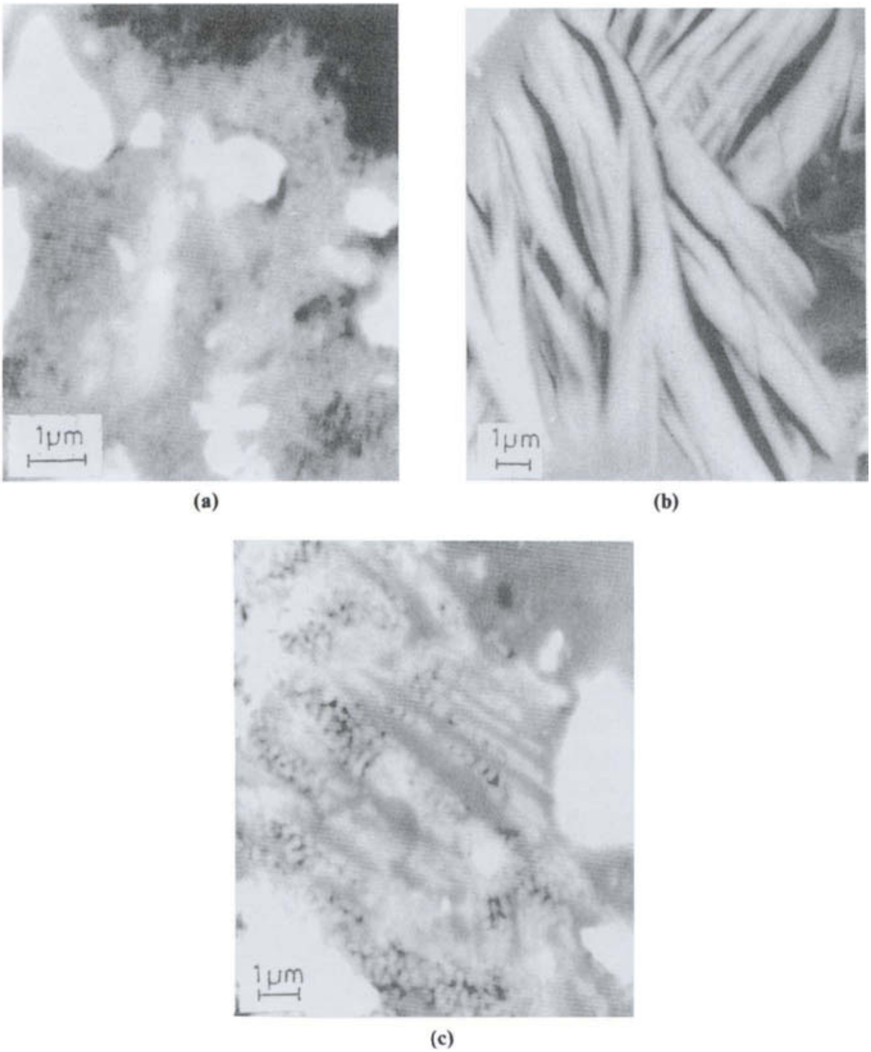


Fig. 13.6(b) SEM micrographs showing well-formed C_2AH_8 (courtesy of D. Sorrentino).



(a) (b) (c)

Fig. 13.7 BSE micrographs of polished sections of hydrated CAC showing (a) CAH_{10}, (b) C_2AH_8 and (c) C_3AH_6.

CAH_{10} no longer forms and the stable phase C_3AH_6 occurs early in the hydration process. It has been claimed that the formation of C_3AH_6 is always preceded by the transitory formation of some C_2AH_8, even at temperatures up to 90°C,[51] but the direct formation of C_3AH_6 from CA [equation (13.3)] can take place after some C_3AH_6 has been nucleated. This phase rapidly becomes the only hydrate present when hydration occurs at temperatures above 50°C. Equations (13.4) and (13.5) show the conversion of the metastable hydrates, the rate of these reactions is dependent on temperature, moisture state and possibly other variables such as the water/cement ratio. The crystallisation of AH_3 gel to gibbsite is also highly temperature dependent and sluggish at ambient temperatures.

The higher C/A ratio of $C_{12}A_7$ favours the formation of C_2AH_8, and very little CAH_{10} is detected in the hydration of this phase at ambient temperatures. The hydration of $C_{12}A_7$ is very exothermic so the formation of the stable hydrates generally occurs sooner.

In industrial calcium aluminate cements, CA and $C_{12}A_7$ are the only phases which react significantly at early ages. Despite the presence of small amounts of $C_{12}A_7$, CAH_{10} is the predominant hydrate at low temperatures, below 15°C.[32,52] Figure 13.8 shows typical DTA traces for Ciment Fondu cured at 20, 30 and 38°C[53] which illustrate the changes in the hydrates formed. This figure also indicates significant quantities of 'gel' (section 13.5.1) at all the temperatures.

13.5.3 MECHANISM OF HYDRATION

The mechanism of hydration of the calcium aluminates is generally accepted to be 'through solution', i.e. by dissolution of the anhydrous phases followed by precipitation of the hydrates from solution.

On shaking together either of the pure compounds CA, $C_{12}A_7$ or calcium aluminate cement and excess water at room temperature, a supersaturated solution with a CaO/Al_2O_3 molar ratio a little above unity is formed. The concentration of this solution rises fairly rapidly to a maximum with the CaO/Al_2O_3 molar ratio remaining around 1.1–1.2. After reaching the maximum concentration the solution becomes opalescent, a solid is precipitated and the concentration then falls abruptly (Figure 13.9).[54-57] The time at which the maximum is reached increases as the water/cement ratio increases, while the maximum concentration attained decreases slightly. However, the ratio of lime to alumina concentrations in solution at the maximum remains roughly the same.

The changes in lime and alumina concentrations in solution have been studied and interpreted by Barret and coworkers.[58,59] Instead of plotting the ionic concentration of lime and alumina against time, the concentration of alumina in solution is plotted against the concentration of lime at the same time for a series of readings. The resulting curves show the development of the solution concentration over time on the $CaO-Al_2O_3-H_2O$

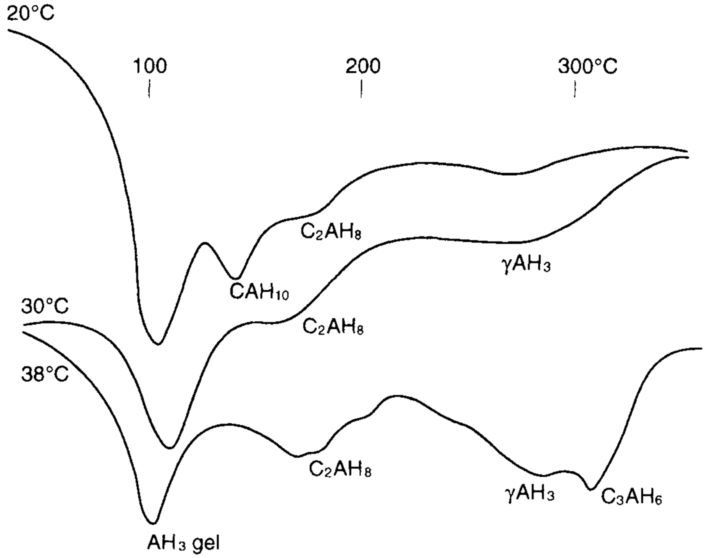
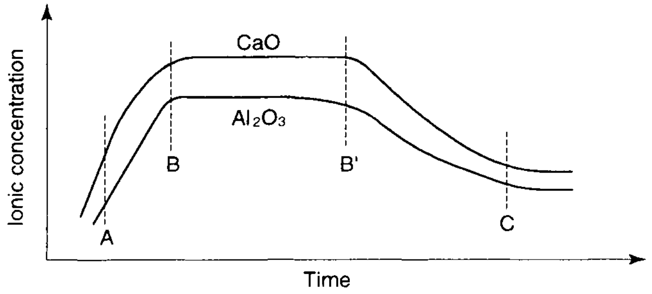


Fig. 13.8 Differential thermal analysis (DTA) curves of CAC cured at 20°C (upper), 30°C (middle) and 38°C (lower).



A → B represents the dissolution period;
B → B' represents the nucleation period;
B' → C represents the bulk precipitation period;
C → represents continued simultaneous precipitation/dissolution.

Fig. 13.9 Evolution of the concentration of calcium oxide and alumina in solution during the hydration of CA.

diagram. The solubility curves of the hydrate phases, from experimental studies (e.g. Refs 60–63) or thermodynamic calculations,[58] can be plotted on the same diagram (Figure 13.10).

The hydration mechanism can then be interpreted as follows. Initially, on addition of water the anhydrous phases (CA or $C_{12}A_7$) dissolve without precipitation of any hydrates. If the solution concentration rises above a critical level of supersaturation for either C_2AH_8 or AH_3, a small amount to these hydrates will precipitate, but the solution concentration will then fall below the level of supersaturation necessary for precipitation. As a consequence, the concentration of the solution tends to follow a line between the two curves, along which the solution is below the critical level of supersaturation for both hydrates such that there is no significant precipitation of either phase. This line is called the 'line of minimum instability' and has a C/A ratio slightly greater than unity, in accord with the earlier experimental observations. With continued dissolution of the anhydrous phases the concentrations in solution increase to a limit, attributed to the equilibrium solubility of the anhydrous phases with hydroxylated surface layers. After an induction period, during which the nuclei attain critical size, massive precipitation of the hydrates occurs and the concentrations in solution drop to the hydrate solubility curves. (A more detailed account of the hydration mechanisms of CACs can be found in Ref. 46.

This thermodynamic representation can also be used to explain the variation in the hydrates formed with temperature. The solubility of all the hydrates changes with temperature, but that of CAH_{10} is especially sensitive. As the temperature increases up to 27°C, nucleation of this phase becomes increasingly disfavoured relative to C_2AH_8.

13.5.4 HYDRATES FORMED BY THE PRESENCE OF SILICA

Pure gehlenite does not seem to react with water but the compound present in calcium aluminate cement contains other oxides in solid solution, and there is evidence that it is more reactive. The presence of gehlenite hydrate (C_2ASH_8), also called strätlingite, in CAC pastes has been reported by several authors.[35,64,65] Strätlingite might also arise from

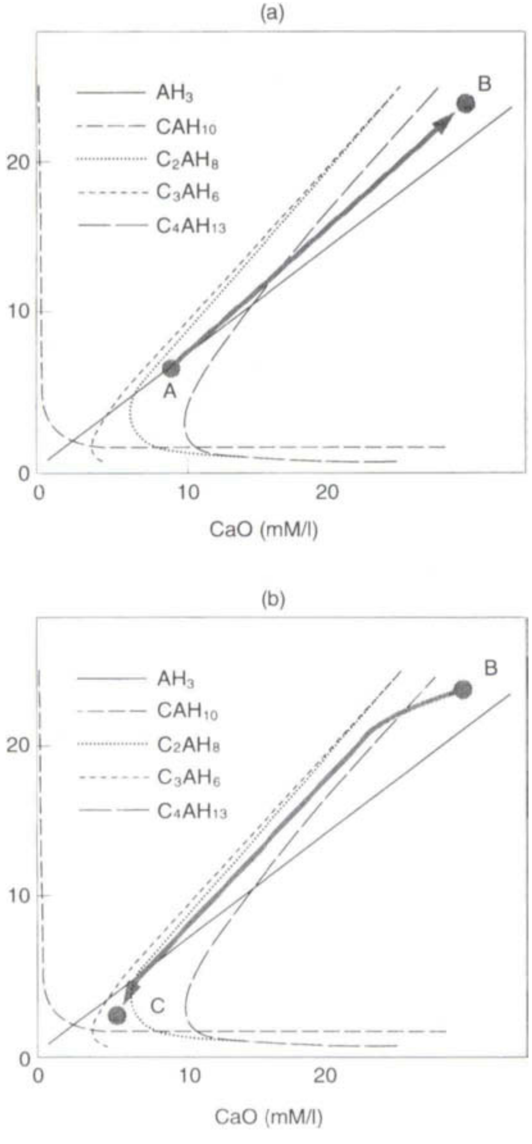


Fig. 13.10 Calculated solubility curves for the calcium aluminate hydrate with the evolution of the solution concentration during dissolution (a) and precipitation (b) superimposed. (Letters correspond to those in Figure 13.9.)

hydration of C_2S in the alumina-rich solution formed by the cement. Strätlingite may also form with additions containing reactive silica such as blastfurnace slag or silica fume, as discussed further in section 13.5.7.

Microanalyses of old samples of CAC concrete indicate that the hydrogarnet phase based on C_3AH_6 also contains significant amounts of silica.[44]

13.5.5 HYDRATES FORMED BY THE PRESENCE OF FERRITES

At 20°C the reaction of the ferrite solid solution (F_{ss}) is negligible at early ages, but at 30–38°C over 80 per cent can have reacted after several months.[66] Houghton and Scrivener[44,67] found that the apparent degree of reaction of the ferrite phase in pastes of 'Ciment Fondu' was strongly affected by temperature. At 20 and 40°C there was little evidence of reaction of this phase, whereas at 70 and 90°C a substantial amount of reaction occurred even after a few hours' hydration. However, the details of the hydration reactions of ferrites in calcium aluminate cements are still not clear.

Studies of the hydration of F_{ss} alone indicate that $C_2(A,F)H_x$ is only formed during the hydration of F_{ss} rich in alumina,[68] which is not generally the case in calcium aluminate cements. Nevertheless, this phase has been reported to occur in CAC pastes,[69] perhaps due to the presence of the calcium aluminates. When ferrites rich in iron are hydrated alone, $C_4(A,F)H_x$ is usually formed at low temperatures, together with an amorphous form of hydrous iron oxide.[70–73] The ratio of A/F in the hydrates is always found to be higher than that in the anhydrous material. However, although Schwiete and Ludwig[74] detected $C_4(A,F)H_x$ in suspensions (w/c = 10), its occurrence in CAC pastes has not been reported. At temperatures of 25°C and upwards $C_3(A,F)H_6$ is formed in amounts increasing with time and temperature. The extent to which iron can enter into solid solution in the hydrogarnet phase in CAC pastes is controversial,[70,72,75] and may be affected by the presence of silica.

The other iron-containing phases have very low reactivity irrespective of temperature.

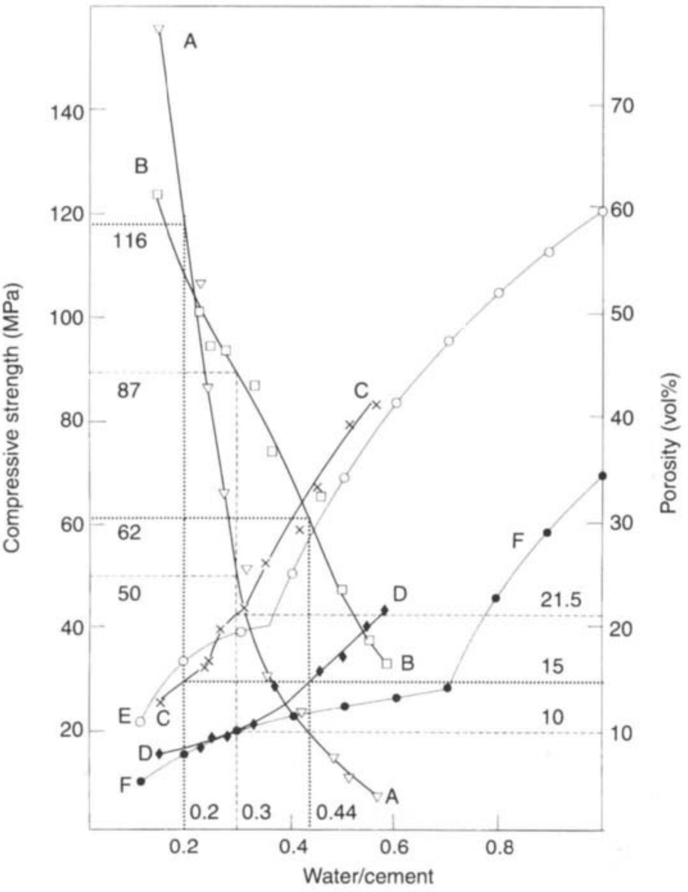
13.5.6 COMBINED WATER AND VOLUME CHANGES DURING HYDRATION

The volume changes occurring on hydration can be calculated from the densities of the hydrate phases (Table 13.2). These are discussed in detail by George.[53] The amount of water needed for complete hydration, also known as the critical water/cement ratio, depends on the nature of the hydrates formed. For a typical standard grade CAC containing about 50 per cent CA and 30 per cent ferrite, the critical water/cement ratio at low temperatures (principal hydrate CAH_{10}) is 0.7. For high temperatures, at which the stable hydrates C_3AH_6 and gibbsite are formed, it is 0.35. (This compares with a value of around 0.3 for Portland cements.) Experimental data[76] for CAC pastes hydrated at 10°C and 70°C agree well with these theoretical values for the pastes hydrated at the higher temperature and for those hydrated at the lower temperature for water/cement ratios below 0.4 (Figure 13.11). Water added in excess of the critical w/c = 0.35 will not be combined in the stable hydrates and will only contribute to the porosity of the paste, with an adverse effect on strength, as illustrated in Figure 13.12.

As with the hydration reactions in Portland cements the solid volume of the hydrates formed is greater than the volume of anhydrous compound from which they form, but less than the total volume of the anhydrous plus liquid water:

$$V_{\text{anhydrous}} + V_{\text{water}} > V_{\text{hydrates}} > V_{\text{anhydrous}}$$

The overall decrease in volume or 'chemical shrinkage' for the hydration of monocalcium aluminate is 16 per cent for the formation of CAH_{10}, and 25 per cent for the formation of C_3AH_6 and AH_3. This results in an average volume decrease for standard grade CACs of 10–12 per cent, similar to that for Portland cements. This difference does not



Curing	*Hydrate*	*Property*	*Curve*
7 days at 70°C	$C_3AH_6 + AH_3$	Compressive strength	A
		Porosity	C
		Porosity	E
7 days at 10°C	CAH_{10}	Compressive strength	B
		Porosity	D
		Porosity	F

Fig. 13.11 Porosity and compressive strength of neat Ciment Fondu pastes as a function of water/cement ratio.

correspond to the macroscopic shrinkage of concrete (section 13.7.1) which is about two orders of magnitude lower, as with Portland cement concrete.

The volume changes occurring during the conversion of the metastable to stable hydrates may also be calculated.

$$3CAH_{10} \rightarrow C_3AH_6 + 2AH_3 + 18H \qquad (13.6)$$

$$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H \qquad (13.7)$$

In reaction (13.6) the volume of the solids is reduced to just below half, and in reaction

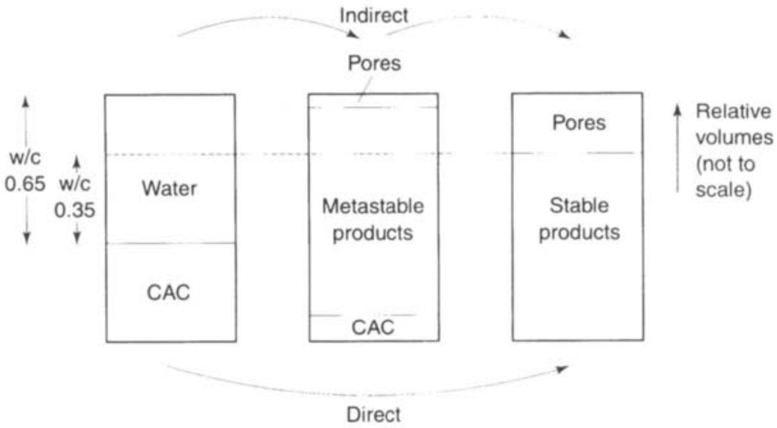


Fig. 13.12 Volume repartition of components in a CAC paste during hydration via the metastable hydrates or directly to the stable hydrates.

(13.7) to about two-thirds of the original volume. However, it must also be noted that water is released during these reactions, which is then available to react with any remaining anhydrous cement leading to a subsequent increase in solid volume. It is more straightforward to consider the long-term volume changes in terms of the direct reaction to C_3AH_6 and AH_3 as indicated in Figure 13.12.

13.5.7 HYDRATION OF MIXTURES OF CALCIUM ALUMINATE CEMENT WITH OTHER MATERIALS

CAC + reactive siliceous materials

Recently there has been considerable study of the effect of siliceous additives on the hydration of CACs. In general it has been observed that these lead to the formation of strätlingite as one of the hydrate phases. Strätlingite (C_2ASH_8) is an AFm phase closely related to C_2AH_8. In contrast to C_2AH_8, strätlingite is stable relative to hydrogarnet at ambient temperatures.

Majumdar and coworkers at the Building Research Establishment, UK, have made extensive study of mixtures of CAC and slag,[77 82] which have been patented under the name BRECEM.[83,84] With slag contents of around 50 per cent, C_2ASH_8 becomes the dominant hydrate at temperatures up to 40°C. However, even at 40°C significant amounts of C_3AH_6 are still formed. In addition, Fentiman *et al.*[85] found that this phase is again the dominant hydrate when hydration occurs at temperatures of 45°C or above. At early ages the strengths of 50:50 CAC/slag mixtures are about half those of CAC alone. However, the blends show continuous strength gains up to 2 years, without a minimum in strength associated with the conversion process. At higher temperatures above 40°C the strengths of the blends are considerably reduced (Figure 13.13).

Bentsen *et al.*[86] studied mixtures of CAC with 30 and 50 per cent silica fume, but only reported results up to 7 days' hydration. In these blends strätlingite was also found to be the dominant hydrate after 1 week, for temperatures of 40°C or below, but at higher temperatures C_3AH_6 had already formed after 1 day. Similar findings were reported by Marcdargent *et al.*[87]

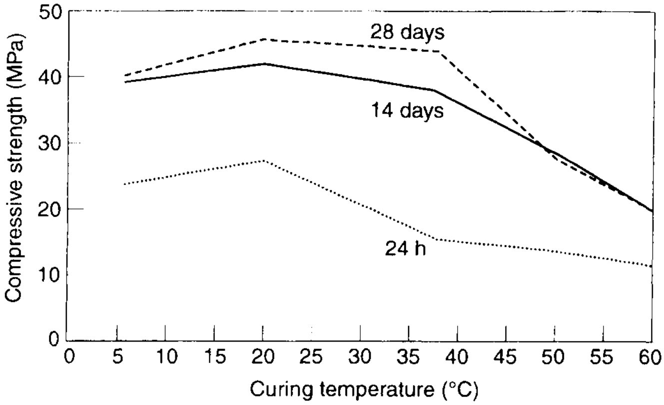


Fig. 13.13 Strength development for Fondu/slag concretes cured at different temperatures.

Ding, Fu and Beaudoin have investigated the effect of a wide range of siliceous additives including silica fume, fly ash, ground granulated blastfurnace slag, zeolites and sodium silicate on the hydration of CAC at temperatures up to 38°C.[88] [91] In all cases strätlingite was formed. Initial strengths were lower than CAC alone, but additions of sodium salts, which increased the pH, were found to increase the rate of strätlingite formation and strength development (see also section 13.6.2).

CAC + Portland cement

The variation in setting time of mixtures of a Portland and a calcium aluminate cement is shown in Figure 13.14.[92] It can be seen that over a range of compositions very rapid or even flash set occurs. This phenomenon is used in practice to produce rapid-setting mortars, usually in conjunction with admixtures. The range of compositions over which flash set occurs is very variable and depends principally on the type of Portland cement used, especially the amount and type of sulfate it contains. The amount of CAC in the CAC–OPC mixture needed to produce rapid set varies between about 20 and 50 per cent

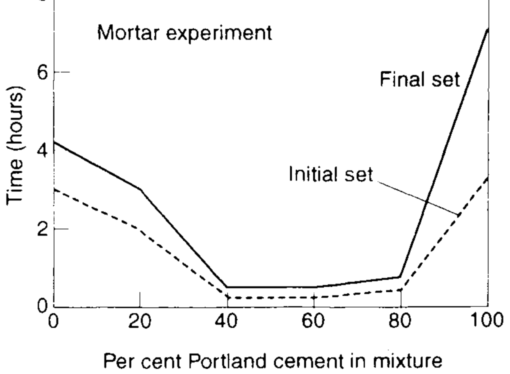


Fig. 13.14 Variation in setting time for mixtures of Portland and calcium aluminate cement.

for the standard grades of CAC. CACs containing higher proportions of monocalcium aluminate, or more finely ground, may produce rapid set at lower levels of addition.

The mechanism responsible for flash setting is not fully understood. It is possible that the setting is due to the uncontrolled reaction of the C_3A (in the Portland cement) after depletion of the sulfate by reaction with the CAC. However, the early formation of ettringite or the acceleration of the reaction of CAC or both may play a role.

Rapid-setting mixtures may develop strength in a few hours but, in the absence of admixtures, the strength develops very slowly thereafter, remaining around 5–10 MPa for several days. This is due to the retardation of the reaction of the calcium silicates in the flash-setting mixtures. However, this pattern of strength development can be significantly modified by admixtures.

Table 13.3 shows the development of compressive strengths in a range of OPC–CAC mixtures, to show the type of behaviour found. It is important to note that the precise values are very dependent on the particular OPC and CAC used and the presence, if any, of admixtures.

The hydrates which form in OPC–CAC mixtures change according to the relative proportions of the two cements. At low levels of CAC ($< \sim 20$ per cent) C-S-H remains the dominant hydrate and alumina is present in the form of ettringite, calcium aluminomonosulfate or C_4AH_x, depending on the age and the exact composition of the cements. For these mixtures the metastable hydrates C_2AH_8 and CAH_{10} are not formed, so the conversion of these to C_3AH_6 is irrelevant. Mixtures rich in CAC (OPC $< \sim 20$ per cent) develop essentially the same hydration products as pure CAC (described above). In between these two extremes the development of hydrates is complex, with the possible formation of the mixed calcium aluminosilicate strätlingite (C_2ASH_8) in addition to other hydrates.

CAC + calcium sulfate

Formulations based on mixtures of CAC and calcium sulfate are used extensively in the field of building chemistry (section 13.10.7). In these systems the initial hydrate formed is ettringite ($C_3A \cdot (C\bar{S})_3 \cdot H_{32}$), which has a high water content (46 per cent by weight). With correct formulation, this high capacity of ettringite to bind water can be used to produce products which are rapid drying as well as rapid hardening. The development of hydrates and of mechanical properties depends on the relative proportions of the components and also on the type of calcium sulfate, i.e. hemihydrate, gypsum or anhydrite. Bayoux *et al.*

Table 13.3 Compressive strengths (MPa) of 1:2:3 concrete, w/c = 0.55[93]

OPC (%)	CAC (%)	3 h	6 h	1 day	7 days	28 days
100	0	0	0	5	21	33
90	10	0.4	1	2	15	21
75	25	4	4	6	10	13
60	40	6	6	8	11	12
40	60	2	7	18	22	22
25	75	2	11	28	41	44
10	90	0	10	39	53	58
0	100	0	8	48	63	72

have reported an extensive study of these mixtures.[94] In many systems there are other mineral components such as lime or Portland cement. In practice these mixtures also contain several organic admixtures which further complicate the chemical reactions which occur.

As discussed above, the different nature of hydrates formed in these systems means that the normal conversion reaction seen in the hydration of CAC alone does not occur.

13.5.8 HEAT OF HYDRATION

While the total heat evolved during hydration (~500 kJ/kg) is of the same order as for Portland cements, the much more rapid hydration leads to its evolution over a shorter period of time (Table 13.4).[95] Figure 13.15 shows the adiabatic temperature rise of a CAC paste at w/c = 0.4. It can be seen that the greater part of the heat evolution from alumina cement occurs over a period of some 10 h and that after 24 h the further evolution is slight.

13.6 Setting and strength development

13.6.1 SETTING

The setting time of calcium aluminate cement is similar to that of Portland cement. It is tested by the Vicat needle method on a paste at standard consistence (24–28 per cent water). The British and European Standard (BS EN 196-3) requires that the initial setting time shall be not less than 2, and the final setting time not more than 8 h. Some typical comparative data on the setting time of calcium aluminate and Portland cements are shown in Table 13.5. In comparison with Portland cement the time between initial and final set is much shorter for CACs; this may be especially noticeable in concretes and mortars. The setting time can be regulated by the use of admixtures (section 13.8).

Table 13.4 Heats of hydration of CAC and OPC (kJ/kg)

Type of cement	6 h	1 day	5 days	7 days	28 days
Calcium aluminate cement	340	445	445		
Ordinary Portland cement[96]				~350	~400

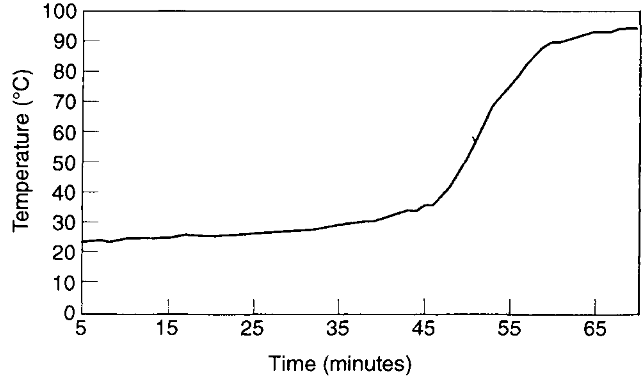


Fig. 13.15 Adiabatic temperature rise during the hydration of standard grade CAC at w/c = 0.4.

Table 13.5 Setting times of CAC and Portland cements

	Initial, h:min (SD)	Final, h:min (SD)
Calcium aluminate cement	3:55 (±0:35)	4:10 (±0:35)
Rapid-hardening Portland cement	2:10 (±1:30)	2:50 (±1:40)
Ordinary Portland cement	3:00 (±1:20)	4:00 (±1:10)

In calcium aluminate pastes and mortars the setting time decreases slightly in the temperature range 0–10°C, then increases to a maximum around 25–30°C, and decreases again above 30°C (Figure 13.16).[97-105]

The maximum in setting time corresponds to the transition from CAH_{10} to $C_2AH_8 + AH_3$ as the hydrate phases which nucleate first, as described in section 13.5.3. The temperature at which this maximum in setting time occurs is affected by the ratio of $C_{12}A_7/CA$ in the cement. In bulk concretes these changes may not be observed, due to local temperature increases from the heat of hydration of the cement.

13.6.2 STRENGTH DEVELOPMENT AND CONVERSION

The long-term strength of calcium aluminate cement results from the formation of the stable hydrates, C_3AH_6 and gibbsite. When hydration occurs in small sections at ambient temperatures the appearance of these stable hydrates is preceded by the formation of the metastable hydrates, CAH_{10} and C_2AH_8. As the metastable hydrates have a high proportion of combined water and low densities, they rapidly fill the space originally occupied by water and give high early strengths. These early strengths must be regarded as transient before the eventual formation of the stable hydrates.

During the conversion of the low-density metastable hydrates to the stable hydrates with a higher density, there is an increase in porosity and decrease in strength, but also a release of water [section 13.5.6, equations (13.6) and (13.7)]. If the initial water/cement ratio has been kept low, anhydrous cement will remain after the initial formation of metastable

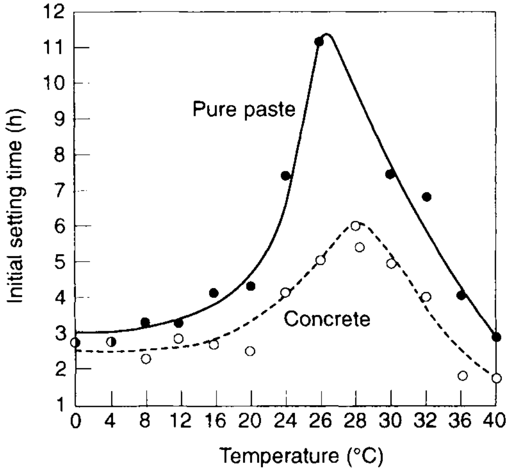


Fig. 13.16 Variation in setting time with temperature.

hydrates. This anhydrous cement is then available to react with the water released by the conversion reaction, leading to an increase in strength. A typical strength evolution curve is shown diagrammatically in Figure 13.17. As the processes of conversion of the metastable to stable hydrates on the one hand, and of further hydration of anhydrous material on the other, may occur simultaneously, the time at which the minimum strength occurs (point B) does not necessarily correspond to a state of complete (100 per cent) conversion, i.e. absence of metastable hydrates.

The process of conversion cannot be prevented so design must be based on the long-term strength (σ_m). In temperate climates, concretes may take several years to reach this minimum strength, before increasing again due to secondary hydration. However, this minimum strength may be first achieved very rapidly (in under 12 h) as indicated by point A in Figure 13.17.

In concretes more than a few decimetres in size the heat of hydration will increase the temperature of the concrete and rapid formation of the stable hydrates will occur. In this case the gain in strength will be effectively continuous as also shown in Figure 13.17.

Generally, at equivalent water/cement ratios, Portland cement concretes are somewhat stronger than CACCs. Therefore for structural concrete CACCs offer no advantage over PCC on strength alone. They would, however, be the materials of choice in situations where their particular properties (e.g. rapid hardening, good resistance to chemical attack, abrasion resistance) are critical factors.

'Intrinsic' strength of calcium aluminate hydrates

For any cement paste (or concrete) the porosity has an overriding effect on the strength and it is difficult to control the porosity independently of the type of hydrate formed. However, it is interesting to compare the strengths of converted and unconverted calcium aluminate cement pastes at equivalent porosities from the data of Cottin and Reif[76] (Figure 13.11; Table 13.6).

Although the interpretation is complicated by the presence of unreacted cement in these samples, these data suggest that the 'intrinsic' strengths of the high-temperature hydrates ($C_3AH_6 + AH_3$) are considerably greater than those of the low-temperature hydrate

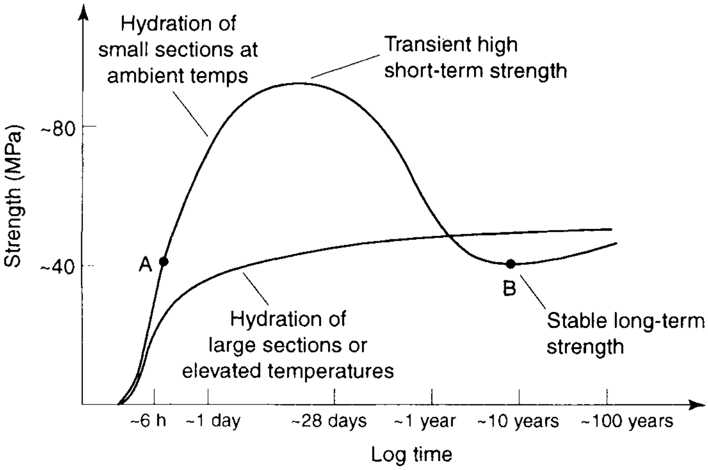


Fig. 13.17 Schematic strength development curves for calcium aluminate cement concrete at w/c ~ 0.4 and cement content of 400 kg/m^3.

Table 13.6 Strengths of unconverted and converted CAC pastes at equivalent porosity

	7 days at 10°C, 'unconverted'		7 days at 70°C, 'converted'	
Porosity (%)	w/c	Strength (MPa)	w/c	Strength (MPa)
12.5	0.40	71	0.15	133
15	0.44	62	0.2	116
21.5	0.58	33	0.3	50

(CAH_{10}). It has also been found that strengths of about 480 MPa can be achieved in hot pressed pastes of CAC containing C_3AH_6 and AH_3,[106] where the porosity is reduced to less than 4 per cent.

Effect of water/cement ratio

As with Portland cements the most significant factor affecting the strength of pastes, mortars or concretes made with CAC is the water/cement ratio (w/c). Figure 13.18 shows some of the results of a large-scale testing programme.[107] Concrete prisms of 70 × 70 × 280 mm were cast at total w/c = 0.33, 0.4, 0.5 and 0.67. All the prisms were cured for 4 h in moist air at 18°C and then for 48 h under water at temperatures of 10, 20, 30, 50, 70 or 90°C. After 52 h the prisms were placed in three exposure conditions; under water at 18°C, sheltered outdoors or exposed outdoors for up to 10 years.

The graph shows the strength results for the concretes cured initially at high and low temperatures. At 70°C (a temperature often attained in massive concrete) only stable hydrates were present after 52 h (curve a). On subsequent exposure in outdoor conditions, the concretes continued to gain strength with time as shown, after 3 months (curve b) and 3 years (curve c). In the concretes cured at 10°C, only metastable hydrates were present after 52 h (curve x). However, these concretes subsequently undergo conversion. Curve y

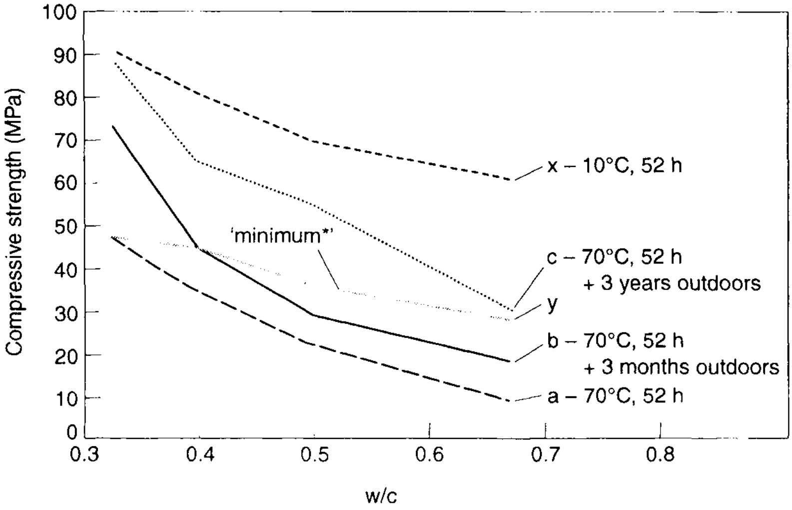


Fig. 13.18 Influence of w/c on strength for different curing conditions.

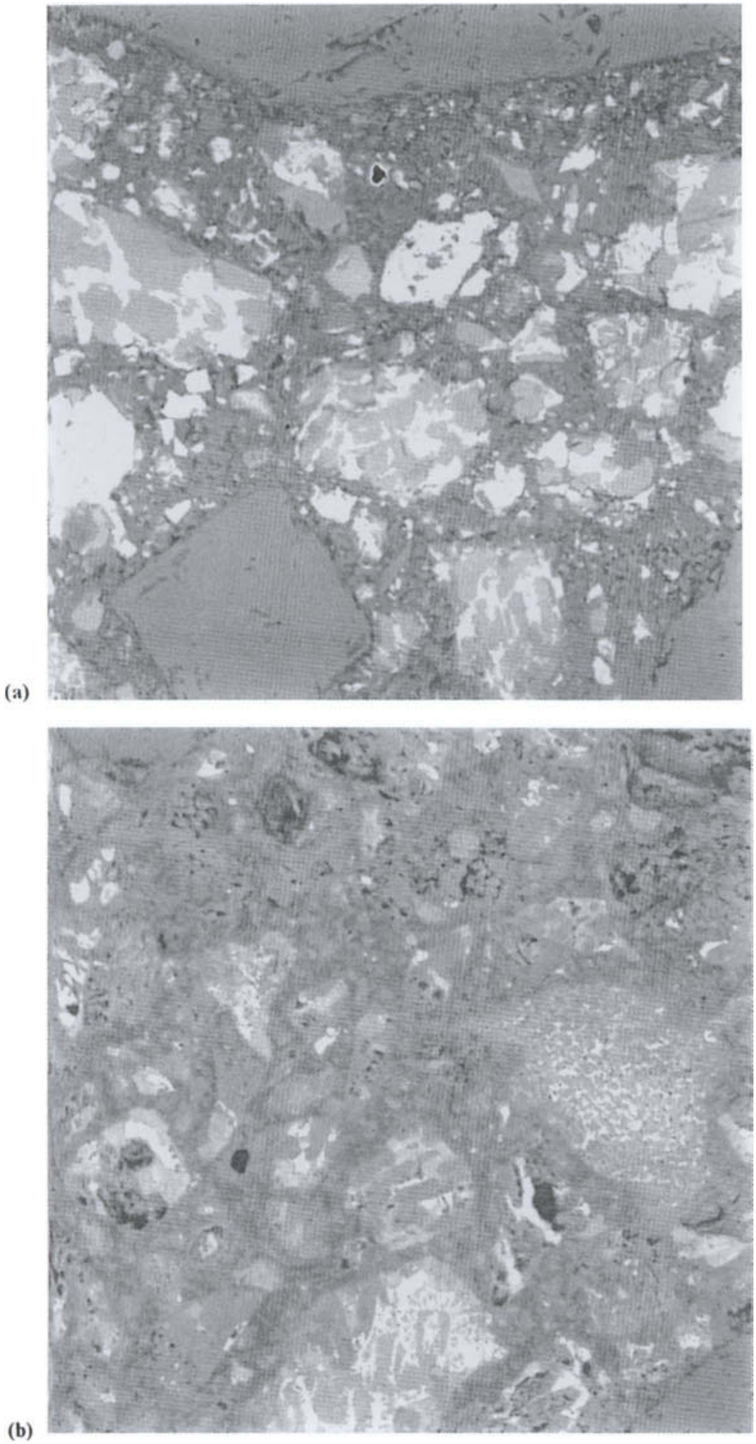


Fig. 13.19 Backscattered electron images showing the microstructure of CAC concrete at w/c = 0.4 hydrated 7 days at 20°C (a) and 70°C (b).

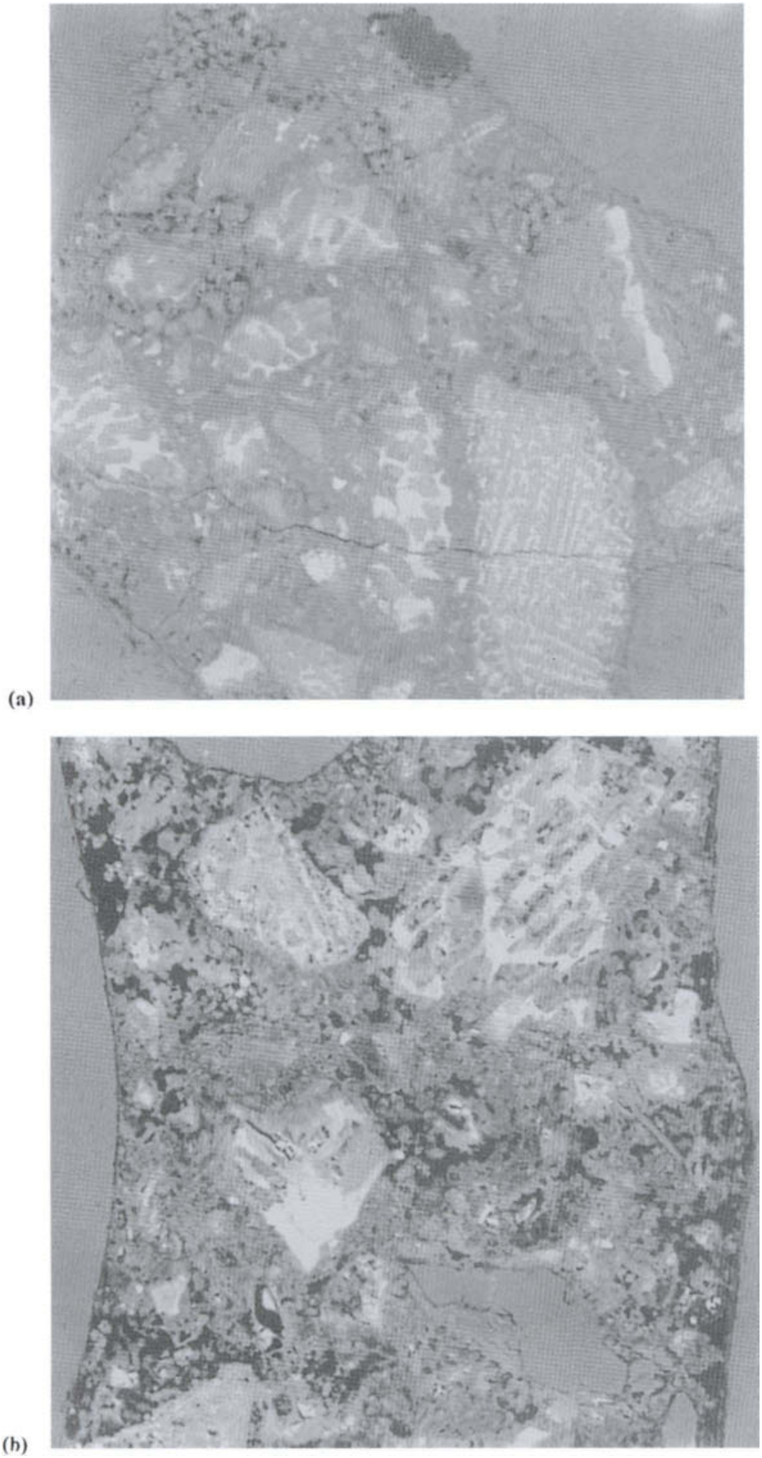


Fig. 13.20 Backscattered electron images showing the microstructure of CAC concrete at w/c = 0.7 hydrated 7 days at 20°C (a) and 70°C (b).

shows the minimum strengths measured, irrespective of exposure condition, for the concretes cured initially at low temperatures.

First, it is important to note the sensitivity of the compressive strength to water/cement ratio under the different conditions of curing. When the initial reaction leads to the formation of the metastable hydrates (curve x, 10°C), increasing the water/cement ratio from 0.33 to 0.67 reduces the strength by 33 per cent (91 to 60.5 MPa). However, when the initial hydration leads to the formation of the stable hydrates the strength reduction for the same change in water/cement ratio is 80 per cent (46.5 to 9 MPa). This means that measurements of strength due to the metastable hydrates cannot predict the stable long-term strength of a concrete (this is discussed further in section 13.6.2). The reason for this difference can be seen clearly from the microstructures shown in Figures 13.19 and 13.20 for concretes at water/cement ratios of 0.4 to 0.7 respectively, in each case, hydrated either at 20°C or at 70°C for 7 days. Due to the low density and high water content of the metastable hydrates, these rapidly fill the available space, even at high water/cement ratios, giving the low-porosity microstructures seen in Figures 13.19(*a*) and 13.20(*a*). As discussed in section 13.5.6, the critical water/cement ratio for formation of the stable hydrates is about 0.35 (equivalent to about 0.4 total water/cement ratio in concrete), so water/cement ratios higher than this will result in excess porosity in the long term. The reality of this can be seen in the dramatic difference between the low-porosity microstructure in Figure 13.19(*b*) and the high-porosity microstructure in Figure 13.20(*b*). For structural concrete the total water/cement ratio should be below 0.4, to ensure good long-term strengths.

Total or free water/cement ratio. The current guidance (e.g. prENV 197-10) for calcium aluminate cement concrete refers to total water/cement ratio. Up until the 1970s the water/cement ratio for a concrete invariably referred to the total water added to the concrete. Subsequently concrete technologists have tended towards the use of 'free' water/cement ratios, the free water being the total water minus that absorbed by the aggregates. The absorption by aggregates is usually measured after 24 h in water. This corresponds to the period of most rapid hydration in Portland cements, during which time it is realistic to imagine that originally dry aggregates can absorb water from the concrete. However, CACs react much faster with the available water, so it is improbable that the aggregates would be able to absorb water from the concrete over such a long period. Work by Montgomery[108] showed that concretes mixed with dry aggregates (Thames Valley gravel) at total water/cement ratios of 0.35, 0.4 and 0.5 had lower strengths than concretes of the same mix proportions mixed after leaving the aggregates in the total mix water for 24 h. According to conventional thinking these two mixes had identical 'free' water/cement ratios (Table 13.7). These results show that the water taken up by dry aggregates from the concrete during hydration of CACs is indeed much less than the amount absorbed by the aggregates over 24 h.

Most of the available data on CACCs originate from concretes gauged on the basis of total water/cement ratios, with dry laboratory aggregates. Thus it is incorrect to convert these values to free water/cement ratios, based on assumed values of aggregate absorption over 24 h.

Due to the fact that all measures of long-term performance are based on total water/cement ratios and to the negative effect of water/cement ratios above 0.4, both on long-term strength and on durability, it is important to consider the total water/cement ratio for CAC concretes. It is clear that the imposition of a maximum total water/cement ratio will pose problems for the production of concretes with aggregates which absorb

Table 13.7 Strengths of concretes with different mixing protocols[107]

	20°C, 90% RH, 1 day			38°C, under water, minimum strength		
w/c	0.35	0.4	0.5	0.35	0.4	0.5
Dry aggregates	74.0	64.5	55.5	45.5	37.5	21.5
Soaked aggregates	78.5	74.0	59.0	57.0	41.5	24.5

water rapidly. In these cases supplementary testing should be carried out to ensure that satisfactory converted strengths and durability are obtained at the water/cement ratio used.

Effect of temperature

The temperature to which CAC concretes are exposed during their lifetime has a very important effect on the rate of conversion. However, it is clear that, in terms of the expected lifetime of many applications, conversion will occur on a relatively short timescale (5–10 years or less). Therefore, design must be on the basis of the stable long-term strength.

Temperate ambient temperatures. The progress of conversion in long-term tests is usually discussed in terms of the strength relative to the unconverted strengths.[52] Concretes continuously immersed in sea water in the UK (average temperature 8°C) for 30 years showed little change from the unconverted strength,[52] but parts of the same concretes exposed to the air had strengths relative to the unconverted strength of 80–90 per cent for w/c = 0.3 and 50–60 per cent for w/c = 0.48. Most studies on concretes exposed in temperate climates or to laboratory tests at 18–25°C indicate that substantial conversion has occurred after 5–10 years[109,110] and the effects on strength may be significant after as little as 1 year.[111] After the failure of structures in the UK in the 1970s (section 13.6.4) a large number of structures containing CACC prestressed beams were surveyed. The ages of these ranged from 5 to more than 10 years and the vast majority were found to be highly converted.[112] In many of these cases water/cement ratios in excess of the current guidance of 0.4 had been used (typically 0.5 or higher); nevertheless the converted strengths (>21 MPa) were comfortably greater than the required design strengths.

As explained above, the conversion of the metastable to stable hydrates, combined with the continuing hydration of the unreacted cement, results in a strength curve which passes through a minimum. This can clearly be seen in long-term strength data for concretes exposed externally in France (Figure 13.21).[109]

38°C. A vast amount of data exists on the behaviour of calcium aluminate cement concrete and pastes at 38°C (100°F), as this temperature was used in many studies to accelerate the formation of the stable hydrates. Curing at this temperature was also used by the Lafarge Aluminous Cement Company during the 1970s and 1980s as a quality control measure. These studies indicate that precuring at a lower temperature (e.g. 20°C), for as little as 1 day, will significantly delay the rate of conversion. For example, when the concrete is immersed in the water bath immediately after casting the minimum in strength occurs at 5 (±1) days. However, if the concrete is precured for 1 day at 18°C the minimum occurs after 3 months. Nevertheless a comparison of the minimum strengths for the two curing

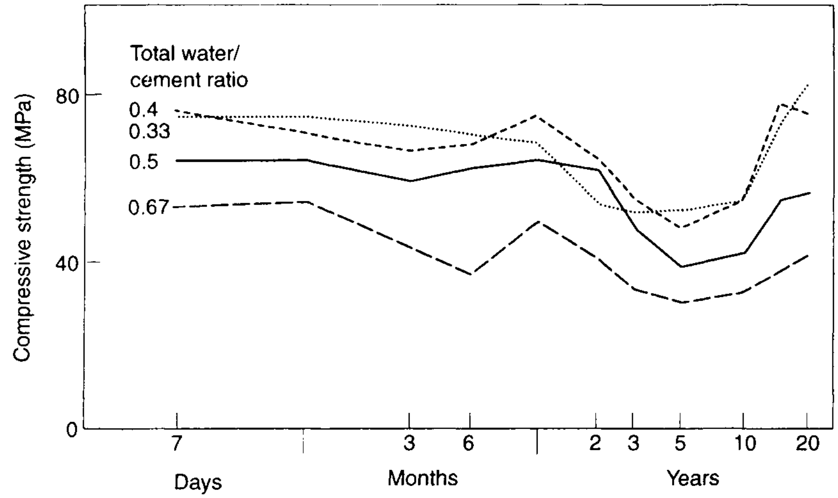


Fig. 13.21 Long-term strength of Ciment Fondu concrete showing minima due to conversion.

regimes indicates that these are very similar, with neither condition giving systematically higher or lower strengths.

Higher temperatures. As described in section 13.5.8, the rapid hydration of CAC leads to greater adiabatic heating than does that of Portland cement. In sections more than a few decimetres in thickness, this results in the concrete reaching temperatures up to ~80°C (Figure 13.22).

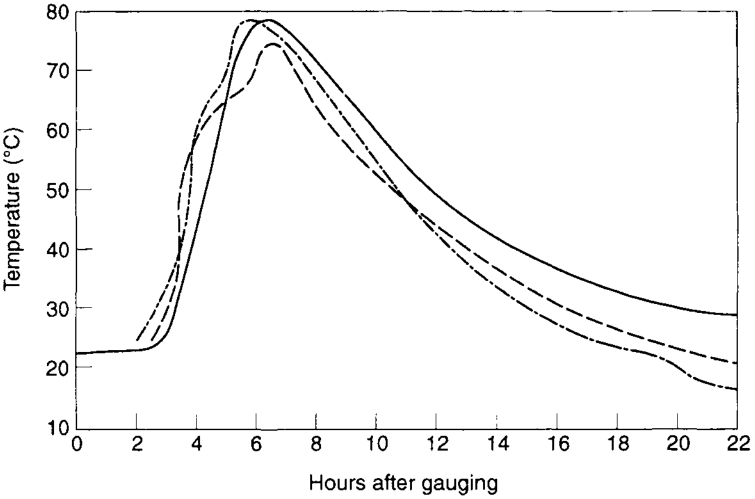


Fig. 13.22 Temperature rise in a beam 35 × 180 cm, measured at mid-height and at mid-thickness of the beam: —— on the beam, · · · one-quarter southward and — — one-quarter northward. Cement content = 500 kg/m^3. Form removed and concrete sprayed with water 5 h after concreting for 20 h.

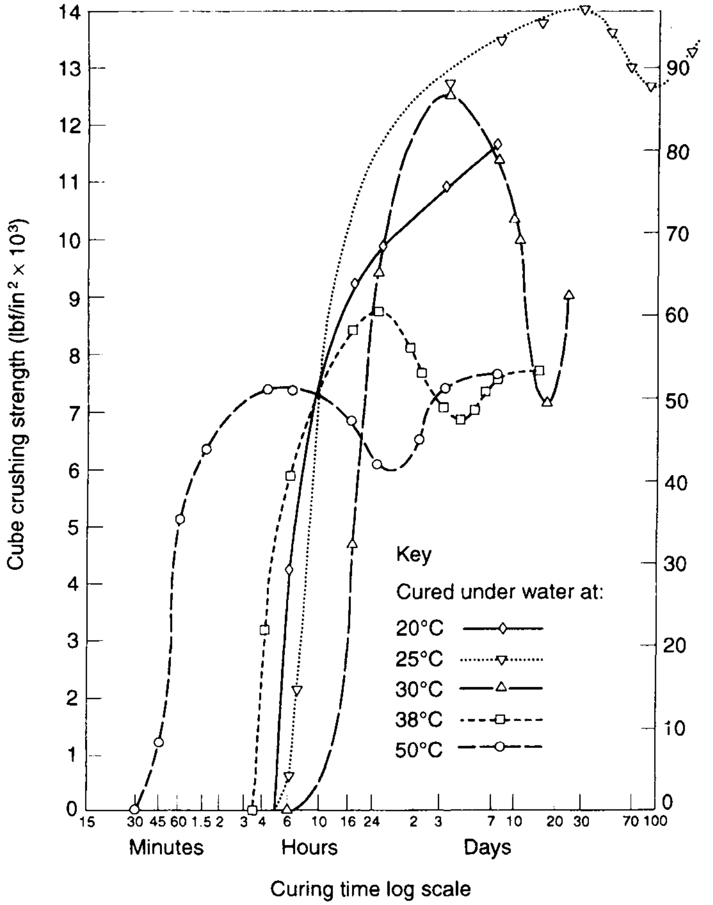


Fig. 13.23(a) Effect of temperature on strength development at 20–50°C.

The most extensive study of the effect of temperature on strength development is that made by French *et al.*,[113] the principal results of which are shown in Figure 13.23. Above about 30°C there is an approximately log-linear relationship between the time at which the minimum in strength occurs and the temperature. For temperatures of 70°C or higher, the minimum strength occurs within several hours and, for practical purposes, the strength development with time is effectively one of uniform increase.

Data from long-term studies of massive concrete are shown in Table 13.8. The 1 m^3 was cast in the laboratories of the BRE in 1995 and the measured internal temperatures reached over 80°C. The other two examples were bridges built in France, Frangey in 1969 and Paganin in 1987. For both of these projects test blocks were cast with the same concrete as the structures themselves and were of large enough dimensions to reach the same internal temperatures. The strengths measured are of cores from these test blocks, except for the 26-year Frangey results which are of cores taken from the bridge itself. In these examples, of concrete in which self-heating led to the early formation of the stable hydrates, no reversion of strength is observed.

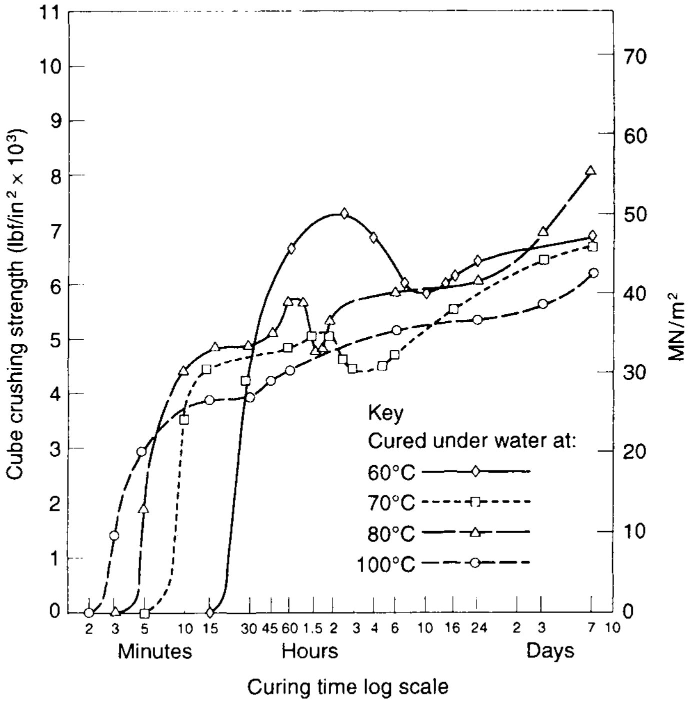


Fig. 13.23(b) Effect of temperature on strength development at 60–100°C.

Other factors affecting strength development

Several other factors have an effect on the rate of conversion and strength development. The rate of conversion is significantly reduced at low relative humidities. However, in practice, even under nominally 'dry' conditions substantial conversion will occur in 5–10 years.

The type of aggregate used may have quite a significant effect on strength. Concretes made with limestone aggregates may have strengths about 20 per cent higher than those made with a silico-calcareous aggregate, while those made with a wholly siliceous aggregate may be about 20 per cent lower. Some of this difference is due to variations in the rate and extent of absorption of water, but the bond between paste and aggregate is also important. The use of synthetic aggregates chemically close to the composition of CACs leads to very high concrete strengths, due to the strong binding between aggregate and paste.

Aggregates containing soluble alkalis should be avoided as these may lead to alkaline hydrolysis (section 13.9.7).

Tests for long term strength

Under virtually all practical conditions, conversion is inevitable. However, provided the water/cement ratio is 0.4 or less, the stable, converted strengths are perfectly satisfactory for most purposes. Therefore, any design must be made on the basis of this converted strength and testing of the concrete should ensure that it has a satisfactory strength in the converted condition. As discussed above, there is no unique relationship between converted and unconverted strengths. Thus early age strengths measured on normal-sized cubes of

Table 13.8 Strength development of cores[a] taken from massive concrete

	w/c	Cement content (kg/m^3)	48 h	28 days	3 months	6 months	1 year	5 years	10 years	15 years	26 years[b]
1 m^3, 1995	0.4	446	38.0	47	49.5	48	53.5				
Frangey bridge plus test blocks	0.4	450					54.1	58.1	63.4	57.9	48.7–63.4 (av. 54.7)
Paganin bridge plus test blocks	0.4	500		36.7	41.5	50.4	58.6	66.7			

[a] NB strengths from cylindrical cores are systematically ~80 per cent of the strength measured on cubes.

[b] Strengths of 10 cores taken from the bridge itself.

concrete cast at ambient temperatures will not give a reliable indication of the long-term strength. There has been considerable study of methods of curing which accelerate the conversion process in order to provide an early indication of the converted strength of a particular concrete.

As discussed above, if cubes are placed in a water bath at 38°C directly after casting, the minimum in strength occurs after 5 days, and this minimum gives a good, conservative estimate of the minimum strength which will occur *in situ*. The recent technical report of the Concrete Society[1] concludes that

> for relatively small concrete sections, a 5-day curing regime in water at 38°C can give a good and confident prediction of minimum *in situ* strength ... For larger sections, for higher ambient or service temperatures or for concretes cast into insulating formwork ... A more secure and therefore preferred method for estimating *in situ* strength is to cast specimens under conditions which will represent those expected in the real construction.

To generate data for concrete which experiences temperatures in excess of 38°C, work is in progress to study the practicality of a test method using higher temperatures or based on semi-adiabatic curing in insulating moulds.

Conversion inhibitors

As described in section 13.5.7, mixtures of CAC with reactive siliceous materials may give strätlingite as one of the hydrates, such that further reaction to form the hydrogarnet phase, C_3AH_6, is very much reduced. However, it is not clear whether conversion is really prevented or just slowed down. Several studies of hydration at temperatures above 38°C (which are likely to occur in sections of any significant size) indicate that the formation of C_3AH_6 still occurs readily.

Another major drawback to such systems is the initial slow rate of strength development, which is very similar to that of much cheaper Portland cements. The addition of sodium salts, which increase the pH, improves the rate of strength development, but such additions could entail a risk of alkaline hydrolysis (section 13.9.8) in the long term.

13.6.3 PLACING, WORKABILITY AND CURING

As with Portland cement concrete the cement content necessary to achieve a workable concrete increases with decreasing water/cement ratio. Figure 13.24 shows the relationship of slump to water/cement ratio for various cement contents. In order to achieve a workable concrete at $w/c = 0.4$ a minimum cement content of $400\,kg/m^3$ is necessary. To ensure good-quality well-compacted concrete, best practice, as for Portland concrete, should be observed, e.g. thorough mixing and vibration. For a given water/cement and aggregate grading CAC is easier to compact than Portland cement, although before vibration the concrete may appear to have poor workability.

It is frequently noted that CACC should be demoulded as soon as possible and the surface sprayed with water. In some cases this is presented as a means of avoiding conversion by cooling the concrete. As shown in Figure 13.22, the temperature rise in concrete sections of significant size occurs before demoulding at 4–6 h and the hydration in the interior of such sections leads to the stable hydrates. In reality, water spraying avoids dusting of the surface, due to dehydration. The high amount of heat evolved during hydration can lead

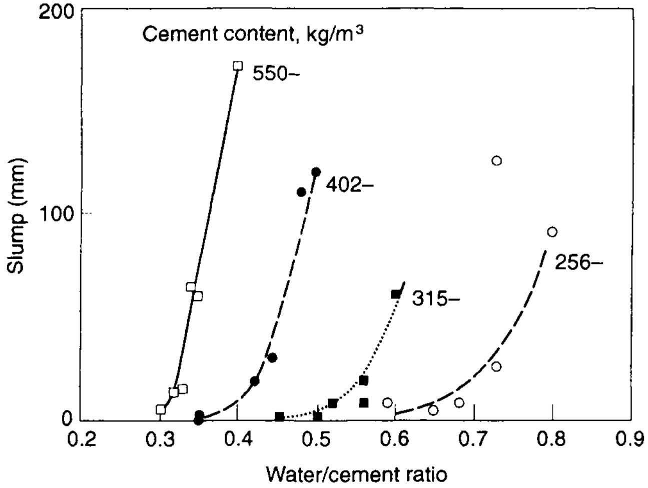


Fig. 13.24 Relationship of slump to water/cement ratio.

to significant evaporation of water from the surface, particularly in good-quality concretes of low water/cement ratio and high-cement concrete. Prevention of water loss by spraying or other means is important to ensure that adequate water is available for continuing hydration. This process was adopted in all the large-scale projects shown in Table 13.8.

When CAC mortars or concretes are cured under water, a white gelatinous deposit may occur on the surface. This is due to the superficial dissolution of the cement phases and the deposition of hydrated alumina gel and other hydrates. This phenomenon only affects a thin surface film of the concrete and has no effect on strength development.

13.6.4 PROBLEMS ENCOUNTERED IN THE USE OF CACC AND DEVELOPMENT OF GUIDANCE

When CAC first came into use after World War I the high capacity of the metastable hydrates to combine water led to the adoption of a minimum water/cement ratio for concrete. By the 1930s the poor performance of concretes at high water/cement ratio after conversion started to be recognised, but water/cement ratios similar to those used for Portland cement at the time (~0.6) continued to be common. The continued incidence of failures led to the French government imposing prohibitive restrictions on the use of CAC in the public sector in 1943.[114]

In the 1960s a number of failures occurred in Bavaria, Germany, owing to corrosion of prestressing wires by concrete made with a CAC produced as a blastfurnace by-product. This led to the discontinuation of use of CACs for construction purposes in Germany. However, extensive investigations elsewhere in Europe concluded that normally CAC provided good protection to reinforcement and that this was an isolated incident attributable to the blastfurnace type of CAC and to poor-quality prestressing wire.

Meanwhile, in France an extensive programme of long-term testing established the necessity of maintaining the w/c < 0.4 and cement content $> 400\,\mathrm{kg/m^3}$ for good-quality concrete which would maintain adequate strength after conversion and give good durability in chemically aggressive environments. This led, in the 1970s, to the removal of the earlier prohibitions on the use of CAC, and their replacement by guidance recommending a maximum water/cement ratio of 0.4 and a minimum cement content of 400 kg/m^3.

The development of guidance in the UK is extensively discussed in the Concrete Society Technical Report no. 46[1] and is only summarised here. In the UK an extensive market for CAC in prestressed concrete developed in the 1950s and 1960s. From the earliest codes of practice it is clear that the effects of conversion on strength were well known. However, this led to advice aimed at limiting or preventing conversion, i.e. trying to avoid the inevitable. For example, the 1965 revision to CP114[115] recommended

- the avoidance of wet or humid service conditions and in-service temperatures above 80°F (27°C);
- control of heat of hydration temperatures during curing by
    - imposition of an upper limit on cement content of ~400 kg/m^3, with no lower limit;
    - cooling during curing by spraying with water;
    - early stripping of formwork.

Although the maximum water/cement ratio for prestressed concrete was 0.4, this would have been very difficult to achieve with the maximum cement content of 400 kg/m^3. Some mix designs had aggregate to cement ratios up to 9:1, for which the water/cement ratio to achieve placement would have been 0.5 or higher.

In 1973 there were two collapses of structures involving CACC prestressed beams: at the Camden School for Girls (built 1955) and at the Bennett Building of the University of Leicester (built 1965). In both cases the investigation reports found reductions in strength of the CACC roof beams, but concluded that these had been of minor consequence to the failures. Instead, the major cause of failure was inadequate resistance of support nibs to the roof beams against horizontal tensile forces due to thermal movements. After the collapse, one of the roof beams in the Bennett Building was tested to destruction and found to have adequate strength for the design, despite a high degree of conversion. Other beams were reused in the repair of the roof.

In 1974 there was a further collapse of some roof beams over a swimming pool at the Sir John Cass School in Stepney. In this case the investigation found the cause to be principally the loss of strength resulting from conversion of the concrete, aggravated by subsequent chemical attack by sulfates. The concrete in this case was continually wet due to water leakage and condensation. There was evidence that the concrete did not fully meet the code requirements for cement content and water/cement ratio. 'The high strength development potential of CAC allowed too high a water/cement ratio to be used yet the required minimum short-term strength was still achieved'[1] (section 13.6.2).

These events led to changes in the Approved Documents to the UK Building Regulation which effectively prevented the further use of CAC in buildings.

Further problems occurred in Spain in the 1990s, where the collapse occurred of the roof of an apartment building, which contained prestressed concrete beams made from both CAC and Portland cement. Again the concrete did not adhere to the current guidelines on water/cement ratio and cement content. A further factor implicated in the failure was the use of aggregates with soluble alkalis, which could have led to the occurrence of alkaline hydrolysis in conditions of water leakage or in warm humid environments.

Over 80 years of use of CACC have shown that well-made good-quality concrete has a very good track record of field performance. However, it may also be surmised that CACC is more sensitive to misuse than Portland cement, due to the temporary high early strengths which may be developed even at high water/cement ratios. Therefore correct use of CACC must be on the basis of converted strengths for structural design and strict quality control of the mix design. To ensure good long-term strength and durability a water/cement ratio below 0.4 and therefore a cement content above 400 kg/m^3 are recommended.

13.7 Other engineering properties

Large quantities of data previously published[52,93] on the engineering properties of CAC concrete relate to mixes with water/cement ratios and cement content outside the currently recommended limits and are therefore not presented here.

13.7.1 DENSITY

The density of hydrated pastes and concretes obviously depends on the water/cement ratio and type and amount of aggregates. The density of a typical concrete at w/c = 0.4 with a dense aggregate (aggregate/cement = 4.5) is about 2500 kg/m^3.

13.7.2 SHRINKAGE

The macroscopic shrinkage of calcium aluminate cement concrete in air is very similar to that of Portland cement concrete. However, this shrinkage occurs considerably more rapidly under similar conditions. Typically nearly half of the total drying shrinkage will occur within 1 day for CAC concrete, compared to about 7 days for Portland cement concrete. Table 13.9 shows comparative values.[116] The shrinkage of the CACC is measured from 6 h due to its rapid hardening as opposed to 24 h used for the start of measurements for Portland concrete. No change in macroscopic dimensions is normally observed during the conversion reaction. To avoid cracking due to the rapid shrinkage of CACCs, the bay size of unreinforced slabs is usually limited to about 3 m.

In applications where the early strength of CAC is not essential (for example, pipe linings) shrinkage cracks may be avoided by heating the concrete during curing to promote the formation of the stable hydrates, which result in a concrete which is less susceptible to cracking.

13.7.3 CREEP

Earlier work, discussed by Robson,[93] indicates that there is no clear difference between the creep of CAC concrete and that of OPC concrete. The relative magnitudes change with time, probably due to the different strength development curves. Most of this work referred to unconverted concretes at water/cement ratios of 0.5–0.7

Some data do exist for converted concrete made according to current guidance. During the construction of the Frangey bridge, referred to in section 13.6.2, the opportunity was taken to check the creep of the fully converted CAC concrete.

Table 13.9 Shrinkage of test pieces 40 × 40 × 160 mm, 20°C, 50 per cent RH (μm/m)

Age	6 h	1 day	3 days	7 days	14 days	28 days
Ciment Fondu	0	200	500	600	680	700
OPC 55	–	0	160	300	500	650

Table 13.10 Deformation and creep of converted CAC

	Deformation (μm/m)	
Age (days)	Shrinkage	Creep
1	21	192
2	86	150
6	160	342
8	139	364
13	192	289
30	128	482

A relatively high load of 15 MPa was applied to 70 × 70 × 280 mm prisms after curing for 24 h at 80°C. The results, summarised in Table 13.10, indicate satisfactory performance. The long-term creep of CACCs does not appear to have been studied.

13.7.4 THERMAL PROPERTIES

The coefficient of thermal expansion of concretes depends mainly on the aggregates. However, the thermal expansion of CAC paste is lower than that of OPC paste. With careful selection of aggregates, CAC concretes can be made which can withstand repeated exposure to fire (NB 'fireproof' OPC concrete is designed to withstand a single exposure). In addition to the refractory uses discussed below (section 13.10.10), CAC concretes are used, for example, as chimney linings and for fire training buildings.

13.8 Admixtures

The use of admixtures with CAC is commonplace. They are used in the same way as with Portland cements, in order to modify particular properties such as setting, rheology, strength and adhesion.

As with Portland cement, in many cases the admixture will have side effects in addition to those for which it was originally intended. Some of these secondary effects may be quite severe and it is always prudent when using admixtures of any kind to carry out trial mixes to determine the extent of the principal and secondary effects.

Most commercially available admixtures have been developed for use with Portland cement, and whilst many of these have similar effects with CAC, this is not invariably the case. Some admixtures will have a retarding effect on the setting and hardening, which may or may not be desirable depending on the application.

Many admixtures, particularly when used in products such as proprietary mortars, are used in combination with each other. For example, water reducers often have a retarding effect and this may be compensated for by the use of a suitable accelerator. Set accelerators will usually enhance the short-term strength, whilst retarders may reduce the normal rapid-hardening properties of CAC. However, in the long term, the strength of an accelerated mortar or concrete may be less than it would otherwise have been, whereas higher ultimate strengths are often found in retarded systems.

In general, substances which increase the pH value of the solution tend to accelerate the set and vice versa. The effects of admixtures may be sensitive to concentration, and substances which retard at low concentrations may accelerate when present in greater quantities. For example, small additions of calcium sulfate, e.g. 0.25 per cent, retard the set, but additions of 1 per cent may reduce the time of the final set below 30 min. The nature of calcium sulfate will also have an effect, the hemihydrate form (plaster) being the most effective in acceleration and the anhydrous form (anhydrite) having little effect on setting time.[93] Sodium sulfate and potassium sulfate at 0.5 per cent concentration have some accelerating effect and magnesium sulfate a retarding one. It seems probable that this behaviour may vary with concentration, as with calcium sulfate. The presence of sugar can inhibit setting and hardening entirely, as occurs with Portland cement. An addition of 1 per cent can delay the set for a day or more, and even with considerably smaller amounts the retardation may be marked.

The effect of the addition of various salts and other substances on setting time are summarised in Table 13.11, although in some cases these may vary with the particular cement tested. This may account for the conflicting results reported from different tests. Damidot *et al.*[105] have explained the apparently anomalous effect of admixtures which retard at low concentrations and accelerate at high concentrations in terms of the separate effect of the admixture on the dissolution and induction period of the hydration (section 13.5.2).

A tentative synthesis of the effect of various ions on setting behaviour has been made by Currel *et al.*[117] the order and magnitude being given as follows:

- for cations, $Li \ll Na < control < K \leqslant Ca < Mg < Sr < NH_4$
- for anions, $OH \ll control < Cl < NO_3 < Br < acetate$

13.8.1 ACCELERATORS

Lithium salts are the most efficient and widely used accelerators. Setting times of just a few minutes may be obtained with relatively low additions (~0.1 per cent). This phenomenon has been explained by the precipitation of lithium aluminate hydrate which acts as a heterogeneous nucleation substrate.[118]

Table 13.11 Effect of various substances on setting time of calcium aluminate cement

Accelerators	Retard at low concentrations and accelerate at high concentrations	Retarders
Lithium hydroxide	Magnesium chloride	Sodium borate
Lithium carbonate	Calcium chloride	Sodium chloride
Lithium sulfate	Barium nitrate	Sodium nitrate
Lithium chloride	Acetic acid	Potassium sulfate
Lithium nitrate	Calcium sulfate hemihydrate	Potassium chloride
Calcium hydroxide	Calcium formate	Barium chloride
Potassium hydroxide		Sodium gluconate
Potassium carbonate		Sodium citrate
Sodium hydroxide		Citric acid
Sodium carbonate		Hydrochloric acid
Sodium sulfate		Glycerine
Sulfuric acid (very dilute)		Sugar

The addition of hydrated and reground CAC added to the unhydrated cement also causes acceleration,[93,119] as does the addition of Portland cement,[93] plaster[94] or lime.[120] Many proprietary rapid-setting mortars are based on mixtures of CAC with these latter materials (sections 13.5.7 and 13.10.7).

13.8.2 RETARDERS

As noted in Table 13.11, chlorides are in general retarders (with the notable exception of lithium chloride). Of particular note is calcium chloride, which has a strong accelerating effect on Portland cement, but is a strong retarder for CAC, and use of this compound is not recommended.[93] Similarly, sea water should not be used for gauging CAC due to the retarding effects of chlorides and their potential deleterious effects on reinforcement.

Hydroxycarboxylic acids – citric, tartaric, gluconic – and their salts are strong retarders of CAC.[93] The sodium salts of these acids are often used in conjunction with accelerators (generally lithium salts) to produce proprietary controlled-set mortars and concretes. Some of these salts, notably sodium citrate, also have marked water-reducing properties, since they increase the fluidity of the paste at low water/cement ratios.

Many other inorganic compounds have a retarding effect,[93] including boric acid and borates, lead and copper salts, ethylenediamine tetraacetic disodium salt, glycol, glycerine, sugars, flour, casein, starch and cellulose products. Accidental contamination with these compounds should be avoided as setting can be severely delayed or suppressed altogether. The effects of a variety of other substances on the setting[121] and hydration rate[122] of CAC have been reported.

13.8.3 WATER REDUCERS, FLUIDIFIERS AND PLASTICISERS

A number of compounds already noted as set retarders also have a water-reducing effect. Sodium citrate[123] is probably the most common of these, and although sodium gluconate also has some water-reducing properties,[124] it is not as effective as sodium citrate. Similarly the disodium salt of ethylenediamine tetraacetic acid (EDTA) has a good fluidifying action[125] and, although this too is a retarder, its retarding effects are less marked than those of sodium gluconate and sodium citrate.

Some water reducers that are widely used for Portland cements are also effective with CAC. Lignosulfonates have long been used; however, these also are retarders, the retarding effects being due to residual sugars; low-sugar varieties are available. The so-called superplasticisers, such as melamine and naphthalene formaldehyde condensates, have limited use for CAC concrete as their effects are very short lived.[126]

Methyl cellulose improves the plasticity and reduces bleeding of CAC but again causes retardation.[93] Bentonite may be added at 2–4 per cent where maximum plasticity is required;[93] however, there will be a consequent strength loss.

13.8.4 AIR-ENTRAINING AND FOAMING AGENTS

Proprietary air-entraining agents mainly based on neutralised vinsol resins do not entrain as much air in CAC as with Portland cement.[93] At 3–4 per cent entrained air, mortars are more plastic and bleeding is reduced.

Although Robson reports that aluminium powder is not as effective with CAC as it is with Portland cement[93] due to its lower alkalinity, George[127] states that volume expansions of up to 20 per cent may be achieved with 0.3 per cent by weight of aluminium powder. This admixture has been used in proprietary grouts to prevent shrinkage during the plastic state; however, it is ineffective after the cement has hardened.

Foaming agents such as alkyl aryl sulfonate (detergent) or hydrolysed protein may be used to produce foamed mortars.[93] This may be achieved by vigorous mixing or more effectively by producing a stable foam and then stirring it into a cement slurry.

13.8.5 LATEX AND POLYMER RESINS – FORMULATED PRODUCTS

Both natural and synthetic latex have been successfully used in CAC in order to produce proprietary mortars, screeds and surface coatings. These are often used to produce chemically resistant floor toppings, where CAC performs well compared to Portland cement.[93] Styrene butadiene latex is used to improve bonding to many substrates[93] as are many other polymer resins, such as acrylic polymers, poly(vinyl acetate) and epoxy resins.

In addition to improving adhesion and flexural strengths, the very wide range of polymer admixtures available today is used to enhance the physical properties of many formulated products. These include repair mortars, tile adhesives, grouts and self-levelling floor screeds. CAC is used in such products either as the main cementitious binder or, more often, mixed with other hydraulic binders such as Portland cement, plaster, gypsum and lime. Great skill is required when formulating such products since the incorrect use of mixtures of these materials can lead to undesirable effects such as flash setting, cracking and uncontrolled expansion (see also section 13.10.7).

13.9 Durability of CAC concrete

13.9.1 GENERAL CONSIDERATIONS

As with Portland cement concrete the durability of calcium aluminate cement concrete is not an absolute, but a function of the quality of the concrete and of the environment to which it is exposed. The original motivation for the development of calcium aluminate cements was to produce a material which would be more resistant to degradation in the presence of sulfates, and there are many examples of excellent field performance under these and other 'aggressive' conditions. At the same time examples of poor performance have also occurred. Analysis of good and bad performance indicates that the most important factors determining durability are the water/cement ratio and the concomitant cement content. This relationship is fundamentally the same as for Portland cement concretes.

Almost all degradation processes are determined by the ingress of chemical species into the concrete. The resistance, or otherwise, of the concrete to such ingress is largely determined by its pore structure – the overall level of porsosity and its connectivity. The pore structure, in turn, is determined by the volume of water added to the concrete during mixing and the degree of reaction of the cement. However, there is no simple relationship between the overall level of porosity and its connectivity.

Long-term laboratory tests[128] suggest that to show good durability, CAC concretes should have a porosity below 12 per cent, which corresponds to a water/cement ratio of below 0.4 for converted concretes. This water/cement ratio corresponds to that recommended for good long-term strength, and in many applications the consideration of durability may be as important, if not more so, than strength.

Field performance and laboratory testing

The best guide to the durability of concrete in a given environment (whether made with Portland or calcium aluminate cement) must be field performance under equivalent conditions. Unfortunately this is rarely available, particularly in situations where performance over long time scales is required. This, and an increasing concern with the poor durability of (Portland) concrete over the past few decades, have led to the widespread study of the use of short-term laboratory testing to predict long-term field performance. Such an approach has mixed blessings.

For example, the measurement of permeability (resistance to the flow of water or gas) has been of considerable value in indicating the factors in (Portland) concrete which increase durability, e.g. low water/cement ratios, good curing and the (proper) use of slag, fly ash or silica fume. Although such measurements can be useful in ranking the relative performance of different concretes, no consistent quantitative relation has been found between permeability measurements and the rate of degradation, or service life, in practical conditions. The most probable explanation for this is that many processes, such as absorption and diffusion, rather than fluid or vapour flow, may determine the rate of ingress. In addition, many processes involve reaction or binding of the ingressing species by the cement hydrates, which will also affect their rate of penetration.

Very little data appear to exist on the permeability of CACC. Dunster *et al.* measured the O_2 permeability of some old CACC taken from structures. In two cases of 60-year-old concretes with water/cement ratios around 0.6, a marked difference was found between the permeability of the outer 50 mm ($0.6-1.7 \times 10^{-17}\,m^2$) and the interior ($187-385 \times 10^{-17}\,m^2$).[129] However, for a 25-year-old concrete made according to the guidelines of $w/c < 0.4$, cement content $> 400\,kg/m^3$, values of $0.1-0.7 \times 10^{-17}\,m^2$, were measured irrespective of sample depth.

Surface densification of CACCs

The above data indicate that there may be a marked difference between the properties of the near-surface and interior regions of CAC concrete. The occurrence of a dense layer at the surface was noted early on by several authors. Figure 13.25 shows microstructures from the near-surface and interior of a 60-year-old concrete from factory pilings exposed to sea water.[44,67,130] The surface microstructure is dense with a porosity of the paste component of 2–4 per cent (measured by image analysis of backscattered electron micrographs), whereas the interior clearly has a much higher porosity of about 17 per cent, typical of a converted concrete at this high water/cement ratio. The precise conditions for the formation of the dense surface layer are not yet clear. Differential thermal analysis and X-ray diffraction indicate the presence of CAH_{10}, AFm phases [e.g. C_2AH_8, CAH_{10}, C_2ASH_8, $C_3A{\cdot}CaCl_2{\cdot}H_{12}$ (Friedel's salt)] and amorphous phases, e.g. 'AH_3 gel'. The formation of this layer could be due to some dehydration of the surface during the early stages of hydration and the later reaction of the unhydrated cement. It is also possible that ingressing ions such as chloride or sulfate may stabilise the hexagonal hydrate phases. Kurdowski[131] also noted the formation of a densified layer in CACCs exposed to strong chloride solutions.

13.9.2 SULFATE RESISTANCE

Calcium aluminate cement concretes have been used in sulfate water for over 80 years. Over this period there have been consistently good reports of the performance of this

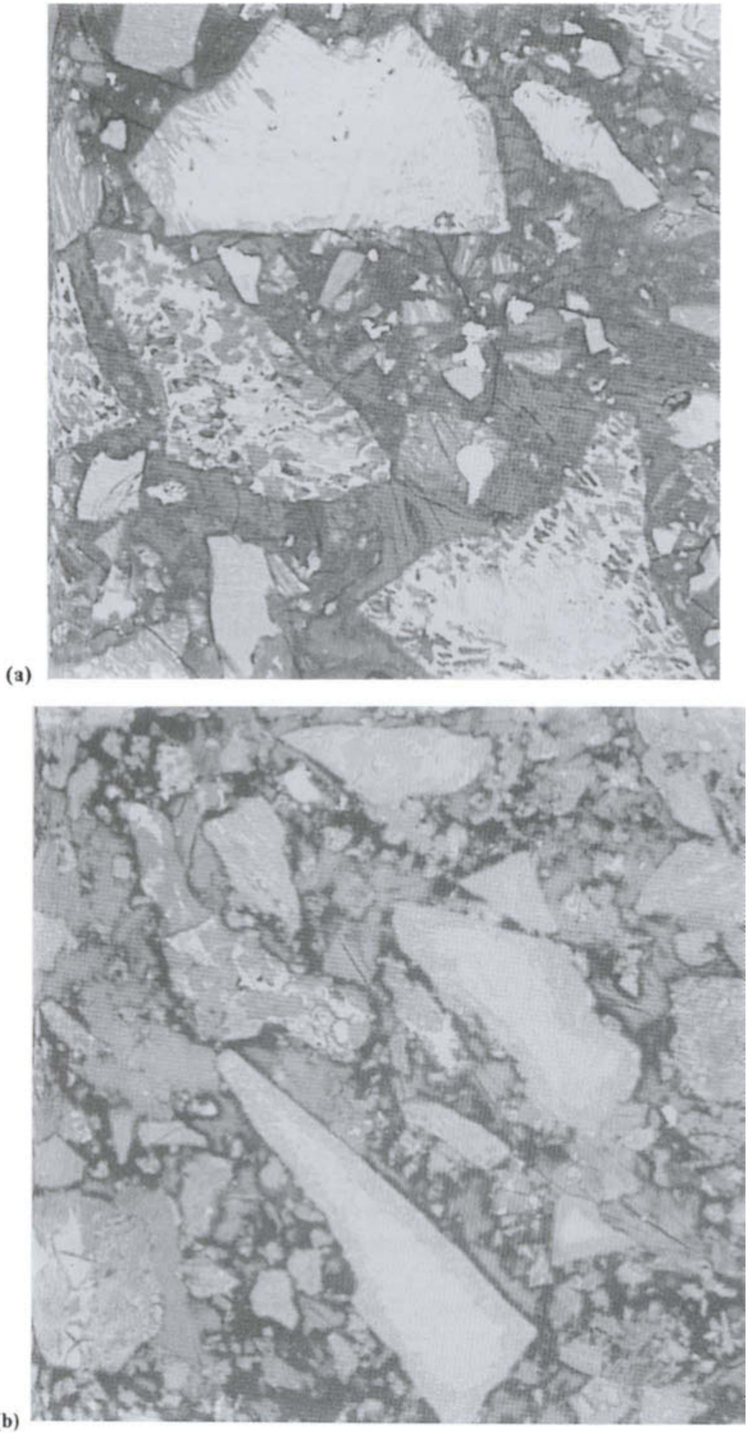


Fig. 13.25 Microstructures from the near-surface (a) and interior (b) of a 60-year-old concrete from factory pilings exposed to sea water at Dagenham, UK.

material both in structures and in long-term field trials. In contrast to the situation with Portland cements, it appears that sodium sulfate solutions may be more aggressive to CAC concretes than magnesium sulfate solutions.

Between 1916 and 1923 over 7000 tonnes of CAC were used in the construction of the P.L.M. Railway in France, which runs through regions containing anhydrite and gypsum. No problems have been experienced with this construction and test specimens immersed in water saturated with calcium sulfate showed no signs of attack even when anhydrite was used as an aggregate.[9] Miller and Manson[132] studied the performance of concretes in the highly sulfated waters of Medicine Lake, South Dakota, for 20 years. The condition of the CAC concretes after this time was excellent, with a gain in strength in many cases. The Portland cement concretes failed within 5 years, while sulfate-resisting Portland concretes lost 20 per cent of their strength in 5 years and nearly half in 10 years. Midgley[133] studied an example of a foundation in soil containing Epsom salts (magnesium sulfate). After 18 years only the immediate surface of the concrete had been attacked and the maximum depth of penetration was 3 mm. Bate[134] reviewed long-term sulfate resistance tests and concluded that good-quality CACC not subjected to elevated temperatures performs well in sulfate-rich environments.

In 1970 a long-term field and laboratory investigation into sulfate resistance of concrete, including CACCs, was started by the UK Building Research Establishment (BRE). The field study involved exposure in the sulfate-rich soils of Northwick Park, London (0.26 per cent SO_3). The results up to 15 years have been reported by Harrison[135,136] and Crammond.[137] The CAC concretes in this study had total water/cement ratios varying from 0.47 to 0.6. All samples were noted to form a dense surface layer which had a low content of the cubic (converted) hydrates. After 15 years the physical condition of all the CACCs exposed in the field was good. The overall sulfate content of the highly converted cylinders was not found to be significantly greater than that of the slightly converted piles, and there was negligible penetration of sulfate into the fully compacted cylinders. The main sulfate mineral present was ettringite, although substantial amounts of sulfate were present within amorphous phases.

Cubes were also exposed to sulfate solutions in the laboratory – 1.5 per cent SO_3 as Na_2SO_4, 1.5 per cent SO_3 as $MgSO_4$ and 0.35 per cent SO_3 as $MgSO_4$. After 15 years there was significant deterioration of the cubes at the higher water/cement ratios (0.53–0.6). In many cases this deterioration had taken the form of expansion within the cube, causing surface cracking. The suggested mechanism was that the sulfates eventually penetrated the dense surface layer of the concrete and formed ettringite in the porous interior, which led to expansion. At the lowest water/cement ratio (0.47) there were some signs of deterioration in one cube in the 0.35 per cent SO_3 as $MgSO_4$ solutions, but three cubes in this, and all the cubes in the higher concentration solutions were in excellent condition.

There are no comparable data yet available for concretes made in accordance with the current guidelines of $w/c < 0.4$ and cement content $> 400\,kg/m^3$. Some preliminary results from the BRE[138] indicated that sections cut from the interior of a $1\,m^3$ block after 28 days disintegrated rapidly in high-concentration sulfate solutions, although a sample from the same concrete containing an original cast surface shows no signs of deterioration after 2 years.

Despite considerable study the precise mechanism of degradation in sulfate solutions, even of Portland cement concretes, is not clear. Many authors attribute degradation to the expansive formation of ettringite and this reasoning lies behind the development of sulfate-resisting Portland cements (SRPCs) with low C_3A contents. However, certainly in magnesium sulfate solutions, it is clear that decalcification of the C-S-H phase and formation of brucite are important degradation processes. Many authors have ascribed the good performance of CACs to the absence of calcium hydroxide, but this is too simplistic. Undoubtedly the calcium aluminate hydrates can react to form ettringite even at comparatively low concentrations of SO_4^{2-}. However it is not clear under what circumstances the formation of ettringite is destructive. Clearly the penetration of sulfate into concretes with a dense surface layer is slow, and this may be in part due to the absorption of sulfate by amorphous phases, in addition to the low porosity.

Additions of CAC to OPC generally lower the sulfate resistance relative to the pure OPC concrete. Small additions of OPC to CAC have little effect relative to the performance of pure CAC concrete. Mixtures of CAC–slag show good durability in sulfate solutions.[139]

13.9.3 PERFORMANCE IN SEA WATER

Lea[52] (pp. 630–8) discusses at length many long-term trials up to 20 or 30 years made in the first half of the twentieth century. In most cases Portland cement, Portland cement with slag and/or other pozzolanic additions and calcium aluminate cements were compared. Tests were made in Germany, Belgium, France, Norway, USA and the UK in both cold and warm waters. The consistent conclusion from all the trials was the importance of high cement contents (usually a lower limit of 400 kg/m^3 is stipulated) and low water/cement ratios for all cement types. In fact, this is stressed more for the Portland cement concretes than for the CAC concretes. Portland cements with C_3A contents above 12 per cent did not perform well, but at lower contents there semed to be little effect attributable to this phase. Above and beyond these effects, the CAC concretes consistently outperformed the Portland cement concretes and most of the blended concretes; the latter at best gave equivalent performance.

In addition to these trials, an extensive study has been made of two structures which have shown good performance in sea water over 60 years (Figure 13.26).[67,74,129,130] In both these cases, dense surface layers were found extending into the concrete for some 50 mm (section 13.9.1). In these regions concentrations of sulfate and chloride were quite

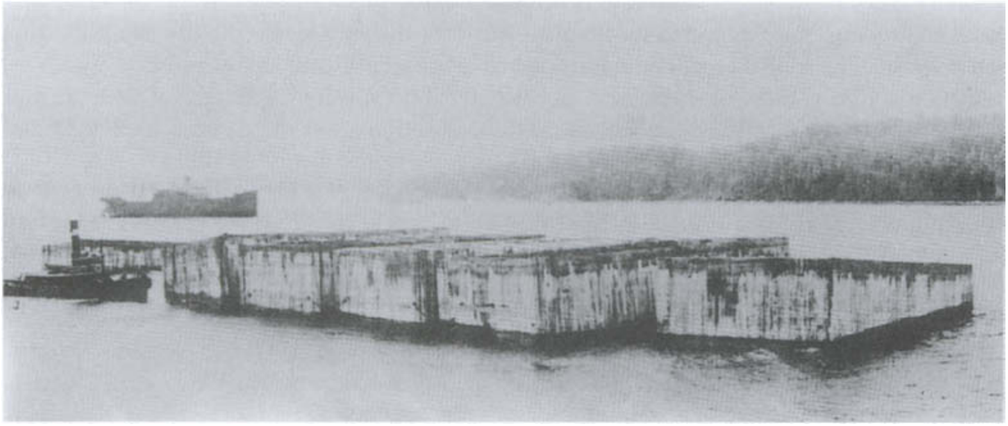


Fig. 13.26 CAC concrete cribs used in the construction of a pier at Halifax, Canada in 1930.

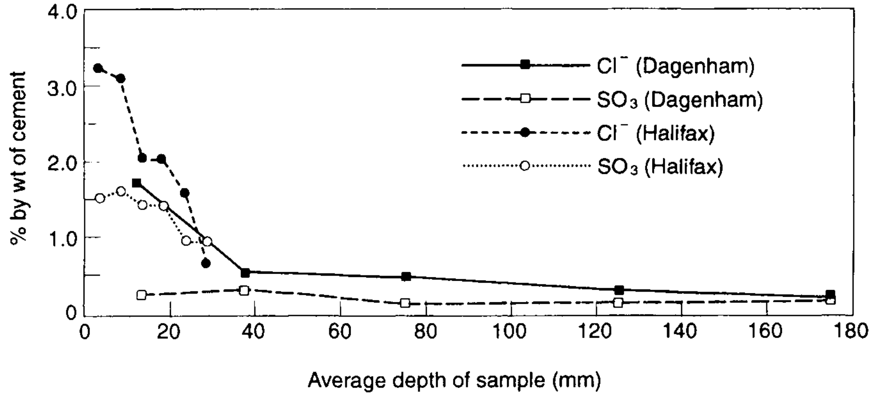


Fig. 13.27 Sulfate and chloride penetration in concrete at Halifax Pier B, Canada, and Ford Dagenham factory, UK (tidal).

significant, mainly in the form of AFm phases (Freidel's salt, $C_3A{\cdot}CaCl_2{\cdot}H_{12}$ and monosulfate, $C_3A{\cdot}C\bar{S}{\cdot}H_{12}$, randomly interlayered with C_2AH_8 and C_2ASH_8), but also in an indeterminate form within the amorphous hydrous alumina gel. Beyond the dense surface layers the concentrations of these ions were low (Figure 13.27).[129]

In most practical cases CAC concretes made in the first half of the twentieth century would have had water/cement ratios in excess of the presently recommended limit of 0.4. Many of these have performed well, although several of the field trials identified the importance of high cement content (i.e. low water/cement), and in a minority of cases high water/cement ratios resulted in poor performance. It may be speculated that the variability of performance at high water/cement ratios could depend on the formation of a dense surface layer to protect the relatively porous interior.

At lower water/cement ratios the difference in porosity and permeability between the interior and exterior is less marked. At early ages the interior of concrete which self-heats and converts rapidly may have a relatively high porosity, but it will also contain anhydrous cement, which will continue to react and densify the interior. George[140] found that in laboratory testing only hot-cured (surface as well as interior) specimens at total $w/c \geqslant 0.6$ showed any sign of attack after 5 years.

13.9.4 REINFORCEMENT PROTECTION

The pH of CAC paste pore solution is normally about 11.6 during the first few hours of setting and then rises to about 12.2–12.4 after 12 h.[141] [143] Although the alkali content of CACs is low, it is released into the pore water during hydration and concentrated as the water is taken up in the hydration products. Due to the lower binding capacity of calcium aluminate hydrates for alkali ions, the pH of mature CAC pastes is very similar to that of Portland pastes.[143] These pH levels are clearly sufficient to maintain reinforcement steel in the passive state, as confirmed by experimental measurements.[143,144] Experimental measurements also confirm that the conversion reaction has very little effect on the pH and the steel remains passivated. As with Portland cement, depassivation may occur due to the presence of chloride or to carbonation of the paste; these are discussed below.

13.9.5 CHLORIDES

Effect on hydration

The strength development of calcium aluminate cement is adversely affected by the presence of calcium chloride in the mixing water, since it acts as a retarder. There are conflicting reports of its effect on conversion, Goñi *et al.*[144] report that the presence of chloride at levels of 0.4 and 1 weight% (as NaCl) in the paste favoured conversion. On the other hand, Macías *et al.*[143] report that the hydration and conversion was slowed down in mixes containing 3 weight% NaCl. Both groups of authors report the formation of Friedel's salt, ($C_3A{\cdot}CaCl_2{\cdot}H_{12}$), although the amount of this phase was reduced at higher temperatures and it was destroyed by carbonation. Macías *et al.* also suggest that chloride may enter into solid solution with other AFm phases, as suggested by the microanalyses of the concretes exposed to sea water described in section 13.9.3.

Effect on reinforcement corrosion

There are few studies of the effect of chloride on reinforcement corrosion in CAC pastes. Goñi *et al.*[144] found that additions of 0.4 per cent Cl^- did not induce corrosion, but that at 1 per cent addition, active corrosion started after about 30 days and continued for 40 days, before the steel became passive again (equivalent OPC samples remained passive throughout). Macías *et al.*[143] found that active corrosion occurred in all samples with 1.8 per cent Cl^- addition, but was marginal in the sample cured at 25°C (with the highest degree of chloride binding).

Chloride ingress

There appear to be no published studies on the rate of chloride ingress into CAC under laboratory conditions. The studies of the concretes exposed to sea water indicated that the presence of a dense surface layer inhibited significant ingress (section 13.9.3; Figure 11.27). Macías *et al.*[143] suggest that chloride binding as Friedel's salt could be a significant factor in slowing down the ingress of chloride into CAC concrete. Unpublished work indicates that the rate of chloride ingress into young, rapidly converted concrete, with the surface removed, may be very rapid.[145] However, tests of chloride ingress under an imposed current carried out by the Florida Department of Transportation[146] showed that unconverted CAC concretes outperformed OPC concretes by more than an order of magnitude.

13.9.6 CARBONATION

The reaction of atmospheric CO_2 with CACs will lead eventually to the formation of $CaCO_3$ and AH_3, irrespective of the nature of the hydrates present, corresponding to the following reactions:

$$CAH_{10} + CO_2 \rightarrow CaCO_3 + AH_3 + 7H_2O \qquad \Delta G = -82.25\,\text{kJ} \qquad (13.8)$$

$$C_3AH_6 + 3CO_2 \rightarrow 3CaCO_3 + AH_3 + 3H_2O \qquad \Delta G = -230.41\,\text{kJ} \qquad (13.9)$$

Monocarboaluminate may be formed as a transient reaction product.

In the absence of alkalis the carbonation of converted CACC leads to an increase in strength,[147] as for Portland cement concrete. Of course, the main concern with carbonation is the possibility of corrosion of the reinforcing steel. As for Portland concrete, active corrosion requires both moisture and oxygen in addition to the loss of steel passivity; thus, even when the concrete is carbonated, the rate of corrosion of reinforcing steel in interior concrete is likely to be low.

Studies of CAC concrete beams in buildings in the UK indicate that after 20–30 years most of these have carbonated to the depth of the reinforcement, a rate comparable to Portland cement concrete.[148] Nevertheless, as expected for interior concrete, only a very small minority show signs of corrosion.

To understand the effect of carbonation of CACCs on reinforcement corrosion, a major study was started by the UK Building Research Establishment in 1993.[149] After 1 year the measured carbonation depths were fairly high. For the good-quality CACC (w/c = 0.4) the carbonation depths at 4 years have increased very little from 1 year, such that they compare favourably with those of good-quality Portland concrete. However, the poor-quality (w/c = 0.8) CACC shows a rapid increase in carbonation depth. This again indicates the sensitivity of CACC to correct use.

In young concretes, carbonation depths can be measured with phenolphthalein indicator. However, in old concretes it is difficult to see the colour change with this indicator. Studies suggest that bromocresol purple might be more effective under these conditions.[150] Otherwise carbonation depths can be identified very clearly in thin sections by optical microscopy under crossed polars.

Laboratory tests indicate that reinforcement steel is not passivated in CACC which has undergone accelerated carbonation.[143,149,151] However, thermodynamic calculations indicate that under natural carbonation conditions it may be possible to maintain a high pH at the carbonation front.[152] This may explain why corrosion is sometimes not observed in CACC, even in the presence of moisture and oxygen. Dunster *et al.*[149] found that the rate of corrosion in concrete carbonated under laboratory conditions was more sensitive to the relative humidity than is usually seen with Portland concretes. At 65 per cent RH the corrosion current was only 0.1 $\mu A/cm^2$, which is borderline for active corrosion. In Portland concrete, Constantinou and Scrivener[153] found virtually no difference in the corrosion rate between 95 and 70 per cent RH.

13.9.7 BEHAVIOUR IN THE PRESENCE OF ALKALIS

Aluminium hydrate (AH_3) can dissolve as aluminate ions at high pHs. In laboratory tests very little effect on weight loss or mechanical properties is observed up to pH 13, with evidence of degradation only at pH 14. Nevertheless the use of CAC in highly alkaline media is not recommended.

Lafuma[154] and Midgley[155] report that the presence of alkalis accelerates the conversion of CAC. However, Beaudoin[89 91] found that in mixtures containing siliceous additives alkalis increased the rate of strätlingite formation and reduced the rate of conversion to C_3AH_6.

13.9.8 ALKALINE HYDROLYSIS

Alkaline hydrolysis is the name given to a phenomenon which is in fact the catalysis of carbonation by alkali. A mechanism for this process was first published in 1936.[156] In poor-quality porous concrete this may result in a dramatic loss of strength. Macroscopically it appears to be characterised by a white dusty precipitation on the surface of the concrete.

The reactions involved may be written as follows:

$$\begin{aligned}&2Na^+(aq) + CO_3^{2-}(aq) + \underset{(CAH_{10})}{CaO \cdot Al_2O_3 \cdot 10H_2O(s)} \rightarrow \\ &\qquad CaCO_3(s) + 2Na^+(aq) + 2Al(OH)_4^-(aq) + 8H_2O \quad (13.10)\end{aligned}$$

$$2Na^+ + 2Al(OH)_4^- + CO_2 + 3H_2O \rightarrow 2Na^+(aq) + CO_3^{2-} + 2Al(OH)_3(s) \quad (13.11)$$

When written in this ionic form it can be seen that the Na^+ ions in fact play no direct part in the reaction. Overall the reactions which occur in alkaline hydrolysis are the same as those occurring in ordinary carbonation, i.e. equations (13.10) and (13.11) may be combined as

$$CO_2 + CaO \cdot Al_2O_3 \cdot 10H_2O \rightarrow CaCO_3 + 2Al(OH)_3 + 7H_2O \quad (13.12)$$

In many texts the sodium and alumina ions produced in equation (13.10) are written as $NaAlO_2 \cdot xH_2O$, and some workers have claimed the occurrence of this compound as a solid phase in concretes subject to alkaline hydrolysis.[157,158] The compound $Na_2[Al_2O_3(OH)_2] \cdot 1.5H_2O(NAH_{2.5})$ can only exist in extremely concentrated NaOH solutions (at least 10 M);[159,160] so it would be unlikely to precipitate in pastes or concretes under normal circumstances. The structure of the synthesised compound[160] also indicates that the X-ray pattern for this phase is quite different from that reported in the JCPDS powder diffraction file (card no. 29-1165) for NAH_6, which appears to correspond to a mixture of AH_3 polymorphs.[161]

It appears that the catalysis of the reaction by alkalis leads to the loss of strength in poor-quality concretes with high water/cement ratios, but the precise physical aspects of this 'destruction' are not understood. The alkali metal ions increase the solubility of CO_2 in solution, making it more available. The solubility of alumina is also increased and if there is sufficient passage of water, material may be lost, leading to loss of strength of the concrete. AH_3 may also recrystallise in the alkali solution giving large crystals, which may also weaken the concrete. Dunster *et al.*[162] have reported a microstructural study of a field case of alkaline hydrolysis in which large areas of paste appeared to have been leached away and large crystals of norstrandite (a polymorph of AH_3) were observed.

For alkaline hydrolysis to occur with detrimental effects, four conditions are necessary:

- high humidity
- high porosity
- presence of free alkali
- presence of CO_2.

Field cases are uncommon, but have been diagnosed in several countries. In France, this type of deterioration occurred where a porous calcium aluminate cement had been used to fix electricity transmission poles into Portland blocks. In this case the alkalis in the Portland cement could be drawn up into the calcium aluminate cement concrete by capillary action and concentrated by evaporation near the concrete surface where carbonation could occur. (NB under normal circumstances, contact of CAC concrete with OPC concrete does not cause a problem since the alkali concentration in the Portland concrete is similar to that in the CAC concrete and too low to cause alkaline hydrolysis.) In the UK a case occurred when alkaline cleaning fluid had leaked from a drain onto a concrete beam.[163] Another case is reported in a poor-quality concrete beam, exposed to persistent roof leakage.[162] In Spain it is thought that alkaline hydrolysis may have occurred where aggregates containing soluble alkalis were used.

Alkaline hydrolysis has proved difficult to reproduce in the laboratory. In a series of experiments aimed at understanding the deterioration in the electricity transmission pole case, a water/cement ratio of 0.7 had to be used before alkaline hydrolysis could be triggered.[164]

The low levels of alkali in the CAC itself do not induce alkaline hydrolysis. Neither is alkaline hydrolysis induced when good-quality CAC concrete is placed adjacent to hardened Portland concrete. Microscopical examination of cores taken through the boundary between Portland and Fondu concrete, from a 14-year-old viaduct,[165] showed no evidence of interaction between the two cements beyond a few hundred micrometers and no evidence of any degradation.

13.9.9 BEHAVIOUR IN THE PRESENCE OF ACIDS

No cement, whether Portland or calcium aluminate, is thermodynamically stable in acidic conditions. Therefore the choice of appropriate material must be made in terms of service life in a given medium.

Two factors determine the rate of acid attack:

- the quantity of acid necessary to dissolve a given quantity of the cement – *the neutralisation capacity*;
- the speed of acid consumption – *corrosion kinetics*.

Portland cement pastes consist mainly of calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). Below pH 7 both these phases are quickly attacked to leave a skeleton of silica and gypsum.

$$\text{C-S-H} + \xrightarrow{H_2SO_4} CaSO_4 + SiO_2(aq)$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$

In calcium aluminate cements the hydrates consist of calcium aluminate hydrates and hydrous alumina gel or gibbsite. This latter is inert to acid attack above pH 4. Attack of the calcium aluminate hydrates above pH 4 leads to the precipitation of more AH_3 gel which then acts as a diffusion barrier, greatly slowing down the reaction:

$$C_3AH_6 + 6H^+ \rightarrow 3Ca^{2+} + 2Al(OH)_3(s) + 6H_2O$$

In the domain above pH 4 the neutralisation capacity of Portland cement is higher than that of CAC, but this is greatly outweighed by the protective effect of the precipitated AH_3 and CACs are attacked much more slowly.

At pHs lower than 4, the AH_3 reacts with the acid and dissolves:

$$AH_3(s) + 6H^+ \rightarrow 2Al^{3+} + 6H_2O$$

This reaction of six moles of acid with each mole of alumina greatly increases the neutralisation capacity. So even in this pH regime the attack of CAC is much slower than that of Portland cement. In addition, the progressive dissolution of AH_3 means that the interior of the concrete is mostly protected from the full acid strength.[166]

Bayoux *et al.*[167] studied the durability of CAC pastes and mortars in various acids at concentrations of 0.01, 0.1 and 1 N. The variation in weight loss was more dependent on

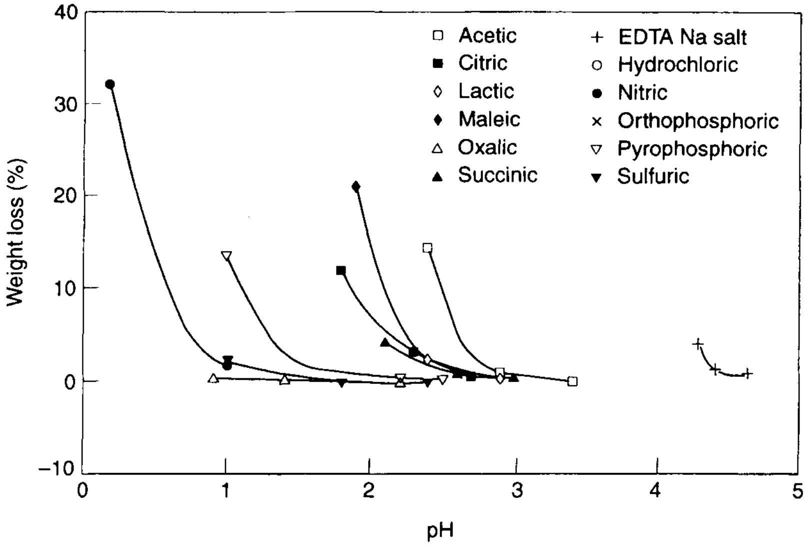


Fig. 13.28 Weight loss (per cent) as a function of solution pH after eight renewals for different acids.

the concentration of the acid than the pH (Figure 13.28), so the pH threshold for rapid dissolution was lower for strong acids than for weak acids.

Bacteriological corrosion

A particular case of acid attack, relevant to the use of CACCs as linings for sewage pipes, is that of bacteriological corrosion. Sulfates in the sewage are converted to sulfide by anaerobic bacteria (found in the thin slime layer which develops on the sewer walls in direct contact with the effluent flow). The sulfide is released in the form of dissolved hydrogen sulfide into the effluent stream. The rate of production of H_2S is governed by a number of parameters, including the amount of sulfate in the effluent stream, ambient temperature, flow speed and effluent level.

When the concentration is high enough, or due to turbulence, H_2S volatilises from the effluent and, carried by convection currents, it accumulates at the crown of the pipe, where it oxidises to elemental sulfur. A second set of aerobic bacteria (*Thiobacillus thiooxidans*) then uses the sulfur as food and excretes sulfuric acid as a waste product. It is this sulfuric acid which goes on to attack the concrete.

The activity of bacteria can induce pH values as low as 2, but practically there are large variations of pH from place to place and the attack may be highly localised.

Comparison of the performance of cements is complicated by interactions between bacteria development and chemical composition of the cement, and thus simple testing with sulfuric acid is not representative of the practical situation. Tests in a special chamber built to simulate corrosion in sewers[168,169] indicate a good performance of CACs compared to Portland or blended blastfurnace cements. Figure 13.29 shows the comparative weight loss of these cement types over 1 year. Examples of field performance are discussed in section 13.10.5.

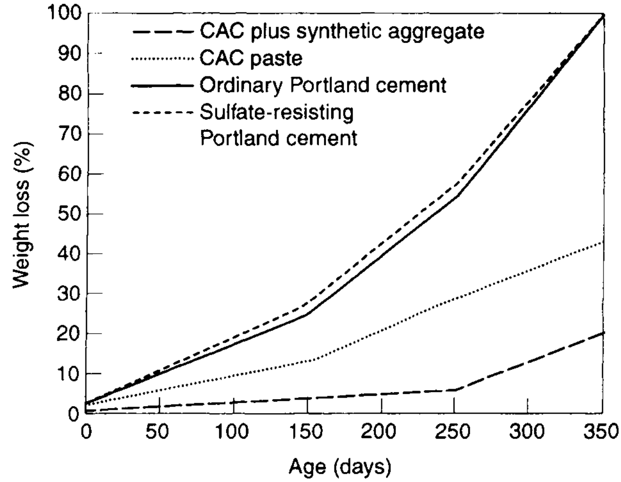


Fig. 13.29 Weight loss due to biogenic attack of CAC and Portland cements after 1 year of accelerated testing approximately equivalent to 24 years as a sewer.

13.9.10 FREEZE-THAW

Field experience with CAC concretes has shown that they can resist freeze–thaw damage in extreme environments for long periods. For example, CACC used to build a pier in the port of Halifax, South Scotia, Canada is still in service after undergoing about 1000 freezing cycles over 60 years.[151] Laboratory experiments and in-service monitoring indicate that for CAC concretes to have good resistance to freeze–thaw cycles, they must be of low porosity (below 13 per cent). This is similar to the conclusions for Portland cement concretes. The limited data regarding the freeze–thaw performance of air-entrained CAC concrete indicate that it is comparable to air-entrained Portland concrete.[170] However, good-quality CAC concrete with w/c < 0.4 is likely to be freeze–thaw resistant even without air entrainment.

13.10 Applications

13.10.1 RAPID HARDENING

As previously stated, CACs have a very similar setting time to ordinary Portland cements, which can also be regulated by the use of admixtures. However, after set, hardening is extremely rapid allowing fast stripping of formwork and putting into service within 6–24 h. This property means that calcium aluminate cements can provide a valuable solution in certain situations. Table 13.12 gives some examples of these types of applications (Figure 13.30). It is important to reiterate that in these situations design was on the basis of converted strength.

13.10.2 ABRASION AND IMPACT RESISTANCE

Good-quality, well-compacted calcium aluminate cement concrete offers very good resistance to abrasion, i.e. loss of surface material by mechanical action. This property is

Table 13.12 Examples of applications of calcium aluminate cements where rapid hardening is required

Situation	Problem	Advantage of use of CAC concrete
Concrete ferry slipway, English Channel	The original Portland concrete had deteriorated in the sea water. Repair with Portland concrete would take several days, necessitating the construction of caissons to keep out the sea water during casting and construction	CAC concrete was supplied in ready-mix trucks. The old concrete was removed and new concrete poured. Hardening was sufficiently rapid to allow the job to be completed between two consecutive high tides
Motorway slab repairs, Bangkok 1989–1990	There was a need to minimise traffic disruption	With CAC concrete the work was completed during the night and the road reopened to traffic the following morning
Bridge deck enlargement, Southern Alps, France, 1989	The bridge was the only connection across a ravine between two neighbouring communities	Using CAC concrete the bridge was widened from 4.5 to 8 m and reopened in 12.5 h. The extra cost was only 3 per cent

exploited in its utilisation in such applications as industrial floors and dam spillways. The best performance is obtained when CAC is used with a chemically similar synthetic aggregate ('Alag'). Figure 13.31 shows the comparative performance of various CAC and Portland cement concretes in an abrasion test in which the volume lost is measured after exposure to a sand–water jet. Installations in spillways of hydroelectric dams have shown good performance to date (12 years after installation).

13.10.3 USE AT LOW TEMPERATURES

The rapid heat evolution of calcium aluminate cement concrete during hardening is beneficial when concrete is placed at low temperatures. Table 13.13 compares strength development of RHPC (rapid-hardening Portland cement) and CAC at low-temperatures.[171] In these data the water/cement ratios of the CAC concrete were above the limit presently recommended. A lower water/cement ratio of 0.4 and correspondingly higher cement content would increase the self-heating and strength development at low temperatures.

In practice it is found that provided the temperature at which the concrete mix is placed is sufficient to keep it above freezing until hydration starts, that is, for about 3 h, the heat evolution will suffice to raise the temperature enough to ensure hardening. Calcium chloride is not an accelerator for calcium aluminate cement, but other accelerators are effective and allow good hydration even if the aggregates are below freezing point.

This property has been used in numerous applications, particularly in Canada where CACC has been used to build foundations in frozen ground. Another recent application was to provide temporary support for a tunnel being bored through artificially frozen ground. CAC concretes are also used for repairs in industrial cold stores.

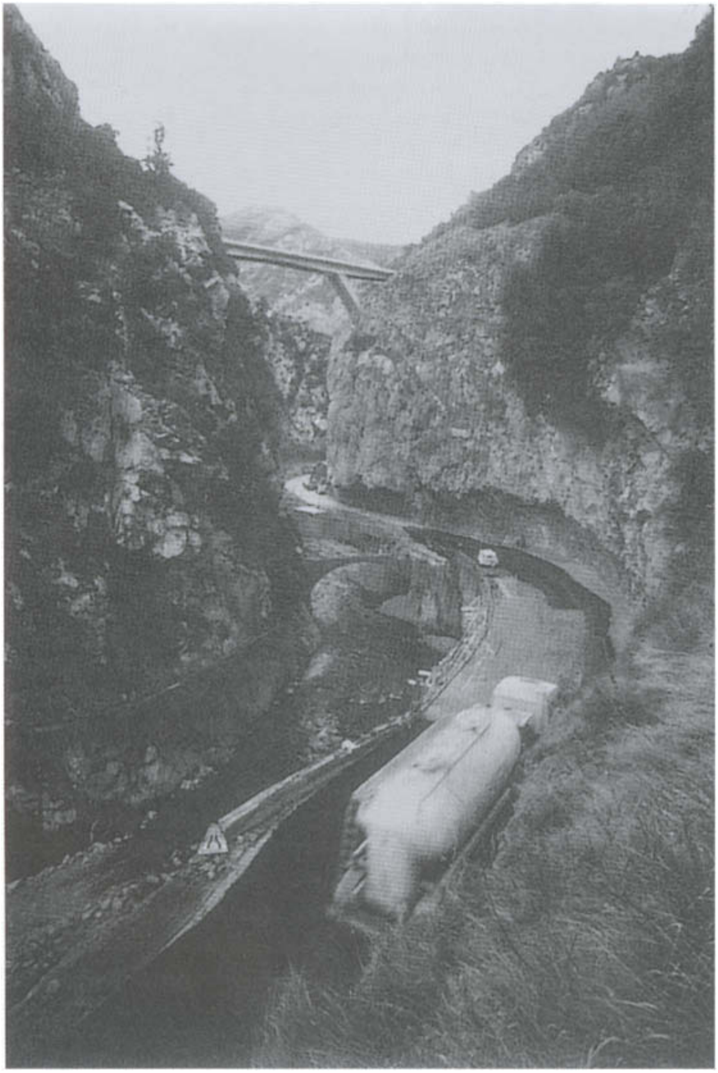


Fig. 13.30 Bridge widened with CAC concrete.

13.10.4 INDUSTRIAL FLOORS

Industrial floors are an important application which may make use of a range of CAC concrete properties:

- impact and abrasion resistance in areas of heavy traffic or loads;
- chemical and acid resistance, including milk, sewage, natural oils, processing plant, fruit juice and slaughterhouse blood;
- temperature tolerance to cold in cryogenic handling facilities and to heat in foundries, steel and aluminium mills where repeated cycling to over 200°C may occur.

The performance of the concrete is highly dependent on the choice of appropriate aggregates (section 13.10.10) and on mix design (especially low water/cement ratios). The

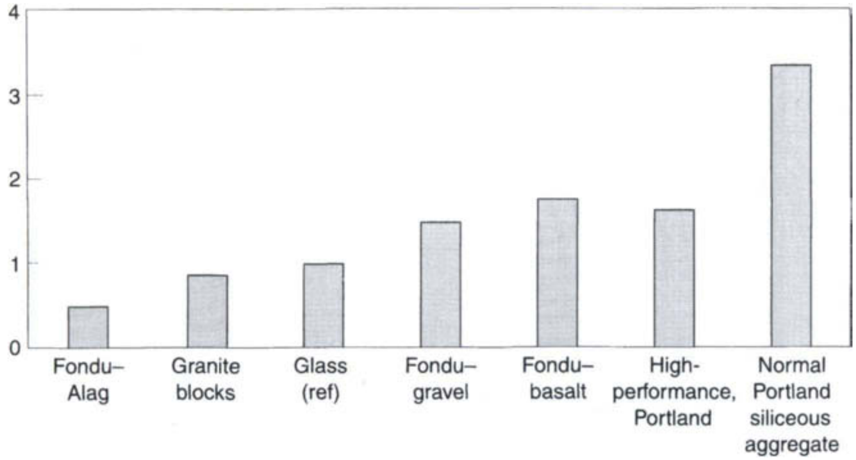


Fig. 13.31 Comparative performance of CAC and Portland concrete in an accelerated abrasion test.

finish of CACC floors requires additional human resources to achieve a good surface finish in the shorter 'open time' between initial and final set when the final trowelling occurs. Curing should take account of the faster heat evolution to protect the surfaces from drying out. Cleaning methods should avoid the use of high pH substances often used in industrial applications.

13.10.5 PIPES

Sewage pipes

Calcium aluminate cements have a long history of successful use as linings and coatings for sewage pipes and in associated wastewater applications. Their performance in these applications is related to good abrasion and acid resistance.

Table 13.13 Strength development of CAC and rapid-hardening Portland cement concretes at low temperatures

		Strength (MPa)[a]			
Temperature (°C)	Cement	6 h	16 h	1 day	2 days
18	CAC	24	39	40	45
18	RHPC	0	4	12	23
12	CAC	21	36	39	41
12	RHPC	0	1	3	43
6	CAC	19	36	37	39
6	RHPC	0	1	1	7
0	CAC	5	33	35	39
0	RHPC	0	0	1	2

[a] Concrete prisms 70 × 70 × 280 mm, cement content 350 kg/m^3, w/c = 0.5.

Several examples of long-term performance exist. Solid calcium aluminate sewage pipes were installed in Australia (Mildura, Victoria, and Bundaburg, Queensland) in the 1950s. When last inspected in 1990 these were found to be in good condition. Also in the 1950s, centrifuged Portland concrete pipes lined with 13 mm (0.5 in) of calcium aluminate mortar were laid in Kuala Lumpur; these are still in use today. Since the 1960s, many kilometres of solid calcium aluminate sewage pipes were used in Durban, South Africa. In the 1980s concrete pipes lined with calcium aluminate mortar were laid in Cairo, Egypt.

Calcium aluminate cements are used extensively for lining ductile iron pipes.[172] The process of centrifugal spinning allows very low water/cement ratios down to 0.3 to be achieved.

Potable and 'soft' water

CACs are used in such applications where the water is particularly aggressive to Portland cement. Under such conditions the possibility of aluminate leaching is a concern. In 'hard' waters, with significant Ca^{2+} in solution, the degree of aluminate leaching is extremely low; however, Portland cements also perform well in these environments, so CACs present no advantage. In 'soft' waters the performance of Portland cement is unsatisfactory and CAC can provide a solution. Under such conditions, the level of aluminate leaching drops to a low level after a short period of contact. In large pipes with a high volume of water flow the aluminate concentrations in the water will not be significantly affected and will remain well below acceptable levels. For any situation, careful assessment should be made of the possible impact of aluminate leaching.

CACs also have a good record of performance in other applications where resistance to 'soft water' is important, such as snow melt runoff, natural spring waters and 'pure' waters used in industrial applications.

13.10.6 MINES AND TUNNELS

Significant quantities of CAC are used in mining and tunnelling. In mines the two principal uses are 'mine packing' and rock bolts.

Mine packing is used mainly in coal mining where the rock is weak. A low-cost rapid setting and hardening material is needed to provide roof support, but the level of strength needed is not very high. This is provided by a system based on CAC and calcium sulfate, which react to form ettringite.[173] The high binding capacity of ettringite for water allows very high water/cement ratios to be used up to 2.5 (which makes the material low cost). Bentonite is also included to prevent sedimentation.

Rock bolts are used to anchor iron bars into mine roofs and tunnel walls to stabilise the rock. These need to set and develop a 'pull' strength very quickly; this is achieved by formulating CAC with various additives and fillers.

In tunnels CAC concrete is used for precast linings, allowing rapid turnaround of moulds. Set accelerators for Portland cement are also manufactured for shotcreting.

13.10.7 BUILDING CHEMISTRY

A major area in which calcium aluminate cements are used today is that of building chemistry. This term covers a wide range of non-structural products used in construction, such as floor levellers and screeds, rapid tile grouts, rapid repair and expansive mortars. In such products, calcium aluminate cements are usually part of a complex formulation, which may contain ten or more components. The mineral part of the formulation may include, in addition to CAC, calcium sulfates, Portland cement, free or hydrated lime or calcite. The admixtures may include accelerators and retarders, superplasticisers, resins, anti-foaming agents, etc., to control such properties as flowability, working time, bleeding or other rheological characteristics. Relatively little has been published about the mechanisms of hydration in such complex systems and most formulations are developed from experience.

The advantages of calcium aluminate cement in these products are various. Some of the simplest products are rapid mortars and grouts which are based on mixtures of Portland cement and CAC as described above (section 13.5.7), in which the addition of CAC accelerates the setting and hardening. However, even in these relatively simple cases, admixtures may have a dramatic effect, not only on the time of set but also on early and ultimate strength development.

The more sophisticated formulated products often consist mainly of CAC with calcium sulfate (section 13.5.7), in which ettringite is the principal hydration product formed along with a substantial quantity of poorly crystallised or amorphous hydrous alumina gel. In these systems the formation of ettringite may be manipulated to achieve rapid drying, controlled expansion or shrinkage compensation.

The white colour of the grades of CAC with low iron content is another attribute which is utilised in the formulated products where aesthetic appearance is important.

13.10.8 ENVIRONMENTAL APPLICATIONS

Calcium aluminates have the property of combining with minerals and organic anions. This gives them possibilities of use for the treatment of liquid or solid wastes. The compounds formed during hydration or by ionic exchange on hydrated products have been known for a long time.[174]

In the presence of anions the addition of calcium aluminates will lead to the formation of AFm phases $C_3A{\cdot}(CaX_2){\cdot}nH_2O$, or $C_3A{\cdot}(CaY){\cdot}nH_2O$, or AFt phase (ettringite type): $C_3A{\cdot}(CaX_2)_3{\cdot}nH_2O$, or $C_3A{\cdot}(CaY)_3{\cdot}nH_2O$. The useful property of these compounds, of interest for environmental applications, is their low level of solubility.

In order to maximise the formation of the compounds it may be necessary to add extra lime with the calcium aluminate. The relevant quantities may be easily calculated from the stoichiometry of the phases.

This application is of interest for the disposal of fly ash resulting from a combustion process, such as municipal waste or industrial waste incineration. According to many national regulations, these wastes have to be solidified and stabilised before used as landfill or recycled in building materials. Most of the stabilisation processes are based on the use of a hydraulic binder, such as Portland cement, slag or calcium aluminates.

The sequence of hydration reactions in a mixture of 84.5 per cent of fly ash and 15.5 per cent calcium aluminates at a water/cement ratio of 2.7 has been analysed by XRD diagrams.[175] Chemical analysis of a municipal solid waste fly ash gave 10.5 per cent of chlorides in the form of alkali chlorides and 8.3 per cent of SO_3, mainly as anhydrite and some as gypsum. The CaO content was 19.3 per cent. Excess lime was used to favour complex calcium aluminates formation. After 4 h only traces of anhydrite were detected and a maximum of ettringite was observed. After complete consumption of sulfates, monochlorocalcium aluminate starts to form, until the calcium aluminate is totally consumed, after about 2 days.

In mixtures of CAC and silica fume hydrated in the presence of caesium ions, it has been found that zeolitic phases are formed which dramatically reduce the leaching of the caesium.[176]

13.10.9 MACRO-DEFECT-FREE (MDF) CEMENT

So-called macro-defect-free (MDF) cements, invented in 1983,[177] are composite materials which have very high flexural strengths. Cement is processed with a very small amount of water and a relatively high addition of polymer. The processing consists of a high-shear mixing process followed by heat curing. The final composite consists essentially of anhydrous cement grains bound together by polymer and a cement hydrate–polymer interphase. The excellent mechanical properties were originally attributed to the extremely low porosity and absence of large flaws – hence the name.

In this application calcium aluminate cements show far superior performance to Portland cement, which has been explained by the formation of a chemical bond between aluminium (and possibly iron) ions and the polymer molecules.[178,179] Recent work with high-resolution electron microscopy and electron energy loss spectroscopy has elucidated further details of the microstructure of these materials.[180]

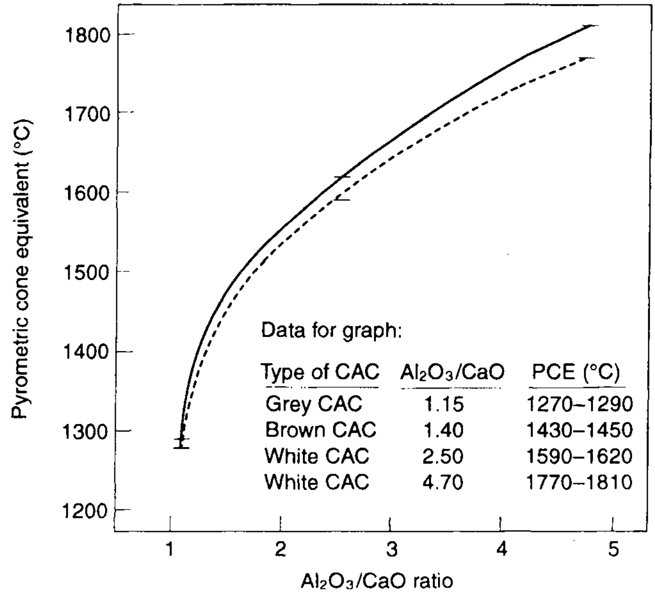
Utilisation of this material has been impeded by difficulties in controlling the process parameters and by the sensitivity of the material to moisture. In moist environments MDF cement loses strength due to degradation of the polymer phase. Considerable research has been directed at resolving these problems (e.g. Refs 181, 182) and industrial development is taking place in several countries including Japan, Italy and the USA.

13.10.10 HEAT-RESISTANT AND REFRACTORY CONCRETES

Although calcium aluminate cements were not originally developed for their heat-resistant properties, this application has become one of the most important today. The high lime and silica contents of Portland cement render it unsuitable to produce refractory concrete for use at high service temperatures, due to the formation of low melting point eutectics. The refractoriness of calcium aluminate cements increases in proportion to the alumina/lime ratio, thus the higher alumina content white CACs may be used at higher temperatures than the basic grades made by fusion.

The capacity to resist high temperatures, and recycling between high and ambient temperatures, are associated with the absence of hydrated lime (portlandite, $Ca(OH)_2$) in the hardened cement. At temperatures above ~500°C the hydrated lime in Portland cement is dehydrated to quicklime (CaO). This is a reversible reaction[183] and subsequent cooling and exposure to moisture will lead to disruption of the concrete. Hydrated lime is not formed during the hydration of calcium aluminate cement and, although the hydrates that are formed (section 13.5.1) are dehydrated at high temperature, they are stable in themselves or form stable compounds with the aggregates used.

Figure 13.32 shows the relationship between the Al_2O_3/CaO ratio and refractoriness. However, this is not the upper limit of the service temperature of concretes made with these cements. The aggregates used in refractory concretes may extend the service temperatures 100–200°C beyond the fusion point of the pure cement by formation of higher melting point eutectics.[184] Thus combinations of the commercially available CACs having alumina contents of 40–80 per cent with the very extensive range of heat-resisting, insulating and refractory aggregates has led to the development of hundreds of proprietary refractory



Data for graph:

Type of CAC	Al_2O_3/CaO	PCE (°C)
Grey CAC	1.15	1270–1290
Brown CAC	1.40	1430–1450
White CAC	2.50	1590–1620
White CAC	4.70	1770–1810

Fig. 13.32 Relationship between Al_2O_3/CaO ratio and refractoriness.

concretes, known in the industry as 'castables'. Table 13.14 gives an indication of the composition of some of these concretes.

The high-temperature performance of modern refractory concretes is now equivalent to or better than some refractory bricks (see below). The major thermal industries, including steel, non-ferrous metals, ceramics, potteries and petrochemicals, could not function today without refractory calcium aluminate cements.

Heat-resistant concretes

Concretes resistant up to 900–1000°C are generally referred to as heat resistant rather than refractory. These concretes are based on the standard grey CAC (~40 per cent Al_2O_3) together with aggregates such as granite, basalt, whinstone and traprock. Such concretes are dense and abrasion resistant and are used for floors in industries such as steel, foundries and aluminium where hot metal spillage or splashing may occur (section 13.10.4).

A more specific use for such concretes is in the construction of fire training areas and buildings. In these structures fires may be set and extinguished many times during a day and a typical structure is likely to have a lifetime of several years. The structural integrity of Portland cement concretes would be rapidly destroyed in these conditions and only CACs are suitable.

Conventional dense refractory castables

Castable refractories tend now to be classified according to their cement contents, conventional castables being the term used for the traditional type of refractory concrete, having 15–25 per cent CAC. The refractory and thermal properties of these castables are governed by the type of cement used (40–80 per cent alumina) and the aggregates (Table

Table 13.14 Heat-resistant and refractory concretes

Cement type	Al_2O_3 (%)	Aggregate type	Approximate temperature limit (°C)
Heat-resistant concretes			
Grey CAC	40	Granite/whinstone/basalt	700–800
Grey CAC	40	Emery	1000
Grey CAC	40	Alag™	1100
Brown CAC	50	Olivine	1200
Dense refractory concretes			
Grey CAC	40	Chamotte (42–44% Al_2O_3), molochite	1300
Brown CAC	50–55		1400
White CAC	70		1450
Grey CAC	40	Sillimanite, gibbsite	1350
Brown CAC	50–55		1450
White CAC	70		1550
Grey CAC	40	Brown fused alumina	1400
Brown CAC	50–55		1550
White CAC	70		1650
White CAC	80		1750
White CAC	70	White fused alumina	1800
White CAC	80		1850
White CAC	70	Tabular alumina	1800
White CAC	80		1900
Thermally insulating concretes			
Grey CAC	40	Pumice, diatomite	900
Grey CAC	40	Vermiculite, perlite	1000
Grey CAC	40	Lytag™, Leca™	1100
Brown CAC	50	Expanded chamotte	1300
White CAC	70	Bubble alumina	1700
White CAC	80		1800

13.14). These products have been in use for many decades and were, until the 1980s, the only type of hydraulically bound refractory castable in use.

Whilst these concretes are still very widely used, their mechanical performance at high temperatures is limited by the relatively high cement content. Since the refractoriness of a castable is strongly related to the Al_2O_3/CaO ratio, the drive to produce higher alumina content cements has led to the development of CACs with 80 per cent alumina.[183] These cements, with aggregates such as fused or tabular alumina, can produce castables with a temperature resistance up to 1800–1900°C.

However, their mechanical performance at temperature, although very good, is limited by the lime (CaO) content of the cement. In order to push the performance even higher, cements with 90 per cent alumina were tried, but these were never widely used.[185] Low-cement castables (see below) were developed in order to improve further the mechanical performance of refractory concretes at high temperatures.

Insulating concretes

Typical dense refractory concrete has a relatively high thermal conductivity, and thus in any heat-retaining vessel, furnace, kiln, etc., the heat losses would be high unless thermally insulated. CACs with suitable lightweight and heat resistant aggregates (Table 13.14) may be used to produce insulating concretes with thermal conductivities in the range 0.15–0.5 W/(m K). The hot-face temperature limit of these concretes is governed by the performance of the aggregates and these should be selected on the basis of temperature and thermal performance required. It is common practice to combine a dense hot-face refractory concrete with an insulating backing concrete in order to control the thermal gradient in the furnace wall and limit heat losses. In extreme cases, different grades of CAC (40–70 per cent Al_2O_3) may be used in the cold and hot faces. Since these cements are all compatible with each other, such concretes can be cast monolithically.

High-technology castables

In the mid 1980s, refractory castables with cement contents of 5–8 per cent were developed. These became known as low-cement castables (LCC) or in the USA as low-water castables. The technology which allowed such concretes to be developed, was dependent on two main factors:

- theories of particle packing and optimised granulometry;[186,187]
- the availability of ultrafine silicas (silica fumes) and aluminas.

In a conventional castable, the cement would normally be the finest ingredient. Good-quality silica fume has a mean particle size in order of magnitude lower than cement and thus allowed the formulation of continuous grading curves down to sub-micrometre levels. The water demand of such systems is optimised at its lowest level by the filling of interstitial voids with these very fine particles (hence the term low-water castables). The binder in these systems consists of roughly equal quantities of CAC, silica fume and reactive aluminas, hence the cement content is reduced to about 5 per cent.[188]

The simultaneous reduction of the cement content of the castable, together with refractory properties of the alumina and silica at high temperatures, led to a significant improvement in the refractory performance of these materials.[189,190]

During the 1980s and 1990s the technology which led to the development of LCCs was improved by the use of additives and superior grades of fume silica and alumina, and thus cement contents were pushed even lower to 3–5 per cent. These products became known as ultra-low cement castables (ULCC) and refractory performance was again improved.

The latest technology has concentrated on two areas. The rheology has been optimised such that castables can now be placed without mechanical vibration, these are known as self-flow castables (SFC),[191] and ultrafine refractory aluminas have been used to replace the fume silica with the objective of further increasing the temperature resistance.[192]

High-performance refractory concretes have in many cases now replaced refractory bricks, bringing improved performance, life and ease of installation and repair.

Refractory concretes for reducing atmospheres

In some industries the furnace atmosphere in certain processes is severely reducing, leading to high carbon monoxide (CO) levels in the gases. Refractories containing iron or iron oxide compounds are attacked by carbon monoxide,[193] leading to disruption of the concrete or bricks.

The standard grey CAC contains about 16 per cent of iron oxides, mainly in the form of ferrites (section 13.4.2) and castables made with this cement are rapidly attacked in reducing atmospheres at ~500°C or above.

During grinding all cements pick up a certain amount of 'tramp' iron due to the wear of mill charge and lining plates. If excessive, this also can cause problems in reducing atmospheres and control of this 'tramp' iron is essential for satisfactory performance.

The so-called mid-range CACs having alumina contents of 50–60 per cent will normally have iron oxide contents of about 3 per cent or less. These cements, and the higher range cements, having virtually no iron compounds, are suitable for concretes used in furnaces with reducing atmospheres.

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14

Special Cements

John Bensted

14.1 Introduction

There are an enormous number of special cement systems in existence and it is quite beyond the scope of this book to be able to consider them all in detail. This chapter has been written on the basis of understanding the main types of special cements that are either in regular use or present some noteworthy features.

Four main cement types are considered, namely oilwell, decorative, chemical and non-standard Portland-based and other cements.

Oilwell cements are discussed in detail, because of the paucity of information available in many texts in oilwell cements. Since they are largely used in conjunction with additives, a knowledge of these additives is necessary in order to appreciate more fully how these cements behave in the field. Consequently there has been some discussion of oilwell cement additives.

Decorative cements have also been described at some length in view of their aesthetic importance in construction.

The main types of chemical cement reported in the technical literature are outlined. Many of them are proprietary products. In consequence, methods of manufacture are not always readily available, nor in a number of instances have the respective hydration chemistries been fully elucidated.

Non-standard Portland and some other cements are also described. Several of these have useful properties for certain specialised applications, which are outlined in the text. Commonly used cements such as masonry filler, sulfate-resisting and blended types are excluded from consideration here, since they are discussed elsewhere in the book.

14.2 Oilwell cements

14.2.1 GENERAL

Oilwell cements find a wide application in the exploration for and the production of oil and gas. They fulfil the requirements for materials forming low-viscosity slurries, which remain pumpable to considerable depths and can be tailored to harden rapidly once in place. Their primary function is one of sealing to prevent the flow of fluids other than where this is specifically required in the well. The major application is in primary cementing, which refers to the process whereby, at several stages during drilling, the borehole is lined with a steel casing (or tube) down which the cement slurry is pumped and then displaced up into the annular space between the casing and the borehole wall.[1] [7] Oilwell cements can also be used for sealing water wells, waste disposal wells and geothermal wells. A cemented well is illustrated diagrammatically in Figure 14.1.

The chemical and physical properties of oilwell cements are given in relevant specifications such as the API Specification 10A. Outside the USA, the most frequently used oilwell cement is API Class G, whilst within the USA (apart from California, the Rocky Mountain region and Alaska) Class H is more usual. These cements must reach an arbitrarily defined consistence (100 Bearden units of consistence or 100 Bc) at not less than 90 min and not more than 120 min. The time taken for the cement slurry to achieve 100 Bc is known as the thickening time.

As the depth of the borehole increases, the temperature rises and the cement slurry has to remain fluid, even at these elevated temperatures, for the time necessary to complete the cementing operation. Two different temperatures are defined in the hole. The temperature attained by the slurry (or mud) as it circulates through the hole is known as the bottomhole circulating temperature (BHCT). This is lower than the maximum temperature which occurs when circulation is stopped with the cement in place at the bottom. The latter is the bottomhole static temperature (BHST), which is often used as the basis for the curing temperature for compressive strength tests. The cement at the bottom of the hole during circulation will be subjected to a pressure equal to the pumping pressure plus the hydrostatic head of mud and slurry in the hole. Therefore, total pressure also increases with the depth of the hole.

Individual well conditions may dictate the use of cement slurries with densities ranging from 1.0 to 2.1 kg/L, pumping times from 2 to 6 h, temperatures from freezing to 200°C or more and pressures up to ~ 140 MPa or even greater.

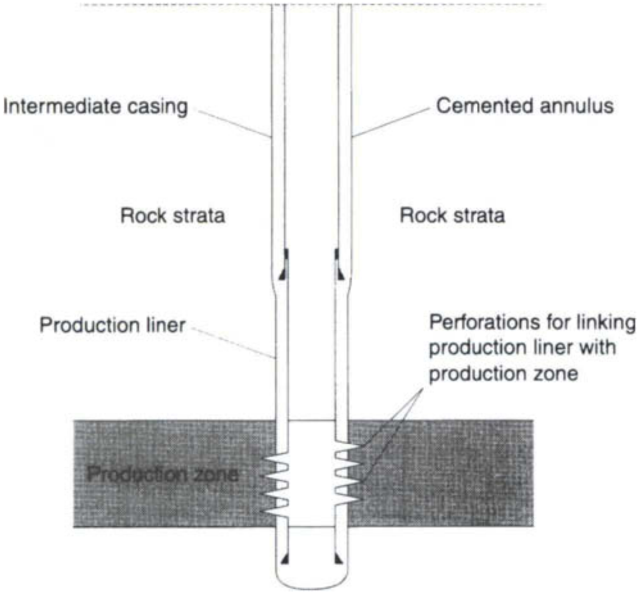

Fig. 14.1 Diagrammatic representation of a cemented oilwell (courtesy P.V. Maxwell-Cook, Palladian Publications Ltd).

14.2.2 OILWELL CEMENT STANDARDS

The American Petroleum Institute (API) Standard, known as API Specification 10A, used in most countries, now specifies eight classes of oilwell cements for use at different well depths (Table 14.1). Oilwell cement is defined by the API for Classes A–H as the product

Table 14.1 API classes of oilwell cement as defined in API Specification 10A

Coverage This specification covers requirements for manufacturing eight classes of well cements. This includes chemical and physical requirements and physical testing procedures

A well cement which has been manufactured and supplied according to this specification may be mixed and placed in the field using water ratios or additives at the users' discretion. It is not intended that manufacturing compliance with this specification be based on such field conditions

Classes and grades Well cement shall be specified in the following Classes (A, B, C, D, E, F, G and H) and Grades (O, MSR and HSR)

Classes A, B and C	The product obtained by grinding Portland cement clinker, consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an interground addition. At the option of the manufacturer, processing additions[a] may be used in the manufacture of the cement, provided such materials in the amounts used have been shown to meet the requirements of ASTM C 465
Class A	Is intended for use when special properties are not required. Available only in ordinary (O) grade (similar to ASTM C 150, Type I)
Class B	Is intended for use when conditions require moderate or high sulfate-resistance. Available in both moderate sulfate-resistant (MSR) and high sulfate-resistant (HSR) grades (similar to ASTM C 150, Type II)
Class C	Is intended for use when conditions require high early strength. Available in ordinary (O), moderate sulfate-resistant (MSR) and high sulfate-resistant (HSR) grades (similar to ASTM C 150, Type III)
Classes D, E and F	The product obtained by grinding Portland cement clinker, consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an interground addition. At the option of the manufacturer, processing additions[a] may be used in the manufacture of the cement, provided such materials in the amounts used have been shown to meet the requirements of ASTM C 465. Further, at the option of the manufacturer, suitable set-modifying agents[a] may be interground or blended during manufacture. This product is intended for use under conditions of moderately high temperatures and pressures. Available in moderate sulfate-resistant (MSR) and high sulfate-resistant (HSR) grades
Classes G and H	The product obtained by grinding Portland cement clinker, consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an interground addition. No additions other than calcium sulfate or water, or both, shall be interground or blended with clinker during manufacture of Class G well cement. This product is intended for use as a basic well cement. Available in moderate sulfate-resistant (MSR) and high sulfate-resistant (HSR) grades

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[a] A suitable processing addition or set-modifying agent shall not prevent a well cement from performing its intended functions.

obtained by grinding clinker, consisting essentially of hydraulic calcium silicates, to which no additions other than set-modifying agents have been interground or blended during manufacture. A suitable set-modifying agent is defined as one which has no deleterious effect on the durability of the hardened cement and causes no retrogression in strength. Well cements include any class of cement defined above and may also include optional additives to obtain necessary performance. No specifications are written for blends of well cement and most optional additives. Cements of Classes A–H are all based upon Portland cement compositions. The API specification is being accepted as an international (ISO) standard.

Class J cement has been officially deleted from the API classification, because it is rarely used. This cement is not a true Portland cement, but is based upon a β-dicalcium silicate–silica composition in approximate proportions 60:40, respectively. Class J cement was designed for cementing wells above ~110°C, where hydrothermal hydration takes place.[8] The rate of hydration is slow compared with Portland-based oilwell cements, because of the lack of tricalcium silicate. It is a similar type of cement to belite–silica cement (BSC) used in the CIS (former USSR) for cementing hot wells.[5,6]

Definitions used in oilwell cementing have been tabulated in the *API Bulletin on Well Cement Nomenclature* (API BUL 10C). Various countries have their own oilwell cement standards. Their requirements are highlighted elsewhere.[9]

API Class A cement has to be specially selected for compliance with the API cementing properties, because not all ordinary Portland cements will necessarily have satisfactory properties for this particular usage. Class B cement is used for similar purposes to Class A cement where the effects of sulfate-bearing soils and waters must be counteracted. Class C cement, which is also used for the same range, is a rapid-hardening cement that may or may not be sulfate resistant.

Class D, E and F cements also contain chemical retarders in quantities suitable for producing thickening times under the conditions defined. The level of retardation increases from Class D through Class E to Class F. They are all moderately or highly sulfate resistant. These cements are seldom employed now, because well conditions are rarely identical with the API Schedules for these cements and may in some circumstances require the use of additional additives that could be incompatible with the preblended retarder incorporated in these cements.

Class G and H cements are manufactured as basic cements, and are more strictly controlled with respect to chemical and cementing properties, with the object of providing consistent properties. Both cements are available as moderately or highly sulfate-resistant types. Class H cement differs from Class G in being a relatively coarse-ground cement. Typical surface areas (Blaine method) for Class G and Class H cements generally lie in the range 270–350 and 220–300 m^2/kg, respectively.

The chemical and physical requirements of API Class A–H cements are summarised in Tables 14.2 and 14.3, respectively. The water requirements are given in Table 14.4.

The chemical requirements are undertaken by modern instrumental or classical gravimetric methods to check that the chemistry of the cements corresponds to the desired requirements.

The physical requirements are evaluated using some standard and some specialised procedures. Fineness is generally measured as surface area, with the Wagner turbidimetric method being used in API Specification 10A for Class A, B and C cements (ASTM C 115) or, alternatively, the air permeability test (ASTM C 204). Autoclave expansion is no longer included (ASTM C 151). For the cementing properties, however, special apparatus is necessary for examining thickening time and compressive strength requirements

Table 14.2 Chemical requirements of API Class A–H oilwell cements (per cent)[a]

	Cement class					
	A	B	C	D, E, F	G	H
Ordinary grade (O)						
Magnesium oxide (MgO), maximum	6.0		6.0			
Sulfur trioxide (SO_3), maximum	3.5[b]		4.5			
Loss on ignition, maximum	3.0		3.0			
Insoluble residue, maximum	0.75		0.75			
Tricalcium aluminate ($3CaO \cdot Al_2O_3$), maximum[c]			15			
Moderate sulfate-resistant grade (MSR)						
Magnesium oxide (MgO), maximum		6.0	6.0	6.0	6.0	6.0
Sulfur trioxide (SO_3), maximum		3.0	3.5	3.0	3.0	3.0
Loss on ignition, maximum		3.0	3.0	3.0	3.0	3.0
Insoluble residue, maximum		0.75	0.75	0.75	0.75	0.75
Tricalcium silicate ($3CaO \cdot SiO_2$):						
Maximum[c]					58	58
Minimum[c]					48	48
Tricalcium aluminate ($3CaO \cdot Al_2O_3$), maximum[c]		8	8	8	8	8
Total alkali content expressed as sodium oxide (Na_2O) equivalent, maximum[d]					0.75	0.75
High sulfate-resistant grade (HSR)						
Magnesium oxide (MgO), maximum		6.0	6.0	6.0	6.0	6.0
Sulfur trioxide (SO_3), maximum		3.0	3.5	3.0	3.0	3.0
Loss on ignition, maximum		3.0	3.0	3.0	3.0	3.0
Insoluble residue, maximum		0.75	0.75	0.75	0.75	0.75
Tricalcium silicate ($3CaO \cdot SiO_2$):						
Maximum[c]					65	65
Minimum[c]					48	48
Tricalcium aluminate ($3CaO \cdot Al_2O_3$), maximum[c]		3	3	3	3	3
Tetracalcium aluminoferrite ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$) plus twice the tricalcium aluminate ($3CaO \cdot Al_2O_3$), maximum[c]		24	24	24	24	24
Total alkali content expressed as sodium oxide (Na_2O) equivalent, maximum[d]					0.75	0.75

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[a] Methods covering the chemical analyses of hydraulic cements are described in Ref. 10.

[b] When the tricalcium aluminate content (expressed as C_3A) of the Class A cement is 8 per cent or less, the maximum SO_3 content shall be 3 per cent.

[c] The expressing of chemical limitations by means of calculated assumed compounds does not necessarily mean that the oxides are actually or entirely present as such compounds. When the ratio of the percentages of Al_2O_3 to Fe_2O_3 is $\leqslant 0.64$, the C_3A content is zero. When the Al_2O_3 to Fe_2O_3 ratio is >0.64, the compounds shall be calculated as follows:

$$C_3A = (2.65 \times \%\ Al_2O_3) - (1.69 \times \%\ Fe_2O_3)$$
$$C_4AF = 3.04 \times \%\ Fe_2O_3$$
$$C_3S = (4.07 \times \%\ CaO) - (7.60 \times \%\ SiO_2) - (6.72 \times \%\ Al_2O_3) - (1.43 \times \%\ Fe_2O_3) - (2.85 \times \%\ SO_3)$$

When the Al_2O_3/Fe_2O_3 ratio is <0.64, an iron–alumina–calcium solid solution [expressed as $ss(C_4AF + C_2F)$] is formed and the compounds shall be calculated as follows:

$$ss(C_4AF + C_2F) = (2.10 \times \%\ Al_2O_3 + (1.70 \times \%\ Fe_2O_3) \text{ and } C_3S = (4.07 \times \%\ CaO) - (7.60 \times \%\ SiO_2) - (4.48 \times \%\ Al_2O_3) - (2.86 \times \%\ Fe_2O_3) - (2.85 \times \%\ SO_3)$$

[d] The sodium oxide equivalent (expressed as Na_2O_{eq}) shall be calculated by the formula:

$$Na_2O_{eq} = (0.658 \times \%\ K_2O) + \%\ Na_2O$$

Table 14.3 Physical and performance requirements of API Class A–H oilwell cements (metric units given in parentheses)

						Cement class							
						A	B	C	D	E	F	G	H
Mix water, per cent of the weight of cement						46	46	56	38	38	38	44	38
Fineness (specific surface area) minimum (m²/kg)[a] –turbidimeter						150	160	220					
–air permeability						280	280	400					
Free fluid content, maximum (mL)												3.5	3.5
Compressive strength test													
Curing time	*Schedule number*	*Curing temperature (°F)*	*(°C)*	*Curing pressure (psi)*	*(kPa)*	*Minimum compressive strength, psi (MPa)*							
8 h curing time		100	(38)	Atmos.		250 (1.7)	200 (1.4)	300 (2.1)				300 (2.1)	300 (2.1)
		140	(60)	Atmos.								1500 (10.3)	1500 (10.3)
	6S	230	(110)	3000	(20700)				500 (3.5)				
	8S	290	(143)	3000	(20700)					500 (3.5)			
	9S	320	(160)	3000	(20700)						500 (3.5)		
24 h curing time		100	(38)	Atmos.		1800 (12.4)	1500 (10.3)	2000 (13.8)					
	4S	170	(77)	3000	(20700)				1000 (6.9)	1000 (6.9)			
	6S	230	(110)	3000	(20700)				2000 (13.8)		1000 (6.9)		
	8S	290	(143)	3000	(20700)					2000 (13.8)			
	9S	320	(160)	3000	(20700)						1000 (6.9)		
Pressure temperature thickening time test													
Specification test schedule number		*Maximum consistency (15–30 min stirring period (Bc)[b])*				*Minimum thickening time (min)*							
4		30				90	90	90	90				
5		30										90	90
5		30										120 max.	120 max.
6		30							100	100	100		
8		30								154			
9		30									190		

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[a] Determined by turbidimeter apparatus described in Ref. 11.

[b] Bearden units of slurry consistency (Bc). Bearden units of consistence obtained on a pressurised consistometer as defined in Section 8 of API Specification 10A and calibrated as per the same section.

Table 14.4 API Specification 10A requirements for water/cement ratios

Class of cement	w/c ratio	US gallons of water per 94 lb sack of cement[a]
A, B	0.46	5.19
C	0.56	6.32
D, E, F, H	0.38	4.29
G	0.44	4.97

[a] 1 unit = 0.08678 dm^3/kg cement.

under conditions which tend to simulate those present downhole; these tests are quite different from those undertaken on cements used for construction purposes.[12,13]

The API has determined average conditions from well data, mostly obtained from the Gulf of Mexico and southwestern USA, and has applied these to form the conditions of testing for API purposes – the standard operation schedules for thickening time testing given in API Specification 10 and later modified for Recommended Practice 10B. Depending upon the geothermal temperature gradient, holes of the same depth in different geographical locations frequently exhibit different bottomhole temperatures.

Since in practice the cements are used in the form of aqueous slurries produced by injection of the cement into a fast-moving stream of water, the laboratory test cement is made into a slurry in a specified high-speed blender to the appropriate density. The API requirements for water/cement ratios are shown in Table 14.4.

The chemical limits for API oilwell cements are mainly taken from ASTM C 150 for construction Portland cements with some modifications and are shown in Table 14.2. For instance, the maximum tricalcium aluminate content of the high sulfate-resistant grade (HSR) cements is 3 per cent, not 5 per cent as for ASTM Type V cements. Where compound composition is specified, the calculations are based on the Bogue formulae, depending upon whether the ratio of alumina to iron oxide is greater or less than 0.64. According to the relevant ASTM methods in C 114, which are 'wet' analytical procedures, the calculations use the Al_2O_3 content found by deducting Fe_2O_3 from the combined R_2O_3 result and not the 'true alumina' determined directly. X-ray fluorescence analysis is increasingly being employed worldwide for the main chemical analysis of oilwell cements. The free lime is not deducted from the total CaO in these calculations. Determination of free lime is not a mandatory requirement for API oilwell cements, despite the influence that free lime in quantities above ~ 1.0 per cent can normally have on cement properties such as retardability (see below). No chemical limits were specified for Class J cement.

The physical limits are summarised in Table 14.3. These include fineness, in terms of specific surface area, determined by the Wagner turbidimeter method in ASTM C 115 or by the air permeability method in ASTM C 204 for Class A, B and C cements. Correlation between the Wagner surface area and that found by air permeability methods such as Blaine and Lea–Nurse is not universally good, but for given milling conditions a satisfactory control can be achieved using an air permeability procedure.

Cementing tests involve compressive strength, thickening (or setting) time and free water determinations. These are carried out on oilwell cement slurries prepared by the API Specification 10A standard method to the water content (slurry density) usually employed for the particular class of cement. (See Appendix on p. 840 about ISO standardisation.)

14.2.3 STANDARD TESTING PROCEDURES

Thickening time

Thickening time is essentially a setting time under conditions of controlled temperature and pressure ramps, designed to simulate conditions for a given well depth. It is defined in API BUL 10C as the time required for a cement slurry of a given composition to reach a consistence of 100 Bearden units of consistence (Bc), determined by the methods outlined in API Specification 10A. Bearden units are arbitrarily defined and are related to poise (or N s/m^2) units.

Thickening time measurements are undertaken on a high-temperature–high-pressure consistometer. This is a test machine that has a rotating cylindrical slurry container, equipped with a stationary paddle assembly and enclosed in a pressure chamber. In the conventional consistometer this chamber can withstand pressures of 207 MPa and temperatures up to 204°C. A heating element is used to raise the temperature of the cement slurry by heating oil at a rate of up to 3°C/min. The thickness or consistence of the cement slurry is monitored by measurement of the torque on the stationary stirring paddle. The cement slurry is mixed according to API specifications (35 s in a blender on high speed) and placed in the high-temperature–high-pressure consistometer. The temperature and pressure are increased according to the appropriate API schedule, which depends upon the depth. The consistence is measured continuously until 100 Bc is reached. The time taken to achieve 100 Bc is the thickening time. The test is designed to simulate the full bottomhole conditions of circulating temperature and total pressure.

Compressive strength

Compressive strength tests are undertaken by pouring the cement slurry into 2 in (5.08 cm) cube moulds in the manner specified in API Specification 10A. The moulds are then subjected to a curing regime appropriate to the simulated well temperature conditions that are employed. With shallow well tests for Class A, B or C cements, simple water-bath curing at atmospheric pressure and 100°F (38°C) is employed. For the basic cements of Class G or H not only is the same compressive strength test used as for Class A, B or C cements, but also a higher temperature test at 140°F (60°C), which likewise has water-bath curing at atmospheric pressure. For deeper well tests involving Class D, E and F cements, the bottomhole static temperature is obtained by adjusting the heating rate over a 4 h period and maintaining this until about 45 min from the end of the test period. The 2 in (5.08 cm) cubes are in all instances cooled to 80°F (27°C) before determining the compressive strength in an appropriate hydraulic testing machine.

In these tests the maximum pressure applied during curing is 3000 lb/in^2 (20.7 MPa) and not the bottomhole total pressure. The reason for this is based upon data collected by the API, which demonstrated that increasing the curing pressure from atmospheric to ~ 13.8 MPa increased the compressive strength appreciably but applied pressures > 13.8 MPa had little further effect. However, in more recent times with a trend towards deeper drilling in many parts of the world, which involves bottomhole total pressures considerably in excess of 20.7 MPa, the appropriateness of some of these tests for simulating well conditions has been questioned. There is a need for high-pressure–high-temperature compressive strength tests for cement slurries in very deep wells, because high pressures as well as high temperatures influence cement reactivity.

Ultrasonic cement analysers (UCAs) are now commonly used to assess compressive strength continuously and non-destructively developed by cement slurries being cured under simulated downhole conditions. Bulk compressibility is obtained from the time taken by the ultrasound to pass through the cement being cured, which can be correlated with compressive strength.[14]

Free fluid (free water)

Specification tests for the free fluid (free water) of cement slurries apply only to Class G and H cements. The cement slurry is poured into an atmospheric pressure consistometer and stirred at 80°F (27°C) for 20 min. The slurry is then remixed in a high-speed blender for 35 s and then used to fill a 250 mL glass cylinder sealed to prevent evaporation. The supernatant water obtained after 2 h while standing quiescent is removed and measured. This is the free fluid content and is a measure of the amount of bleeding that takes place under the test conditions.

Because of the criticism that this test does not reliably simulate conditions downhole, an operating free-fluid test has now been included in API Recommended Practice 10B. This involves heating the slurry under pressure according to the appropriate schedule employed and, after the slurry reaches the maximum temperature and pressure, cooling to 194°F (90°C), if necessary, in 20 min. After the slow release of pressure and removing the slurry cup from the consistometer, a procedure similar to the aforementioned is followed. The operating free fluid is more appropriate for field usage under simulated conditions of testing. It is an optional test and no limits are specified. Often a maximum value of 4.0 mL for operating free fluid is felt to be appropriate when cementing in vertical wells.

Cement slurry stability can also be measured by a settling test.[15]

Soundness

Unsoundness refers to a large expansion taking place in certain defective cements after thickening and hardening has taken place, causing a disruption of the hardened cement. This phenomenon results from the very slow hydration of certain constituents, namely free magnesium oxide and free calcium oxide, and can be exacerbated by the presence of excess sulfates. Since unsoundness in cements is not revealed until after a long period of time, accelerated tests such as autoclave expansion are required for its detection.

The soundness of API oilwell cements used to be tested according to ASTM C151 autoclave expansion of Portland cement. The maximum acceptance requirements for the soundness or autoclave expansion test were 0.80 per cent for cements of Classes A–H. The MgO content of these cements is limited to 6 per cent for minimising unsoundness. Most HSR Class G and H cements in which the MgO and free lime contents are low generally have very small autoclave expansions in the approximate range 0–0.05 per cent, which are well below the 0.80 per cent limit formerly given in API Specification 10. In these cases unsoundness is not a problem. This test is no longer included in API Specification 10A.

Rheology

The term rheology relates to the viscosity (or fluidity) of the cement slurry when subject to mixing and pumping through the system. When the cement is used, it is normally mixed by feeding it from a storage silo into a fast-moving stream of water (a Venturi-type mixer). Then, the slurry moves into a slurry box which often incorporates a screen to remove large particles; from here it is transferred by suction through a pump which subjects it to positive pressure to pump it through the casing or drill pipe to the bottom of the hole and into the annulus. A good bond with the steel casing and the wall of the hole as drilled is necessary. This means that the slurry must have a low viscosity as long as possible before the thickening action sets in. It must be easy to move after a period of quiescence (for example, due to a pump breakdown).

The only 'viscosity' limit specified in the API is the maximum of 30 Bc during the 15–30 min period of the specified thickening time test. Another test method for rheological properties is given in the API Recommended Practice 10B using a rotational viscometer – a rotating cylinder and bob type, which enables measurements of plastic viscosity, yield value and gel strength to be made. However, no guidance is given about limits for the results obtained. The only other 'viscosity' test suggested in API Recommended Practice 10B is the atmospheric consistometer method, which works on the same principle as the thickening time test machine, again with no limits applied.

The problem with such viscometric procedures is that they are laboratory tests and do not reliably simulate many conditions downhole. Good simulation would be difficult to achieve, since the actual viscometric behaviour of a given cement slurry is highly dependent upon the precise conditions to which it is subject during mixing, pumping and placement. There is certainly a need for more high-pressure–high-temperature rheological data for use in cementing deep wells.

Arctic (permafrost) testing procedures

Special procedures have been adopted in API Recommended Practice 10B for simulating Arctic conditions for cementing in such environments, but no limits have been set for these tests.

The dry cement should be stored overnight at 20°F (−7°C) and mixed with ice water in a chilled blender to produce a slurry of temperature 40 ± 2°F (4 ± 1°C), the mixing water being expressed on the basis of 100 parts of solids. Thickening time is performed on an atmospheric pressure consistometer at 40°F (4°C). For compressive strength determinations, the samples should be cured at 20°F (−7°C) and 40°F (4°C) for the desired testing periods of 1, 3 and 7 days. A test involving 7-day freeze–thaw cycles is also carried out and the compressive strengths of cubes are normally examined after one and three cycles at 14 and 42 days, respectively.

Permeability

Permeability is a measure of the capacity of a porous medium to transmit fluids or gases and is usually measured in millidarcies (mD); 1 mD = 0.9868×10^{-15} m^2). A porous medium has a permeability of 1 darcy when a pressure of 1 atmosphere on a sample 1 cm long and 1 cm^2 in cross-section will force a fluid of 1 cP (10^{-3} N s/m^2) viscosity through the sample at a rate of 1 mL/s. The permeability of set oilwell cement to water can be undertaken by a standard procedure using a cement permeameter laid down in API Recommended Practice 10B. A differential pressure of 100–1400 kPa is utilised to force water through the sample in the cement permeameter for a maximum of 15 min or until ~1 mL has been forced through the sample into an appropriate measuring tube. The flow rate should be measured at least twice. The water permeability of the set cement is calculated from Darcy's law, which states that the rate of flow of a homogeneous fluid through a porous medium is proportional to the pressure or hydraulic gradient and to the cross-sectionl area normal to the direction of flow and inversely proportional to the viscosity of the fluid:

$$K = 14\,700 \frac{Q \mu L}{AP} \tag{14.1}$$

where K = permeability (mD), Q = flow rate (mL/s), μ = viscosity of water (cP), L = sample length (cm), A = sample cross-sectional area (cm^2), P = differential pressure for the above (psi; 1 psi = 6.895×10^{-3} MPa). The curing conditions of pressure, temperature and time should be stated. No limits for permeability are given in API Recommended Procedure 10B.

Set cements have very low permeabilities – much lower in fact than those of most producing formations and can be of importance when considering zone isolation. At temperatures below ~90°C the permeability of set cement decreases with age and temperature, and after 7 days of curing is usually too low to measure. Those of set cements are normally below ~0.1 mD. Permeability can be controlled in low-temperature wells where necessary by densification and above ~110°C by densification and the use of silica flour. When lightweight slurries are employed, the permeability is commonly limited to 0.1 mD

The permeability of set oilwell cement to gas is normally higher than that to water, but measurements of the former are less reliable, since it is difficult to obtain good representative samples for the laboratory measurement of gas flow. Cements that have set for 3–7 days have a gas permeability ~0.1 mD.

Fluid loss (filtration) control

Fluid loss refers to the volume of filtrate lost to the permeable material due to the process of filtration. Control of fluid loss from oilwell cement slurries is of major significance when cementing deep liners and in squeeze cementing operations,[1–4] since flow is restricted by the increase in slurry viscosity and consequent rapid deposition of filter cake when such losses occur through the permeable formations. Temperature, pressure, time and permeability are the main factors affecting fluid loss. In API Recommended Practice 10B details of standard 30 min test procedures for measuring the fluid loss of cement slurries at 100 or 1000 psi (0.7 or 6.9 MPa) or higher pressures are described. These use a filter press consisting of a suitable frame and cylinder assembly with a filter medium comprising a 325-mesh (45 µm) screen (ASTM E 11) supported on a 60-mesh (250 µm) or appropriate lower mesh screen. Bottomhole temperature can be simulated with a heating jacket. For simulating downhole placement, the cement slurries are examined on an atmospheric pressure or pressurised consistometer for a given time schedule before removal and pouring into the filter cell. The test period is timed from the instant of initial pressure application. Filtrate readings are taken at 0.25, 0.5, 1, 2 and 5 min and thereafter at 5 min intervals until 30 min has elapsed. For slurries that dehydrate in <30 min and tests of shorter duration than 30 min, an interpolated 30 min value is calculated. The API fluid loss result is the quantity of fluid in millilitres, measured or extrapolated, which has been filtered during the 30 min period multiplied by 2. No API limits are given for fluid loss.

API fluid loss values on neat cement slurries (where practically measurable) lie well above 1000 mL. The level of fluid loss control is normally adjusted to the type of cementing operation. Values below 200 mL are usually preferred and sometimes may need to be ~50 mL or less.

Particulate properties

Fineness, in terms of specific surface area, is determined by the Wagner turbidimetric method (ASTM C 115) for Class A, B and C cements, where minimum values of 150, 160 and 220 m^2/kg are required respectively in API Specification 10A, or alternatively for these three classes of cement, by the air permeability test method (ASTM C 204), where the minimum values required are, respectively, 280, 280 and 400 m^2/kg. There are no mandatory surface area requirements for cements of Class D–H. It should be remembered that correlation between the Wagner surface area and the surface area found by air permeability methods such as Blaine and Lea–Nurse[12,13] is not universally good, but for given milling conditions during cement production a satisfactory control can be achieved using an air permeability procedure. Indeed, for practical purposes most manufacturers and users check the surface areas of oilwell cements by the Blaine or Lea–Nurse method.

The particle size distribution of oilwell cements can be a useful test.[16] Significant differences in the particle grading between two cements from a given source can indicate appreciably different chemical reactivities of the cements, but comparisons between individual cements from different plants are less easy to correlate in terms of cementing performance. There are no API requirements for particle size distributions.

14.2.4 OPERATING CONDITIONS

The API testing schedules discussed can, of course, be adapted for use in actual downhole conditions found in a well. However, rather more is commonly required for ensuring that a particular oilwell cement can be successfully employed for cementing the annulus. It must be borne in mind that the borehole would not pass through perfect geological strata. There will be layers of varying mechanical strength, which will include some hard, some friable and some subject to sloughing. The permeability of the strata will vary, and also some strata will be fissured to varying degrees. These faults will be observed by the experienced drilling team and measures taken in designing a cementing formulation to ensure that a good cementing job will be carried out. These include the use of various appropriate additives (see below).

14.2.5 NON-STANDARD OILWELL CEMENTS

Various other cements are marketed in addition to the normal Portland type varieties for specialist purposes.[17 19] Alinite cement (see also section 14.5.3) has found some application as a lightweight slurry extender, like API Class C cement, on account of its rapid-hardening properties, although batch-to-batch variability has been encountered as a problem on a number of occasions.[20]

Pozzolanic oilwell cements are often utilised in lightweight extension. Dicalcium silicate–silica cements, like the former API Class J[18,19,21] and BSC (belite–silica cement)[5,6] in the CIS, have been employed in high-temperature (~ 120°C and above) well cementing. Portland blastfurnace slag cements and slag-based materials are commonly used in the CIS as basic oilwell cements, but have not been used so regularly around the world. Further possibilities for using slag cements in well cementing operations have been discussed.[22] Various novel cements have been employed for specialist cementing jobs. Several of these cements are briefly described in Table 14.5, where their key differences from standard Portland oilwell cements and main types of usage are summarised.[23] Fuller details of the possibilities for novel cement usage in well cementing are given elsewhere.[17 19]

Table 14.5 Examples of non-standard cements used in well cementing[23]

Cement	Composition	Cementing action	Use in well cementing
Pozzolanic	Portland cement and pozzolan (~50:50 by volume) and ~2% bentonite	Pozzolanic component reacts in alkaline cementitious medium to give C-S-H. This reaction is slow. Bentonite initiates restriction of water mobility	Production of lightweight cement slurries of s.g. *ca.* 1.6–1.8
Slag	Portland clinker and ground granulated blastfurnace slag (ggbs) + ~4–7% gypsum	Granulated slag reacts in alkaline cementitious medium to give C-S-H. This reaction is slow and supplements that of Portland cement component	General cementing. Mostly used in CIS, seldom in Western world. Cementing efficiency depends on good granulation (high glass content)
	Ggbs and sand	Poor hydraulicity at ordinary temperatures, better at high temperatures. C-S-H and other products formed below ~110°C. Sand prevents strength retrogression above ~110°C by permitting formation of tobermorite etc.	High temperature cementing (above ~110°C), mostly in CIS
	Activated ggbs	Formation of C-S-H	Drilling mud to cement conversion
Dicalcium silicate (belite)–silica e.g. Class J, belite–silica cement (BSC)	β-Dicalcium silicate/quartz sand ~60:40 by weight	Steady hydration at elevated temperatures to give C-S-H, tobermorite etc.	High-temperature cementing. Seldom used in Western world, because of difficulty in accurately controlling hydration
Silicate, hydrothermal	Sodium silicate and silica (hydratable) and polyvalent metal ion source	Formation of hard insoluble silicates	Plugging of high-permeability zones
Calcium aluminate	Monocalcium aluminate (main cementing phase)	Formation of insoluble calcium aluminate hydrates. Ceramic bond forms by solid-state reactions increasingly above 700°C	As refractory cement, such as in fireflood and thermal recovery wells. In Arctic cement compositions for low-temperature cementing
Microfine	Portland (including sulfate-resisting Portland) cements or Portland cements with ggbs or alkali activated ggbs ground finely to 500–1000 m^2/kg or more and very low particle sizes (< *ca.* 15 μm)	Formation of calcium silicate hydrates like C-S-H	Where high penetrability is required, as in repairing tight casing leaks in squeeze operations[19]

Table 14.5 (*Cont'd*)

Cement	Composition	Cementing action	Use in well cementing
Magnesium oxychloride (Sorel)	Mainly magnesium oxide and magnesium chloride (acid soluble)	Main phases formed are $Mg_3(OH)_5Cl \cdot 4H_2O$ and $Mg_2(OH)_3Cl \cdot 4H_2O$, plus $Mg_2OHClCO_3 \cdot 3H_2O$ and $Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O$ in presence of CO_2 or carbonates. In refractory use, the main binder at 300–450°C is $3MgO \cdot Al_2O_3 \cdot 0.5SiO_2 \cdot nH_2O$	Temporary plugging operations. As refractory cement up to 850°C with siliceous and aluminous aggregates
Calcium phosphate	Hydroxyapatite $Ca_5(PO_4)_3OH$ and boehmite γ-AlOOH, derived from $NH_4H_2PO_4$-based fertiliser and calcium aluminate cement	Hydrothermally catalysed *in situ* phase transformations	Resistance to alkali carbonation by supporting intermediate casing and protecting casing from aggressive fluids in geothermal wells to 300°C
Resin or plastic cements	Class A, B, G or H type cement blended with water, resin and catalyst	Resin bonding, which is polar at angles to main C–C chain is very strong and supplements cement bonding	Selective plugging of open holes, squeezing perforations and cementing waste disposal wells at *ca.* 15–95°C, especially in highly aggressive, acidic environments
Expansive	Portland cement and expansive component	Expands slightly during first few days of hydration as C-S-H is formed from Portland cement component	Improving zone isolation. Can cement over cavernous vugs
Thixotropic	e.g. Portland cement and $CaSO_4 \cdot 0.5H_2O$ (gypsum cement)	Hydration of $CaSO_4 \cdot 0.5H_2O$ to gypsum and reaction with cement to form ettringite produces thixotropic properties as the cement thickens up. Gypsum cement is quick setting, develops a high gel strength rapidly once motion stops and has a slight linear expansion ($\sim 0.3\%$)	Well plugging. Cementing across weak formations. Lost circulation control
Arctic	Blend of Class G or H type cement with gypsum, ferrite phase and salt (NaCl) or Calcium aluminate cement with fly ash or natural pozzolan diluent	Formation of normal hydration products like C-S-H Formation of calcium aluminate hydrates	Low-temperature cementing (to ~ -10°C) of conductor and surface casing with adequate thickening and compressive strength development (low heat liberation to avoid damage to permafrost)

14.2.6 MANUFACTURE OF OILWELL CEMENTS

Oilwell cements are manufactured using the same raw materials and processes[12,13,24] as for ordinary, moderate or high sulfate-resistant Portland cement. The compound composition obtained will, of course, vary within the set limits of the appropriate specification, depending upon the targets set by the manufacturer. This takes into consideration the materials and plant available, as well as the route which gives the best quality control.

The manufacture of oilwell cement may be summarised by reference to the basic cement Class G. Certain modifications are necessary in comparison with the production of sulfate-resisting Portland cement for the construction industry. Construction cements need to be more reactive so that satisfactory compressive strength development can be achieved at early stages, whilst for oilwell cementing the cements need to be less reactive to give an adequate placement time that can allow for stoppages, and also to prevent excessive quantities of additives such as retarders and dispersants being necessary to control the rate and manner of thickening of the cement slurry. For consistency of response to the effect of additives, during oilwell cement manufacture, variations in materials, proportioning and processing must be minimised at all stages during the process. The onus is on the manufacturer to maintain consistently a 'good housekeeping' policy at the plant.

Class G cement is made from a raw meal containing a calcareous component (such as chalk or limestone), an argillaceous component (clay or shale), a source of iron oxide (such as haematite or pyrites residues) and, if necessary, a small addition of quartz sand to allow sufficient silica to be present *in toto* in the raw meal. The composition of the raw meal is designed to produce a clinker of suitable reactivity for oilwell cement usage. For HSR as opposed to MSR Class G cement, relatively more iron oxide needs to be incorporated in the raw feed to produce more ferrite phase at the expense of tricalcium aluminate. These components are ground together to achieve a fine homogeneous mix either with water in a slurry (wet process) or in a grinding mill in the dry state (dry process). From the slurry tanks or grinding mills the raw meal is fed to a rotary kiln, where it is burned to the point of incipient fusion (*ca.* 1400–1450°C). Combination is completed and a clinker is produced, which is cooled on leaving the kiln. The free lime content of the clinker should not normally exceed ~ 1 per cent for low-MgO cements or ~ 0.5 per cent for high-MgO cements, otherwise the cement is likely to have poor retardation, rheology and fluid loss properties.

Oil and gas are commonly used kiln fuels, although coal or lignite of low ash content and some petroleum coke may be used if reducing conditions within the kiln can be avoided. Reduction causes some change of iron(III) to iron(II), as a result of which less ferrite phase is formed and more tricalcium aluminate is produced than would normally be expected. The iron(II) substitutes for calcium in the clinker phase being formed, which creates a more difficult combinability and necessitates harder burning. Overburning should in any event be avoided, because it produces a clinker which is insufficiently reactive from the oilwell cementing viewpoint. In addition, reduction in the kiln assists dissociation of alkali sulfates present in small quantities, which causes the released alkali metal ions to become incorporated in solid solution in the main clinker phases. Such incorporation in the tricalcium aluminate phase alters its chemical reactivity and causes potential deliquescence in the clinker produced. Sulfur dioxide produced by the effects of the volatilisation may assist in producing undesirable build-ups in the kiln and possible blockages. The overall effects of reduction on the cement are to give rise to poor rheological properties, poor development of compressive strength, poor handling problems, normally faster thickening, and a greater susceptibility to aeration. Slowly cooled clinker also gives rise to a faster-setting (thickening) cement.[25]

After cooling, the clinker is ground with up to about 2–4 per cent gypsum in a grinding mill to produce a Class G cement with a surface area in the range *ca.* 270–350 m^2/kg. The grinding temperature should be kept as low as possible to minimise dehydration of gypsum to hemihydrate or soluble anhydrite. Excessive gypsum dehydration can cause two problems: (1) false set or early stiffening, which can give rise to rheological problems during pumping and/or placing; and (2) extra sulfate ions in solution in the slurry which can accelerate alite (tricalcium silicate) hydration and thus cause the cement to be unacceptably reactive. Gypsum addition is normally kept low, giving a total cement SO_3 content within the range *ca.* 1.7–2.3 per cent, again to minimise the acceleration of the hydration reaction of alite with sulfate. The cement produced is then stored under dry conditions in a silo prior to despatch.

Class H cement is produced by a similar process, except that the clinker and gypsum are ground coarser to give a cement with a surface area generally in the range *ca.* 220–300 m^2/kg. Experience involved in the production of MSR Class H oilwell cement has been described.[26]

Class A and Class C (ordinary type) cements are manufactured like ordinary (or ASTM Type I) and rapid-hardening (or ASTM Type III) Portland cements, respectively. For a Class A cement the surface area may have to be kept relatively low and for both Class A and Class C cements, the free lime content might need to be low (as discussed earlier for Class G cement), in order to satisfy oilwell cementing requirements and additive response. However, Class B cement is made in a similar way to Class G, except that slight changes may need to be made to optimise the manufacturing process, because the cementing requirements for Class B cement are somewhat different (less stringent) from those of Class G cement.

For the preretarded cements of Classes D, E and F, where they are still manufactured, it may be necessary to blend in the retarders in appropriate blending tanks rather than to grind them in with the clinker and gypsum. This is to ensure homogeneity of distribution and consistency of cement performance from batch to batch in complying with the appropriate API Schedules. These cements differ primarily in the level of retardation present, Class D being the least retarded and Class F the most retarded. Class F cements commonly contain *ca.* 35–40 per cent silica to avoid strength retrogression at the higher temperatures commonly encountered; Class E cements sometimes do too.

Generally speaking, for oilwell cement usage, higher levels of product quality and of quality control at the plant are required than for the different types of Portland cements made for the construction industry. This is necessary because of their being subjected to more exacting conditions of reaction – thickening and hardening – under different conditions of temperature and pressure downhole. Also, developments in drilling technology, such as the construction of slim-hole wells[27] and the greater use of horizontal and extended reach wells[27(a)] to maximise oil and gas production from various fields, demand the manufacture of higher-quality oilwell cements (high batch-to-batch consistency in performance and relatively low reactivity under downhole conditions) for the successful cementing of such wells. In multilateral well technology,[28] for instance, cemented junctions can be very important for providing mechanical integrity at junctions between the main wellbores and the branches. The cemented junctions are made by cementing a liner into a branch wellbore and working over the portion of liner and cement that extends into the main wellbore.[29] Not surprisingly, such sophisticated cementing operations need oilwell cements that have been manufactured to a high quality.

In the future it is highly likely that greater use will be made of cement extenders such as ground granulated blastfurnace slag (ggbs)[30] pulverised fly ash (pfa), metakaolinite and other partially burned clays, suitable natural pozzolans and microsilica. Such usage would be for either technical or economic reasons or both. Portland blastfurnace cement is known to function as a basic oilwell cement under appropriate conditions[30] and has the added bonus of sulfate resistance. Portland pozzolanic cements containing pulverised fly ash, metakaolinite and natural pozzolans may also be able to perform similar functions. All need to undergo rigorous laboratory tests first. The extender can be either ground in at the cement plant with the Portland clinker and gypsum, or could be added to the Portland cement by careful on-site blending. Microsilica already has a number of specialist uses in well cementing (section 14.2.7). Since microsilica is an active pozzolan, the properties of any Portland cement mix with microsilica under downhole conditions are decidedly different from those of other extenders due to the greater reactivity of the microsilica.

14.2.7 ADDITIVES USED WITH OILWELL CEMENTS

In the oil industry, unlike the construction industry, all chemical additions to cement are called additives. The term admixture is not normally employed here.

For optimum characteristics of oilwell cement slurries, chemical additives are mixed with the cement slurry to tailor requirements to the particular downhole conditions. This is particularly true of the basic oilwell cements Class G and Class H, where a wide variety of downhole conditions are encountered during cementing in different locations. Additives may be used in dry or liquid (aqueous solution) forms. Liquid additives are commonly preferred on offshore rigs for convenience of storage and ease of use. However, errors in mixing are easier than with dry additives blended in with the cement, where the main problem is in ensuring good homogeneity. Fuller details of additives used for oilwell cements are given elsewhere.[31]

Additives can be broadly classified into 10 different categories, which are discussed in this section. It should be borne in mind when categorising additives, that particular additives may be multifunctional. For instance, a lignosulfonate will function as a retarder, as a dispersant, as a fluid loss additive to some extent, and as a water reducer. All these functions have to be taken into account when designing the appropriate well cementing formulation.

For given well conditions, a well cementing service company will normally recommend and supply the oilwell cement and proportions of additives in order to obtain a satisfactory cementing job. Most service companies have their own brand names or designations for such materials which are, in many instances, of similar composition for similar use. Improvements have taken place over the years for producing the required cement slurry properties and to extend the range of use as both depth and temperature have increased.

Retarders

Retarders are used for lengthening the thickening times of oilwell cement slurries, and allow longer pumping times and improved flow properties. Examples include calcium and sodium lignosulfonates (up to ~95°C),[32] sugars, polyhydroxyorganic acids of sugar origin (high-temperature retarders) such as calcium or sodium gluconate, calcium or sodium glucoheptonate, glucodeltalactone, citric acid, tartaric acid, phosphonates, gums and starches. Borax ($Na_2B_4O_7 \cdot 10H_2O$) and other borates are often used as retarding aids with other retarders, such as lignosulfonates, to extend their temperature range of effective use. Sodium chloride (common salt) retards hydration above ~20 per cent.[33] Mechanistic and other aspects of retardation such as S-curve formation (Figure 14.2) are discussed elsewhere.[34-39]

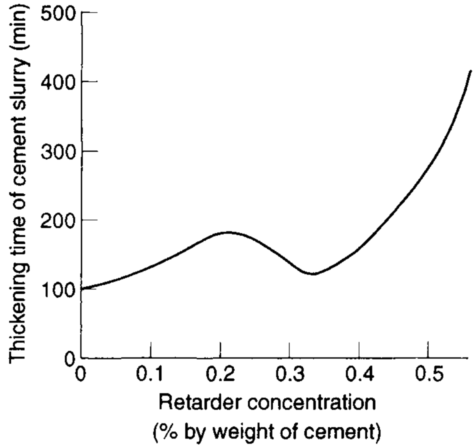

Fig. 14.2 S-curve formation for thickening time.

Accelerators

Accelerators are employed for decreasing thickening times and increasing early compressive strength when cementing surface casing and conductor strings below ~40°C. Examples include calcium chloride (2–4 per cent), sodium chloride (*ca.* 1–4 per cent), sodium silicate (*ca.* 2–4 per cent), sodium aluminate (up to ~5 per cent) and using sea water for the cement slurry. Very high concentrations of salts often retard hydration by altering the ionic strengths of the solution phases. There is no universal mechanism of cement acceleration.[40]

Weighting agents

In deep wells, where high pressures are experienced, cements need their slurry densities to be increased in order to prevent blow-out of the cement slurry, so that effective cementing can take place. Such materials should normally have a specific gravity (s.g.) of *ca.* 4.2–5.0, have a low water requirement, a cement strength which is not significantly reduced, have little effect on cement pumping time, and have a particle size distribution compatible with that of the cement in order to prevent bleeding. Examples include haematite (Fe_2O_3; s.g. 5.0), iron-base spent catalyst (IBSC; s.g. 4.5), ilmenite ($FeTiO_3$; s.g. 4.7), barite ($BaSO_4$; s.g. 4.2), galena (PbS; s.g. 7.5) and, for slurries up to 2.16 kg/L, densified slurries containing sand (s.g. 2.23).[31,41]

Lost circulation controllers

Lost circulation is defined as the total or partial loss of drilling fluids or cement to high-permeability zones, cavernous formations and natural or induced fractures during the drilling or completion of a well. Lost circulation controllers form low-permeability bridges across the openings that are accepting fluids. For logistical reasons such materials are nowadays normally added to drilling fluids in advance of cementing rather than to the oilwell cement slurries. The key properties are the size and shape of their grains and also their rigidity and density.[4 7] Such additives include blocking granules such as walnut shells, lamellated materials like cellophane flakes and fibrous materials such as nylon fibres.

Lightweight additives – extenders

The most commonly used extender is bentonite (s.g. 2.65), which is often referred to simply as 'gel'. An approximate formulation for bentonite is $Al_{1.67}$ $Mg_{0.33}$ $[(OH)_2/Si_4O_{10}]_{0.33}$ $Na_{0.33}$ $(H_2O)_4$. Bentonite absorbs water and swells, being able to hold several times its own weight of water. Depending upon the particular requirements, quantities of bentonite ranging from 2 to 12 per cent by weight of cement, or even more, can be used. For each 1 per cent added, the water can be increased by ~5.3 per cent and slurry densities of 1.44–1.56 kg/L can be achieved. Bentonite can be used either dry-blended or prehydrated. Two per cent bentonite by weight of cement prehydrated in fresh water will normally absorb as much water as 8 per cent dry blended. Dry-blended bentonite does not hydrate so well, because of partial inhibition from calcium ions in the cement slurry.

Attapulgite, or 'salt gel' (s.g. 2.89) has been used as an alternative to bentonite when sea water is used, or in saturated salt slurries, where bentonite is less efficient. It has the approximate formulation $(Mg,Al)_2[OH/Si_4O_{10}]\cdot 12H_2O$. Attapulgite hydrates differently from bentonite in that its clusters of fibrous needles become dispersed in water.[4] Attapulgite has now been banned in cementing operations in many countries because of the similarity of its fibres to asbestos fibres. Granular forms of attapulgite are still permitted in some locations.

Other materials ued for lightweight extension include natural or synthetic pozzolans, such as pulverised fly ash (s.g. 2.0–2.6), sodium silicate (s.g. 2.64), microspheres, ceramic beads, glass beads, foam cement with nitrogen, diatomite ($SiO_2\cdot xH_2O$, diatomaceous earth) – a naturally occurring mineral with a high water requirement (s.g. 2.1–2.2), gilsonite – a naturally occurring asphaltite (s.g. 1.07), crushed coal (s.g. ~1.3) and expanded perlite – a siliceous glass of volcanic origin (s.g. 2.2–2.4). Both gilsonite and perlite may require 2–6 per cent bentonite additions to stop flotation in the slurry mix.

Strength retrogression inhibitors

Portland cements suffer from strength retrogression at temperatures above *ca.* 110–120°C and also a loss in impermeability owing to the formation of large crystals of α-dicalcium silicate hydrate $[Ca_2(HSiO_4)OH]$. Additions of, say, 35 per cent silica sand or silica flour favour the formation of tobermorite $[Ca_5(H_2Si_6O_{18})4H_2O]$, a good, strong binder of high impermeability which has a smaller crystal size and overcomes the problems of strength retrogression.[42,43] Silica sand is coarser (generally 75–210 μm particle size) than silica flour (<75 μm).

Fluid loss control additives

Fluid loss control additives are employed for maintaining a constant water/solid ratio in cement slurries downhole by controlling the rate of water loss to adjacent permeable zones through suitable viscosification; otherwise the cement slurries would lose water by filtration into these zones. This filter loss may be static or dynamic. If sufficient water is lost, the cement either produces non-strengthening filter cake-type deposits, or it may flash set. Typical fluid loss controllers are polyacrylamide, polyethyleneamines, carboxymethylhydroxyethylcellulose (CMHEC) and hydroxyethylcellulose (HEC). Latex is sometimes employed, but has high foaming during mixing with the slurry and is expensive.

Dispersants (friction reducers, thinners or turbulence inducers)

Dispersants improve the flow properties of the cement slurry by breaking up cement agglomerates and freeing the water. They produce slurries at lower viscosity and allow turbulent flow conditions to be reached at lower pump pressures. Dispersion of the cement particles involves modifying the electrostatic interactions at the surfaces to produce charged particles that mutually repel each other and thus keep apart. The mechanism of dispersion has been discussed.[4,4(a)] Common dispersants include sulfonated naphthalene formaldehyde condensate (SNFC), sulfonated melamine formaldehyde condensate (SMFC), lignosulfonates, sodium chloride (salt), polyacryamides and organic acids such as citric acid, which is a good saltwater dispersant.

Defoamers and deaerators

The main cause of foaming is the use of additives in cement slurries such as salts of organic acids. Excessive foaming results in pump cavitation and loss of suction head during the cementing operation, as well as creating difficulties in circulating and measuring slurry density. Defoamers are added in small quantities (~ 0.2 per cent by weight of cement) either in solid or liquid (solution) form to remove foaming during the mixing of cement slurries. They do not normally remove all entrained air from the slurry. Defoamers used include lauryl alcohol, poly(propylene glycol) and lower sulfonate oils. They act by lowering surface tension and remaining insoluble in water.

Deaerators are more powerful and remove entrained air as well as foaming from cement slurries. They are utilised in small quantities similar to defoamers. Slurry weights can be altered by as much as 4–5 per cent by the presence of entrained air. Like foaming, air entrainment mainly arises through the use of additives in cement slurries, such as lignosulfonates and other retarders. Deaerators employed include dibutylphthalate, tributylphosphate (less so nowadays because it can cause nausea) and silicone polymers such as polydimethylsiloxane.

Miscellaneous additives

Thixotropic agents. Thixotropic agents are added to oilwell cement slurries to produce thixotropic properties downhole, which are needed to overcome problems of lost circulation by sealing off lost circulation zones or achieving good annular fill across incompetent zones. Examples of thixotropic agents include calcium sulfate hemihydrate ($CaSO_4 \cdot 0.5H_2O$), which functions on the basis of its false setting properties[44–46] in hydrating to gypsum:

$$CaSO_4 \cdot 0.5H_2O + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O \tag{14.2}$$

and which can be used (*ca.* 8–12 per cent by weight of cement) up to $\sim 80°C$, and mixtures of aluminium sulfate and iron(II) sulfate[47] that generate gypsum *in situ* and proceed to the formation of ettringite in the cement slurry. Proprietary organic-based mixtures, such as guar gum–benzoquinone–sodium carbonate mixture[48] and titanium, zirconium or hafnium chelates with cross-linkable agents, such as titanium chelates with water-soluble cellulose ethers, poly(vinyl alcohol) and acrylamide polymers,[49] are also sometimes used.

Salt slurries for cementing of salt strata. For cementing through salt strata, slurries are employed that contain either very high (18 per cent by weight of water to saturation) or very low quantities of salt (between zero and several per cent). Details of these slurries are discussed in some detail elsewhere.[4]

Gas migration controllers. Impermeable acid systems are used to control gas migration following the cementing operation, which arises by percolation through the thickening cement, when it is neither truly a slurry nor truly solid, if the hydrostatic pressure in the cement column falls below the pore pressure of a gas zone across which the cementing is being done. Gas migration is generally checked by a polymeric additive system containing a suitable fluid loss controller, retarder and dispersant that can effectively block the pores. *In situ* generation of hydrogen gas bubbles from finely ground aluminium pellets and also microsilica (normally used as a 50 per cent aqueous slurry in concentrations of 10–50 per cent by weight of cement) have also been used. Highish rates of cement shrinkage during hardening can encourage gas migration.

Foamers. Although the presence of foam is normally detrimental, for the production of ultra-lightweight cement slurries with densities as low as 0.72 kg/L, appropriate foaming agents (such as cationic or anionic surfactants in small quantities) are utilised to assist in generating and stabilising the foamed cement slurry being pumped downhole. Gaseous nitrogen is incorporated directly into the slurry as a foam density control agent, in order to produce an effective ultra-lightweight system. Foamed cement slurries are used mainly for primary cementing of weak formations, for overcoming lost circulation in cavernous vugs, for squeeze cementing of depleted zones, for zonal isolation and for heat insulation.[1,4]

Colouring materials. Colouring materials are employed to check whether or not cement slurries return to the surface during well cementing and to assist in determining circulation volume. Dyestuffs such as methylene blue, phenolphthalein or fluorescein, or pigments such as the black, red or yellow iron oxide at the 0.1 per cent level, or even mica (in larger quantities), are sometimes used to colour cement slurries. Mica is generally satisfactory for examining subsea returns, whereas a carbide slug is of more use on land and offshore for the determination of circulation volume. In a number of instances, dilution and/or mud contamination may dim and cloud the colours of the dyestuffs, rendering them ineffective.

Mud-to-cement conversion. Drilling mud solidification has for many years been considered the 'ideal solution' for bonding casing to the borehole walls, so that effectively the cementing stage is eliminated. In the Shell mud-to-cement system,[50 52] the water-based drilling mud is converted into cement by adding ground granulated blastfurnace slag (ggbs) and alkali activators such as caustic soda and soda ash to a drilling mud treated with appropriate activators and retarders. The advantages of this process include the ability to obtain good placement and compressive strength development over a wide temperature range, together with good zonal isolation and environmental benefits by not necessarily having to dispose of the drilling mud. Disadvantages include the severity of stress cracking in the hardened slag-muds, complex slurry design, logistical problems of mud dilution, added storage and replacement of a portion of the active mud system while tests are being conducted.[53]

More research and development is clearly necessary in order to ascertain how widely this process can be applied to different well conditions. Although many problems remain to be addressed, including durability, it is very probable that this process will continue to be used for well cementing even if universality is unlikely to be a realistic option in the future.

14.2.8 HYDRATION OF OILWELL CEMENTS

Ordinary hydration

Oilwell cements are usually based upon Portland cement compositions, which comprise four principal clinker mineral phases: tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_6$) and a calcium aluminoferrite of more variable composition (approximately Ca_2AlFeO_5), to which some calcium sulfate in the form of the dihydrate gypsum ($CaSO_4 \cdot 2H_2O$), or its derivatives like hemihydrate ($CaSO_4 \cdot 0.5H_2O$) or natural anhydrite ($CaSO_4$), have been incorporated during the manufacturing process to regulate thickening behaviour. In situations where sulfate resistance is required, the quantities of tricalcium aluminate must be reduced, because this phase is the most susceptible to sulfate attack.[54] The hydration of ordinary and sulfate-resisting Portland cements has been described in various texts.[44,45,55] Compressive strength is obtained mainly from the reaction of the silicate phases to form calcium silicate hydrate. Tricalcium silicate is the principal cementing phase, whereas dicalcium silicate (usually in the β form) reacts at a much slower rate to form similar hydration products. Early compressive strength is largely obtained from tricalcium silicate, but at later ages (e.g. 28 days and beyond) the contribution from β-dicalcium silicate becomes very important. None of the principal cementing phases is pure – all contain several per cent of impurities in solid solution, which are derived from the raw materials and the fuel, and may be affected by the manufacturing process. These give rise to hydration products, which again are not pure products and contain impurities in solid solution. The hydraulic behaviour of the cementing phases is influenced by the presence of these impurity ions.

At surface temperatures or just above, the silicates react with water to form an amorphous calcium silicate hydrate, which can be represented approximately as follows:

$$2Ca_3SiO_5 + 6H_2O \rightarrow \text{`}Ca_3Si_2O_7 \cdot 3H_2O\text{'} + 3Ca(OH)_2 \qquad (14.3)$$

$$2Ca_2SiO_4 + 4H_2O \rightarrow \text{`}Ca_3Si_2O_7 \cdot 3H_2O\text{'} + Ca(OH)_2 \qquad (14.4)$$

The aforementioned reactions are not normal dissolution and precipitation types, but arise topochemically at the clinker silicate surfaces. The equations given above are only approximate, because the calcium silicate hydrate formed, known as C-S-H, is in reality a very poorly crystalline non-stoichiometric material consisting principally of dimeric units at first, but which subsequently slowly polymerise after a few days to give higher linear units like pentamer and thence octamer, and so on, with the passing of time.

The appearance of a hardened MSR Class H oilwell cement hydrated for 4 months at a water/cement ratio of 0.38 is illustrated in Figure 14.3.

The hydration products from the tri- and β-dicalcium silicate phases at up to ~100°C do not differ essentially from those formed at ambient temperature. However, there may be some differences in microstructure and morphology. No changes in the mechanism of hydration have been reported in the temperature range from ambient to 90°C, although more polysilicate hydrate in relation to dimer has been found in calcium silicate hydrate pastes at 65°C than at 25°C.[56] At elevated temperatures the hydration of β-dicalcium silicate is accelerated in relation to that of tricalcium silicate, which could be related to the higher solubility of silica and lower solubility of calcium hydroxide under these conditions.[57]

The solubility product and morphology of C-S-H formed in sodium chloride or sodium hydroxide solution are not very different from those of C-S-H produced in water. Na^+ ions are incorporated in the C-S-H gel. This C-S-H easily reverts to the normal C-S-H after dispersing in water.[58]

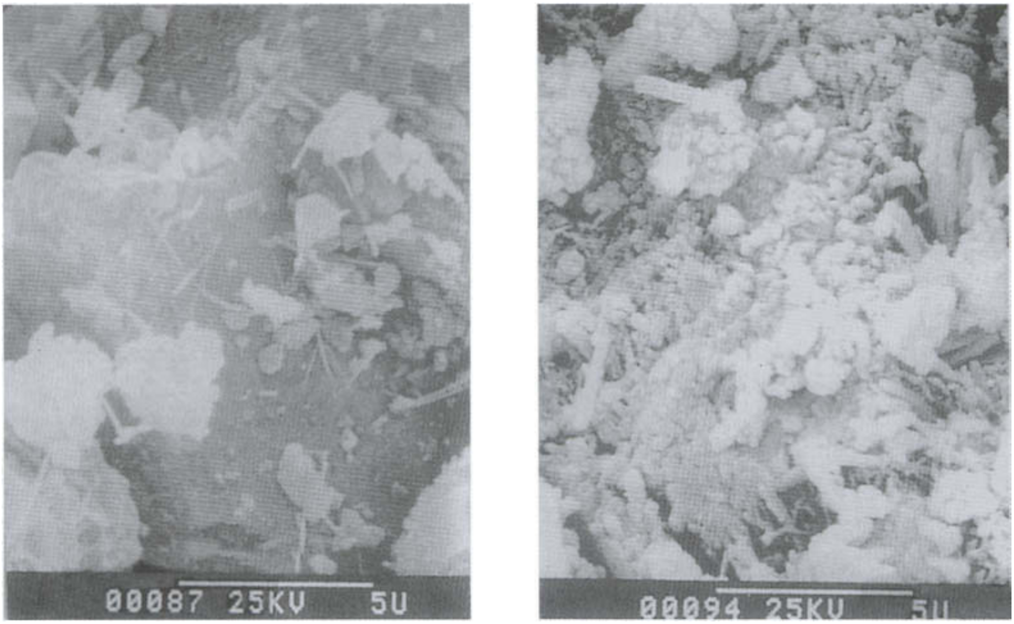

Fig. 14.3 MSR Class H oilwell cement (scale bars 5 μm). (a) Unhydrated, showing clinker particles and rodlets of gypsum. (b) Hydrated at water/cement ratio = 0.38 for 4 months at 27°C, revealing dense formation of C-S-H, hexagonal platelets of calcium hydroxide and 'monosulfate-$C_4(A,F)H_{13}$' (AFm phase) plus some rodlets of ettringite (AFt phase).

The tricalcium aluminate and calcium aluminoferrite phases react with the added calcium sulfate to form ettringite, the rate of the former reaction being faster than that of the latter:

$$Ca_3Al_2O_6 + 3\{CaSO_4\cdot 2H_2O\} + 26H_2O \rightarrow Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O \quad (14.5)$$

$$\begin{aligned} &Ca_2AlFeO_5 + Ca(OH)_2 + 3\{CaSO_4\cdot 2H_2O\} \\ &\quad + 25H_2O \rightarrow Ca_6[Al_{0.5}Fe_{0.5}(OH)_6]_2(SO_4)_3\cdot 26H_2O \end{aligned} \quad (14.6)$$

In practice only one form of ettringite is produced, since the effects of solid solution between ettringite derived from the aluminate and ettringite derived from the aluminoferrite plus their containing impurities from the parent clinker phases means that there is just one continuous mass of ettringite being formed. The parent phases in respect of ettringite formation at best make only secondary contributions to thickening and the development of compressive strength.[32,36] Only very small quantities (sometimes none) of tricalcium aluminate are normally present in the API HSR cements of Classes B–H, where most (if not all) the ettringite arises from the aluminoferrite phase; this reaction is somewhat slower than that of tricalcium aluminate and also requires the presence of calcium hydroxide to react. When the gypsum is effectively used up, commonly after several hours, ettringite changes to the monosulfoaluminate hydrate $Ca_4[(Al,Fe)(OH)_6]_2SO_4\cdot 6H_2O$ which readily enters into solid solution with the calcium aluminate hydrate $Ca_2(Al,Fe)(OH)_7\cdot 3H_2O$ formed at this stage from aluminate and aluminoferrite reacting with water.[46]

Some calcium hydroxide is present at the beginning of hydration, where the aqueous phase of the cement slurry can be considered for simplicity as essentially a limewater medium, being derived from some hydration of the small free lime content:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (14.7)$$

Alkalis are present in oilwell cements in small quantities, both in the form of alkali sulfates and incorporated in the main clinker phases. They exist potentially as sulfates if sufficient SO_3 is present in the clinker, and the preferred sulfate form is potassium sulfate (K_2SO_4). A series of double alkali sulfates can also exist, namely calcium langbeinite [$K_2Ca_2(SO_4)_3$] and potassium sodium sulfate [$(K,Na)_2SO_4$]. The alkali metal ions from the sulfates readily enter solution when the cement is mixed with water and accelerate the early hydration reactions, particularly those of tricalcium silicate and tricalcium aluminate. Limits of 0.75 per cent equivalent Na_2O are included in API Specification 10A for Class G and H cements to permit adequate thickening times to be achieved downhole.

Some free magnesium oxide (MgO) may be encountered with high magnesia-containing oilwell cements. This hydrates slowly to the hydroxide:

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (14.8)$$

which may crystallise as brucite. Its effects on oilwell cement properties are similar to those of free lime.

Class C cement is a rapid-hardening Portland cement (ASTM Type III) and its early hydration chemistry is accelerated. For this reason a higher water/cement ratio of 0.56 is permitted for achieving a suitable thickening time and higher early compressive strength development. The retarded cements of Classes D, E and F take longer to achieve thickening by virtue of their lower rate of hydration of tricalcium silicate. Class H cement is coarser than Class G from the same source and ordinarily will hydrate at a slower rate, since the rates of clinker phase reactions decrease with coarser surface areas. Class H cement is designed for use at lower water/cement ratios than Class G cement, such as 0.38 specified in API Specification 10A for achieving suitable thickening and compressive strength, although in practice it is often used at much higher water levels (e.g. 46 per cent) in cementing formulations. Likewise, Class G cement is also often employed in cementing formulations at water levels different from the 44 per cent by weight of cement specified.

Hydrothermal hydration

Different products are formed when oilwell cements are hydrated under high temperature and pressure conditions. The calcium silicate hydrates formed under such conditions range from X-ray amorphous to highly crystalline phases. A number of studies have been reported.[42,43,56,59 75]

Normally, oilwell cements are employed with ~35 per cent of strength retrogression inhibitor, such as silica flour, in higher-temperature wells above ~120°C, for preventing, or at least minimising, the formation of α-dicalcium silicate hydrate [$Ca_2(HSiO_4)OH$], a dense orthorhombic phase that is deleterious in having high permeability and low compressive strength, and sometimes also (above 202°C) tricalcium silicate hydrate [$Ca_6Si_2O_7(OH)_6$], a similarly deleterious crystalline material. With the incorporation of the strength retrogression inhibitor, tobermorite [$Ca_5(H_2Si_6O_{18})\cdot 4H_2O$] is normally the first crystalline phase to be produced. Formation of tobermorite in wells is commonly associated with low permeability and good compressive strength. Above about 150°C, tobermorite will transform to two other crystalline phases, xonotlite [$Ca_6Si_6O_{17}(OH)_2$] and gyrolite [$Ca_8(Si_4O_{10})_3(OH)_4 \cdot \sim 6H_2O$], which both have a lower impermeability and compressive strength than tobermorite. Gyrolite will subsequently transform at ~250°C to truscottite [$Ca_7(Si_4O_{10})(Si_8O_{19})(OH)_4 \cdot H_2O$], which is weaker than gyrolite and is less permeable. Xonotlite and gyrolite generally have good compressive strength and moderate impermeability from the viewpoint of oilwell cementing. Thermodynamic calculations of the principal and secondary reactions in the $Ca(OH)_2$–SiO_2–H_2O system have been made for explaining the observed reactions.[74]

Calcium hydroxide is not commonly encountered under hydrothermal conditions, since it reacts in the system, usually together with the added silica, in forming the more crystalline calcium silicate hydrates observed. The corresponding effects of magnesium hydroxide have not been studied in detail in hydrothermal cement systems.

Amongst substituted calcium silicate hydrates formed under hydrothermal conditions in cementitious systems are pectolite ($NaCa_2HSi_3O_9$) and scawtite [$Ca_7(Si_6O_{18})CO_3 \cdot 2H_2O$]. Pectolite is a sodium-substituted calcium silicate hydrate formed above 150°C and is produced when tobermorite is exposed to sodium salt solutions. Pectolite generally has higher permeability and similar compressive strength in comparison with xonotlite, although combinations of pectolite and truscottite usually have permeabilities slightly lower than that of xonotlite.[42] Scawtite is a calcium silicate carbonate hydrate which is commonly encountered in trace quantities in high-temperature wells, where it enhances cement performance. Its formation appears to be impeded in the presence of significant quantities of aluminium and alkali metal salts. Aqueous solutions containing carbon dioxide appear to enter the pores of the hydrating cement and react with the cement surfaces, producing scawtite and releasing silica, which may seal small fractures and pores. However, scawtite shows poor performance and brittleness when present in large amounts. It is formed from cements with 35 per cent silica and < 10 per cent sodium carbonate, sodium hydrogencarbonate or finely ground calcium carbonate in the temperature range 215–315°C. Scawtite is basically a xonotlite structure in which 5.3 per cent CO_2 replaces part of the silica content.[42,56]

The form in which the silica is present is very important for the sequence of reactions that occur. The poorly cementitious products formed when silica sand is used in place of silica flour for completing high-temperature wells that contain very saline brines have already been discussed in the section on additives under 'Strength retrogression inhibitors'. With condensed silica fume (of very high surface area, $\sim 20\,000\,m^2/kg$), the silica reacts faster than the lime to form initially an amorphous hydrate, which then reacts with more lime to form gyrolite and truscottite, without normally passing through the tobermorite stage.

So far, the silicate hydration products have been discussed, but not the hydration products of the aluminate and aluminoferrite phases. Hydrated aluminate and aluminoferrite phases such as the calcium monosulphoaluminate hydrate $Ca_4[(Al,Fe)(OH)_6]_2SO_4 \cdot \sim 6H_2O$ in solid solution with the calcium aluminate hydrate $Ca_2(Al,Fe)(OH)_7 3H_2O$ have not commonly been observed under these conditions. Ettringite is not stable to hydrothermal conditions and would not normally be detected. At least some of the Al^{3+}, Fe^{3+} and SO_4^{2-} ions become incorporated in the calcium silicate hydrate systems in some form of solid solution. No aluminoferrite-derived phases have been independently established, presumably because Fe(III) undergoes extensive solid solution with Al(III) and is readily incorporated in the aluminate and aluminosilicate products formed under hydrothermal conditions. Hydrogarnet and strätlingite are formed in the temperature range 100–200°C.

The conditions in actual wells are not ideal.[64] The standard conditions for equilibrium transformations[74] are nonexistent. Thus the actual hydration products formed in a given well will depend upon the precise conditions occurring in that particular well and may include calcium silicate hydrates and related minerals as well as various calcium aluminate – and aluminosilicate-based compositions of different types from those described above.

Low-temperature hydration

Comparatively little work has been done so far on the low-temperature hydration of oilwell cements. Binder systems based upon Portland cement (API Class G oilwell cement) and upon Portland blastfurnace cement have been found to hydrate effectively in the temperature range *ca.* 0 to −20°C only when salt solutions are used in preparing the slurries. With appropriate levels of sodium chloride or calcium chloride or mixtures of these two salts, the cement suspension can set within 4–10 h at sub-zero temperatures. Class G cement was found to hydrate more effectively at these low temperatures than Portland blastfurnace cement.[76] Details of low-temperature cementing have been described.[77]

Morphological differences and complex effects with accelerating additives have been found when Class G cement hydration at 5°C has been compared with that at 20°C.[78,79] At 5°C, in particular, there are optimum concentrations for acceleration, above and below which retardation may take place.[78]

Sulfate resistance

The majority of oilwell cements used in the field are sulfate resisting, such as the MSR or HSR types in the API Specification 10A classification. There are two reasons for this usage:

- Sulfates are commonly found in a number of formation waters and can affect the set cement downhole. Sodium and magnesium sulfates are often encountered in such waters. Sulfate attack arises by reaction within calcium hydroxide from the set cement to form gypsum:

$$SO_4^{2-} + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2OH^- \qquad (14.9)$$

which in turn reacts with the monosulfoaluminate–calcium aluminate hydrate solid solution in the set cement to form ettringite, which can be represented thus:

$$Ca_4[(Al,Fe)(OH)_6]_2 \cdot SO_4 \cdot 6H_2O + 2\{CaSO_4 \cdot 2H_2O\} + 16H_2O$$
$$\rightarrow Ca_6[(Al,Fe)(OH)_6]_2(SO_4)_3 \cdot 26H_2O \qquad (14.10)$$

Formation of gypsum and particularly of ettringite occupies larger volumes than the starting materials, causing disruptive expansion. Full details of sulfate attack are described elsewhere.[12,13,54] Sulfate resistance is increased by replacing tricalcium aluminate by ferrite, which severely reduces the rate of ettringite formation in reaction (14.10), and by lowering free lime, or by including a pozzolan in the cement which effectively reacts with the calcium hydroxide formed and thus renders it unavailable for reaction with extraneous sulfates. Sulfate attack is normally only a problem in practice for a bottomhole static temperature below ~60°C, where ettringite exists as a stable phase.

Even with sulfate-resisting cements, the sulfate resistance is appreciably lowered if the alite (C_3S) content is above 60 per cent.[80] This effect presumably arises because the higher the alite content, the greater the propensity to form calcium hydroxide upon hydration, which can then react as in equation (14.9). At low temperatures below ~10°C prolonged effects of sulfate (in conjunction with carbonate) attack can produce the non-binding calcium carbonate silicate sulfate hydrate known as thaumasite, details of which are considered elsewhere.[81,82]

- When tricalcium aluminate is largely replaced by ferrite, the cement slurry becomes more workable and rheological behaviour is positively assisted. Hence it is often useful to employ a sulfate-resisting oilwell cement even in conditions where sulfate resistance is not specifically required.

14.2.9 EFFECTS OF AERATION (EXPOSURE)

When oilwell cements become exposed to dry air, no significant chemical reaction or deterioration of the cement properties arises, but upon exposure to moist air, some reaction with this water (hydration) and/or reaction with carbon dioxide (carbonation) occurs, which can affect the cementing properties downhole. Such processes of hydration and carbonation are referred to as aeration.

The main hydration products of Portland-type cements are susceptible to carbonation in the presence of moisture; the greater the concentration of carbon dioxide, the greater the rate of carbonation.[83] Indeed, the calcium aluminate hydrates appear to be even more susceptible than the calcium silicate hydrates in this respect. The ultimate products of carbonation are normally alumina gel (which can change with time to crystalline gibbsite [$Al(OH)_3$]) and calcite ($CaCO_3$) for the calcium aluminate hydrates, with iron(III) oxide gel as well in the case of ferrite, and silica gel (which can change with time to crystalline silica [SiO_2]) and calcite for the calcium silicate hydrates. Other forms of calcium carbonate, such as vaterite and aragonite may also be produced during carbonation, but calcite is the most commonly encountered stable end product.

Reactions of tricalcium and β-dicalcium silicate with water and carbon dioxide have been shown to obey a decreasing volume, diffusion-controlled mechanism.[84] The degree of carbonation increased with the following parameters:

- temperature of reaction;
- specific surface area of the particles;
- time of aeration;
- relative humidity of the reacting environment;
- partial pressure of carbon dioxide.

The end products were found to be aragonite and silica gel although, in the presence of water vapour, calcite was observed to be the preferred form of calcium carbonate produced. Work on carbon dioxide uptake in C-S-H[85] suggests that the carbon dioxide absorbed reacts in a random manner with the silicate lattice to form a 'solution' of calcium and carbonate ions in a 'solvent' of randomly crosslinked silica gel.

Carbonation of the aluminate and aluminoferrite phases can result in the initial formation of 'hexagonal plate'-type phases of the type $Ca_4[(Al,Fe)(OH)_6]_2CO_3 \cdot 5H_2O$. Formation of the monocarboaluminate hydrate from tricalcium aluminate and calcium carbonate is very rapid.[86] Ultimately, the monocarboaluminate hydrate will be further attacked by carbon dioxide in the presence of moisture; calcium carbonate and alumina gel or gibbsite will be formed.

The effects of carbonation are generally worse with small laboratory samples where surface/volume ratios are much higher than with bulk specimens and where permeability or porosity is high, allowing penetration by moist carbon dioxide.

The effects of aeration on the properties of Class G oilwell cement have been examined.[87–89] Exposure to air results in increased thickening times, decreased compressive strengths and generally higher free water contents. The same trends have been found in the presence of 0.2 per cent calcium lignosulfonate retarder. In non-aerated cement, the thickening time corresponds to the occasion when *ca.* 5–8 per cent of C-S-H is formed, and is akin to setting with construction Portland cements,[90,91] except that reaction is enhanced due to the higher-temperature profile in the examination of thickening time. In aerated cement, carbonation interferes with this development, as a result of which it takes longer to achieve a similar level of C-S-H and thickening times are therefore increased. As has been indicated earlier, C-S-H arises from hydration of the cement silicate phases, primarily tricalcium silicate (alite) and to a lesser degree β-dicalcium silicate (belite). Compressive strength is a manifestation of further development of C-S-H and, because of the interference from carbonation, lower compressive strengths are achieved as a result of aeration. Interference from carbonation results in the production of some silica gel and calcium carbonate.

Problems of carbon dioxide corrosion have also been highlighted in connection with enhanced oil recovery from wells,[92] and the effects of carbon dioxide and carbon dioxide-containing fluids upon calcium silicate hydrates found in geothermal well grouts.[93–95] Thaumasite can also be formed by a combination of aeration and sulfate attack on C-S-H at low temperatures.[82,96–98] It has no binding power and is thus detrimental when formed. It is not known so far to be a problem in well cementing.

Aeration also influences the hydration of the aluminate and aluminoferrite phases, which normally react with the added calcium sulfate (usually gypsum) and water to produce ettringite. The formation of ettringite permits orderly hydration prior to thickening, and makes a minor contribution to thickening, but has minimal effect on compressive strength development. Aeration tends to attack ettringite destructively as it is being formed by producing some gels of alumina and iron oxide plus gypsum and thus interfering with these processes. The lower cementitious reactivity of aerated cements can readily be followed by conduction calorimetry.[87,99]

Free water content generally tends to rise with exposure,[87,88] although the individual results are often quite variable. Normal cement hydration reactions bind water, whereas carbonation releases water as calcium carbonate is formed. However, the formation of some calcium monocarboaluminate hydrate from the aluminate and aluminoferrite phases also binds some water. The general trend is for free water to increase upon exposure, owing to the dominant effect of aeration being the production of calcium carbonate with the corresponding release of water.

Exposure of oilwell cement, either in bulk or in small laboratory samples, to atmospheric moisture can significantly change its physical and chemical properties. Cementing formulations can be considerably in error if based upon the testing of poorly packaged cement samples that are aerated in consequence. This may lead to shorter pumping times than is desirable, with consequent underdisplacement. Greater attention needs to be paid to the choice of container used to transport samples to laboratories and the avoidance of unnecessary exposure to atmospheric moisture prior to testing. Consideration should be given to greatly improving the removal of water from compressed air used in pneumatic transfer and storage systems.

14.2.10 GENERAL CONSIDERATIONS

The requirements for oilwell cements are much more stringent than those for construction cements. This is not altogether surprising, because oilwell cements are expected during usage to withsand a wide range of temperature and pressure effects, as well as different types of rock formations, problems of strata, underground waters containing dissolved salts, etc., which construction cements are not exposed to in a given environment. Oilwell cements thus need to be of a high degree of consistency in the batches from their source and to behave consistently with the various additives put into the cementing formulations to cope with the actual conditions of a given well. Consequently their manufacture needs to be very tightly controlled; in storage and transport unnecessary exposure to moist air should be avoided and the testing procedures need to be applied with great care to obtain reliable data with the avoidance of aeration. The hydration of oilwell cements is commonly more complicated than for construction cements because of thermal effects and the influences of salts in the rock formations and downhole waters. Additives commonly modify the hydration of the oilwell cements and their behaviour needs to be more fully understood. These points have all been reviewed.[31,100,101]

With increased exploration around the world for sources of energy like oil and gas, many wells are being drilled and cemented. Some of these are in remote locations, whilst others are deeper than has been common practice hitherto. Because of this, the functions and performance of oilwell cements need to be appreciated to a greater degree, so that successful completion of wells in a wide variety of difficult circumstances can be undertaken with the greatest level of efficiency.

14.3 Decorative Portland cements

14.3.1 GENERAL POINTS

Decorative Portland cements such as white cement have an important aesthetic role in making exposed concrete surfaces, such as on buildings, bridges and swimming pools, more attractive to the environment. Also, the visual appearance of various mortars and renderings can be improved. The most widely used decorative cement is white Portland cement. Coloured Portland cements are less commonly encountered than white Portland cement. For obtaining white or light-coloured concrete, especially selected white or light-coloured sand and stone aggregates are needed. As with normal concrete, suitable performance and durability will only be achieved if the concrete is placed and properly compacted using good site practice. Details of white cement application have been detailed previously.[102] The visual appearance of decorative products is illustrated in Figure 14.4. White calcium aluminate (high-alumina) cements are also used in decorative applications (see also the discussion in Chapter 13).

14.3.2 MANUFACTURE OF WHITE PORTLAND CEMENT

The manufacture of white Portland cement requires suitable, carefully selected raw materials and special processing to avoid contamination during production which would adversely affect the whiteness of the product.[103-106] The grey colour of normal Portland cements is caused primarily by the iron oxide content, so this needs to be kept as low as possible in a white Portland cement. The raw materials for white Portland cement manufacture are chalk or limestone and china clay, which are selected for their low iron oxide content. Of the four main phases of Portland cement, normally only the calcium aluminoferrite phase (C_4AF) is essentially coloured and this material imparts the characteristic grey colour to Portland cements. Chromium and manganese oxide contents may also have a significant

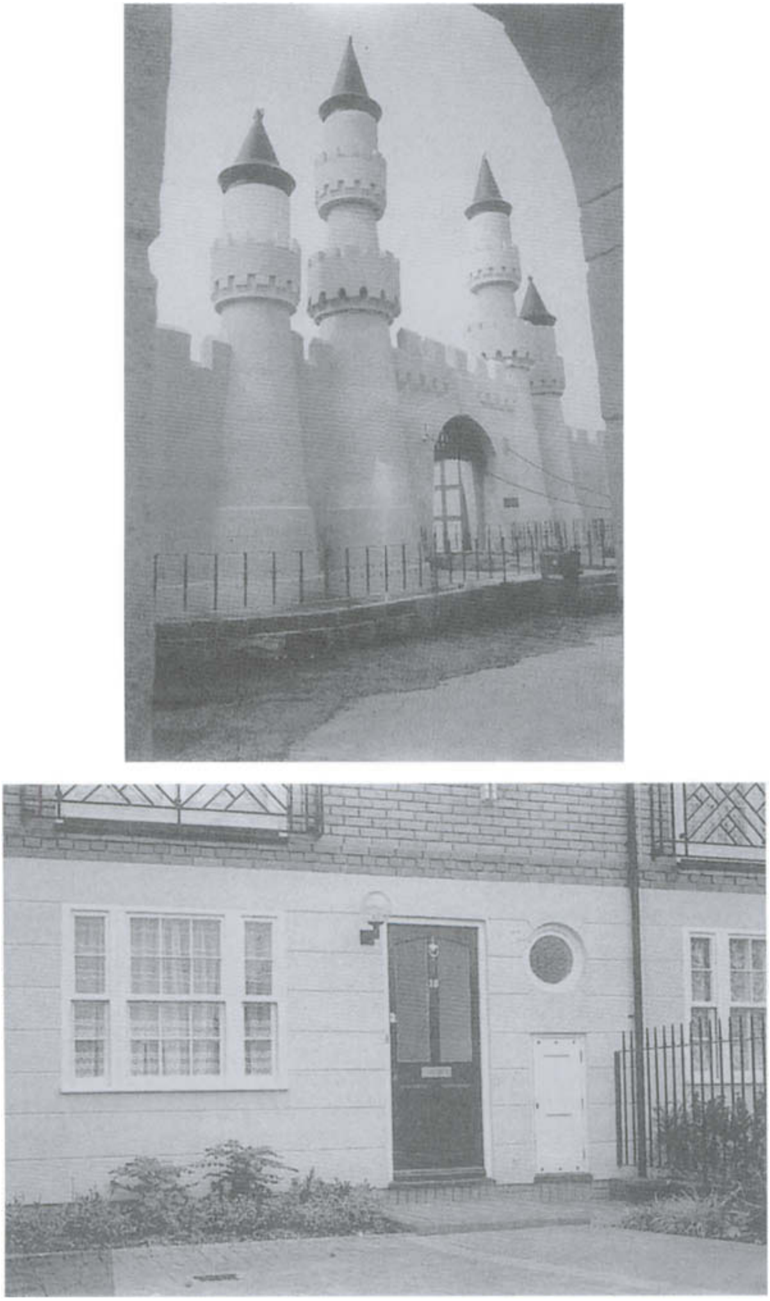

Fig. 14.4 Examples of the use of cement-based decorative finishes for external aesthetic appearance (courtesy P. J. Cook, Snowcem PMC Ltd).

effect upon the colour of Portland cements. In general, the higher the C_4AF content, the darker grey its colour. For white Portland cement it is necessary to reduce the Fe_2O_3 content to below ~0.4 per cent. Further decreases below this level have only a small effect in producing increased whiteness.[103,104] Because of the lack of sufficient iron-containing material, which normally acts as a flux during the burning of the raw materials in rotatory kilns, combination of the raw materials is more difficult than for ordinary grey Portland cements. Higher burning temperatures than usual (*ca.* 1550–1600°C) are often necessary to achieve clinkering. Cryolite (sodium aluminium fluoride) has at times been added as a flux to aid in burning. Oil or gas is normally used as the fuel, since with coal the ash acts as a contaminant. Quenching the clinker appropriately in a reducing atmosphere aids whiteness,[106] because reduction of Fe(III) to Fe(II), Mn(III) to Mn(II) and Cr(VI) to Cr(III) or better to Cr(II) results in a significant lowering of colour intensity. The cooled clinker is then ground with a pure white gypsum in a grinding mill with ceramic media or pebbles rather than the more efficient steel balls in order to avoid contamination of the product with iron. Brightening agents such as titanium dioxide are sometimes added to the clinker as well.[106] These brightening agents are substances which have a higher degree of whiteness than the white clinker. They should be applied cautiously, if employed, because of their non-hydraulic nature. White cement has also been produced from electric arc furnace (EAF) reducing slags.[107] These byproducts of EAF steelmaking, when ground with white gypsum and a suitable activating additive give an alternative white cement to the more commonly encountered Portland-based type.

14.3.3 WHITE PORTLAND CEMENT REQUIREMENTS

For a white Portland cement the key requirement is whiteness, followed by the workability and compressive strength properties. Determination of the whiteness is usually based upon measurement of the reflectance by standard procedures.[106] Although there are no specific standards for white cement manufacture in Western Europe, such cement is normally manufactured to comply with the standard requirements for ordinary and/or rapid-hardening Portland cement (e.g. BS 12), such as for setting and compressive strength development. Chemical compositions of white Portland cements are shown in Table 14.6 for illustrative purposes. Standards do exist for white Portland cement in a number of countries. These are classified in the *Cembureau World Cement Directory.*

14.3.4 HYDRATION CHEMISTRY OF WHITE PORTLAND CEMENT

White Portland cement often has a very low alkali content, caused by alkali loss through volatilisation in wet process manufacture as well as through the choice of pure raw materials, and also a generally higher free lime content (CaO) than is commonly obtained for most ordinary Portland cements, because of fluxing problems, and in addition lower magnesia (MgO) contents, again through the choice of purer raw materials. The C_4AF phase is normally low (commonly ~1 per cent) because of the low iron content. These factors all influence the actual hydraulic behaviour of the white cement.

The hydration behaviour of Portland cements is well known.[46] Less ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31–32H_2O$) is commonly formed than for ordinary Portland cements[108] from the tricalcium aluminate (C_3A) phase. Such behaviour is similar to that of very low-alkali grey Portland cements.[109] This arises when lower alkali levels are present in white cement; the solubility of lime increases whilst that of sulfate (SO_4^{2-}) decreases. Hence less SO_4^{2-} ions are available in solution for reacting with C_3A and there is insufficient calcium aluminoferrite phase present to react with the lime to form ettringite and thus afford at least some degree of compensation for the low SO_4^{2-} ion solubility. Indeed there

Table 14.6 Examples of white Portland cement compositions (per cent)

	Cement			
	1	2	3	4
C_3S	46.4	38.1	67.1	63.6
C_2S	33.6	40.8	12.5	22.9
C_3A	9.7	10.4	8.5	4.7
C_4AF	1.1	0.8	1.4	0.9
SO_3	2.6	2.8	2.3	1.8
Free lime	2.5	2.9	2.6	2.5
K_2O (t)[a]	0.19	0.22	0.11	0.17
K_2O (w/s)[b]	0.03	0.03	0.03	0.05
Na_2O (t)	0.14	0.14	0.09	0.07
Na_2O (w/s)	0.04	0.04	0.02	0.02

[a] t = total.
[b] w/s = water-soluble fraction.

is very little ferrite phase present to augment the production of ettringite. Hydration of the alite (C_3S) and belite (β-C_2S) phases appears to be somewhat low in comparison with ordinary Portland cement at a similar surface area, presumably due to the low alkali, magnesia and other impurity ion contents as well as the fairly low sulfate content of the white cement investigated.[110] These common differences in hydraulic behaviour of white Portland cement compared with ordinary Portland cement should not adversely affect technical performance. More rapid setting and higher early compressive strength can be achieved by grinding the white clinker and gypsum to high surface areas of rapid-hardening fineness during manufacture, should the need arise. In this way the rate of hydration of white Portland cement can be raised above that of ordinary Portland cement, and has been observed in studies of hydration behaviour.[111]

14.3.5 COLOURED PORTLAND CEMENTS

Coloured Portland cements are produced by intergrinding suitable pigments with white or normal grey Portland cement. This permits a more uniform and durable concrete to be produced than simply mixing concrete with pigments, because of difficulties with the latter in obtaining a uniform colour across the concrete.[112] The majority of cement pigments are inorganic.[103,104]

Coloured Portland cements (red, orange, yellow, green, blue, black, etc.) are mostly based upon white Portland cement with up to 10 per cent or more of added colour pigment. Some types are in fact based upon ordinary grey Portland cement, but this cannot be used satisfactorily for most types of coloured cement because the grey colour cannot always be optimally covered up. Pigments for use in cement are covered by appropriate specifications such as BS 1014.[103,104] Such pigments need to possess the following properties:

- non-detrimental to the cement;
- not affected by the cement;

- good colour durability when exposed to light and different weather conditions;
- finely divided;
- do not contain soluble salts.

The colour of each particular coloured cement can be checked by appropriate colorimetric procedures.

Pigments approved in BS 1014 are given in Table 14.7 together with the limits specified for (1) matter volatile at 105°C for powders, and (2) matter soluble in water. Procedures for determining the compositions of the pigments, their colour and staining power are given. In addition, the pigments must not significantly affect the setting time or compressive strength development of the cement. The initial set must not be less than 45 min and the final set not more than 10 h, and the difference for both setting times between the mixes with and without added pigment not more than 30 min. The mean compressive strength of the mix containing the pigment should not differ by more than 20 per cent from the mean compressive strength of the mix without pigment. Recommendations on proportions of pigments, pale colours, blended pigments and the use of pigment dispersions are also given in BS 1014. Pigments can also be added to or ground in with white calcium aluminate cements to produce a range of decorative finishes. Few countries have specific standards for coloured Portland cement.[103,104]

Table 14.7 Pigments for use in Portland cement[103,104]

Pigment	Composition	Volatile matter at 105°C for powders, maximum (%)	Matter soluble in water, maximum (%)
Chromic oxide green	Cr_2O_3, 95% min.	0.5	0.5
Red iron oxide	Fe_2O_3, 94% min. (Class 1) Fe_2O_3, 50% min. (Class 2)	3.0	3.0
Carbon black	Amorphous free C	Within 2% absolute of amount stated by vendor	1.0
Black iron oxide	Fe_2O_3, 80% min. (Class 8)	1.5	2.5
Yellow iron oxide and iron hydroxide	Fe_2O_3, 83% min. (Class 4) Fe_2O_3, 70% min. (Class 5) Fe_2O_3, 45% min. (Class 6)	4.0	2.5
Brown iron oxide and iron manganese oxide	Fe_2O_3, 70% min. (Class 10) Fe_2O_3, 45% min. (Class 11) Fe_2O_3, 40% min. (Class 12)	4.0	2.5
Titanium dioxide, white	TiO_2, 98% min. (anatase type) TiO_2, 97% min. (rutile type)	0.5	0.6
Phthalocyanine blue	Cu phthalocyanine CI pigment blue 15	1.0	2.0
Phthalocyanine green	Polyhalogenated Cu phthalocyanine CI pigment green 7, 41 or 43	1.0	2.0

The pigment shall not contain compounds or other impurities, such as lead or zinc compounds, capable of adversely affecting the setting and strength development of Portland cement.

By agreement between the contracting parties, limits for metal oxide content other than those given in the table may be specified.

Coloured cements in concrete may undergo fading at the surface. Although such colour fluctuations may be attributable to mix design or to the composition of the concrete, the main reason for fading is usually efflorescence, which can be a serious problem in coloured concrete. Efflorescence refers to the leaching of lime compounds leading to the formation of salt deposits on the concrete surface. This can arise when water percolates through poorly compacted concrete or through cracks or along badly made joints, and when evaporation can take place at the concrete surface.[112] Efflorescence is manifested by effects ranging from hazy white layers to thick white crusts spoiling the exposed concrete surfaces. This is caused primarily by calcium hydroxide (portlandite), one of the Portland cement hydration products, which is slightly soluble in water, migrating to the concrete surface through the capillary system of the concrete by aqueous transport and evaporated to leave the solid calcium hydroxide [$Ca(OH)_2$], which then reacts with atmospheric carbon dioxide to form calcium carbonate:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O \qquad (14.11)$$

Any water penetrating the surface of the concrete can dissolve soluble calcium salts and give rise to secondary efflorescence, which tends to be more patchy than primary efflorescence. The mechanisms of primary and secondary efflorescence have been discussed in some detail.[113] [115] Efflorescence can be effectively treated in a number of ways.[115]

- sandblasting the surface of the concrete;
- washing the concrete with an appropriate dilute acid such as hydrochloric acid (HCl); or
- relying upon natural weathering.

The hydraulic performance of coloured cement is basically similar to that of the parent white or grey Portland cement. The rate of hydration of coloured Portland cements, like that of white cement mentioned earlier, can be increased by finer grinding of the clinker and gypsum phases present[111] (certain organic pigments if used may lead to a slight retardation in setting). However, the pigments do not normally contribute to compressive strength development, so the ultimate strength attained may be somewhat lower than that of the parent white or grey cement at the same surface area, but should ordinarily comply with standards for Portland cement such as BS 12. Mixes which are slightly richer than usual should be employed to compensate for the non-hydraulicity of the pigment. Like white cement, there are no British or other Western European standards for coloured Portland cements, but the specialised manufacturers of these products do have their own specifications for their use.

Production issues and achievements in manufacturing white and coloured cements have been addressed. For obtaining a high-quality white clinker for white cement or as the base for coloured cement production, the important roles of the system for whitening the clinker and the need to enrich the limestone raw material have been emphasised.[116]

14.3.6 CEMENT PAINTS

The term cement paint is applied to paints based upon Portland cement with the addition of pigments, fillers, accelerators and water-repellent substances. These paints are supplied as dry powders and mixed with water before use. For the lighter colour paints a white Portland cement is used, but for darker colours ordinary Portland cement can be substituted as a base. Titanium dioxide and zinc sulfide are used to improve the opacity of white and lighter-coloured cement paints. Other pigments need to be of the lime-fast type and conform to appropriate standards such as BS 1014. Hydrated lime and siliceous fillers are also incorporated. Calcium or aluminium stearate and similar materials are added to improve the waterproofing qualities of exterior paints, as well as an accelerator (commonly calcium chloride) to ensure that the paint will set before it dries out.

Powder cement paints are governed by standards such as BS 4764. In this standard the product should consist essentially of Portland cement, complying with BS 12, pigments and extenders. The extenders should be limestone (including chalk) or siliceous material, as specified in BS 1795, or hydrated lime. Whenever possible, the pigments should comply with BS 1014.

Cement paints are used for decorative purposes to give a matt finish and for improving resistance to rain penetration by choking any fine fissures and blocking wide pores. These paints are suitable for use on porous building materials such as brickwork, stonework, concrete, cement renderings, building blocks, brick and asbestos-cement, but not on metal, timber products, gypsum plaster or bituminous felt. Because they are resistant to the alkali in cement and permit moisture in walls to dry out freely, they are particularly suitable for the immediate decoration of cement products. Recommendations for the use of powder cement paints are given in appropriate standards such as BS 4764. Examples of the usage of cement-based decorative finishes for external aesthetic appearance are depicted in Figure 14.4.

14.4 Chemical cements

Many different types of chemical cement have been produced. A number of the more important ones are highlighted and the chemical aspects of cementation, where known, are discussed. Many of these are proprietary products and details of their manufacture and mode of action are frequently not readily available.[117] Acid–base cements have been discussed in some detail.[118]

14.4.1 MAGNESIUM OXYCHLORIDE (SOREL) CEMENT

Magnesium oxychloride or Sorel cement is made by mixing powdered magnesium oxide (magnesia) with a concentrated solution of magnesium chloride. The principal phases formed are $Mg_3(OH)_5Cl{\cdot}4H_2O$ and $Mg_2(OH)_3Cl{\cdot}4H_2O$. With atmospheric CO_2 attack, two other phases are formed – $Mg_2OHClCO_3{\cdot}H_2O$ and $Mg_5(OH)_2(CO_3)_4{\cdot}4H_2O$. Dissolution of MgO in the $MgCl_2$ solution leads to formation of a gel (setting) and occurs before the crystallisation of the other hydrates takes place. Sorel cements have, for a given porosity, better mechanical strengths than ordinary Portland cements. The bonding mechanism in this cement is similar to that of gypsum cement.[17,119] Sorel cements also have a noteworthy adhesion to salt (sodium chloride).

The key to effective chemical reaction is the quality of the magnesia, which needs to have been produced by consistent, adequate burning. Underburning produces an excessively reactive product and overburning an insufficiently reactive material.

The hydration reactions are complex and can be represented basically as follows:

$$5MgO + MgCl_2 + 13H_2O \rightarrow 2\{Mg_3(OH)_5Cl{\cdot}4H_2O\} \tag{14.12}$$

$$3MgO + MgCl_2 + 11H_2O \rightarrow \{Mg_2(OH)_3Cl{\cdot}4H_2O\} \tag{14.13}$$

$$3MgO + MgCl_2 + 2CO_2 + 7H_2O \rightarrow 2\{Mg_2(OH)_3Cl{\cdot}4H_2O\} \tag{14.14}$$

$$5MgO + 4CO_2 + 5H_2O \rightarrow Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O \quad (14.15)$$

$$Mg_3(OH)_5Cl \cdot 4H_2O + 2CO_2 \rightarrow Mg_2OHClCO_3 \cdot 3H_2O + MgCO_3 + 3H_2O \quad (14.16)$$

$$MgO + MgCl_2 + 2MgCO_3 + 7H_2O \rightarrow 2\{Mg_2OHClCO_3 \cdot 3H_2O\} \quad (14.17)$$

$$Mg_2(OH)_3Cl \cdot 4H_2O + CO_2 \rightarrow Mg_2OHClCO_3 \cdot 3H_2O + 2H_2O \quad (14.18)$$

$$MgO + 4MgCO_3 + 5H_2O \rightarrow Mg_5(OH)_2(CO_3)_4 \cdot 4H_2O \quad (14.19)$$

Resistance to water depends upon the transformation of the hydroxychloride hydrates to the insoluble carbonates and can be improved by the incorporation of certain additives. These additives can be inorganic, such as phosphates, borax and calcium sulfate–silicate mixtures, or organic, such as resins, melamine urea and formaldehyde. Such additions normally cause a slowing down in compressive strength development. Sorel cements have high early strengths and can be used with many different kinds of aggregates in large quantities, such as glass fibres, wood and expanded clays.

Sorel cement has been used on occasions in the CIS, particularly with siliceous and aluminous aggregates, as a refractory oilwell cement at up to 850°C.[120] The principal binder at 300–450°C had been identified as a hydrated magnesium aluminosilicate having the composition $3MgO \cdot Al_2O_3 \cdot 0.5SiO_2 \cdot nH_2O$.

Sorel cements are most commonly employed for industrial flooring, due to their elastic properties and resistance to accumulated static loads. Their main disadvantages are dimensional instability, poor freeze–thaw resistance and lack of resistance to atmospheric agents – they are significantly water soluble and release corrosive solutions.

There have been various developments of Sorel cements. For example, one product consists of Sorel cement with up to 10 per cent of a water-soluble ammonium salt such as ammonium chloride and sometimes also similar quantities of an aminoplast.[121] These additives are included to give the Sorel cement better resistance against magnesium sulfate present in the inflow of water or brine to be sealed and also better setting properties. Another Sorel cement product consists of a stoichiometric mixture of magnesium and calcium oxides, carbonates and sulfates, which is hydrated in chloride-containing waters. This particular cement mix is described as reacting by polymerisation to form a magnesium hydroxy-sulfate/chloride polyhydrate of high compressive strength.[122] A water-resisting Sorel cement was obtained by including a suitable additive containing H_3PO_3 to the $MgO–MgCl_2–H_2O$–fly ash system. This allowed the formation of a stable phase, $5\,Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, together with the insoluble phase $Mg_2P_2O_7$ in the hardened magnesium oxychloride matrix.[123]

14.4.2 MAGNESIUM OXYSULFATE CEMENT

Magnesium oxysulfate cements can be produced by adding magnesium chloride solutions to calcium sulfates or calcium phosphate–sulphate mixtures. The magnesium oxysulfate cements formed can be regarded as variants of Sorel cements. The phosphates, where present, improve the rheological properties of the cement pastes and their water resistance. Alternatively, magnesium oxide can be treated with sulfuric acid to form magnesium oxysulfate cements. The following phases have been identified in the latter instance, depending upon the temperature and pressure conditions.[119]

- $3Mg(OH)_2 \cdot MgSO_4 \cdot 8H_2O$
- $5Mg(OH)_2 \cdot MgSO_4 \cdot 3H_2O$

- $Mg(OH)_2 \cdot MgSO_4 \cdot 5H_2O$
- $Mg(OH)_2 \cdot 2MgSO_4 \cdot 3H_2O$
- $2Mg(OH)_2 \cdot 3MgSO_4 \cdot 5H_2O$
- $MgSO_4 \cdot H_2SO_4 \cdot 3H_2O$
- $3Mg(OH)_2 \cdot MgSO_4 \cdot 4H_2O$.

They give compressive strengths which are comparable to those of Sorel cements.

The main use to date of magnesium oxysulfate cements has been for making lightweight insulating panels.

14.4.3 ZINC OXYCHLORIDE CEMENT

Reaction of zinc oxide with zinc chloride in water gives an extremely hard zinc oxychloride cement product, which (unlike Sorel cement) is not attacked by acids or boiling water. The main hydrated products are two zinc oxychloride hydrates, $4ZnO \cdot ZnCl_2 \cdot 5H_2O$ and $ZnO \cdot ZnCl_2 \cdot 2H_2O$. The former product is very stable and insoluble, but is associated with very poor workability, whilst the latter is not stable in water and can cause excessive solubility and leaching. Since both products are normally formed together, zinc oxychloride cement does not appear to have sufficiently reliable properties to justify practical application.

14.4.4 ALUMINIUM OXYCHLORIDE CEMENT

Aluminium oxychloride dissolves in water to give a very concentrated Al^{3+} solution. Small changes in pH causes a hydrolysis with the formation of alumina gel that binds refractory aggregates:

$$2Al(OH)_2Cl + (n-1)H_2O \rightarrow Al_2O_3 \cdot nH_2O + 2HCl \tag{14.20}$$

The cement can produce a concrete having refractory properties up to 1500°C. During heating, hydrogen chloride is produced, which is corrosive to metals. Despite this problem, aluminium oxychloride cements are becoming more extensively used in ceramics and metallurgy because of their ease of handling. Their detailed properties are not as yet known.

14.4.5 SILICOPHOSPHATE CEMENT

Silicophosphate cement commonly consists of wollastonite powder ($CaSiO_3$) and buffered phosphoric acid. Setting normally takes place within 30 min. A compressive strength of up to 50 MPa is developed within 4 h. Factors affecting strength development are the particle size of wollastonite, the phosphorous pentoxide (P_2O_5) content of the liquid and the liquid/powder ratio.[119] It appears that an acid–crystal surface interaction occurs, which in consequence reduces the apparent surface area of the wollastonite, thus freeing the bonding constituents for matrix development. The cementitious system develops ~30 per cent of its 28-day compressive strength in 2 h. However, the tensile bond strength of silicophosphate cement compared is very poor with conventional concrete substrates, which reduces its potential applicability.[119]

14.4.6 SODIUM HEXAMETAPHOSPHATE CEMENT

Sodium hexametaphosphate $(NaPO_3)_6$ forms very stable bonds with water and yields a high compressive strength of 64 MPa within 24 h at 120°C.[119] Unfortunately, since the shear strength may be as low as 0.5 MPa, the potential for this cement is limited. A solution produced at 25°C mixed with powdered magnesite can be utilised as a mortar for bonding magnesite brick. High-strength mortars are produced with fireclay aggregate.

14.4.7 CALCIUM PHOSPHATE CEMENTS

Various compositions can be considered for formulating calcium phosphate cements. In principle, any combination of at least two calcium phosphates more soluble than hydroxyapatite would allow hardened cement-type products to be obtained under appropriate conditions. Setting normally occurs within *ca.* 8–22 min at 25°C, with final compressive strengths being ~30 MPa. Detailed aspects of the hydration processes are not yet known. Such cements find application in dentistry[124] and in geothermal wells at up to 300°C for resistance to alkali carbonation (Table 14.5).[125,126] Some typical reactions that arise between calcium phosphates in aqueous suspension are as follows:

- calcium dihydrogen phosphate monohydrate to calcium hydrogen phosphate dihydrate (brushite):
$$Ca(H_2PO_4)_2 \cdot H_2O + H_2O \rightarrow CaHPO_4 \cdot 2H_2O + H_2PO_4^- + H^+ \tag{14.21}$$
- brushite to hydroxyapatite:
$$5\{Ca(HPO_4 \cdot 2H_2O\} \rightarrow Ca_5OH(PO_4)_3 + 2H_2PO_4^- + 2H^+ + 9H_2O \tag{14.22}$$
- tricalcium phosphate to hydroxyapatite:
$$1.67\{Ca_3(PO_4)_2\} + H_2O \rightarrow Ca_5OH(PO_4)_3 + 0.33\,H_2PO_4^- + 0.33H^+ \tag{14.23}$$
- hilgenstockite to hydroxyapatite:
$$1.25\{Ca_4O(PO_4)_2\} + 0.5H_2PO_4^- + 0.5H^+ \rightarrow Ca_5OH(PO_4)_3 + 0.25H_2O \tag{14.24}$$
- tricalcium phosphate to brushite:
$$Ca_5(PO_4)_2 + H_2PO_4^- + H^+ + 2H_2O \rightarrow 3CaHPO_4 \cdot 2H_2O \tag{14.25}$$

Calcium phosphate cements can be synthesised by the acid–base reaction between sodium phosphate [NaH_2PO_4 or $(NaPO_3)_n$] as the acid solution and calcium aluminate cement as the base reactant at 25°C. $(NaPO_3)_n$ gave a cement with a 24 h compressive strength of >20 MPa and a porosity of >30 per cent. It also reacted much more than NaH_2PO_4. Sodium phosphates are alternatives as cement-forming solutions to ammonium phosphates, which are considered environmentally questionable.[127]

Lightweight calcium phosphate cement (LCPC) slurries can be prepared from calcium aluminate cement as the base reactant too, with $(NaPO_3)_n$ as the acid reactant and mullite-shelled hollow microspheres as the lightweight additive. Slurries of density 1.12–1.32 g/cm^3 are produced under hydrothermal conditions.[128] Calcium aluminate cements with C_2AS and CA as the major phases gave LCPC slurries of shortened thickening times, whilst those with CA, CA_2 and α-Al_2O_3 as the main phases produced extended thickening times under geothermal well conditions.[129]

14.4.8 ZINC PHOSPHATE CEMENT

Interaction of zinc oxide with orthophosphoric acid gives a cementitious reaction. Setting is rapid and after 5 min neutral zinc phosphate tetrahydrate has already been formed:

$$3ZnO + 2H_3PO_4 + H_2O \rightarrow Zn_3(PO_4)_2 \cdot 4H_2O \quad (14.26)$$

Reaction is rapid for the first 30 min and is practically complete after 1 day. Compressive strengths of *ca.* 75–100 MPa have been obtained. Calcium phosphate cement has been utilised in dental work.[130]

14.4.9 MAGNESIUM PHOSPHATE CEMENTS

Magnesium phosphate cements were developed to satisfy various needs.[131]

- improving the water resistance of Sorel cements;
- production of a high early strength concrete;
- production of a magnesia-based refractory concrete.

Addition of soluble phosphates to Sorel (magnesium oxychloride) cement improves water resistance by the formation of insoluble complexes. This gives rise to aluminium phosphates with a Al_2O_3/H_3PO_4 molecular ratio of 1.1 or 1.4, or to the calcium phosphate hydrates $Ca_5(PO_4)_3OH$ or $CaH_2PO_4 \cdot H_2O$. The phosphate appears to be adsorbed onto the surface of the hydrating grains, forming an insoluble phosphate layer. These phosphates can also precipitate inside the pores, thus limiting water penetration.

Magnesium phosphate cements produced by reacting magnesia with soluble phosphates have improved resistance to water and freeze–thaw cycles and better dimensional stability than Sorel cements. They are quick setting and frequently need retarding. The setting and hardening mechanism appears to be an acid–base reaction that gives rise to a gel, which is followed by crystallisation of this gel into an insoluble phosphate binder.

14.4.10 MAGNESIA-AMMONIUM PHOSPHATE CEMENT

Magnesia–ammonium phosphate cements have been investigated.[132-135] They consist of a powdered mixture of magnesia, monoammonium dihydrogen phosphate ($NH_4H_2PO_4$), sodium tripolyphosphate ($Na_5P_3O_{10}$) and various inert fillers (commonly including sand), which are added to a controlled quantity of water (commonly 12 per cent) and mixed thoroughly to yield a workable cementitious paste. An exothermic reaction takes place after about 2 min, which leads to setting after 10–15 min and hardening after 30–60 min. The reaction mechanism is of the acid–base type that leads to the formation of crystalline magnesium ammonium phosphate hydrates. The main product is struvite ($MgNH_4PO_4 \cdot 6H_2O$) along with three other hydrates, comprising dittmarite ($MgNH_4PO_4 \cdot H_2O$) schertelite ($Mg(NH_4)_2(HPO_4)_2 \cdot 4H_2O$) and stercorite ($NaNH_4HPO_4 \cdot 4H_2O$) also being commonly observed. The chemical reactions are largely complete within 15 min at 20–25°C when setting takes place, but at 0–5°C setting takes up to 200 min. Magnesia is always present in large excess, so that a particle of magnesia provides a core with reaction products forming as a rim. The reaction can be halted through a lack of either phosphate ions or water. Very high compressive strengths have been obtained after 1 h (24 MPa), which are nearly doubled at 24 h (46 MPa). Between 1 and 28 days the compressive strength gradually increases to reach 55 MPa.[132] A borate retarder can be used instead of sodium tripolyphosphate.

The main hydration reactions of magnesia–ammonium phosphate cement can be summarised by the following chemical equations:

$$MgO + 2\{NH_4H_2PO_4\} + 3H_2O \rightarrow Mg(NH_4)_2(H_2PO_4)_2 \cdot 4H_2O \quad (14.27)$$

$$Mg(NH_4)_2(H_2PO_4)_2 \cdot 4H_2O + MgO \rightarrow 2\{MgNH_4PO_4 \cdot H_2O\} + 3H_2O \qquad (14.28)$$

$$Mg(NH_4)_2(H_2PO_4)_2 \cdot 4H_2O + MgO + 7H_2O \rightarrow 2\{MgNH_4PO_4 \cdot 6H_2O\} \qquad (14.29)$$

$$Na_5P_3O_{10} + 5NH_4H_2PO_4 + 22H_2O \rightarrow 5\{NaNH_4HPO_4 \cdot 4H_2O\} + 3H_3PO_4 \qquad (14.30)$$

14.4.11 MAGNESIA–TRIPOLYPHOSPHATE CEMENT

Reaction of ammonium dihydrogen tripolyphosphate $(NH_4)_3H_2P_3O_{10}$ with powdered magnesia produces a high-strength cement (91.0 MPa at 8 days), which can be accounted for by the relatively low porosity of the material. The triphosphate chain remains intact in the hardened cement, when conditions of good heat transfer are employed during curing, giving the major hydration product $Mg_{2-x}(NH_4)_{1+2x}P_3O_{10} \cdot nH_2O$. Under curing conditions of poor heat transfer there is some decomposition of the triphosphate chain, yielding small amounts of orthophosphates such as struvite ($MgNH_4PO_4 \cdot 6H_2O$) and also pyrophosphate ($P_2O_7^{4-}$). Like magnesia–ammonium phosphate cement, the reaction mechanism involves simple acid–base reactions of the ammonium hydrogenphosphate with magnesia, as well as precipitation reactions caused by the extremely low solubilities of the magnesium ammonium phosphates in water.[136]

14.4.12 MAGNESIA-TYPE CEMENTS

Periclase (MgO) cement can hydrate and form magnesia gel as well as crystalline brucite $[Mg(OH)_2]$. Hydration begins from the surfaces of the cement particles. By this means, the voids and pores are blocked and segmented with the hydration product.[117,137,137(a),138] Through this process, the whole structure is densified and strengthened. The basic cementitious reaction is

$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (14.31)$$

Related to periclase cement is high-lime magnesiochrome cement, which finds application in refractories.[139,140] This particular cement is based upon periclase plus calcium chromate–chromite, a complex mineral produced by the combination of lime with chromic oxide (Cr_2O_3) in an oxidising atmosphere. Hydration is normally performed with a 30 per cent aqueous solution of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) solution at 8 per cent by weight of the cement. The reaction mechanism basically resembles that of periclase cement. However, the products formed are more complex. As well as hydrates they also consist of carbonates, which are formed by the effects of carbonation. The typical products formed can comprise brucite $[Mg(OH)_2]$, magnesium oxychloride $[Mg(OH)Cl]$, calcium chromate dihydrate ($CaCrO_4 \cdot 2H_2O$), calcium monochromite ($CaCr_2O_4$), portlandite $[Ca(OH)_2]$, secondary magnesium carbonate ($MgCO_3$), secondary calcium carbonate ($CaCO_3$) and mixed calcium magnesium carbonates $[(Ca,Mg)CO_3]$.

14.4.13 ALUMINOSILICATE CEMENTS

Aluminosilicate cements are produced by mixing a glass based upon silica and alumina with a phosphoric acid solution. The glass is made by quenching a melt of alumina, silica and a fluorite or sodium carbonate flux. Setting and hardening occur rapidly, setting usually taking only 2–4 min. The reaction mechanism involves dissolution and precipitation.[131] Al^{3+} and Ca^{2+} ions are released from the glass and combine with the ions in solution to precipitate as solid phosphates together with metal fluorides. The main application is in dentistry. Use of these cements is restricted because of a lack of consistency in setting and hardening, poor adhesion, high shrinkage and, unlike some of the cements previously described, relatively poor compressive strengths (16–20 MPa).

Calcium aluminate glass cements have been reviewed.[141]

14.4.14 IONIC POLYMER CEMENTS

Ionic polymer cements are based upon reaction of a solution of a polyalkenoid carboxylic acid (usually 50 per cent polyacrylic acid), metal powder (often zinc), silicoaluminate (commonly a glass) and mineral. Cements containing glass are known as glass ionomer cements. Reaction proceeds via an acid–base mechanism to give an ionic bonded product such as zinc polyacrylate. The reactions between glass and polyacrylic acid are more complicated because they lead to a system containing a glassy part surrounded by a gel (ionic bond) in a matrix formed by covalent C–C bonds. Here the initial stage consists of the release into solution of alumina gel, Ca^{2+}, Na^{+} and F^{-} ions, together with the ionisation of the carboxylic acid. The setting time corresponds to the formation of calcium polyacrylate; the aluminium ions react more slowly.[131]

The setting mechanism of glass ionomer cement can be understood on the following basis.[142] The glass powder, polyacid and tartaric acid solution are mixed. The polyacid dissolves in the solution and ionises:

$$\text{—COOH} \rightarrow \text{—COO}^- + H^+ \tag{14.32}$$

H^+ ions exchange for both Ca^{2+} and Al^{3+} ions in the glass. These ions then form salt bridges with the polyacid:

$$2\text{—COO}^- + Ca^{2+} \rightarrow \text{—COO—Ca—OOC—} \tag{14.33}$$

giving a three-dimensional glass–polycarboxylate gel composite material. Glass particles as well as hydrated calcium and aluminium polycarboxylate (like polyacrylate) are contained in the hardened cement matrix.

Later developments of glass ionomer cements have included the glass polyphosphonate cements produced from poly(vinylphosphonic acid) and glasses of reduced basicity. These give compressive strengths of up to 200 N/mm^2 and acceptable working and setting times, easily satisfying the requirements for dental glass ionomer cements as given in the standards ISO 7489 and BS 6039.[144]

Glass ionomer cements have been superseding aluminosilicate cements in dental applications because of their superior adhesion. They are also used as splinting materials.

14.4.15 ORGANO-MINERAL CEMENTS

Organo-mineral cements are hard, brittle materials produced by reacting alkali silicates with isocyanates. Such materials are used as watertighters in mining. Normally, water glass is mixed with a diphenylmethanediisocyanate (DMDI) to give an emulsion, which hardens to form a two-phase resin. The details of the setting reaction are complex and involve reactions with both water and carbon dioxide.[143] Water enters the organic phase by diffusion and reacts with the isocyanate to give a polyisocyanate resin and carbon dioxide. OH^- ions from the alkaline silicate (water glass) act as a catalyst for this reaction. Carbon dioxide enters the inorganic phase by diffusion and reacts there with the water glass to yield a polysilicate gel and various carbonates and hydrogen carbonates of alkaline and alkaline earth metals, such as $Na_2CO_3 \cdot H_2O$, $Na_2CO_3 \cdot 7H_2O$, $NaHCO_3$ and $Na_3H(CO_3)_2 \cdot 2H_2O$ from the Na^+ ions.

Different distributions of the solid phases in the polysilicate gel can be generated according to the degree of dispersion of the components. Hence both the type of reacting components and their mixing determine the precise properties of the resulting organo-mineral cements. For example, setting times can vary from a few seconds to several weeks. Compressive strengths of the pure hardened cements can reach 30 MPa and flexural strengths 10 MPa.

14.4.16 WATERLESS CEMENTS

Waterless cements are obtained by the chemical reaction of polyelectrolytic resins (like polyacrylic acid) containing 25 per cent solids with a metal oxide (ZnO):

$$ZnO + H_2p \rightarrow Zn \cdot p + H_2O \qquad (14.34)$$

There is a very rapid rate of hardening, with optimal compressive strengths of ~60 MPa being achieved after 24 h and 95 MPa after 5 days at 100 per cent relative humidity. The term 'waterless' refers to the fact that no water is needed to achieve hardening. Water is in fact released during the hardening process. The functional groups of the polymer become bonded to the metal, with water being a by-product, producing a highly crosslinked and strong material at ambient temperature.[145] Possible applications lie in dentistry and bioceramics.

Another 'waterless' cement binding reaction is that of calcium monohydrogenphosphate with tetracalcium oxydiphosphate.[146]

$$CaHPO_4 + Ca_4(PO_4)_2O \xrightarrow{H_2O} Ca_5(PO_4)_3OH \qquad (14.35)$$

This reaction is an acid–base type, which is really

$$H^+ + O^{2-} \rightarrow OH^- \qquad (14.36)$$

There is no actual uptake of water during the course of this reaction, even though the reactants are present in an aqueous medium. Hence the reaction can be described as 'waterless'.

14.4.17 BORATE CEMENTS

Boric oxide (B_2O_3) forms hydrolytically unstable cements with polyacrylic and phosphonic acids, which are quick-setting [1–5 min with poly(vinylphosphonic acid)].[118] Since B_2O_3 is acidic, an acid-base reaction does not take place. It was considered that cement formation arose through the formation of hydrogen-bonded complexes rather than by salt formation.[118,147]

However, in connection with binding for consolidation of sandstone rock formations, solution systems involving certain borates such as potassium tetraborate ($K_2B_4O_7 \cdot 4H_2O$) and disodium octaborate tetrahydrate ($Na_2B_8O_{13} \cdot 4H_2O$) mixed with calcium chloride produced hydrated calcium borate systems of comparable compressive strengths to that produced by calcium silicate hydrate (C-S-H) under similar conditions.[148] Unlike the C-S-H, the hydrated calcium borates were well crystalline. The strong bonding observed here for the hydrated calcium borates appeared to be due to the 'spider's web effect' of extensive three-dimensional hydrogen bonding in all directions within the hydrated calcium borate structures.[149]

14.5 Special Portland-type and other cements

Various special Portland-type and other cements exist which do not fit into the commonly defined categories of cements. These cements are briefly described in this section.

14.5.1 NON-CALCAREOUS AND NON-SILICEOUS PORTLAND-STYLE CEMENTS

Cements can be produced in which calcium is replaced by strontium or barium and silicon by germanium, tin or lead. Calcium cannot be so replaced by magnesium because the magnesium silicates and aluminates have no intrinsic hydraulic binding power in the presence of water, nor can silicon be replaced by titanium for similar reasons. The hydration products of the strontium and barium silicates and aluminates have good binding power. Good compressive strengths are given and sulfate resistance is generally better than for ordinary Portland cements, but hydration is less easily controlled.[150-154] Tri- and dicalcium germanates undergo hydration to form calcium germanate hydrate (C-G-H) which has a strong binding power like the calcium silicate hydrate C-S-H.[148,155-157] Calcium stannates and plumbates also possess hydraulic activity. Calcium selenate can regulate setting in lieu of calcium sulfate.

Such cements have tended to be primarily experimental because of their high cost as well as the dearth of suitable raw material sources. The main interest to date has lain with strontium and barium cements for refractory concrete, and with barium cements for radioactive shielding. On economic grounds the barium cements offer more attraction than the strontium ones, although they are prone to quick setting. Despite the excellent binding power of C-G-H, this material is unlikely to find practical application in view of its expense and lack of general availability. Calcium selenate is likely to be too expensive as well as too toxic to offer any practical advantages over calcium sulfate.

14.5.2 NON-GYPSEOUS PORTLAND CEMENT

The use of gypsum as a regulator for the smooth setting of Portland cement has occurred for so long that in most standards its inclusion is accepted as part of the basic definition of Portland cement. Possible alternatives to the use of gypsum as a set regulator in Portland cement, such as calcium lignosulfonate–sodium hydrogencarbonate mixtures, have been advocated.[158-161] Since the flow behaviour and high water demand of ordinary Portland cement is largely a function of the state of flocculation induced by the gypsum, replacement by a suitable alternative could give beneficial properties to the cement.

The possibility of combining a water-reducing retarder like calcium lignosulfonate with an accelerator such as sodium hydrogencarbonate into an alternative system, both to disperse the ground clinker and to regulate the set of gypsum-free Portland cement, has been investigated. As well as regulating the set and effective dispersion, which considerably reduces water demand, there is very rapid early hydration and strength gain. Also, the character of the hydration products is different. The elongated calcium silicate hydrate gel particles, which are prominent in the usual early-stage Portland cement paste hydration products, are almost completely missing, and the calcium silicate hydrate gel which develops consists of more or less equidimensional particles that rapidly fill the limited space available. The microstructure becomes effectively massive when viewed by scanning electron microscopy after about 2 days. Naturally, no ettringite is produced and no analogues of this material appear to be developed. This cement can hydrate by itself without calcium chloride additions below 0°C (such as at -20°C) and to set and harden acceptably.

Another development is the ground Portland clinker-poly(phenol sulfonate)-alkali metal salt system.[162] The sulfonated product of condensation of phenols with formaldehyde [known as poly(phenol sulfonate)] reacts synergistically with the alkali metal carbonate (or hydrogencarbonate, or silicate) as a strong liquefying system in a suspension of Portland clinker. The liquefying effect of the poly(phenol sulfonate)-carbonate system permits the preparation of cement suspensions that possess practically Newtonian behaviour without yield value at low water/cement ratios (0.20 or less). The synergistic influence of the poly(phenol sulfonate)-carbonate system substitutes for the setting or thickening regulation of gypsum. The ground Portland clinker (specific surface area 250–700 m^2/kg)-poly(phenol sulfonate)-alkali metal carbonate cement differs from conventional Portland cement in giving good rheological behaviour at low water/cement ratios, good compressive strength development (20–40 MPa at 4–5 h, 60–100 MPa at 24 h), the ability to set and harden at low temperatures below 0°C, a rapid rise in compressive strength during short time intervals with elevated external temperatures (steam curing), and high resistance to aggressive media and high temperatures. The microstructure of the hardened pastes is differentiated from that of conventional Portland cement pastes by a high compactness and by the absence of characteristic portlandite (calcium hydroxide) crystals.

Gypsum-free Portland cements (clinker surface area 300–700 m^2/kg) attain compressive strengths of 1–9 MPa after 1–3 h at water/cement ratios of 0.20–0.25. They are composed of crystalline and amorphous material with C/S = 1–5 and C/A = 10–50. At 12–24 h a dense structure is developed which does not alter morphologically, even though the paste strength increases to 100 MPa or more at 28 days. The main binder in this dense structure is a high-lime C-S-H (C/S $\sim$ 2.7) intergrown with very fine $Ca(OH)_2$ and highly dispersed cubic and hexagonal hydroaluminates.[161] Gypsum-free Portland cement made from Portland clinker ground to 300 m^2/kg mixed with a phenol-poly(ethylene oxide) oligomer plasticiser in water gave compressive strengths of 5.3 MPa at 3 days and 54.5 MPa at 28 days in the absence of alkali carbonate.[163]

Gypsum-free slag cement (GFS) is based upon ground granulated blastfurnace slag (300–500 m^2/kg surface area), plasticiser and an alkaline component (hydroxide or silicate).[161] Hardened GFS pastes (water/cement = 0.24–0.26) give compressive strengths at 28 days of 50–90 MPa and > 100 MPa at 180 days. The dense microstructure of these hardened pastes contain C-S-H (low lime) intergrown with highly dispersed hydroaluminates and hydroaluminosilicates. Calcium hydroxide was not detected.

14.5.3 ALINITE CEMENT

The incorporation of calcium chloride in the raw material mixture for Portland clinker production by utilising molten salt technology, has enabled the temperature of clinker formation to be reduced by 400–500°C. This clinker contains alinite, a structural leitmotif of alite (tricalcium silicate) incorporating chloride ions.[132,164,165] The quantitative content by weight of the mineral phases present in alinite clinker varies within the following limits: alinite 60–80 per cent, belite (β-dicalcium silicate) 10–30 per cent, calcium chloroaluminate (Ca_6AlO_7Cl) 5–10 per cent, dicalcium ferrite 2–10 per cent. Weak Ca–Cl bonds are developed which result in alinite clinker being softer than alite and requiring less energy for grinding. Gypsum addition is reported[166] to intensify strength development rather than principally functioning as a regulator of set.

Alinite has also been produced by clinkering steel plant wastes such as fly ash from an in-house power generating plant, limestone fines, mill scale and magnesite dust with calcium chloride as a sintering aid at 1150°C.[167] The optimum calcium chloride addition to the raw mix was found to be 7–8 per cent by weight. These cements have been found to be relatively insensitive to the various impurities in the raw mix and can tolerate higher levels of MgO than Portland cements. This low-temperature clinkering route offers scope for the conversion of industrial wastes into hydraulically setting cements. Alinite cement is compatible with Portland cement and additions of 20 per cent by weight of fly ash can be satisfactorily accommodated. Alinite is stable in impure systems with different elements, but is unstable in the pure system $CaO{-}SiO_2{-}Al_2O_3{-}CaCl_2$. Typical alinite clinker contains alinite (65 per cent), belite (20 per cent), mayenite ($C_{11}A_7{\cdot}CaCl_2$; 10 per cent) and C_4AF (5 per cent).[168] Alinite was ascribed the formulation $Ca_{21}Mg[Si_{0.75}Al_{0.25}O_4]_8O_4Cl_2$. The presence of magnesia appears to be essential for alinite formation.[169] Jasmundite $[Ca_{22}(SiO_4)_8O_4S_2]$, which has S^{2-} instead of Cl^- ions in the crystal lattice, is poorly hydraulic.[170] Later work showed alinite not to have a fixed composition and to be best represented as $Ca_{10}Mg_{1-(x/2)}\square_{x/2}[(SiO_4)_{3+x}(AlO_4)_{1-x}O_2Cl]$ where $0.35 < x < 0.45$ and $\square$ refers to a lattice vacancy.[171] Alinite cement has high early strength properties. The main hydration products of alinite cements are calcium silicate hydrates that appear to incorporate the chloride, which are morphologically different from the poorly crystalline calcium silicate hydrate (C-S-H) found during normal Portland cement hydration below ~100°C. The presence of labile chloride could in theory encourage corrosion of steel reinforcement, but current experimental evidence on this aspect is conflicting. As well as C-S-H, hydration produces calcium hydroxide and an AFm phase $C_3A{\cdot}CaY_2{\cdot}10H_2O$ ($Y = Cl^-, OH^-, \frac{1}{2}CO_3{}^{2-}$), but microprobe analysis could not positively identify Cl^- ions incorporated in the C-S-H gel. Hydration of alinites with different Si/Al ratios has shown no significant differences in hydraulic activity, because of the high degree to which small amounts of free chloride accelerate hydration. Bromide-alinite, in which bromide ions replace chloride, has been made. However, its hydraulic activity has not yet been reported.[172]

Calcium silicate sulfate chloride $[Ca_4(SiO_4)(SO_4)Cl_2]$, a derivative of alinite having an orthorhombic structure,[173] is formed at only *ca.* 600–800°C. It has appreciable hydraulic activity,[174] greater than that of belite. Compressive strengths of 25 MPa at 28 days have been found.[174]

14.5.4 BELINITE CEMENT

Belinite $[Ca_8Mg(SiO_4)_4Cl_2]$ has been synthesised from a calcium chloride melt containing magnesia. Unlike alinite, its hydraulic behaviour is relatively poor and comparable with that of belite β-dicalcium silicate.[175,176]

14.5.5 BELITE CEMENT

Cements based upon mixtures of Portland cement and belite (β-dicalcium silicate) produced by the alkaline sintering of alumina-containing raw materials are manufactured in the CIS.[177] Such cements normally give high later strengths at moderate alkali contents, due to the slower rate of C-S-H formation from belite in comparison with that formed from alite (tricalcium silicate). They are employed as low-heat cements and give increased impermeability to water in concrete as a result of their large belite contents hydrating at slower rates than alite.

A more reactive dicalcium silicate (containing 5 per cent SO_3) has been produced at 750°C from the mineral spongolith and calcium nitrate.[178] Incorporation of SO_4^{2-} ions accelerates the formation of C-S-H in a relative sense. However, such formation is still much slower than that from alite in conventional Portland cements.

14.5.6 HIGH EARLY STRENGTH CEMENTS

Clinkers with high alite (75–95 per cent) and low belite (5–12 per cent) contents have been produced using less energy by lowering the clinkering temperature by ~200°C. This has been achieved by partially substituting the aluminate and ferrite phases of conventional Portland clinker by CaF_2–$CaSO_4$–CaO and SiO_2.[179] When ground with gypsum to produce a cement, high early strength properties are observed.

Additions of calcium fluoride or another suitable mineraliser containing fluoride and calcium sulfate or mixtures of calcium sulfate and alkali metal sulfate, when made to a normal Portland cement raw mix such that part or all of the fluoride and sulfate components are retained within the clinker, give rise to a cement that has enhanced early and late compressive strength when ground to specific surface areas similar to those of normal Portland cements.[180] This high strength may be the result of the combined mineralising action of both the fluoride and sulfate additions leading to the formation of alite crystals of increased hydraulic activity. Enhanced C-S-H formation is observed during early hydration of this special type of Portland cement.

For example, if a slurry of calcium aluminate (high-alumina) cement is mixed with another slurry containing anhydrite and/or gypsum, lime, bentonite and lithium carbonate (accelerator), reaction is brisk and ettringite is a major hydration product:

$$CaAl_2O_4 + 2Ca(OH)_2 + 3CaSO_4 + 30H_2O \rightarrow Ca_6[Al(OH)_6]_2(SO_4)_3 \cdot 26H_2O \tag{14.37}$$

An ultra-rapid hardening cement clinker, consisting of alite, calcium fluoroaluminate ($11CaO \cdot 7Al_2O_3 \cdot CaF_2$) and the ferrite phase, has also been produced.[181] This also gives rise to enhanced C-S-H formation.

Portland cement containing an aluminous clinker with $C_{12}A_7$ improves early compressive strength. The incorporation of accelerators and/or retarders allows a rapidly setting and hardening cement that produces concretes having an acceptable early strength but, at the same time, having a setting time which is controllable even in the presence of contaminants.[182] This cement possesses a composition similar to that of certain expansive cements (see below) and, indeed, upon hydration does undergo some expansion. It acts as a bonding agent in the agglomeration of ores and foundry sands, or where cement slurries have to be pumped for soil stabilisation, or in coal mines where coal measures are employed as aggregates. So far this cement has not been applied in any well cementing situation. During hydration, products such as C-S-H and ettringite from the Portland cement component and calcium aluminate hydrates from the aluminous component are formed. Various ettringite-based mine cements exist, which have rapid setting and early strength development.[183]

Another type of high early strength cement is the proprietary alkali-activated aluminosilicate cement known as Pyrament. Pyrament cement is reported to be an alkali-activated blended Portland–pozzolanic cement containing organic retarder and water reducer.[141]

14.5.7 MICROFINE CEMENTS

Commercial microfine cements were developed in Japan for grouting, after organic grouts had been banned in 1974. (Grouts are materials – including neat cement – injected into a soil or rock formation to change the physical characteristics of the formation.[184]) Microfine cements are produced in classifiers or by ultrafine grinding in a cement mill to a high surface area, commonly 600 m^2/kg or above. They work on the principle that the more finely ground the cement, the greater is the penetrability. A penetrability comparable to that of chemical grouts can be achieved. Microfine cements can be of Portland cement or Portland cement-extender mixes, where the commonest extender used is ground granulated blastfurnace slag. Injection of cement grout under pressure is sometimes used for sealing contraction joints in mass concrete structures such as domes, for repairing cracks in concrete and for tightening water-retaining structures. In use for grouting, the microfine cement is commonly batch-mixed with water and a dispersant or in a two-component mix with sodium silicate in the second tank. With a given commercial microfine cement, the batch system has produced setting times of *ca.* 4–5 h and the two-component mix very rapid setting times of 1–3 min.[184] Microfine cements are increasingly being used in oilwell cementing squeeze repair jobs.[19]

14.5.8 PORTLAND POLYMER CEMENTS

High-strength cements can be obtained when suitable polymers or fibres are incorporated in the Portland cement matrix, by modification of the stress field. Flexural strength in particular is increased considerably. Polymers used for this purpose include those of methyl methacrylate, styrene, vinyl acetate, styrene–acrylonitrile, chlorostyrene, vinyl chloride and polyester–styrene. Mechanical properties and durability are normally improved. These polymers supplement the effect of the Portland cement and do not replace it. Most are attacked by strong alkalis, but some (such as polyester–styrene) give high resistance to strong acids. The fibres used include zirconia glass, asbestos, polyamide (Kevlar), polypropylene, carbon, alumina filament, steel, bamboo and a range of vegetable fibres such as sisal, jute, coir, akwara and elephant grass.[119] Glass fibre-reinforced cement has been extensively discussed.[128]

The mechanical strengthening of Portland polymer cements has been suggested as being primarily due to pore filling by the polymer, which acts as a continuous, randomly orientated reinforcing network. In addition, the polymer also appears to enter into some type of interaction with the hydrated cement and form stable bonds. These largely determine the strength and durability properties of the polymer–cement composites. Such interaction is readily apparent when an ionic monomer such as *p*-vinylsulfonic acid (25 per cent aqueous solution) is added at a monomer level of ~12 per cent to the dry cement and polymerised *in situ* at ambient temperature. This results in decreased porosity and increased fluidity of the material.[185]

The mechanism of interaction of three latex polymer systems [a styrene acrylate, a styrene acrylate with a coupling agent and a poly(vinylidene chloride)] with the hydration products of Portland cement have been investigated by examining the squeezed-out pore solutions from the cement pastes.[186] Interaction was shown to occur between the polymers and Ca^{2+}, SO_4^{2-} and OH^- ions released by the cement during hydration. Initiation for the acrylic-based polymer systems appears to arise through alkaline hydrolysis of the carboxylate groups of the polymers, in which the carbonyl radicals effectively catch the Ca^{2+} ions from the liquid phase of the cement pastes, whilst SO_4^{2-} ions become trapped in the latter. For the poly(vinylidene chloride)-modified pastes, interaction results from dehydrochlorination of the polymer, in which certain species of the broken-down polymer catch the Ca^{2+} ions from solution. However, dosages of 5 per cent or more (v/v of cement composite) poly(vinylidene chloride) could release sufficient Cl^- ions to exceed the tolerable corrosion limits in reinforced concrete.[186]

One noteworthy example of a polymer cement is the so-called macro-defect-free (MDF) cement paste, which is prepared at very low water/cement ratios in the range 0.08–0.20.[187 190] A typical composition of this is 100 parts by weight of Portland or calcium aluminate cement, 0.7 parts of silica powder (0.04 μm) and 16.5 parts of an aqueous solution containing 3.5 parts of polymer [polyacrylamide, hydroxypropylmethylcellulose or hydrolysed poly(vinyl acetate)], which gives a flexural strength of 60 MPa and a compressive strength of 200 MPa. This material has applications in the ceramics field.

Another development to date has involved producing a composite of Portland cement, condensed silica fume (csf) and a superplasticiser for obtaining products of high strength, low permeability and low bulk density.[191] Condensed silica fume has microfiller and pozzolanic effects, whilst the superplasticiser (sulfonated melamine– or naphthalene–formaldehyde condensate) is an effective water reducer, giving water/solid ratios of $\leqslant 0.20$. The hydrated composite has already found some applications as a ceramic and as an asbestos substitute. Cement-based matrices reinforced by randomly dispersed carbon or steel microfibre are generally outperformed when 18 per cent (by weight of cement) microsilica is included.[192]

Cement–zeolite composites can also produce high strengths. Although the strength of a Portland cement–zeolite composite was found to be lower than that of the Portland cement alone at zeolite additions of < 50 per cent, above this level there was a large increase in structural formation and strength gain, which was attributed to the high surface activity of the zeolite.[193]

14.5.9 EXPANSIVE CEMENTS

Expansive cements are usually based upon Portland cement with an expansive component. They expand slightly during the first few days of hydration and can be used to compensate for the effects of shrinkage in normal Portland cement concrete, which is useful for underpinning or other types of repair work, and in the production of chemically prestressed concrete, where the expansion of the cement is utilised to stress the reinforcement.[46] Such a cement has also been employed experimentally to cement over a cavernous vug in a well,[17] but there has been little commercial application to well cementing operations. Expansions of up to 5 per cent under controlled conditions can be given.

There are a number of different types of expansive cement,[131] the most familiar of which are outlined below. Type K expansive cement is commonly produced by intergrinding ordinary Portland cement clinker, an expansive clinker containing kleinite ($3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$) and either gypsum or an anhydrite–gypsum mixture. As well as kleinite, the expansive clinker generally contains alite, belite, ferrite and anhydrite plus some free lime, and is made by sintering limestone, various alumina-containing materials and gypsum at temperatures not exceeding 1300°C in rotary kilns.

Not all sulfoaluminate cements containing kleinite are expansive. Other properties, such as rapid hardening and high early (1–3 days) and late (28 days) compressive strength may be the desired purpose. A mixture of limestone, gypsum, bauxite, silica sand and iron-rich industrial by-product raw meal (in carefully selected proportions) which was sintered at 1280°C and ground to 3700 cm^2/g, with no gypsum being ground in, gave such a cement.[194]

Type M expansive cement is based upon addition of aluminous cement or aluminous slag plus lime to Portland cement.

Type S expansive cement is made from Portland cement clinker with a high C_3A content. This cement has so far found a more limited application than the other two types because of the difficulty of steadily controlling the rate of formation of ettringite from tricalcium aluminate. Ettringite forms very rapidly from C_3A at early hydration times and then the reaction slows down to a very low rate. Even after 7 days, the unreacted tricalcium aluminate content is still appreciable.

At early ages the kleinite phase hydrates more rapidly than the tricalcium aluminate. The reaction rate normally remains relatively high until depletion has taken place.

Calcium sulfoaluminate cements can be produced from industrial by-products such as phosphogypsum, bauxite fines, in pulverised fly ash and ground granulated blastfurnace slag producing the components of these cements, which, when mixed in the proportions $C_4A_3\bar{S}/\beta\text{-}C_2S/C\bar{S}$ of 1.5:1:1 by weight, have given products of acceptable compressive strengths after 1 day and 28 days.[195,196] Shrinkage-compensating cements can contain a prehydrated calcium aluminate (high-alumina) cement-based expansive additive, in which appropriate admixtures can be employed, either to reduce or to increase expansion as desired.[197]

Other types of expansive cement composition contain calcium oxide or even magnesium oxide as the expansive component. The calcium oxide can be obtained by sintering a limestone, clay and anhydrite mixture. This expansive phase contains alite, free lime and some residual anhydrite, and is interground with the ordinary Portland cement clinker. The calcium oxide occurs largely as inclusions in the alite grains and undergoes hydration more slowly as the alite hydrates, resulting in controlled expansive properties.

For temperatures up to 200°C, compositions with slags and silica additions have been proposed.[198] The expansivity of the reaction

$$3CaO\cdot 3Al_2O_3\cdot CaSO_4 + 8CaSO_4 + 6CaO + 96H_2O \rightarrow 3\{Ca_6[Al(OH)_6]_2(SO_4)_3\cdot 26H_2O\} \tag{14.38}$$

is probably due to negatively charged colloidal grains of ettringite with a high specific surface area being formed by a through-solution mechanism; they attract the polar water molecules that surround the crystals, and cause interparticle (perhaps double layer-type) repulsion, which results in overall expansion of the system. Other hypotheses consider expansion to be caused by local transformation of anhydrous phases into hydrates.[46]

14.5.10 HYDROGARNET-TYPE CEMENTS

A synthetic hydrogarnet of composition $3CaO\cdot Al_2O_3\cdot 1.6SiO_2\cdot 2.8H_2O$ was produced by heating a small quantity of water glass with two slags, one containing 25–50 per cent $CaO\cdot 2Al_2O_3$ and the other ~80 per cent $\gamma\text{-}Ca_2SiO_4$ at 100–250°C and 50 MPa pressure for 7 days. A 0.16 water/hydrogarnet mix has been found to be a composition with 27 per cent porosity and a 7-day compressive strength of 126 MPa.[199]

A low water level is necessary to achieve high-strength properties. The cementing properties are very dependent upon the SiO_2/Al_2O_3 ratio; being better at higher silica levels.

Hydrogarnet–gehlenite hydrate cements can be made from hydration (at a water/cement ratio of 0.3–0.4) of calcium aluminosilicate glasses containing 45–55 per cent CaO, 12–26 per cent SiO_2 and 22–40 per cent Al_2O_3.[200] These glasses were ground to an average particle size of *ca.* 10–15 μm and a uniform specific surface area of 350–500 m^2/kg and cured without activators. At low (< 15 per cent) SiO_2 levels, hydrogarnet (C_3AS_3–C_3AH_6 solid solution) was the dominant phase, whilst at higher (> 20 per cent) SiO_2, gehlenite hydrate (C_2ASH_8) predominated. The hydration mechanism involved simultaneous precipitation of the intergranular material to gehlenite hydrate. This can be contrasted with the through-solution mechanism postulated for calcium aluminate (high-alumina) cements. The predominantly hydrogarnet cements had moderate compressive strengths (*ca.* 79–100 MPa), high porosities (20–30 per cent) and excellent chemical and thermal stability, whilst the predominantly gehlenite hydrate cements had high compressive strengths (*ca.* 110–136 MPa), low porosities (1–10 per cent) and instability above 100°C.

14.5.11 HYDROPHOBIC PORTLAND CEMENTS

Hydrophobic Portland cement generally consists of a finely ground Portland cement with a suitable hydrophobic agent such as stearic, oleic or naphthenic acid in small quantities (~0.5 per cent). These hydrophobic agents coat the cement particles and entrain ~1 per cent additional air. They impart a high level of protection to the cement against premature hydration from atmospheric moisture. This is useful when adverse storage conditions are present, which would be unsatisfactory for normal Portland cements. Indeed, hydrophobic cements are used where protection against deterioration during storage is required.[201,202]

Hydrophobic cements are mainly manufactured in the CIS, although some are made from time to time in other countries such as the UK where they have been produced to comply with BS 12 requirements for Portland cement. Such cement has been used in the Falkland Islands, when large-scale construction started in 1982, and there were no covered storage facilities initially for the cement in a cold, damp climate. CIS standards specify the use of 0.08–0.1 per cent oleic acid, 0.1–0.12 per cent naphthenic acids ($C_nH_{2n-1}CO_2H$, where $n = 8$–13) derived from certain crude oils, or 0.2–0.25 per cent soap naphtha derived from the alkali treatment of the oils and containing 50 per cent water.

The main problem with using hydrophobic cement is workability, since the hydrophobic seal is not always readily broken during mixing with water. Desirably low water/cement ratios for structures may not always be practically possible. The hydrophobic agent may itself cause some retardation of hydration. Nevertheless it should normally be possible to produce hardened cement in concrete structures satisfying the requirements of Portland cement standards like BS 12. Hydrophobic Portland cement is often produced to rapid-hardening cement fineness.

Waterproofed or water-repellent Portland cement is sometimes defined separately from a hydrophobic Portland cement as ordinary Portland cement that contains a small quantity of metal (usually calcium) stearate, oleate, naphthenate or laurate, or of a non-saponifiable oil, which has been added during grinding. This cement is used where moist or humid conditions would cause ordinary Portland cement to deteriorate significantly before mixing with water, as in changing rooms of sports clubs. Usually only ~1 per cent of additional air is entrained under normal usage conditions. This cement assists in increasing the water-repellent properties of concrete and renderings by reducing their porosity.

Hydrophobic calcium aluminate cements have also been produced.[202,203]

14.5.12 FERRITE CEMENT

Ferrite cements are produced from the raw materials bauxite, limestone and magnetite to compositions such as $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ or $6CaO \cdot Al_2O_3 \cdot 2Fe_2O_3$ by sintering in furnaces at 1300°C or above. Hydration at 20°C using a water/cement ratio of 0.25 was found to be ~50 per cent complete at 28 days.[204] The main hydration products were

$Ca_2[(Al,Fe)(OH)_5]_2 \cdot 3H_2O$ and $Ca_3[(Al,Fe)(OH)_6]_2$, similar to the materials formed in calcium aluminate cement hydration.[205] Increasing the temperature from 20 to 60°C raised the chemical reactivity and $Ca_3[(Al,Fe)(OH)_6]_2$ became the main hydration product. The compressive strength of $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ after 7 days hydration increased from 37 MPa at 20°C to 74 MPa at 60°C. C_4AF compositions showed a greater reactivity than C_6AF_2 ones. Additions of triethanolamine and sodium carbonate have been found to accelerate the hydration process and the development of compressive strength.

Ferrite cements find use at present as binders in the production of iron ore pellets and compacts. No information is readily available on the long-term durability of these cements.

14.5.13 THERMOPLASTIC CEMENT

If elemental sulfur is heated above 160°C, the melt consists of an equilibrium mixture of long-chain sulfur molecules (some containing up to 1 million sulfur atoms) and short-chain cyclic molecules. Should the melt be chilled to ambient temperature, 'plastic sulfur' is obtained. This consists of long-chain molecules plasticised by the low molecular weight material. The rapid embrittlement of this is caused by the loss of the plasticiser by crystallisation of the low molecular weight material to orthorhombic sulfur. This embrittlement has not yet been reliably controlled. However, there are methods of controlling the crystallisation of sulfur. These have been employed for making new chemically resistant concretes and surface coatings. Hence, whereas elemental sulfur cooled from the melt (below 160°C) gives monoclinic and then orthorhombic sulfur, the formation of which is complete in about 1 day, sulfur containing about 5 per cent (with water) of suitable additives, such as dicyclopentadiene, frequently shows no formation of macrocrystalline orthorhombic sulfur even after 5 years. This technique has been used to make a thermoplastic cement for impregnating Portland cement concrete by casing in moulds in a liquid form at 120–130°C. It gives very good mechanical properties (compressive strength ~50 MPa) and good chemical resistance to acids and oils, but poor resistance to alkalis.[119,131,206] Sulfur can itself bind aggregates upon cooling below the melting point of sulfur (119°C for yellow sulfur), by solidifying and binding the aggregate. It replaces the cement and water components of a regular Portland cement concrete mix.[207,208]

14.6 Conclusion

A wide range of cements that have specialist applications has been surveyed and their advantages and disadvantages discussed where appropriate. The use of special cements will clearly grow in the future in regard to optimising cementing performance for particular operations.[209,210] However, most construction usage will still involve 'ordinary' cements like Portland, sulfate-resisting Portland and blended products with pulverised fly ash, ground granulated blastfurnace slag, etc.

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APPENDIX

INTERNATIONAL STANDARDISATION OF OILWELL CEMENTS

Many API standards, including those for oilwell cements, are in the process of being converted into international and also European standards, because of the global exploration and production of oil and gas, which increasingly requires globally standardised materials and equipment for keeping costs down. API Specification 10A (*Specification for Well Cements and Materials for Use in Well Cementing*) and API Recommended Practice 10B (*Testing of Well Cements*) are in the process of being converted into international standards ISO 10426–1 and ISO 10426–2 respectively, which should be available during 1999. These international standards, by what is known as the Vienna Agreement between ISO and CEN (the European standards organisation), will also be available as European standards.

These standards initially are being based on the API standards with no significant technical changes. When the international standard is issued, then the particular API standard that it has superseded will no longer be worked on for any appropriate revisions by the API but by ISO. So, API Classes of oilwell cements will become ISO Classes. The international standards will be applied globally but used locally. So, for example, in the U.K. these new standards will be designated BS EN ISO 10426-1 and BS EN ISO 10426-2, in Germany DIN EN ISO 10426-1 and -2, in Norway NS EN ISO 10426-1 and -2, in the United States ANSI/API ISO 10426-1 and -2 etc.

ANSI – American National Standards Institute
API – American Petroleum Institute
BS – British Standard
CEN – Comité Européen de Normalisation (European Committee of Standardisation)
DIN – Deutsches Institut für Normung
EN – European Norm
ISO – International Organisation for Standardisation
NS – Norsk Standard

15

Cement Admixtures

Rodney M. Edmeades and Peter C. Hewlett

15.1 Introduction

Concrete in its earlier forms contained minor additions of inorganic and organic materials, whether by intent or accident, the latter resulting from contaminated sands and the use of naturally occurring hydraulic binders such as pozzolanas. Any intended use was empirical, not resulting from chemical awareness. For instance, the use of blood as an air-entraining agent, as well as goat's milk and pig's fat to improve the workability of these early concretes, and of urine to vary the rates of setting and hardening, occurred without any detailed knowledge of the alchemy.

Admixtures should be distinguished from additives and additions in that these materials are usually solids and are added to the cement during its manufacture, e.g. set-controlling gypsum, stearate grinding aids, or as a major component in the manufacture of concretes and mortars, for instance granulated blastfurnace slag, pulverised-fuel ash (pfa) and silica fume added in significant amounts (>10 per cent w/w of cement content).

In the last 30 years interest in admixtures has increased along with developments in concrete and concern about its durability and visual presentation. Over the same period a considerable amount of research and development has also taken place, resulting in greater confidence in the technology of chemical admixtures. Some chosen references are given that should put admixtures into their historical and present-day context.[1 8]

Admixture usage has steadily increased in most industrialised countries, e.g. Australia, Japan, USA and Germany,[9] and in the UK it increased from some 12 per cent of all concrete made containing an admixture in 1975 to ~ 50 per cent in 1991.[10]

Sometimes certain types of admixtures may predominate due to particular conditions, e.g. sustained hot or cold weather periods, extreme exposure and poor concrete-making materials. However, the usage of admixture types is rather random. So what types or categories of materials exist?

First, we can divide admixtures into those that are water soluble and those that are not, or produce an aqueous emulsion or dispersion. The 'solubility' categorisation is given in Table 15.1. In addition to these readily recognisable groups there are a number of miscellaneous materials, for example expansion producers (gas formers), corrosion inhibitors, fungicides and flocculants.

All admixture materials are not used to the same extent and may be split into major and minor groups as far as the UK use is concerned.

Table 15.1 Admixture categories using solubility as a criterion

Soluble (water)	Insoluble
Accelerators Retarders/retarding water reducers (Mortars and concrete) Water-reducing plasticising/fluidifiers Air entrainers Superplasticisers (normal and retarding) Air-entraining mortar plasticisers Permeability reducers (waterproofers) Pumping aids	Plasticisers/workability aids: → Solid particulate → Liquid dispersion → Liquid emulsions Pigments
Viscosity Modifiers	Viscosity Modifiers
Wash water systems	

- Major categories:
  - normal water reducers
  - air entrainers
  - air-entraining mortar plasticisers
  - superplasticisers
  - retarding water reducers
  - mortar retarders.
- Minor categories:
  - accelerators
  - retarding superplasticisers
  - integral permeability reducers (concrete and mortars)
  - pumping aids
  - accelerating water reducers
  - polymer emulsions.

In looking at the physical chemistry of admixture interaction it is not possible to separate their chemistry from that of Portland cement hydration, and indeed that of other cements such as those based on calcium aluminates.

Broadly speaking, admixtures may be regarded as active, interactive and passive. Active admixtures react with a solubilised component of cement such as lime to produce a derivative. It is this derivative that imparts the admixture effect. Accelerators, retarders and waterproofers would comprise this category.

Interactive admixtures are usually surface active and associate with the liquid–air and solid–liquid interfaces, resulting in orientation and adsorption. The active component of the admixture is not changed by these events. Examples are plasticisers, superplasticisers and air entrainers.

Passive admixtures do not change their form in passing into solution or remaining in suspension. Their contribution is mainly physical, by way of molecular entanglement and solvent association in the case of viscosity modifiers, or simply light absorption and reflection in the case of pigments.

Dealing with each category in turn, it should be remembered that Portland cement, sand and water are themselves electrically charged due to the dissociation of surface silanol groups in the case of siliceous aggregates, and multi-phase dissolution in the case of cement. Water also consists of dipoles and dissociated ions. The net effect is that cement has a residual positive charge[11] of *ca.* +10 mV and sand and siliceous aggregates have a net negative charge. In the presence of electrically charged surfactants the system endeavours to reduce electrical potential by positive and negative charges cancelling one another out. The detailed manner of surface orientation depends upon the chemical functionality of the molecules and the resultant charge distribution. The behaviour varies, as will become apparent in the following sections.

15.2 Air-entraining admixtures

These admixtures comprise a group of surfactants which act at the air–water interface in cement paste, thereby stabilising air entrapped during the mixing process in the form of tiny discrete bubbles. They are characterised by possessing a hydrocarbon chain or backbone terminating in a hydrophilic polar group, typically a carboxylic or sulfonic acid group. The sequence, initiated by dissolution and dissociation followed by orientation and adsorption, is shown in Figure 15.1.

Normally used in the form of the sodium salt, the ionised polar group becomes orientated into the aqueous phase, whilst the hydrocarbon chain orients into the air within the bubble (Figure 15.2). The surface tension of water is reduced, facilitating the formation of bubbles

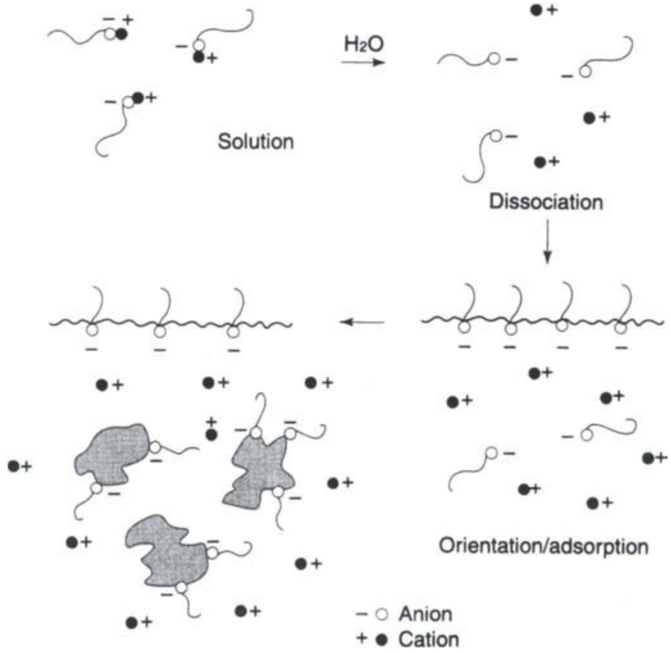


Fig. 15.1 Surface activity and surfactant behaviour.

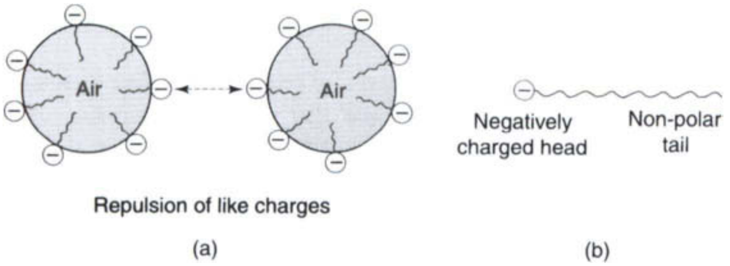


Fig. 15.2 (a) Orientation of surfactant at air bubble surface and (b) anionic air-entraining agent (most common type).

when a concrete or mortar is agitated, and the charged sheath of surfactants surrounding each bubble leads to mutual repulsion, thus preventing coalescence in the form of larger bubbles.

In concrete and mortar this surface charge causes the stabilised bubbles to adhere to the oppositely charged zones on cement and aggregate particles (Figure 15.3). The overall net effect is an aggregate–air–cement–air–aggregate type of bridge, improving the cohesion of the mix and further stabilising the air void system (Figure 15.4).[12] It is apparent that such a system would permit relatively free motion in shear with the stabilised air bubbles acting like compressible bearings. Both the cohesion of the mix and the workability improve. This is important when air is entrained in concrete to improve freeze–thaw durability

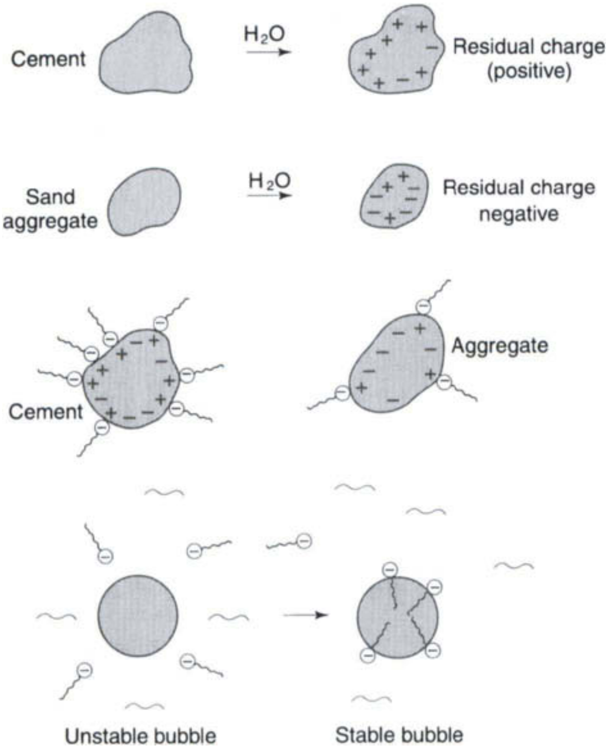


Fig. 15.3 Dissociation and orientation.

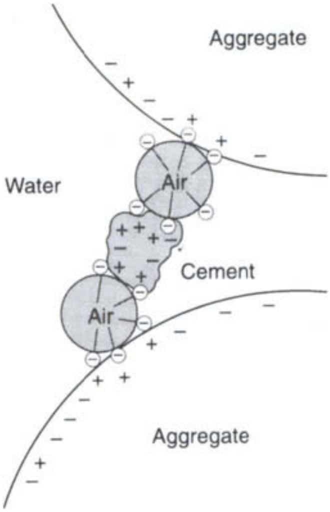


Fig. 15.4 Mechanism by which entrained air voids remain stable within concrete (source: Ref. 12).

because there is a tendency for air to escape if vigorous vibration is employed during placing and compaction.

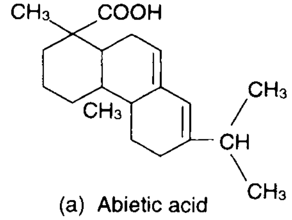
Only a limited number of organic materials are suitable for use as air-entraining admixtures, the earliest and most effective being vinsol resin extracted from pinewood. The active ingredient is sodium abietate, the sodium salt of abietic acid (Figure 15.5(*a*)), which is a complex aromatic molecule derived from the breakdown of natural wood resins. Other derivatives of natural products, such as the soaps of oleic and caproic acid, have been employed in the past but their performance is less reliable than that of modern synthetic air entrainers.

With the increasing scarcity of vinsol resin and wider use of blended cements containing pulverised-fuel ash (pfa), a greater proportion of proprietary air-entraining admixtures are now based on synthetic chemicals. The principal types are anionic, such as the alkylarylsulfonates and alkylsulfates, but a number of non-ionic surfactants have been developed for use in concrete.

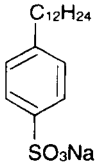
Among the anionic surfactants, sodium dodecyl benzene sulfonate, sodium oleyl sulfate and sodium oleate are well-known examples (Figure 15.5(*b*)–(*d*)). Non-ionic surfactants such as nonylphenolethoxylate are efficient air entrainers but do not perform well in freeze–thaw durability tests (Table 15.2). This is probably due to the lack of an hydrophobic 'tail' oriented towards the interior of the air bubbles, which prevents water intrusion as pressure develops during freezing.

Apart from the nature of the air-entraining admixture and the dosage employed, the air content achieved in any concrete or mortar is influenced by a number of factors (Table 15.3). As a general rule the volume of air entrained decreases with increasing cement content and fineness but increases with increasing alkali content of the cement (peaking at 1.5 per cent equivalent Na_2O). The latter effect may be connected with the increasing pH of the aqueous phase.

Air content also increases with increasing sand content in a mix, and with a decreasing proportion of sand with a particle size $<150\,\mu m$. Higher temperatures lead to a lower air content, as does a high degree of workability. The use of cement replacement materials *per*



(a) Abietic acid



(b) Sodium dodecyl benzene sulfonate

$CH_3-(CH_2)_7-CH=CH-(CH_2)_8-SO_4Na$

(c) Sodium oleyl sulfate

$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COONa$

(d) Sodium oleate

Fig. 15.5 Structure of air-entraining chemicals.

Table 15.2 Freeze–thaw resistance of concrete air-entrained by different chemical types of admixture

Air-entraining admixtures	Air content (%)	Relative classification of freeze–thaw resistance[a]
None	2.0	5
Sodium oleate	5.6	86
Sodium lauryl sulfate	5.8	46
Neutralised wood resins	5.2	57
Phenol ethoxylate	5.2	7

[a] An average of several techniques measuring effect on modulus and compressive strength after freeze–thaw cycling.

se has little effect on the efficiency of air entrainment, but the residual carbon content of pfa (as measured by loss on ignition) can have a dramatic effect, particularly with vinsol resin-type admixtures. This is ascribed to the rapid adsorption of admixture by the amorphous carbon particles in the ash, which can increase the required dosage by a factor of three or four. Synthetic surfactants are less liable to rapid removal from the pore solution and have been recommended for pfa mixes.

Figure 15.6[12] shows the comparative effectiveness of a range of surface-active chemicals

Table 15.3 Factors influencing air content

Increasing air content	Decreasing air content	Example change	Estimated effect (target 5 per cent air content)
Lower temperature	Higher temperature	10–20°C	Reduction 1–1.25%
Higher slump	Lower slump	50–100 mm	Increase of 1%
Sand grading coarser	Sand grading finer	BS 882 Zone 3 to 2 (1 zone width)	Increase <0.5%
Sand content increased	Sand content decreased	35–45%	Increase 1–1.5%
Decrease in sand fraction $<150\,\mu m$	Increase in sand fraction <150 micron	$-50\,kg/m^3$	Reduction of 0.5%
Decrease in cement content inclusive of sand content adjustment	Increase in cement content inclusive of sand content adjustment	$-50\,kg/m^3$	Reduction of 0.5%
–	Inclusion of organic impurities	Inclusion	Positive and negative effects reported
–	Inclusion of pfa	Inclusion	Significant reduction linked to carbon in ash
–	Increase in hardness of water	Increased hardness	Reduction
Increase in mixing efficiency	Decrease in mixing efficiency	Better mixing efficiency	Increase linked to dispersion of admixture
Positive dispensing tolerance	Negative dispensing tolerance	±5%	±0.25%
–	Prolonged agitation	1 h 2 h	Reduction of 0–0.25% Reduction of 1%

with respect to the stable air content of cement pastes. The relative effectiveness of charged surfactants in relation to uncharged molecules is readily apparent.

The combined use with other admixtures, particularly plasticisers and superplasticisers, can affect the volume and stability of entrained air. Admixtures based on lignosulfonates appear to have less effect and may even increase air entrainment. However, there is now a considerable body of evidence that sulfonated melamine and sulfonated naphthalene–formaldehyde condensates can lead to a drop in air content and an increase in the air void spacing factor. This occurs when the superplasticiser is added with the air entrainer at the time of mixing or up to 40 min later.[13]

Although intended to entrain air by a mainly physical action, some admixtures of this type do interact with the cement to a certain extent and affect the course of hydration. In the case of most anionic surfactants, including vinsol resin, high levels of dosage can lead to retardation of C_3S hydration whilst the third (C_3A) hydration peak observed by isothermal calorimetry is accelerated.[14] By contrast, sodium oleate has no effect on C_3S hydration but does accelerate later C_3A hydration.

The entrainment of 3–6 per cent air by volume has a pronounced effect on concrete workability, producing increased mobility and cohesiveness. With the correct bubble size

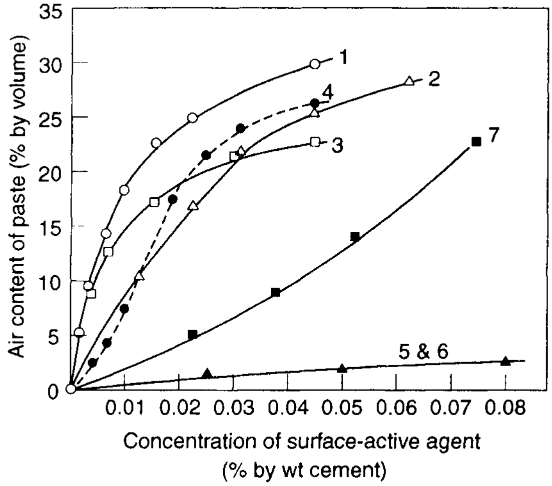


Fig. 15.6 Air-entraining capacities of surface-active agents in cement pastes (source: Ref. 12). Mixing conditions: mixing time 4 min, speed of propeller mixer 1000 rpm. w/c = 0.45 by weight, temperature = 25°C. Surface-active agents: 1, sodium dodecyl sulfate; 2, neutralised 'Vinsol' resin; 3, sodium abietate; 4, tetradecyl trimethyl ammonium bromide; 5, Triton NE; 6, Lissapol N 300; 7, saponin.

(0.02–1.0 mm) and spacing factor of >0.025 mm (preferably 0.05 mm), frost resistance is also ensured without a significant loss in strength, and bleed of the fresh concrete is reduced.

Let us consider what controls the stability of this entrained air. Excess pressure in an air bubble may be represented as

$$\Delta P = \frac{2T}{R} \tag{15.1}$$

where T = surface tension of bubble and R = bubble radius. Therefore, if T is lowered by orientation of surfactant at the air–water boundary, then ΔP is reduced and the bubbles tend to stabilise.

Air is of course trapped in the concrete initially simply by the tumbling or beating action of the concrete in the drum or the pan. It can be calculated that the film thickness of the stabilised bubble is *ca.* 3–6 times the carbon chain length of the surfactant material. There is a minimum chain length of some 12 carbon atoms while an optimum of some 16–18 is required (2–2.5 nm) for the surfactant to act as an efficient air entrainer. For instance, sodium oleate, $CH_3—(CH_2)_7—CH{=}CH—(CH_2)_7{\cdot}CO_2Na$ with a C_{18} chain length is an efficient air-entraining agent. A typical example of an air-entraining agent is abietic acid (Figure 15.5a).

The resins derived from pinewood, i.e. vinsol resin, and various abietates are more effective in the presence of alkali metals such as calcium and sodium, and many admixture combinations are derived by prereacting, say, vinsol resin with caustic soda.

Many simple carboxylates of long-chain compounds are precipitated in the presence of calcium, limiting their use:

$$2(R{\cdot}COO\,Na) + Ca^{2+} \rightarrow (R{\cdot}COO)_2Ca\downarrow + 2Na \tag{15.2}$$

Whilst non-ionic surfactants are less efficient than anionic ones, they are more stable in the presence of calcium ions, when anionic surfactants are precipitated and rely on the sparingly soluble nature of these materials in order to function. Air-entraining agents also affect the viscosity and bleed behaviour of the cement paste. As a rule, the viscosity of paste increases as a result of adsorption, causing water repellency, thus increasing interparticle attraction. Initially the retention of air bubbles causes bridges between cement particles, resulting in a viscosity increase and reduction in the bleed of cement pastes.

In the case of mortars, a high level of air entrainment (10–20 per cent) is usually required to provide a highly workable, medium-strength material which is also frost resistant. Mortar plasticisers, as air-entraining admixtures are usually termed when supplied for masonry and rendering mortars, have supplanted the use of hydrated lime on the majority of building sites. They represent one of the oldest groups of admixtures. Much pozzolan-based Roman concrete owes its longevity to the deliberate or inadvertant use of air entrainment. As a category of admixtures, they have been well reviewed.[12,15]

A recent variant on air-entrained mortars is the strongly retarded versions (up to 36 h) which are designed to permit extended use on sites for bricklaying and similar purposes. Retardation in the delivered container is offset by water/retarder removal by way of suction (~30 per cent) into the porous brick, causing a reduction in total retarder quantity and yielding reasonable setting/hardening times when laid (Figure 15.7).

The retarding component is usually based upon hydroxycarboxylic acid salts and the air-entraining component on vinsol resin or synthetic anionic surfactants. It would seem that the hardened properties of such mortars containing these admixtures are not adversely affected (see Figures 15.8–15.11).

The British Standard for mortar air-entraining admixtures is BS 4887: Part 1: 1986 and that for retarded mortars/air entrainers is BS 4887: Parts 1 and 2. The mortars themselves have to comply with BS 4721.

15.3 Water-reducing/plasticising admixtures

Generally speaking, mixtures of low-viscosity liquids such as water and relatively heavy particles such as cement, sand and aggregates do not remain uniformly mixed once agitation is stopped. Separation of the various phases occurs, resulting in segregation and the upward displacement of water as 'bleeding' occurs. Careful grading of materials and their relative

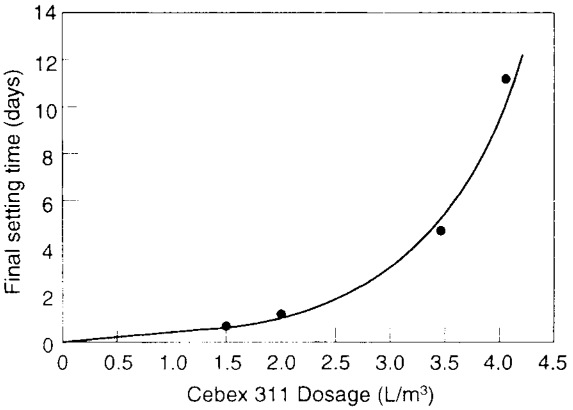


Fig. 15.7 Cebex 311: set time versus dosage in class (III) lime mix (source: Ref. 15).

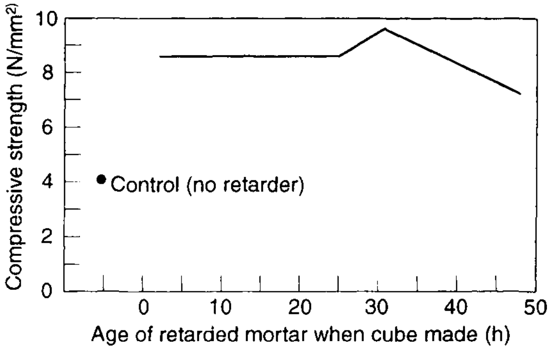


Fig. 15.8 Compressive strength after 28 days of 1:6 retarded mortar (source: Ref. 15).

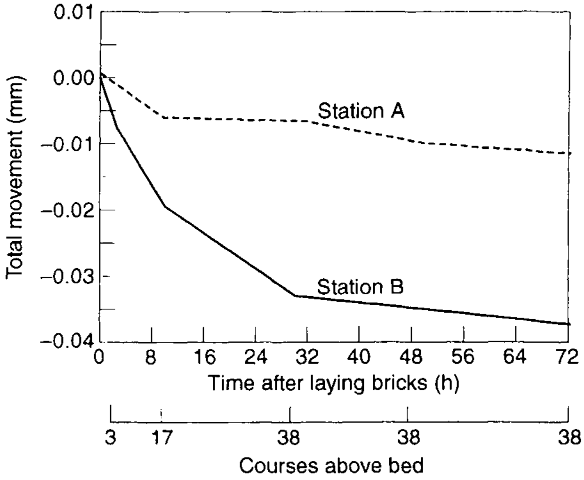


Fig. 15.9 Movement of nominal 10 mm retarded mortar bed between bricks (source: Ref. 15).

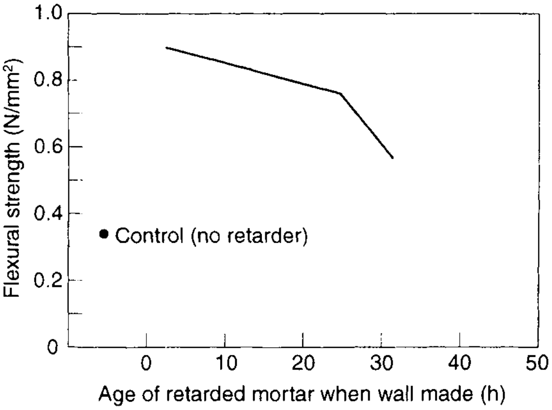


Fig. 15.10 Flexural strength after 28 days of 1:6 retarded mortar brick wallets (source: Ref. 15).

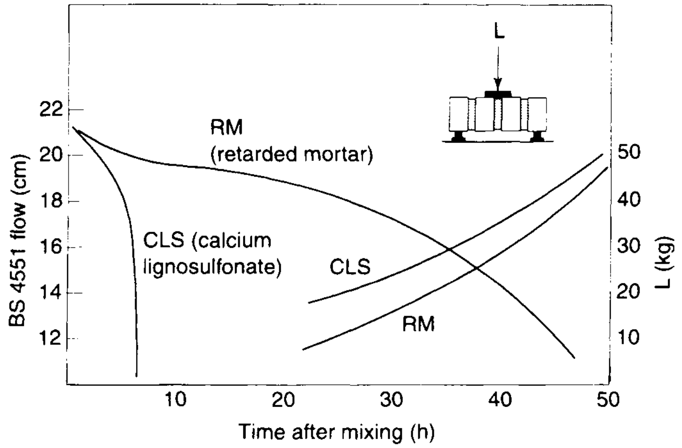


Fig. 15.11 Early flexural strength of masonry (source: Ref. 15).

proportions can offset these effects but the underlying tendency remains. To minimise these effects the water content of the concrete is kept low. This juggling act is what governs the flow or rheology of concrete and mortar mixes. The vague term 'workability' is used to describe these complex effects. In general, workability may be expressed as resistance to flow ($1/r$ = workability). The relationship is shown in Figure 15.12.

The gross yield value can be split into two terms:

- Y_L, or absolute yield value (reflecting internal structure);
- F_R, or internal friction (this term is pressure dependent).

In general the workability of a cement paste is greater than that of the resulting mortar, which in turn is greater than for the resulting concrete. Such a picture has been used to describe concrete as a Bingham body,[16] although others prefer a pseudo-plastic model.[17] Whatever the detail, we can understand admixture action by developing the Bingham model further.

The three stylised diagrams in Figure 15.13 show an initial Newtonian body where the flow is governed by viscosity only. As the water content is progressively reduced, internal

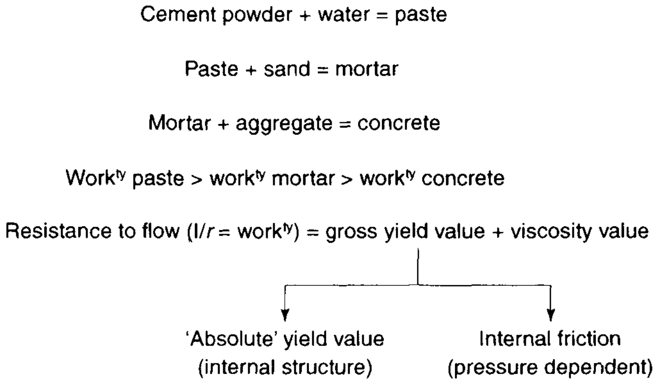


Fig. 15.12 Workability (Work'y) and rheology.

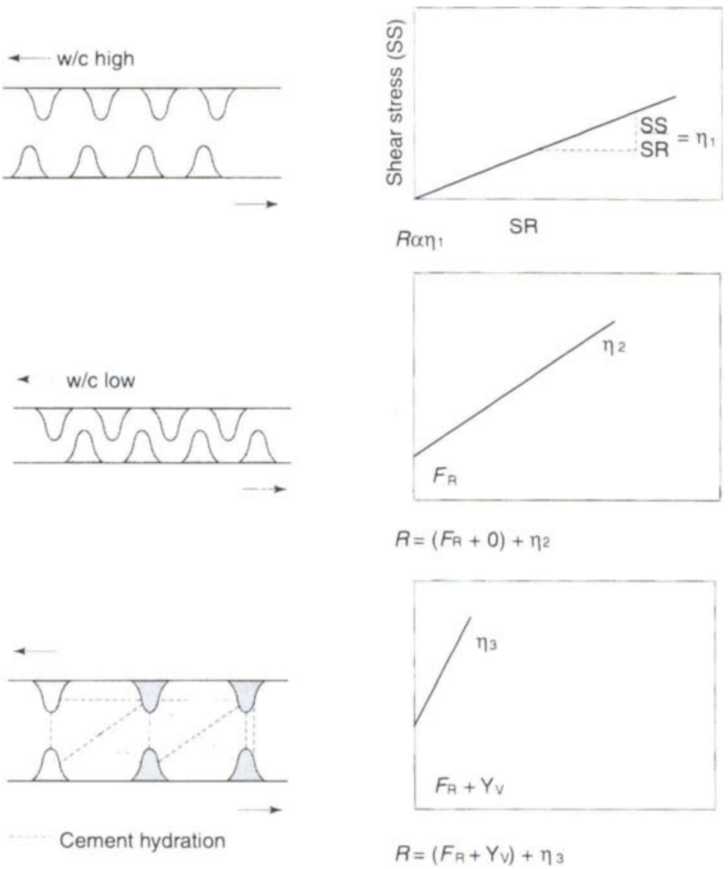


Fig. 15.13 Resistance to flow and internal friction structure and shear.

friction increases causing an intercept on the shear stress axis, and as cement hydration proceeds internal structuring occurs, increasing the yield value further, but of course it now consists of both chemical and physical interactions.

For a concrete or mortar to have facile placing characteristics, $F_R + Y_V$ should be low together with the viscosity η. This state may be achieved using plasticising as well as superplasticising admixtures, permitting the water content to be kept low but sufficient to hydrate the cement, with a water/cement ratio of ~0.26.

Maintaining low water contents whilst achieving an acceptable level of workability results in higher strengths for a given cement content (Figure 15.14)[18] as well as lower permeability (Figure 15.15)[19] and reduced shrinkage (Figure 15.16).[20] Water-reducing admixtures (also referred to as 'plasticisers') are all hydrophilic surfactants which, when dissolved in water, deflocculate and disperse particles of cement. By preventing the formation of conglomerates of cement particles in suspension, less water is required to produce a paste of a given consistence or concrete of a particular workability. This effect is caused by adsorption on the cement surfaces of the high molecular weight anions of which these admixtures are composed, leading to mutual repulsion of individual particles and a reduction in interparticle friction.

As far as surfactant activity is concerned, plasticising admixtures and air-entraining

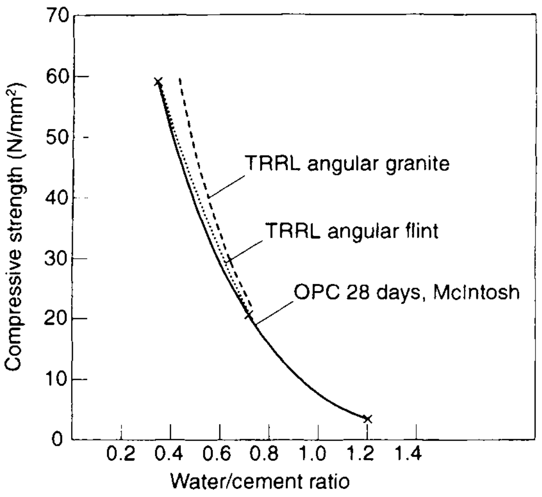


Fig. 15.14 The use of admixtures to maximise cement use (source: Ref. 18).

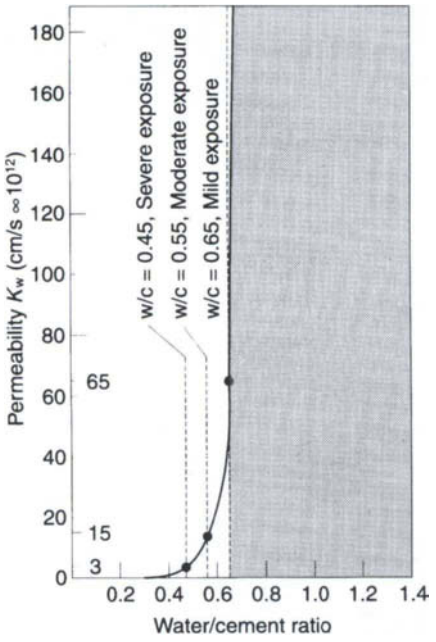


Fig. 15.15 The use of admixtures to improve durability (source: Ref. 19).

agents behave in a similar way. However, due to the various chemical functional groups on the backbone of molecules comprising this group, instead of end-on adsorption occurring, the backbone is preferentially adsorbed, causing the negative end-group to thrust into the solution. The net effect is shown in Figure 15.17(*a*).

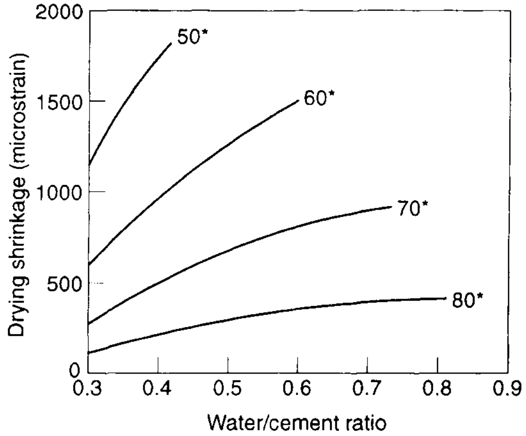


Fig. 15.16 Shrinkage versus w/c ratio and aggregate content for different aggregate contents by volume (*) (source: Ref. 20).

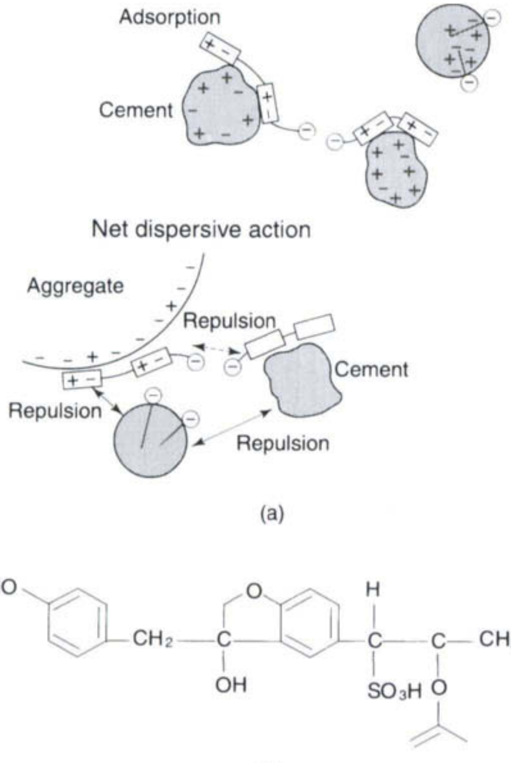


Fig. 15.17 (a) Backbone adsorption resulting in mutual repulsion. (b) Repeating unit of a lignosulfate molecule.

The plasticising action of these admixtures can be utilised in three ways:

- the amount of mixing water required to produce concrete or mortar of a given workability can be reduced, giving rise to a denser, stronger composition;
- increased workability can be obtained for a fixed water content, providing easier placing and compaction;
- both cement and water can be reduced in proportion to give an economic 'corresponding mix' of unchanged workability and strength.

This class of admixture can be further subdivided into normal, accelerating and retarding water reducers, the differences arising from their effect on the setting and hardening of cement compositions.

The requirements of BS 5075: Part 1: 1982 for the different types of water reducer are summarised in Table 15.4.

15.3.1 NORMAL WATER-REDUCING ADMIXTURES

When added to concrete or mortar at the prescribed dosage, these admixtures have no significant effect on the subsequent hydration of the cement. However, the improved dispersion of cement grains can cause a shortening of the stiffening time and enhanced early strength at a constant water/cement ratio.

At high dosage levels, some admixtures used in combination with certain cements (particularly those with low C_3A content, i.e. sulfate-resisting) may cause retardation. This can be offset by incorporating small amounts of an accelerator into the formulation, such as calcium chloride, calcium formate or triethanolamine.

The principal raw materials used in the production of water-reducing admixtures are the salts of lignosulfonic acid and hydroxycarboxylic acids. Less commonly, modified carbohydrates sometimes known as hydroxylated polymers have formed the basis of a series of proprietary admixtures.[21]

Lignosulfonates are obtained as a by-product from the acid sulfite wood-pulping process, and in their crude form contain many impurities such as pentose and hexose sugars. The latter are powerful retarders and are removed by fermentation followed by distillation of the resulting alcohol if the lignosulfonate is to be incorporated into a normal-water reducing admixture. A typical lignosulfonate repeating unit is shown somewhat simplistically in Figure 15.17(*b*) and a typical analysis of a sugar-reduced lignosulfonate given in Table 15.5.

Calcium and sodium salts are most commonly used in admixture production, the former being cheaper but less effective as a water reducer, the latter being more soluble and less liable to precipitation when stored at low temperatures. Lignosulfonates exist in solution as high molecular weight materials (typically 5000–50 000) and are polyelectrolyte microgel units which are roughly spherical in shape (Figure 15.18). These microgel units come about by progressive dissolution of the lignin within the wood that is being pulped, yielding fragments which undergo further degradation into what has been described as an homologous series having a main repeating unit with secondary units attached to it (Figures 15.19 and 15.20).[22,23]

Only those carboxylic and sulfonate groups near the surface of the sphere are ionised, although the sodium salt has been shown to have a higher degree of ionisation than the calcium salt.

Commercial methods of purifying and fractionating crude lignosulfonates have enabled admixtures formulators to select products within a defined range of molecular weights.

Table 15.4 Performance requirements of water-reducing admixtures according to BS 5075: Part 1: 1982[a]

		Workability; compacting factor relative to control mix		Stiffening times Time from completion of mixing to reach a penetration resistance of:				Compressive strength Minimum compressive strength as per cent of control mix concrete at:					
				0.5 N/mm^2		3.5 N/mm^2		24 h		7 days		28 days	
Category of admixture	CAA chart type	Test mix A	Test mix B	Test mix A	Test mix B	Test mix A	Test mix B	Test mix A	Test mix B	Test mix A	Test mix B	Test mix A	Test mix B
Normal water-reducing	C3	At least 0.03; above	Not more than 0.02; below	–	Within 1 h of control	–	Within 1 h of control	–	–	90	110	90	110
Accelerating water-reducing	C4	At least 0.03; above	Not more than 0.02; below	–	More than 1 h	–	At least 1 h less than control	125	125	–	–	90	110
Retarding water-reducing	C5	At least 0.03; above	Not more than 0.02; below	–	At least 1 h longer than control	–	–	–	–	90	110	90	110

[a] Test Mix A contains the admixture at the manufacturer's recommended dosage rate and in all other respects has the same composition as the control mix. Test Mix B contains the admixture at the manufacturer's recommended dosage rate and has the same composition as the control mix, except that the total water/cement ratio is reduced by 8 per cent.

Table 15.5 Typical analysis of lignosulfonate liquor

	Calcium lignosulfonate source (%)	Sodium lignosulfonate (%)
Solids	54	30
Reducing sugars (based on glucose determination): xylose, arabinose, mannose (of a total of 7)	5.8	0.9

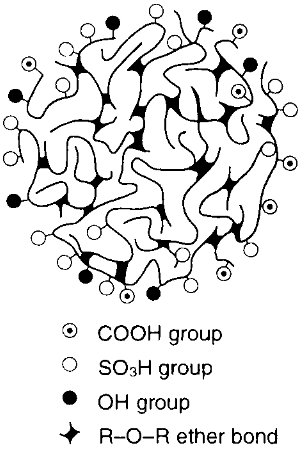


Fig. 15.18 Lignosulfate polyelectrolyte microgel unit.

There is evidence that water-reducing capability increases with increasing molecular weight and decreasing carbohydrate content.[24]

Highly purified lignosulfonates entrain very little air, but cruder commercial materials can cause significant air entrainment, particularly at high dosage. This is often counteracted by the incorporation of air-detraining agents such as tributyl stearate or dibutyl phthalate. Only small amounts (<1 per cent by weight of lignosulfonate) are required to suppress air entrainment completely. These air detrainers are thought to act by impeding the movement of materials within the air water interface which defines the limit of the bubble, such that the bubble increases in size by stretching the interfacial skin; points of weakness arise causing rupture of the skin and hence the bubble. This is known as the Marangoni effect.

Hydroxycarboxylic acids constitute the other most important group of water-reducing chemicals which are normally employed as the more soluble sodium salts in proprietary admixtures. Although the lower molecular weight acids are surface active, the longer-chain acids such as mucic, gluconic and heptonic are favoured for their plasticising action (Figure 15.21). At low dosage levels, sodium heptonate and sodium gluconate behave as normal water-reducing admixtures, but with increasing dosage there is a growing tendency to retard cement hydration. This can be overcome in compound admixtures in which sodium heptonate or gluconate is blended with sodium lignosulfonate, dextrin derivatives and triethanolamine. Proprietary water-reducing admixtures of this type have become available from most major producers.

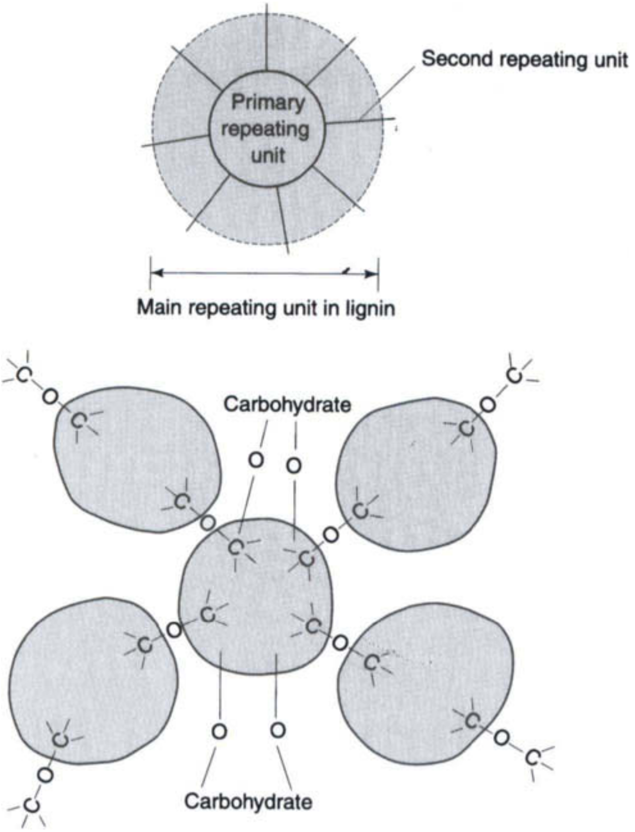


Fig. 15.19 Suggested structure of lignin (source: Refs 22, 23).

15.3.2 ACCELERATING WATER-REDUCING ADMIXTURES

As implied by the name, this type of admixture combines water-reducing capability with the acceleration of cement hydration. The simpler formulations consist of a mixture of calcium lignosulfonate and calcium chloride or, when a chloride-free admixture is required, a blend with calcium formate or sodium nitrite. The relative effects are shown in Figure 15.22. Many of the chloride-free accelerators described later do in practice provide sufficient water reduction to be included in this category.

The principal uses are in cold-weather concreting, and in precasting to enable moulds to be re-used with a minimum of delay. By utilising the water-reducing function, higher strengths can be obtained than from the use of a conventional accelerator such as calcium chloride (Table 15.6).

15.3.3 RETARDING WATER-REDUCING ADMIXTURES

This important class of admixture includes most of the proprietary retarders based on hydroxycarboxylic acids. Their main function is to delay the setting time of concrete without adversely affecting subsequent strength development, whilst at the same time permitting a substantial reduction in water/cement ratio.

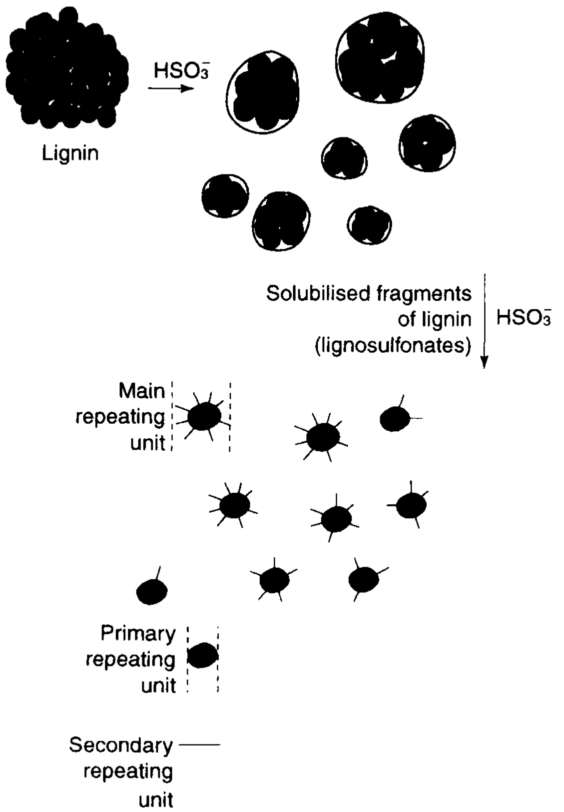


Fig. 15.20 Acid dissolution of lignin yielding microgels of lignosulfonate (source: Refs 22, 23).

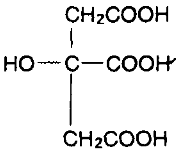
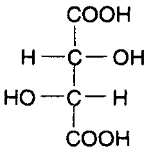
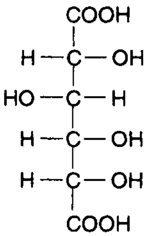
Another group consists of calcium lignosulfonates in which the high sugar content of the crude sulfite lye has been retained (as much as 50–60 per cent by weight of the lignosulfonate solids). The reducing sugars are powerful retarders, but a higher dosage level of this type of admixture (300–1000 mL/100 kg cement) is normally required compared with the hydroxycarboxylic acid type (200–500 mL/100 kg cement). There is also a greater tendency to entrain air, which is usually offset by incorporating an air detrainer.

To avoid the variations in sugar content inherent in the raw material, purified lignosulfonate–hydroxycarboxylic blends are also employed to produce efficient admixtures of this class.

The general effect of all water-reducing admixtures on the properties of mature concrete is beneficial although, if used to improve workability, the accelerating type can lead to slightly increased drying shrinkage and creep.

When used to obtain water reduction, all types give rise to improved strength, lower permeability and better freeze–thaw durability. In the case of 'corresponding' mixes with reduced cement content but maintained workability and strength, both initial surface absorption (as measured by the ISA test[25]) and freeze–thaw durability are improved by the use of lignosulfonate water reducers (Figures 15.23–15.25). This durability is, of course, not as good as that conferred by properly entrained air.

Another aspect to be considered is the dependence of plasticiser effectiveness on the

	Material Citric acid	 Tartaric acid	 Mucic acid
Functionality: OH groups	1	2	4
COOH groups	3	2	2
Molecular weight	192	150	210
Formula			

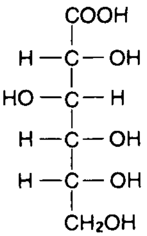
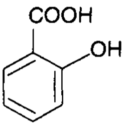
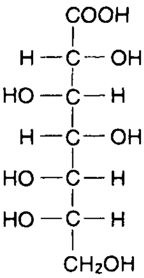
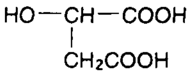
	Gluconic acid	Salicylic acid	Heptonic acid	Malic acid
Functionality: OH groups	5	1	6	1
COOH groups	1	1	1	2
Molecular weight	196	138	230	134
Formula				

Fig. 15.21 Hydrocarboxylic acids used in admixtures.

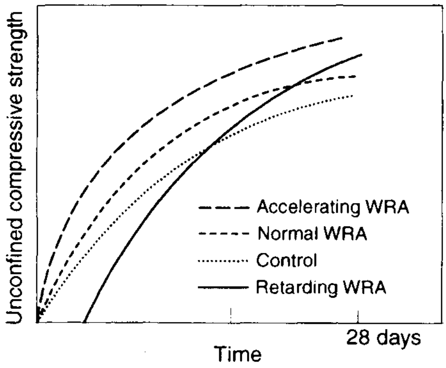


Fig. 15.22 Relative strength development (at 28 days) using different water-reducing admixtures (WRA).

Table 15.6 Achievement of maximum strength from accelerating water-reducing admixtures

Admixture type	None	Calcium chloride solution	Accelerating water-reducing admixture
Mix proportions:			
Cement OPC	1	1	1
Sand (zone 2)	2.2	2.2	2.2
Gravel (20–10 mm)	4.5	4.5	4.5
Water	0.58	0.56	0.52
Admixture	–	Normal dosage (1.5% by weight of cement)	Normal dosage
Properties:			
Slump (mm)	15	15	15
28-day density (kg/m^3)	2450	2465	2450
Average compressive strength (N/mm^2) at:			
7 days	27.1	29.0	32.5
28 days	42.0	45.5	53.2

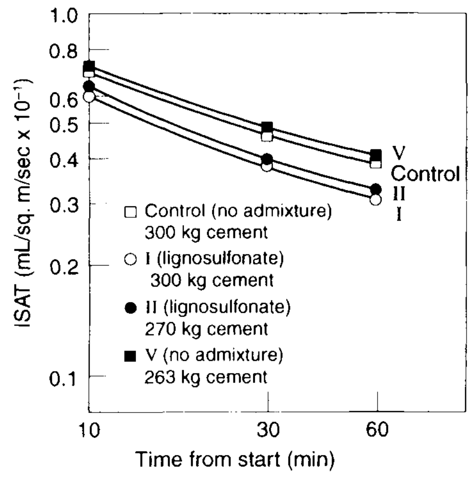


Fig. 15.23 Initial surface absorption test (ISAT) readings for oven-dried concretes containing lignosulfonate water-reducing agents at constant workability (source: Ref. 26).

composition of the Portland cement. Notwithstanding that the cement may be within the range permitted under the standard, the composition can vary from plant to plant. This interdependence is shown graphically in Figure 15.26.[27]

Plasticising and superplasticising admixtures are similar in that both groups cause agglomerates of cement grains to disperse. However, lignosulfonate addition reaches a maximum effectiveness at lower percentages by weight than superplasticisers. The latter increases in effectiveness with addition as shown in Figure 15.25.

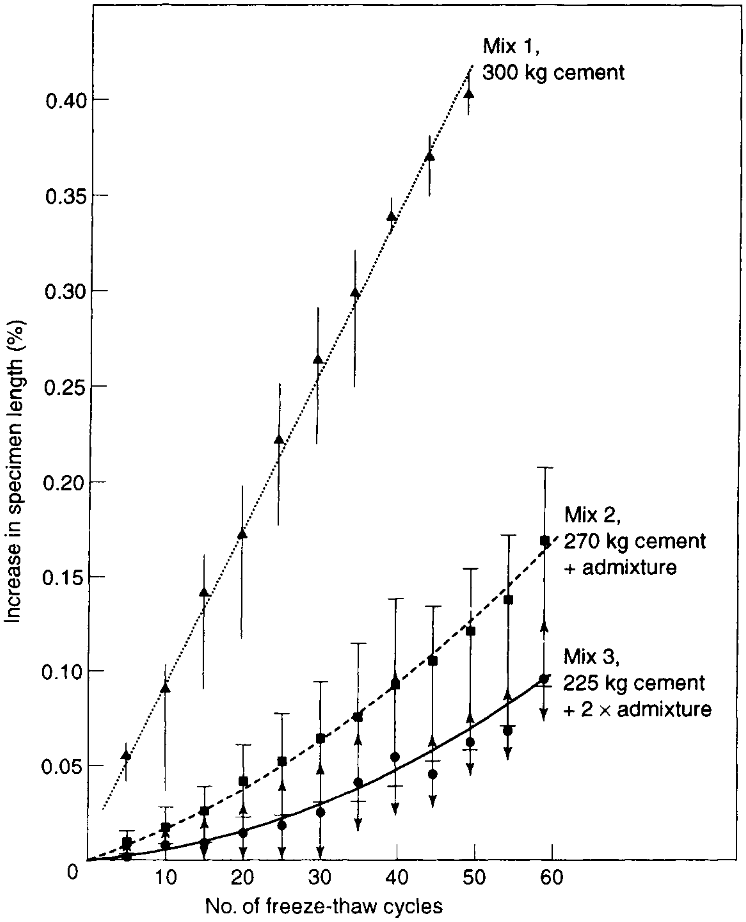


Fig. 15.24 Freeze–thaw tests: length change of specimens (source: Ref. 26).

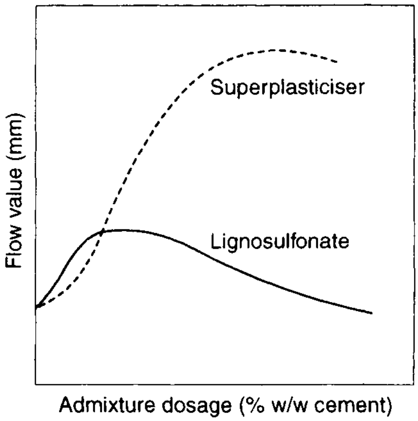


Fig. 15.25 Relative workability: normal water-reducing admixture versus superplasticiser.

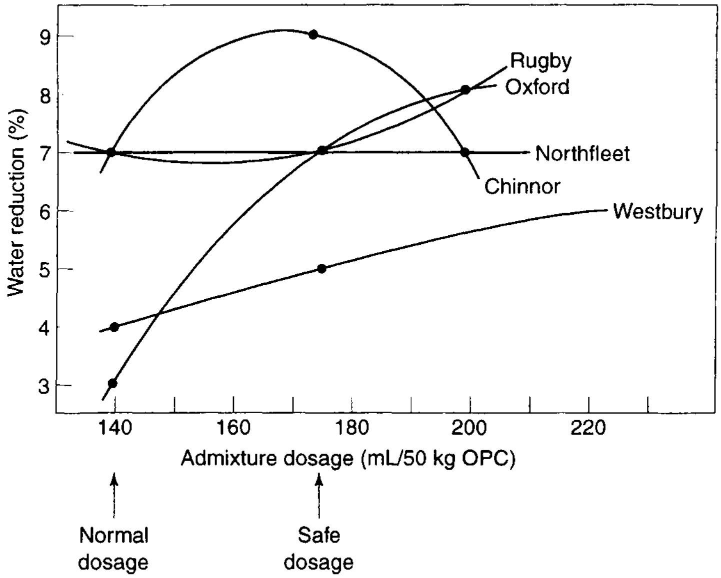


Fig. 15.26 Relationship between admixture dosage and water reduction for normal plasticiser (lignosulfonate) (source: Ref. 27).

The search for cost-effective alternative chemicals continues, and since high costs are not usually welcomed in this category of admixtures there is a tendency to use waste materials. Indeed the use of lignosulfonates resulted initially from just such a motive.

Alkali-treated straw pulp waste liquor has been shown to give normal plasticising and superplasticising properties.[28]

15.4 Superplasticising admixtures

This is a relatively new group of admixtures, although the chemicals comprising them have been known for their dispersing capability since the 1930s. A selection of references is given.[29-36]

These admixtures are also known as superplasticisers or high-range water-reducing admixtures and can be used at considerably higher dosages than ordinary water-reducing admixtures without adverse side effects such as gross retardation of set. A much greater reduction in the volume of mixing water can therefore be made in the case of concretes of normal workability (~30 per cent) or alternatively, 'flowing concrete' can be obtained without excessive addition of water to the mix. The effect on cement paste fluidity of one common type of superplasticiser compared with that of two conventional plasticisers is illustrated in Figure 15.27. All superplasticisers consist of high molecular weight, water-soluble polymers, the majority being synthetic chemicals. Solubility is ensured by the presence of adequate hydroxyl, sulfonate or carboxylate groups attached to the main organic repeating unit, which is normally anionic.

The superplasticisers in general usually fall into four main categories, and attempts were made to classify them in this way when they were first introduced. However, nowadays many proprietary products are blends of two or more active chemicals and the distinctions have become blurred. The four categories are as follows.

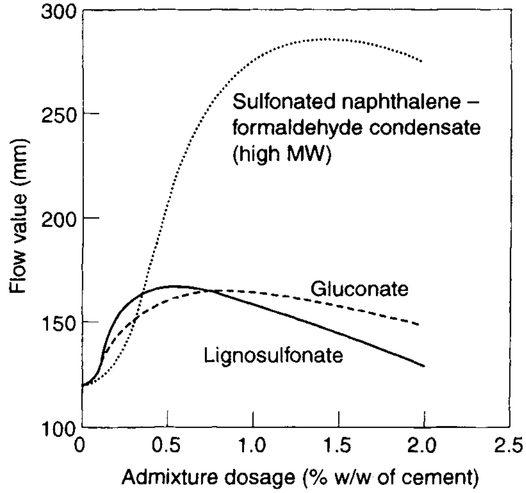


Fig. 15.27 Fluidity of cement paste containing various dispersing agents at constant water/cement ratio.

- Sulfonated melamine–formaldehyde condensates. Developed in Germany and made available commercially in 1964,[37] these synthetic polymers have the structural formula shown in Figure 15.28, with each repeating unit containing one sulfonate group. The condensation number (*n*) is usually in the range 50–60, giving a molecular weight of the order of 12 000–15 000. The sodium salt is very soluble and is favoured for use as an admixture.
- Sulfonated naphthalene–formaldehyde condensates. Developed in Japan and introduced for sale in 1963,[38] these polymers have the structure shown in Figure 15.29. Again, each repeat unit is solubilised by a single sulfonate group, which gives a very soluble salt. The condensation number (*n*) in this case is typically 5–10, giving a molecular weight of the order of 1 000–2 000.
- Modified lignosulfonates: the activity of lignosulfonates shown in Figure 15.27 can be considerably improved by treatment of the crude by-product to remove all carbohydrate impurities, followed by selection of the higher molecular weight fraction. In some processes the basic lye is autoclaved to promote increased polymerisation prior to fractionation. The lignosulfonates which result from this refining process can approach the synthetic condensates in terms of performance, although they have a greater tendency to entrain air.

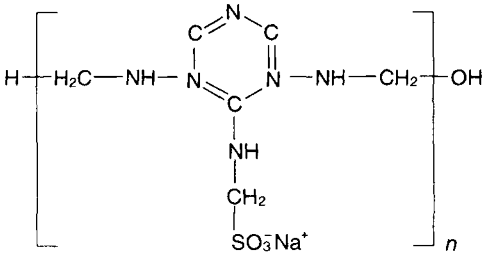


Fig. 15.28 Sulfonated melamine–formaldehyde condensate.

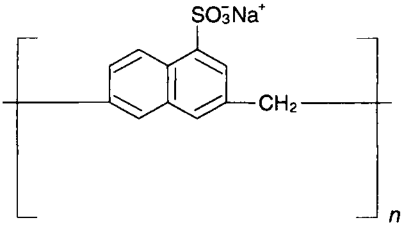


Fig. 15.29 Sulfonated naphthalene–formaldehyde condensate.

- Other synthetic polymers such as sulfonated polystyrene, hydroxylated polymers and copolymer dispersions are used alone or in combination. Superplasticisers with extended workability fall into this miscellaneous category.

All superplasticisers are strongly adsorbed onto cement surfaces, often building up multiple chemisorbed layers on individual grains. The sulfonated naphthalenes do not have the backbone chemical substitution that the sulfonated melamine derivatives possess. Whilst the negative charge build-up resulting in dispersion is similar, the manner of adsorption is not. Multi-layer adsorption has been suggested but evidence is lacking (Figure 15.30).[39]

Mutual particle repulsion leads to a high degree of dispersion, but the polymers employed do not exclude water from the cement surface entirely, and hydration does proceed in a normal manner. Figure 15.31 shows the dispersion of cement agglomerates, giving a more finely divided and uniformly dispersed material, resulting from the build-up of negative charge illustrated in Figures 15.32–15.35.[11,39]

The formation of hydration products on the surface of cement grains tends to negate the improved workability. However, the rate of hydration may well be increased due to the finely dispersed state causing early hydration products resulting in the 'slump loss' phenomenon which can be very pronounced in superplasticised concrete (Figure 15.36).

Workability is greatly enhanced by delayed addition of the superplasticiser, rather than adding it with the mixing water. This allows time for the normal reactions between gypsum and clinker to occur without competition from the superplasticiser. A delay of only a few minutes is adequate for ettringite formation and the establishment of a 'dormant' period

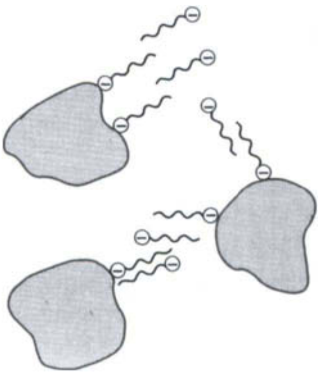


Fig. 15.30 Suggested multi-layer adsorption resulting in dispersion (source: Ref. 39).

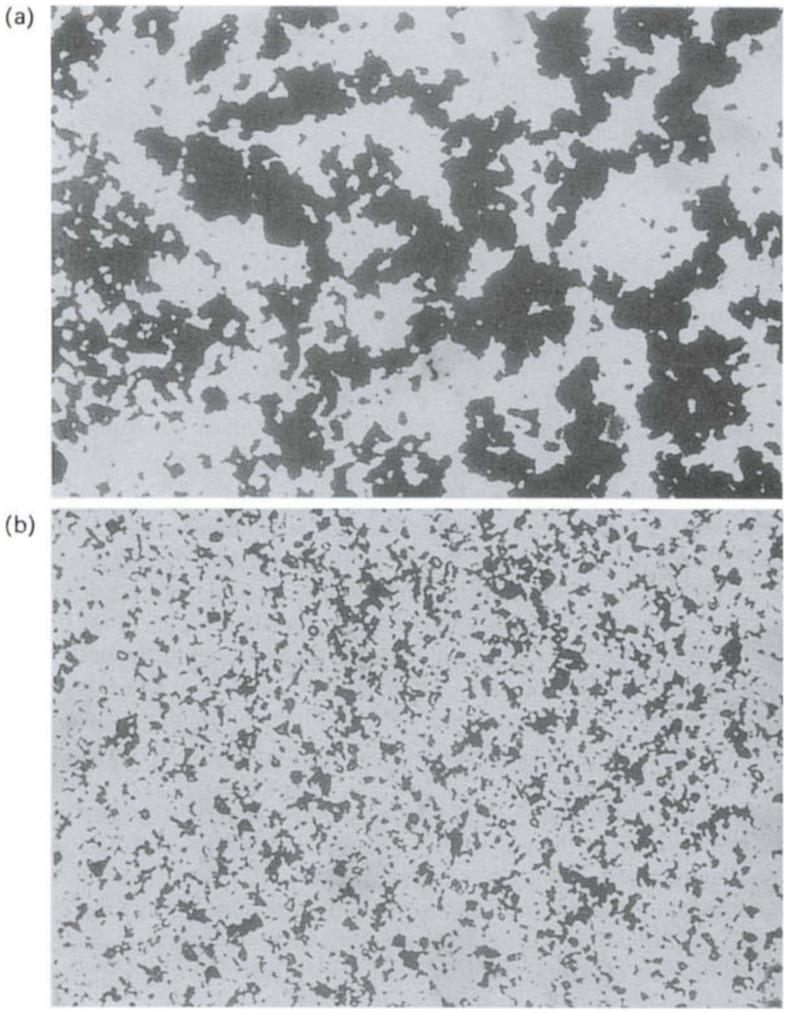


Fig. 15.31 Photographs of dispersed cement grains (a) before and (b) after addition of superplasticiser.

during which only slow changes take place. This competitive effect is shown in Figures 15.37 and 15.38, albeit for a lignosulfonate plasticiser.[40]

Further extension of the period during which superplasticised concrete remains workable can be obtained by repeated additions of admixture. Only small extra dosages are usually necessary to maintain workability.

To avoid the complication of delayed addition and repeat dosing, superplasticers have been developed with improved workability retention. Some are tailor-made polymers[41] in a patented system, while others are superplasticiser–retarder blends which give similar results. They are generally described as retarding superplasticising admixtures as there is in all cases a degree of set retardation when workability is maintained for more than 1 h. The performance requirements (BS 5075: Part 3: 1985) for normal retarding superplasticisers are again given in Table 15.7. The effects of a particular combination of heptonate or boroheptonate/superplasticiser are shown in Figure 15.39[42] and the relevant effect on

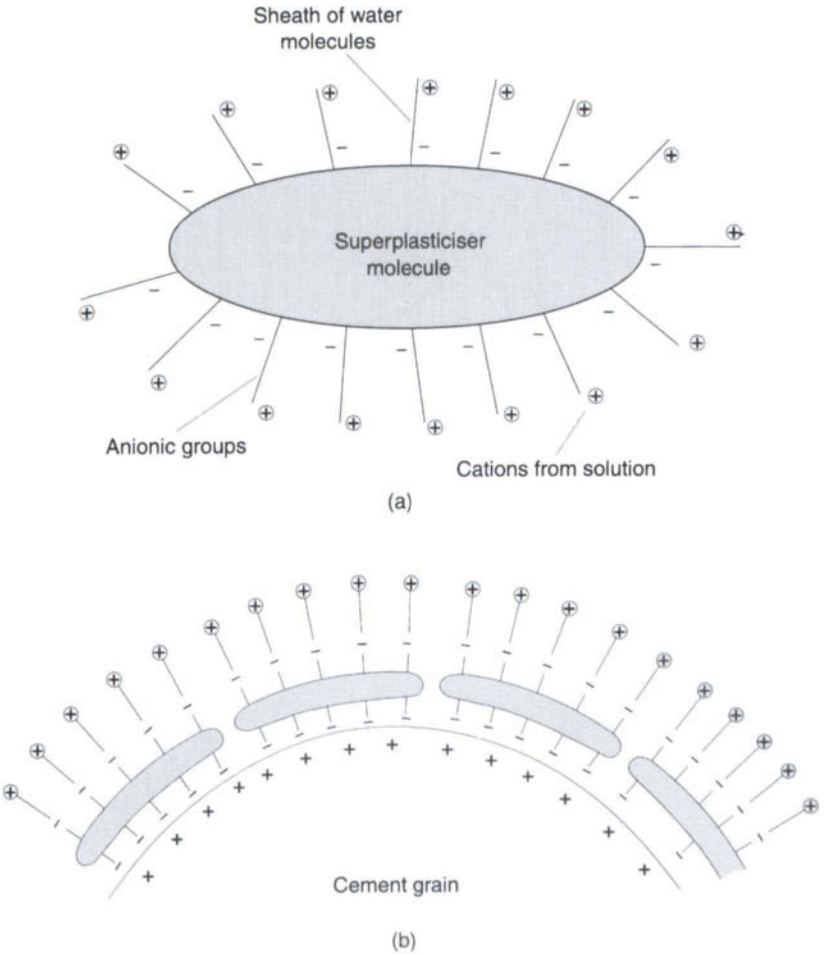


Fig. 15.32 (a) Representation of a superplasticiser molecule and (b) its mode of adsorption on cement (source: Ref. 39).

setting time and strength development in Table 15.8. More recent developments involve the use of zeolites/natural aluminosilicates as carriers for the superplasticiser that is gradually released into the plastic concrete, offsetting the loss in workability.[43]

Superplasticisers perform more effectively with some cements than with others. This is not merely due to the differing proportions of calcium aluminate and silicate phases in the clinker, but can be very dependent on the form of calcium sulfate present in the final cement. Basile *et al.*[44] showed that a cement in which the calcium sulfate was present as the dihydrate showed a much greater water reduction with a standard dosage of category B superplasticiser than a cement containing calcium sulfate hemihydrate. The rate of slump loss was also greater in the latter case.

Superplasticisers also improve the workability of calcium aluminate cement compositions, but generally tend to reduce strength.[45] The effect is dependent on the chemical type of admixture and on temperature. A higher dosage leads to a higher early loss of strength, possibly due to the accelerated conversion of CAH_{10} and C_2AH_8 to C_3AH_6.

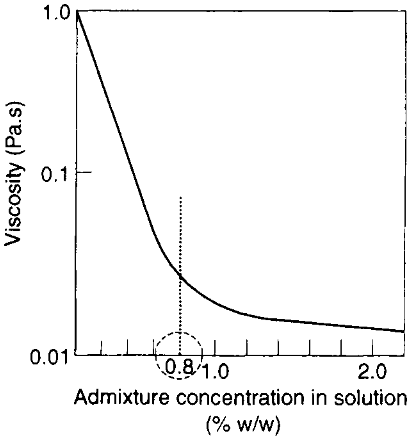


Fig. 15.33 Flow versus dosage of normal superplasticiser (w/c = 0.5; temperature = 20°C (source: Ref. 11).

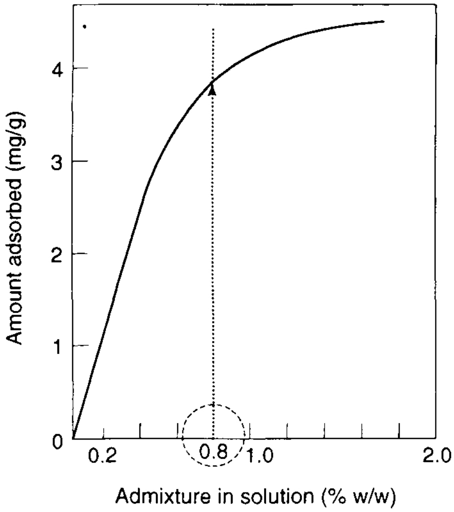


Fig. 15.34 Adsorption isotherm of superplasticiser-cement (category B; w/c = 0.5; temperature = 3 min at 20°C) (source: Ref. 11).

The effect of superplasticisers on cement hydration is mainly due to physical factors rather than chemical interaction. Better dispersion of individual cement grains leads to more efficient hydration and better early strength where no reduction in water content is made.

There is evidence[46] of a finer capillary pore system in cement paste containing a superplasticiser, and that the mean size of portlandite [$Ca(OH)_2$] crystallites is reduced. On the other hand, larger ettringite crystals are formed.[47]

When large reductions in water content are made possible by the use of a superplasticiser, improved strength and reduced permeability of the resulting concrete are an obvious benefit. More controversially, improved freeze-thaw durability has been claimed for high-strength concrete,[48] although other workers claim the need for air entrainment to avoid damage in freezing conditions. This is certainly true for flowing concrete, where the entrainment

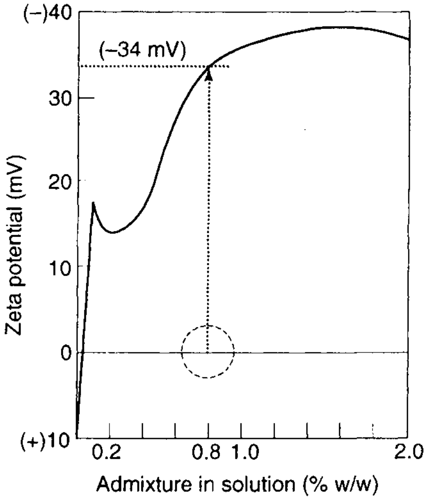


Fig. 15.35 Zeta potential resulting from adsorption (source: Ref. 11).

of stable air of the required bubble size and spacing is made more difficult by the use of superplasticisers.[49,50] In this regard the consequences of air entrainment (added cohesion) and dispersing action are mutually competitive and excluding. A balance can be struck by adding the air entrainer to give the required amount of stable air and then adding the minimum superplasticiser content to give the level of workability required.

In general, long-term durability properties are improved by superplasticisers, but other properties such as drying shrinkage and creep are only marginally affected by these admixtures.

15.5 Retarding admixtures

Admixtures that extend the hydration induction period, thereby lengthening the setting times, are known as retarders. However, they function in different ways. Usually, materials in this category function by reducing the solubility of the hydrating components in cement and so are solubility reducers; for example, gypsum retards the dissolution of aluminate, thus retarding the set of cement. Alternatively, the admixtures react with a component to form a precipitate on the cement particles, imparting a low-permeability coating on the grains, and thus slowing down further hydration.

We are more concerned with the second category of 'coating' admixtures. In the presence of water a cement particle sends out a swarm of calcium ions into the surrounding water, and any substance capable of immobilising or delaying this surge will also slow down the interchanges between the water and the particle, thus retarding the hydration process. Coating admixtures are therefore precipitated primarily on the cement constituents which are most rapidly hydratable, e.g. C_3A, C_4AF and C_3S.

Materials which can slow down the hydration of cement usually work by enhancing the early hydration sheath that surrounds cement grains. They can do this by complexing with the calcium that is liberated on hydration and/or by adulterating the early gel membrane itself. Materials that cause the latter effect are heavy metal salts of tin, lead and zinc. Their action is prolonged and difficult to control. Some sugars (such as sucrose) strongly retard cement hydration at very low dosage, but again their performance can be unpredictable

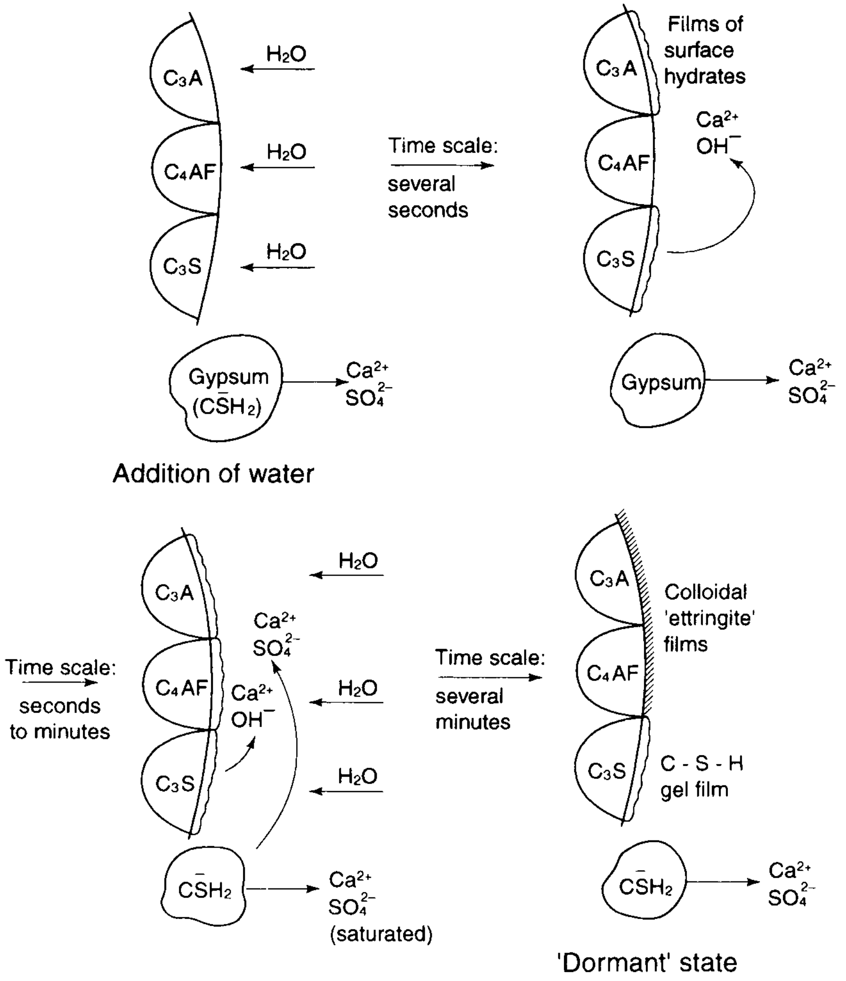
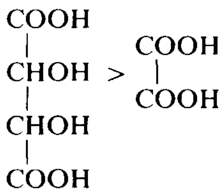


Fig. 15.36 Early hydration reactions of Portland cement: normal behaviour with no admixture present (source: Ref. 40).

and at high dosage 'flash setting' may be induced with some cements. The basic mechanism of early hydration sheath formation and its consequential osmotic rupturing is shown in Figure 15.40.[51]

Materials such as the organic polyacids have calcium salts of low solubility and effectively retard cement hydration. As the carbon chain increases in length, so does the retarding effect, e.g. tartrates are greater retarders than oxalates.



$$\mathrm{HOOC{-}CHOH{-}CHOH{-}COOH > HOOC{-}COOH}$$

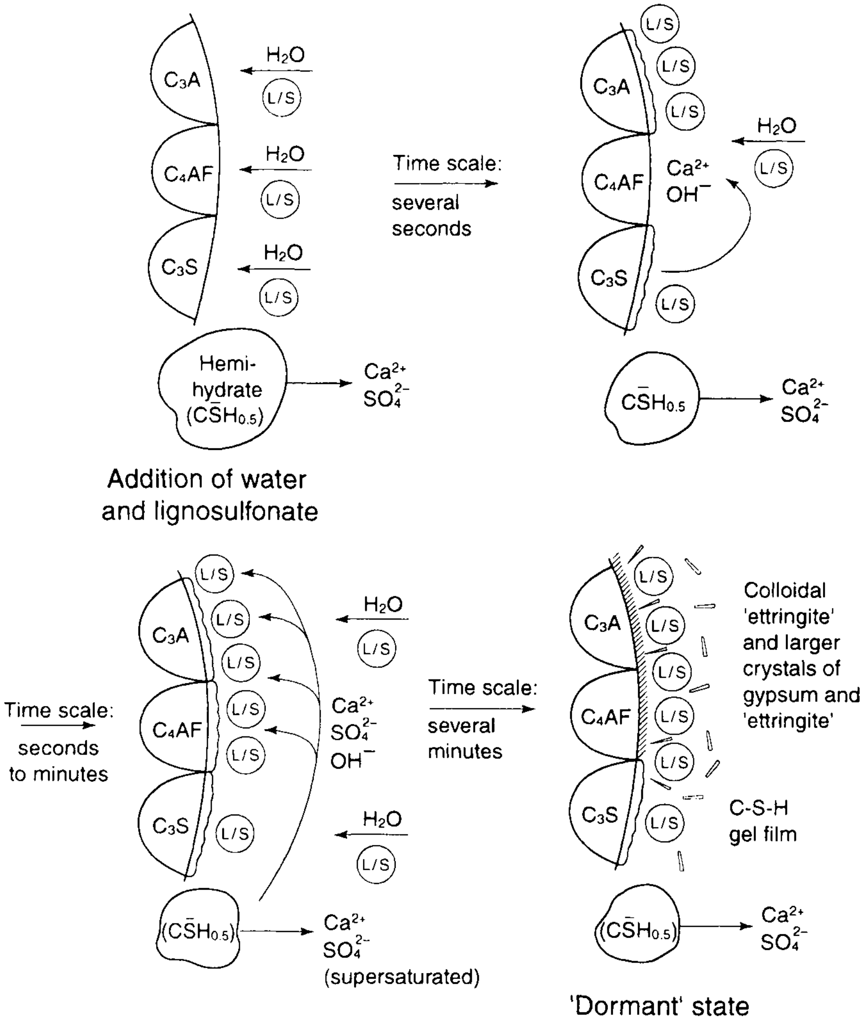


Fig. 15.37 Early hydration reactions of Portland cement: in the presence of lignosulfate (L/S) admixture and with partial dehydration of gypsum (source: Ref. 40).

This group is typified by straight-chain hydroxycarboxylic and carbohydrate materials (hence the loose term 'sugars' that is often used to describe them).

Typical materials within this group are those derived from mono- and polysaccharides such as glucose and sucrose (Figure 15.41) having the general formula $C_nH_{2n}O_n$. These materials are characterised by what is known as the α-hydroxycarbonyl group (Figure 15.42). The effectiveness of the CHOH grouping is shown in Figure 15.43 where sodium tartrate (an effective retarder) is compared with sodium caproate, which does not have the CHOH grouping and does not retard. It will also be apparent that the carbohydrate-type materials also relate to the hydroxycarboxylic acids, but to be effective retarders they have to be used at higher concentrations than when used as retarding plasticisers. Typical of these is gluconic acid, which also relates to the heptonates and boroheptonates, shown in Figure 15.44.

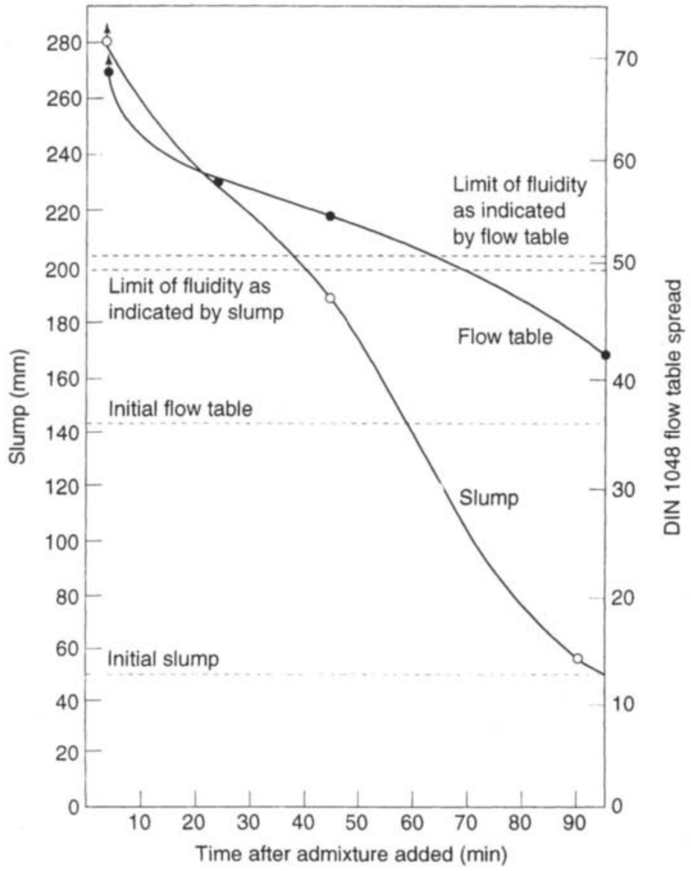


Fig. 15.38 Time-dependent workability using a category B admixture (nominal 300 kg/m^3 gravel aggregate).

Sometimes these so-called sugars may be present as impurities in other admixtures; for instance, unrefined calcium lignosulfonates contain considerable amounts – up to 40 per cent – of polysaccharides or sugar-like materials which can cause retardation on their own account.

The CHOH group is conducive to coating formation. For instance, sodium gluconate [$(CH_2OH)(CHOH)_4$–CO_2Na] is a good retarder by virtue of its capability to form coatings.

Glucose belongs to the carbohydrate family where $x = 6$ and $n = 6$ (Figure 15.41). In the presence of calcium these materials form salts; for instance, glucose forms calcium glucosate and sucrose forms calcium sucroate, sealing off the cement particles from the water, thus causing retardation. Other materials such as starch, sucrose and cellulose which are polysaccharides have the formula $(C_6H_{10}O_5)_n$ also retard by acting with the calcium, but in addition increase the viscosity of the water, slowing reaction (Figure 15.45).

It is interesting to note that glucose is a large molecule measuring some hundreds of nanometres in size and so relatively little material would be required to form a monomolecular layer on the cement, e.g. 1 g of cement which has a specific surface area of some 3000 cm^2 would require a volume of glucose equal to 3×10^{-4} cm^3 which is about 3/10 000 that of the weight of cement – very little goes a long way!

Table 15.7 Performance requirements for normal retarding superplasticisers

Property	Test reference	Type of admixture Superplasticising	Type of admixture Retarding superplasticising
Performance tests and requirements for high-workability test mix concrete A			
Flow	B.3	510–620 mm	510–620 mm
Loss of workability on standing	B.2 B.5	At 45 min the slump shall be not less than that of the control mix concrete at 10–15 min At 4 h the slump shall be not more than that of the control mix concrete at 10–15 min	At 4 h the slump shall be not less than that of the control mix concrete at 10–15 min
Minimum compressive strength as percentage of control mix concrete:	B.7		
at 7 days		90	90
at 28 days		90	90
Performance tests and requirements for water-reduced test mix concrete B			
Slump	B.2	Not more than 15 mm below that of the control mix concrete	Not more than 15 mm below that of the control mix concrete
Stiffening time relative to control mix concrete:	B.4		
for 0.5 N/mm^2		Within 1 h	1–4 h longer
for 3.5 N/mm^2		Within 1 h	–
Minimum compressive strength as percentage of control mix concrete:	B.7		
at 24 h		140	–
at 7 days		125	125
at 28 days		115	115

Note: the strength requirements take into account the usual variation in cube testing and the limited increase in air content allowed with the test mix concretes.

Salts of certain heavy metals, such as tin chloride, and magnesium salts also retard hydration by forming insoluble hydroxides in the presence of lime. For instance, calcium hydroxide has a solubility of 2.2×10^{-2} g/(atom L) whereas tin and magnesium hydroxides have solubilities of 10^{-5} and 10^{-4}, respectively. However, the use of heavy metal salts as retarders is not recommended since their reaction is not predictable and depends much on the content of soluble alkalis.

Adsorption of precipitated materials of one form or another onto the surface of cement particles or the early hydration products retards the hydration process and it becomes diffusion controlled. It should also be noted that the coating film is not completely

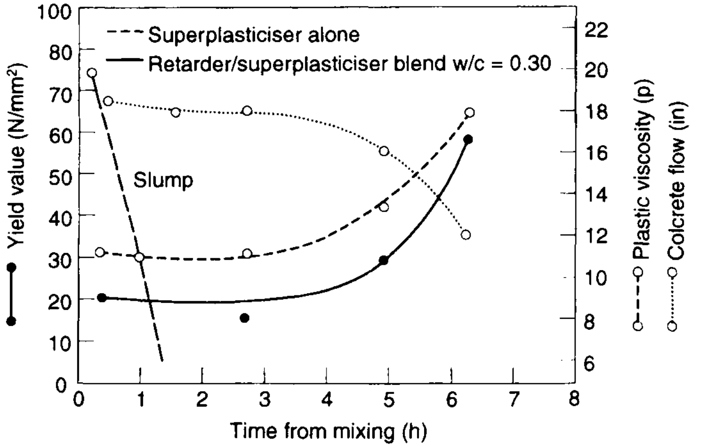


Fig. 15.39 Fluidity of neat cement grouts (source: Ref. 42).

Table 15.8 Setting time and strength development

	Proportion of retarder in superplasticising admixture (%)			
	0	25	50	100
Dosage used to give slump of 200 mm (% of cement)	0.98	0.86	0.73	0.73
Setting time (hours:minutes)				
Initial	8:20	10:50	13:00	15:20
Final	10:30	13:40	16:00	20:00
Compressive strength (N/mm^2):				
7 days	15.8	15.4	14.3	16.7
20 days	21.3	23.5	22.9	24.4

impermeable and the hydration is not permanently prevented, as has been shown by heat of hydration and setting time measurements. It is found that ultimate strengths are often enhanced by using coating-forming retarders, although the mechanism of action is obscure.

The work of Diamond[52] [54] using model compounds such as salicylic acid (a prototype hydroxycarboxylic acid type of retarder) has shown that adsorption occurs mainly on the C_3A phase. The form of precipitate is now considered to be amorphous and the hydration products contain a significant amount of salicylate complexed to aluminium in the form shown in Figure 15.46.

Some practical retarders are often based on phosphates or selected hydroxylated polymers. Soluble phosphates cover a wide range of complex salts, the most useful of which are probably trisodium orthophosphate (Na_3PO_4) and sodium pyrophosphate ($Na_4P_2O_7$).[55] The admixtures retard the first hydration peak of C_3S and considerably extend its duration. Setting of the cement is thus delayed but subsequent strength development can be enhanced. One advantage of this type of retarder is that setting times can be adjusted without unwanted changes in workability, which complicates some construction techniques such as slip forming.

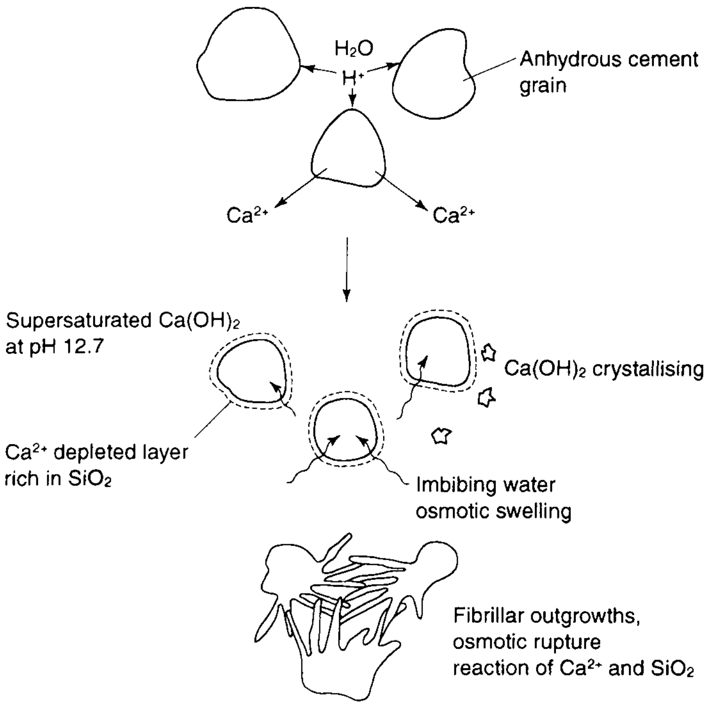


Fig. 15.40 Cement hydration/retardation (source: Ref. 51).

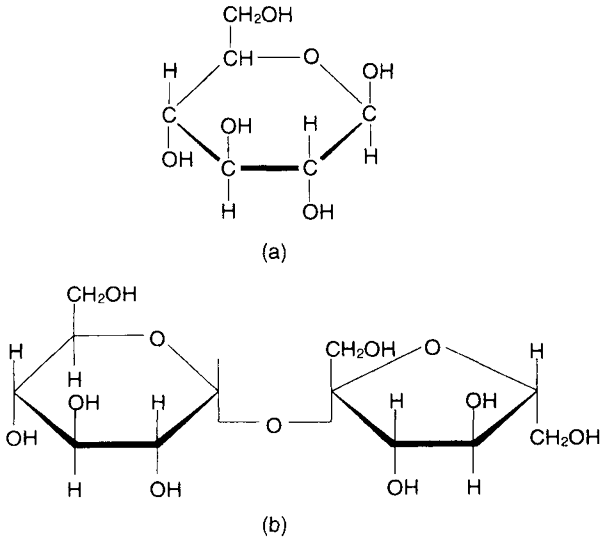


Fig. 15.41 Structure of (a) glucose (a monosaccharide) and (b) sucrose (a polysaccharide).

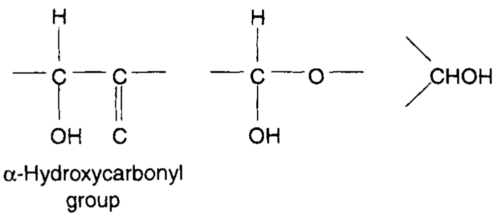


Fig. 15.42 Examples of retarding admixtures (functional groupings).

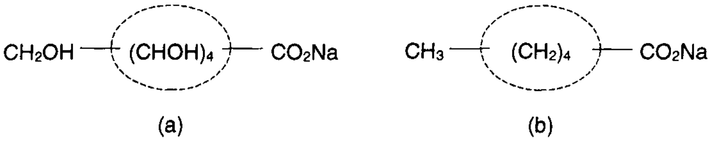


Fig. 15.43 (a) Sodium tartrate, a retarder, and (b) sodium caproate, which does not retard.

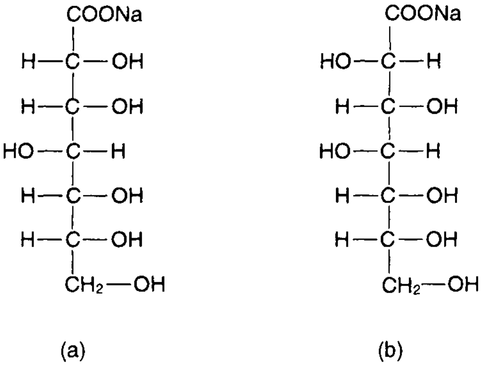


Fig. 15.44 Heptonates. (a) the α isomer (dihydrate, crystalline) and (b) the β isomer (industrial-grade liquid). Boroheptonates are essentially of the β form (liquid).

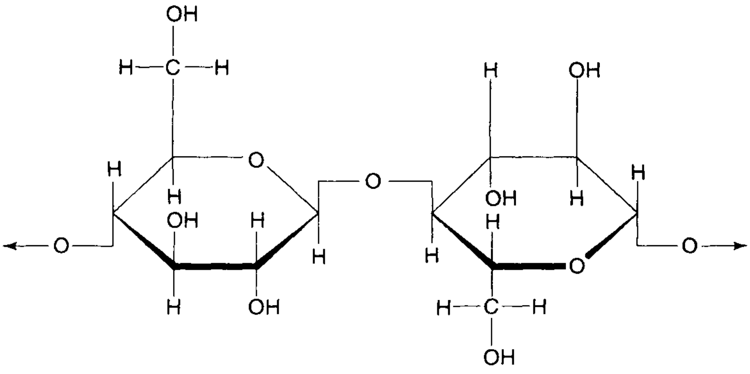


Fig. 15.45 Cellulose.

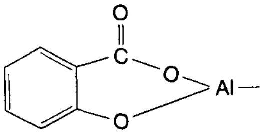


Fig. 15.46 Aluminium salicylate complex.

An important subclass of retarders is widely employed in ready-to-use mortars which can be stored on building sites for up to 48 h. Conventional retarders are used at relatively high dosages in conjunction with suitable air-entraining admixtures, the entrained air assisting in the retention of workability and preventing 'bleed'.

The optimum/compatible blend of retarding and air-entraining admixture is vital to obtain the required properties in the mortar, with a typical 'working life' of 36 h. Figure 15.47 indicates the ideal performance of the mortar and the results actually obtained with proprietary admixture combinations.[56]

Working life can be strongly influenced by the silt content of the sand, which adversely affects both air entrainment and the degree of retardation of cement hydration. The extent of the effect on retardation is shown in Figure 15.48 which indicates the increased dosage of admixtures needed to maintain a given working life as the silt content is increased.

Stiffening and setting of the mortar is brought about by the absorption of water by the bricks or other porous backing. Typically 30 per cent of the water component is removed together with the dissolved retarder, thus hastening the start of cement hydration. This suction removal process would not initially alter the concentration of the retarder but would reduce the overall amount.

The need for adequate suction in the substrate means that water-saturated or dense, impervious masonry will not activate the setting process as intended. In the case of renders and screeds, water loss by evaporation from the exposed surface may concentrate the retarder, hence further delaying set. In extreme cases drying out may occur without any strength development.

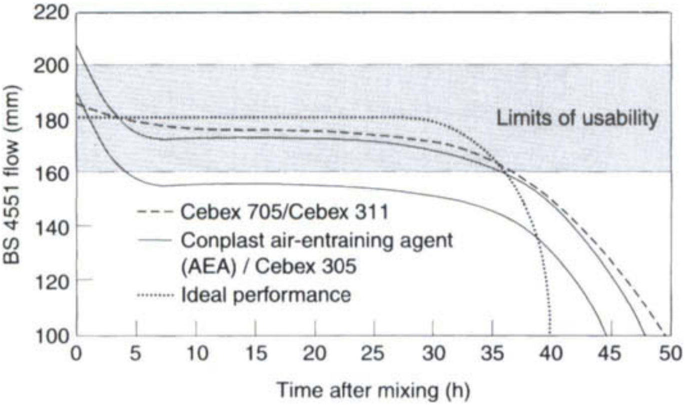


Fig. 15.47 Cebex-retarded mortar development: workability retention (source: Ref. 56).

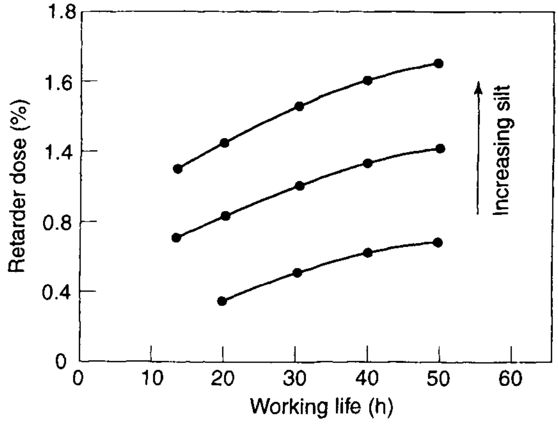


Fig. 15.48 Mortar working life versus admixture dosage (source: Ref. 56).

15.6 Accelerating admixtures[57–63]

This class of admixtures comprises a range of chemicals which influence the rate of cement hydration, thereby shortening the setting time and, in most cases, increasing the rate of early strength development. Two main subdivisions can be identified, although there is some overlap between them.

1. Rapid set accelerators which affect mainly the tricalcium aluminate phase (C_3A) of Portland cement. They are usually alkalis aiding the dissolution of silica and alumina and interfere with the C_3A–gypsum reaction.
2. Accelerators of setting and hardening, which affect mainly the alite (C_3S) phase to promote early strength. These materials are acids or salts of acids which aid the dissolution of lime.

Figure 15.49[64] shows the different ultimate effects between types 1 and 2 above.

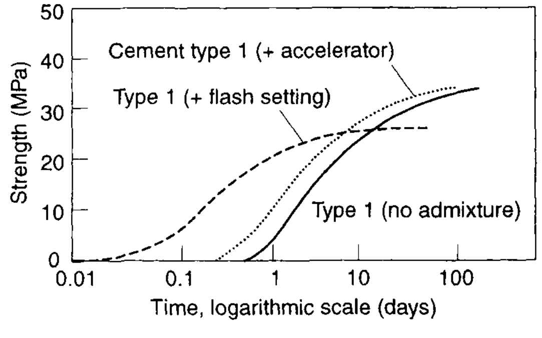


Fig. 15.49 Schematic comparison of strength development with conventional and flash-setting admixtures (source: Ref. 64).

15.6.1 RAPID SET ACCELERATORS

These materials are sometimes referred to as flash- or false-setting admixtures. They are mainly highly alkaline chemicals when in solution, typical examples being alkali metal hydroxides, carbonates, aluminates and silicates. They accelerate the hydration of C_3A, resulting in a considerable evolution of heat and precipitation of insoluble calcium salts, partly derived from the admixture itself. The increase in temperature can also stimulate C_3S hydration, which contributes to early strength, but this is not usually sustained to give high long-term strength.

A few salts derived from strong acids and weak bases (e.g. aluminium chloride) accelerate hydration of the alite (C_3S) and can lead to flash setting at high dosage. Little increase in strength occurs after setting.

This type of admixture finds only limited application in practice, but quick-setting neat cement or mortar compositions are used for plugging water leaks into basements, tunnels and shafts prior to the installation of permanent waterproofing linings.

Another important use is in controlling the set of spray-dried concrete (shotcrete) or mortar (gunite) when applied either for immediate temporary support following excavations in unstable ground, or to build up thick layers of material in a single pass which will not detach from the substrate. By adjusting the dosage accurately, setting can be varied from a few seconds to several minutes, allowing time for the material to travel from the gun to the target and to be compacted by successive layers before initial setting occurs.

The final strength of shotcrete or mortar is adversely affected by the use of accelerators, the penalty increasing with increasing dosage and consequent shortening of setting time. Admixtures for spray concrete have been well reviewed.[65]

Table 15.9[66] gives the results from a field trial of a 3:1 sand/cement gunite accelerated by the addition of a sodium aluminate–sodium carbonate type admixture. Compressive strength was determined on cores taken from panels shot with the standard site equipment and stored in water until tested. With this particular admixture and cement combination, the effective dosage of 5 per cent resulted in a reduction of strength of 60 per cent.

Superior performance has been claimed for rapid set accelerators based on organic chemicals, but little published information is available. Figure 15.50 illustrates the relative rates of stiffening obtained with inorganic and organic accelerators in sprayed concrete.

In the case of 'dry process' shotcrete or gunite, the accelerator may be dispersed as a powder and intermixed with the dry components before they are conveyed pneumatically to the nozzle, or added as a liquid with the mixing water at the nozzle. 'Wet process'

Table 15.9 Effect of gunite accelerator on setting time and strength development[67]

		Unconfined compressive strength (UCS) (N/mm^2) of cores at:	
Accelerator dosage (wt% of cement)	Final set (min)	17 days	28 days
0	200	29.3	37.5
1.5	120	21.0	23.4
2.75	40	17.1	19.5
5.5	10	12.1	14.7

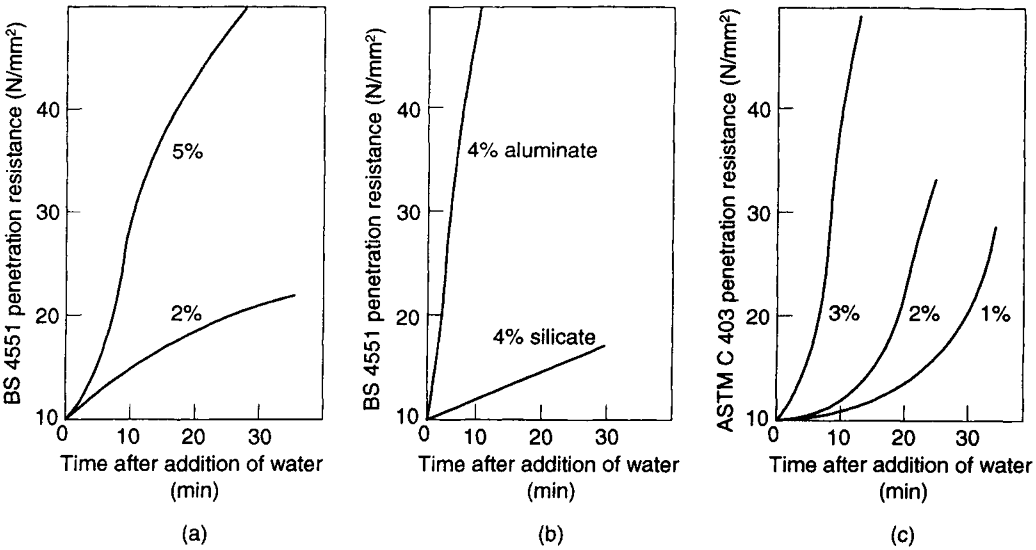


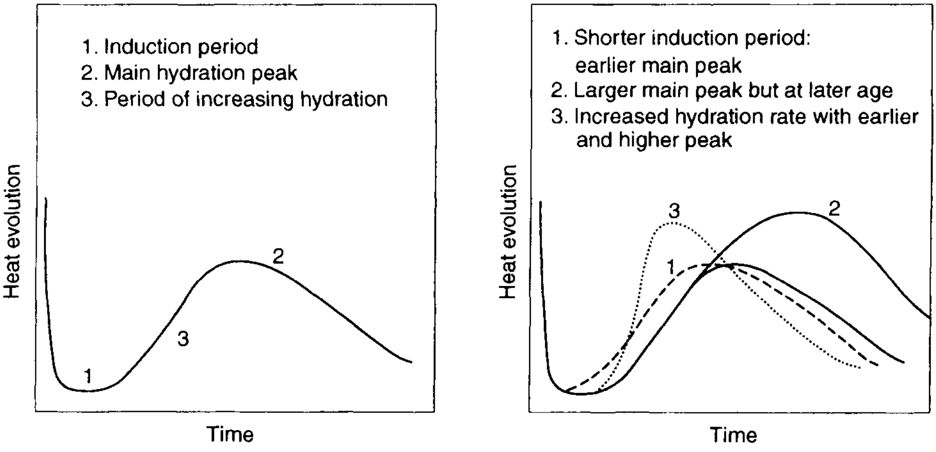
Fig. 15.50 Initial rate of stiffening of a spray concrete mix with various accelerator types (source: Ref. 3). Dosages expressed as per cent by weight for powder accelerators, or by volume for liquid accelerators, of cement weight. (a) Aluminate powder accelerator, (b) aluminate and silicate liquid accelerators, (c) organic accelerator.

shotcrete is premixed with water prior to pumping to the nozzle, and in this case the accelerator is added in liquid form to the stream of compressed air at the gun.

15.6.2 ACCELERATORS FOR SETTING AND HARDENING

This group of accelerators consists of chemicals which principally influence the rate of hydration of the alite phase of Portland cement, resulting in an increase in heat evolution and C-S-H gel formation at an early age. Conduction calorimetry can be used to demonstrate the effect of accelerators on the general hydration of Portland cement, as indicated in Figure 15.51. Comparative curves for calcium chloride and calcium formate are shown in Figures 15.52 and 15.53. Most are soluble salts of alkali and alkaline earth metals in which both the anion and cation contribute to the overall effect of the admixture.

Anions which cause significant acceleration are halide, nitrate, nitrite, formate, thiosulfate and thiocyanate (Figure 15.54)[67] although their activity appears to depend on the identity of the associated counterion. Divalent and trivalent cations such as calcium, magnesium, barium, ferric and aluminium appear to be more effective than monovalent ions such as sodium, potassium and ammonium. These conclusions have been confirmed during attempts to rank the action of admixtures using techniques such as conduction calorimetry,[68] X-ray diffraction analysis[69] and early strength development.[70] Valid comparisons between different chemical admixtures may be drawn when dosages are based on equivalent molar concentrations, and these have confirmed the superiority of calcium chloride. Figure 15.55 and Table 15.10 show the effect of some accelerators on the main hydration peak and on setting time.



(a) (b)

Fig. 15.51 (a) General hydration curve from conduction calorimetry and (b) possible accelerative effects on hydration curve (source: Ref. 3).

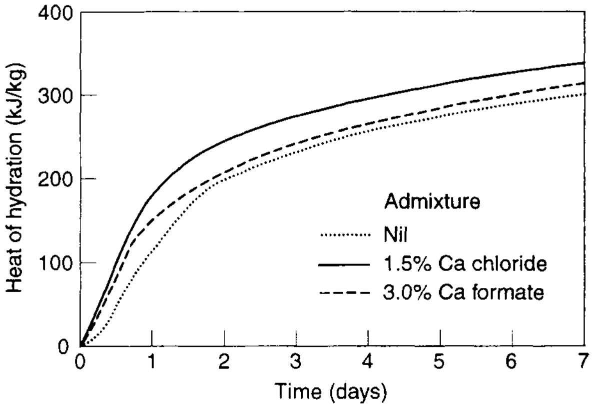


Fig. 15.52 Total heat evolution of OPC with accelerators (w/c = 0.5, temperature = 20°C).

15.6.3 CALCIUM CHLORIDE ACCELERATORS

It is a necessary requirement that an accelerator should be soluble and ionise in the mixing water. In order to accelerate the dissolution of lime, the acid ions should possess sufficient mobility in order to penetrate into the silicate particles. Consequently their size is of major importance. Taking all these requirements into account, calcium chloride is suitable, being the soluble and highly ionised salt of a strong acid, with a very small anion size (0.27 nm compared to 0.34 nm for nitrite and 0.45 nm for formate).

Amines or base accelerators also function by upsetting the dissolution of silica and alumina. Triethanolamine is an accelerator for the initial hydration of Portland cement by disturbing the reaction between C_3A and gypsum, thus accelerating the hydration of C_3A by both increasing the formation of the hexagonal aluminate hydrate and promoting the conversion to the cubic aluminate hydrate; it also accelerates the formation of ettringite.

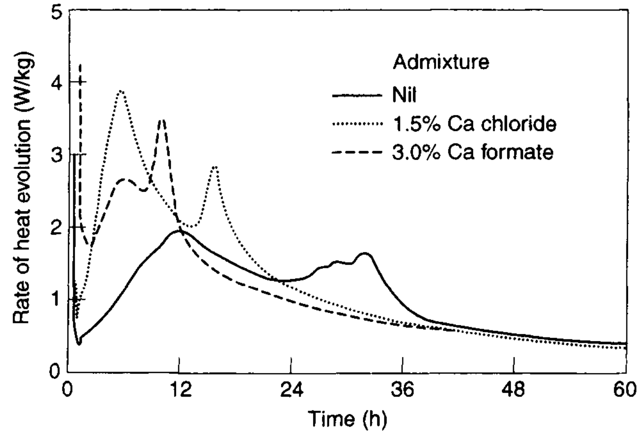


Fig. 15.53 Rate of heat evolution of OPC with accelerators (w/c = 0.5, temperature = 20°C).

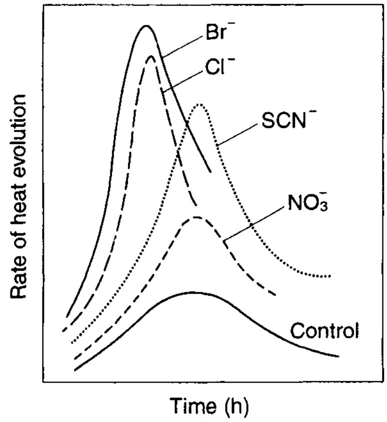


Fig. 15.54 Accelerating anions (source: Ref. 68).

However, triethanolamine may also act as a retarder in the hydration of C_3S. The strongest acids accelerate the most basic cements, e.g. chloride for Portland cements. The strongest bases accelerate the least basic cements, e.g. alkalis, oxalates and aluminates for pozzolanas, slags and high-alumina cements.

In terms of cost, availability, solubility and performance in use, calcium chloride is the ideal accelerating admixture, and has a long history of commercial use. It is particularly effective at low temperatures, when enhanced heat evolution can offset prolonged setting times of concrete during cold weather and provide an additional safeguard against freezing.

As to the mechanism of acceleration with calcium chloride, Rosenberg's[57] work indicates that the acceleration is essentially catalytic and it is the C_3S phase that is most affected. Whilst C_3A and calcium chloride do react chemically to form calcium hydrochloroaluminate of the form $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot xH_2O$, it has little effect during the early hydration of the cement itself. In the presence of gypsum, C_3A reacts preferentially, and only after this reaction is complete does the calcium chloride have any significant effect. The sequence of

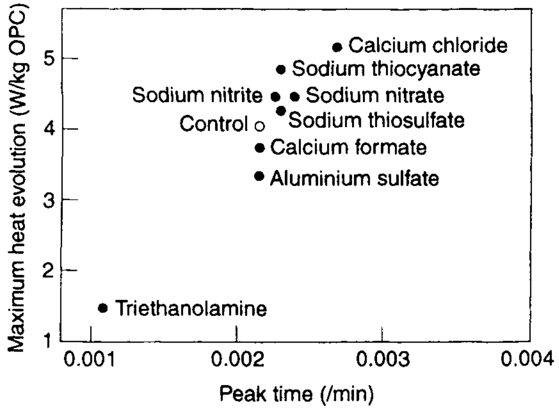


Fig. 15.55 Effect of selected chemicals on main hydration peak (0 M/kg = the control experiment; and 0.05 M/kg OPC).

Table 15.10 Effect of selected chemicals on BS 5075 final stiffening time at constant workability

Chemical	BS 5075 final stiffening time (h:min)	
	0.05 M/kg	0.10 M/kg
Control (mean value)	4:35	4:35
Aluminium sulfate	3:20	Flash set
Calcium chloride	3:30	2:45
Calcium formate	4:20	4:05
Sodium nitrate	4:05	4:05
Sodium nitrite	4:25	4:15
Sodium thiosulfate	4:30	4:20
Sodium thiocyanate	4:05	4:00
Triethanolamine	Flash set	Flash set

reactions in the system $C_3A/CaCl_2/CaSO_4/H_2O$ is as follows.

$$C_3A + 3CaSO_4 + 32H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O \qquad (15.3)$$

No reaction with $CaCl_2$ takes place during this phase.

$$\begin{aligned} CaCl_2 + C_3A + 10H_2O &\rightarrow C_3A \cdot CaCl_2 \cdot 10H_2O \\ &\rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot xH_2O \qquad (15.4) \\ &\text{(calcium hydrochloraluminate)} \end{aligned}$$

After all the $CaCl_2$ has been used, conversion of the trisulfoaluminate to the monosulfoaluminate occurs:

$$\begin{aligned} C_3A \cdot 3CaSO_4 \cdot 32H_2O + 2C_3A \cdot Ca(OH)_2 \cdot 12H_2O &\rightarrow 3C_3A \cdot CaSO_4 \cdot 12H_2O \\ &+ 20H_2O + 2Ca(OH)_2 \qquad (15.5) \end{aligned}$$

The resultant $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$, $C_3A{\cdot}CaCl_2{\cdot}10H_2O$ and $C_3A{\cdot}CaSO_4{\cdot}12H_2O$ form a solid-solution series.

Calcium chloride seems to act as a catalyst of the hydration of C_3S and C_4AF, although there is some evidence of a possible chloride complex in the hydrating C_3S system. The reactions are slow and do not appear to be the cause of accelerated set in Portland cement paste. At high water/cement ratios, the chloride ion reacts to form the hydrochloraluminate and stabilises the formation of ettringite. The aluminate ions produced from C_4AF are also consumed together with the C_3A. Calcium chloride causes small fibrous crystals to appear during hydration, indicative of rapid crystallisation, which in turn may be caused by the highly ionic character of the water phase when calcium chloride is present.

The hydration of the system $C_3A{-}CaCl_2{-}CaSO_4{\cdot}2H_2O$ shows that the calcium chloride primarily accelerates the reaction between C_3A and gypsum. Sulfate reacts first followed by reaction of C_3A and chloride after the gypsum has been used up. Calcium chloride appears to stabilise the formation of trisulfoaluminate (ettringite). After conversion of the ettringite the hydrates which have a hexagonal structure, namely $C_3A{\cdot}Ca(OH)_2{\cdot}12H_2O$, $C_3A{\cdot}CaCl_2{\cdot}10H_2O$ and $C_3A{\cdot}CaSO_4{\cdot}20H_2O$, form solid solutions.

At normal temperatures, shorter setting times and high early strength allow rapid demoulding of precast concrete items and hence shorter production cycles. Rapid repair work using concrete, mortars or grouts is also facilitated. The control of setting time and variation of dosages is very precise.

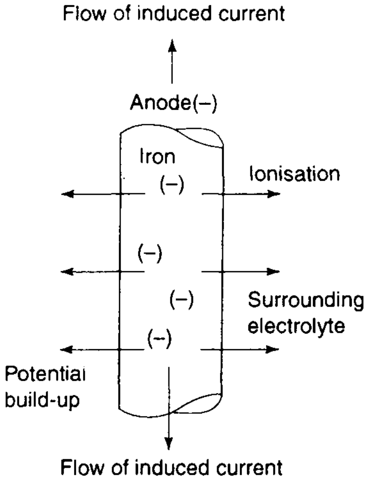
However, when used in reinforced or prestressed concrete, the highly active chloride ions will quickly depassivate the surface of steel, which is normally protected at the high pH of cement paste by an oxide film. This oxide layer increases the oxidation/reduction potential of the metal, thus depassivating it. In the presence of chloride ions the protective layer is broken down because the chlorides of metals are generally soluble. Once this has happened, electrochemical corrosion can occur. The prerequisites are:

- the presence of an electrolyte in contact with the metal;
- the presence of local differences in electric potential (metallic impurities, internal stresses, difference in crystal form);
- the presence of oxygen.

This sequence of events is shown in Figure 15.56. The result of the primary reaction is the transition of iron from metal into solution, which constitutes corrosion. Electrons are liberated at the anode and consumed at the cathode. The presence of chloride gives a good conducting medium and breaks down the passivating layer.

The composition of the cement and the use of replacement materials such as pfa, ground granulated blastfurnace slag (ggbs), and condensed silica fume (csf) all influence the degree to which the added chloride is combined in calcium aluminate hydrates or C-S-H gel, hence the level of free chloride ions in the pore fluid can only be determined by experiment.

There is continuing disagreement on the existence and value of a threshold chloride ion concentration above which corrosion can occur. The importance of the Cl^-/OH^- ion ratio in the pore fluid is also disputed, although there is considerable evidence that a higher pH must be matched by higher chloride levels before corrosion of steel reinforcement will commence. Hauseman[71] concluded that there was a critical Cl^-/OH^- ratio of ~0.6 in the pH range 11.6–12.4, above which corrosion starts, but it has been demonstrated by Rasheeduzzafar *et al.* that in practice concrete pore solutions show a pH considerably higher than 12.5.[72] It has been suggested that 'safe regions' of this ratio can be established for different types of concrete.[73]



(1) Primary reaction
$2Fe - 4\varepsilon \longrightarrow 2Fe^{2+}$ (ionisation)
(metal)
$2Fe^{2+} + 4OH^- \longrightarrow 2Fe(OH)_2\,[FeO, H_2O]$
ferrous oxide hydrate

(2) Secondary reaction
$2Fe(OH)_2 + H_2O_2 \longrightarrow 2FeO(OH)\downarrow + H_2O$ [Rust formation, oxidation to the ferric state]

(3) Cathode reaction
$2H_2O + O_2 + 4\varepsilon \longrightarrow 4(OH)^-$

Fig. 15.56 Corrosion of reinforcement.

Irrespective of these findings, the use of chloride-based admixtures in reinforced or prestressed concrete is now banned, and the level of chloride in most admixtures is limited to 0.1 per cent by mass. Calcium chloride also reduces the sulfate resistance of concrete made with ordinary Portland cements.[74] These problems have led to a renewed search for improved chloride-free accelerators.

15.6.4 NON-CHLORIDE ACCELERATORS

Although not as effective as calcium chloride, several chemicals have been proposed and become commercially available for use as accelerators, calcium formate, de-acidised calcium formate, sodium aluminate and triethanolamine being those most commonly mentioned.

As previously indicated, calcium salts appear to have a superior activity compared with most other metal salts, but they commonly suffer from a low solubility in water. Calcium formate acts in a manner similar to calcium chloride, but high dosages are required and its solubility is considerably less (approximately 17 g/100 g compared with 75 g/100 g at 20°C).

Two or more chemicals are often used in combination to increase the concentration and improve the performance of liquid admixtures, which are preferred to powders for accurate dosing of concrete. Calcium formate sodium nitrite blends have been used extensively,

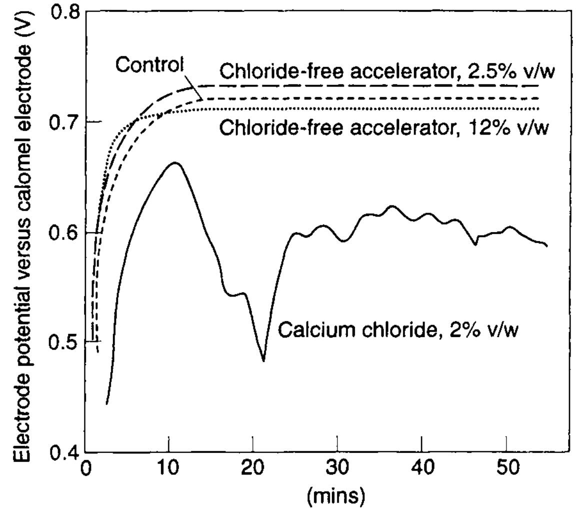


Fig. 15.57 Variation of electrode potential with time during corrosion test (source: Ref. 76).

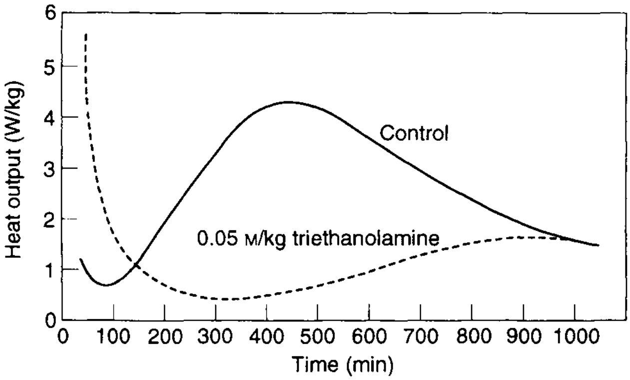


Fig. 15.58 Effect of triethanolamine on Portland cement hydration by conduction calorimetry (source: Ref. 76).

with the added advantage of anti-corrosion properties claimed for their use.[75] Measurement of the electrode potential of steel embedded in concrete at constant applied current density is one method of monitoring the passivity of the steel. Figure 15.57 compares the protection given by a chloride-free accelerator with the breakdown caused by calcium chloride.[76]

A third minor ingredient, triethanolamine, has also been incorporated in some proprietary admixtures to shorten initial setting times. Triethanolamine will combine with aluminium and so provide dissolution of the C_3A in advance of aluminohydrate formation. It is an accelerator of C_3A hydration at low dosage (0.1–0.5 per cent by weight of cement) but at higher dosages causes retardation of C_3S hydration. Figure 15.58 shows the effect of triethanolamine on the main (C_3S) peak during cement hydration at a dosage of 0.4 per cent.[76] The proportion of triethanolamine in compound chloride-free accelerators must therefore be limited, in order for the dosage to be kept below 0.5 per cent at normal levels of addition of the admixture to concrete.

In recent years, calcium nitrite has been manufactured commercially and become available as a proprietary accelerator. This chemical has a reasonably high solubility (~ 50 g/100 g) and is claimed to be almost as effective as calcium chloride. The dosage rate is of the order of 0.3–2.3 per cent (as solids by weight of cement). The toxicity of inorganic nitrites, in contrast to most other chemicals used as cement accelerators, should be noted. Calcium nitrite has also been promoted as a corrosion inhibitor for reinforced concrete.[77] Other non-chloride accelerators have been based on calcium nitrate or sodium thiocyanate. The latter is effective but relatively expensive.

15.7 Water-resisting admixtures

These admixtures (also known as integral permeability reducers, waterproofers or dampproofers) consist of materials which reduce the hydraulic permeability of concrete and mortar, and often confer water repellency to the exposed surfaces. Their efficiency is not readily demonstrated due to the relative impermeability of well-compacted high-quality concrete. These admixtures have been reviewed previously,[78–80] and comprise a disparate group of material types shown in Figure 15.59.

Water may pass through concrete or mortar via interconnected voids within the cement paste matrix or at the paste–aggregate interface. Ignoring defects such as gross voids, cracks or open joints, the interconnected porosity is of two kinds:

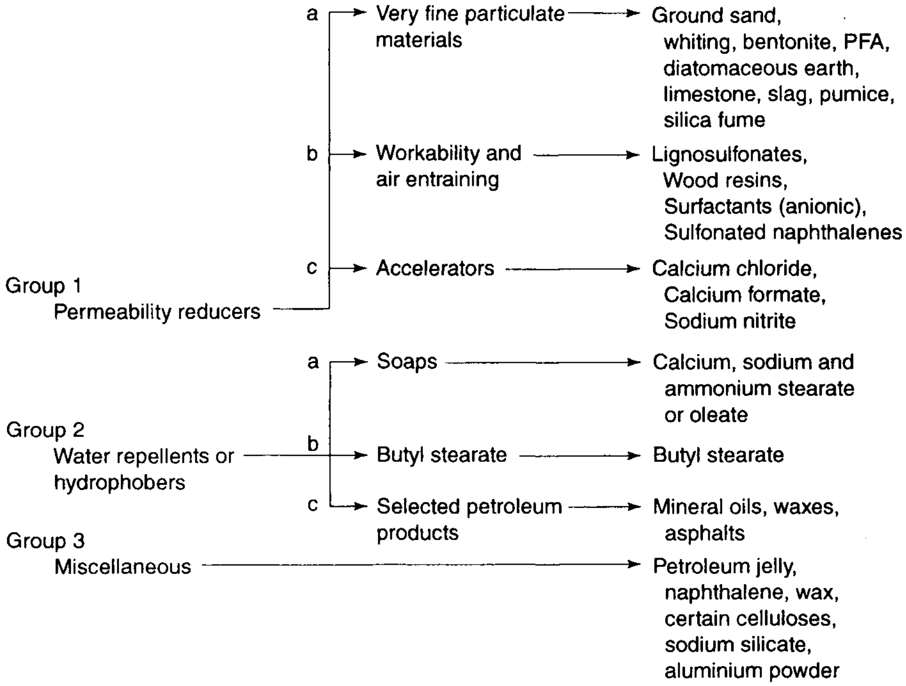


Fig. 15.59 Waterproofing admixtures.

- Micropores in the C-S-H gel, typically of the order of 2–8 nm in diameter;
- capillary pores between cement hydration products which are all that remains of the original interparticle space and are of the order of 1.3 μm.

Micropores appear to be of almost constant size in all cement pastes, and contribute little to percolation flow of water through concrete. These pores are also independent of the original water/cement ratio.

On the other hand, capillary pores vary in size and number depending on the water/cement ratio and maturity of the concrete or mortar. Theoretically, cement pastes with a water/cement ratio of $\leqslant 0.5$ achieve capillary discontinuity after several days of wet curing, and should then be impervious. However, in practice all concretes possess minor defects, which result in a finite hydraulic permeability of the order of 10^{-8}–10^{-10} m/s. This applies to saturated concrete subject to a pressure head of water. Unsaturated concrete in contact with a source of moisture will imbibe water by capillary suction, the magnitude of which can be equivalent to a hydrostatic head of several metres. Normal concrete is thus never completely watertight, and will allow transmission of water in liquid or vapour form. Admixtures intended to improve this situation fall into three main groups (Figure 15.59).

- Group 1. These comprise permeability reducers which lessen the overall porosity by blocking the normal interconnected capillary pores.
- Group 2. Water repellents or hydrophobers which coat the pore surfaces with a water-repellent precipitate.
- Group 3. Miscellaneous items.

We will now deal with each group and subgroup in turn.

15.7.1 PERMEABILITY REDUCERS

These may be very fine inert powders added in sufficient quantity to fresh concrete to reduce the residual pore volume, often in combination with a plasticiser or superplasticiser to maintain workability, or even allow a reduction in the water/cement ratio. Reactive powders (such as condensed silica fume) are to be preferred if they combine with the calcium hydroxide in the pore fluid to augment the C-S-H gel produced by the cement.

Replacement of the coarsely crystalline calcium hydroxide (portlandite) in the cement matrix by C-S-H gel leads to a refinement of the pore system which can reduce hydraulic permeability. However, capillary suction may actually increase, and an alternative strategy is then required.

Very fine particulate materials

Ground sand, whiting, bentonite, pfa, diatomaceous earth, limestone, slag and pumice, colloidal silica (csf) and fluorosilicates comprise in part this group. It is preferred if the finally divided material has some degree of pozzolanic reactivity.

Particulate materials are of real benefit if the concrete mix is low in cement or deficient in fines. However, in cement-rich mixes the effect could be the reverse, since the addition of fine particles could increase the water requirement, leading to a less dense and lower-strength concrete. It could be argued that as long as heat evolution is not a problem, and shrinkage cracking can be avoided, the addition of extra cement to lean mixes is the best means of waterproofing.

Workability and air-entraining admixtures

Incorporating a workability agent or plasticiser reduces the chance of large voids and the lower water requirement offsets bleed. Salts of lignosulfonic acids are commonly used, often in combination with a particulate mineral filler. Incorporation of lignosulfonates may give rise to a finer pore system which, whilst causing high capillary absorption and absorptivity actually increases resistance to the passage of water and hence its hydraulic permeability. Air-entraining agents act in a manner similar to lignosulfonates by imparting improved workability to the mix, allowing less water to be used. The cellular network does not give rise to interconnected voids which would otherwise increase the permeability.

Accelerators

The function of accelerators as permeability reducers is doubtful. The use of calcium chloride, for instance, may improve early permeability and porosity figures simply by advancing the overall hydration reaction of the C_3A and C_3S phases, but the ultimate permeability remains, it would appear, unchanged.

15.7.2 WATER-REPELLENTS OR HYDROPHOBERS

Hydrophobing agents are a group of oily or waxy compounds which are introduced as solutions or suspension into concrete, where they precipitate often as the insoluble calcium salts. These form a water-repellent coating on the concrete surface and on the inner walls of capillary pores, which increases the angle of contact of liquid water and inhibits its wetting capability. In extreme cases water is claimed to be expelled from a concrete or mortar surface rather than adsorbed.

Materials comprising this group are soaps of long-chain fatty acids (stearates, oleates and palmitates), hydrolysable oils (butyl stearate), mineral oils, wax dispersions and asphaltic emulsions. Precipitation usually occurs during the first 24 h after casting and any effect on strength development is of short duration. Some admixtures of this type do tend to entrain air, however, leading to a permanent reduction in strength while the unsaturated aliphatic acids can affect the later ettringite–monosulfate conversion.

Complex water-resisting admixtures may comprise three major ingredients, for example ammonium stearate solution, a sulfonated naphthalene–formaldehyde superplasticiser and an asphaltic emulsion, and can be used at dosages as high as 30 L/m^3 of concrete. At this level of addition, sorbtivity can be reduced by a factor of approximately four and hydraulic permeability by an order of magnitude,[81] although the materials cost of the concrete may be doubled. Chloride ion diffusivity is also reduced by 75 per cent.

Due to the reduced moisture movement in concrete containing these admixtures, dampness and efflorescence can be eliminated. External concrete surfaces exposed to the weather also retain a pristine appearance, because the shedding of surface water discourages the accumulation of dirt and the growth of lichens or moss.

Materials in this group reduce the passage of water through dry concrete, which would normally occur as a result of capillary action and not by means of an external pressure of water. Moisture movement of this type may result in staining, efflorescence and general unwanted dampness. In principle, it is thought that all these materials impart a water-repellent property to the concrete surface, as well as lining and in some cases blocking the pores. The detailed mechanism is obscure, but it has been suggested that the water-repellent action is associated with an electrostatic charge imparted to the walls of the capillaries.

Materials comprising this group are:

- soaps
- butyl stearate
- selected petroleum products.

Soaps

These are usually metal salts and more recently the sulfonium salts of fatty acids, for instance calcium, sodium or ammonium stearate, oleate as well as stearic acid dispersions. The 'soluble' soaps are thought to react with the calcium ions in the aqueous phase of the concrete and so precipitate out as the insoluble calcium salts. It is this precipitate that imparts the hydrophobic coating to the capillary surface as well as blocking some pores in the fresh concrete. The pore system that develops during the later stages of hydration (>24 h) is not affected by this precipitate, hence the saturated permeability is not reduced.

All these materials entrain air, due presumably to their surfactant properties, and dosages exceeding 0.2 per cent by weight of cement are not recommended in order to avoid the likelihood of significant strength loss. On the other hand, improved workability may result from using these soaps, which reduce the formation of cavities and large voids. The optimum dosage should be established by taking regard of the mix design, admixture chosen and final properties required.

Butyl stearate

The hydrophobic action of butyl stearate is similar to that of the soaps described above in that the eventual compound resulting in water repellency is calcium stearate. However, butyl stearate hydrolyses only slowly in the alkaline phase of concrete and slowly produces calcium stearate. As a result, very much less air is entrained and strength reductions are not so serious. This allows higher concentrations to be used which invariably gives improved dampproofness. Slow reaction of the butyl stearate also allows better distribution of the admixture throughout the cement gel.

Selected petroleum products

Mineral oils, waxes, cut-back and emulsified asphalts comprise this group. In the case of the asphalt emulsions, the dispersion is broken by the drying out of the concrete, resulting in hydrophobing and some pore blocking. The other compounds are generally regarded as 'inert' hydrophobers acting mainly in a physical way without obvious reaction with the cementitious components.

Some strength reduction may result due to entrained air, particularly if emulsifying agents have been used to disperse the hydrocarbons. Certain wax emulsions may improve the dampproofness of steam-cured concrete by melting *in situ* and so blocking the pores.

15.7.3 MISCELLANEOUS

Products in this group are considered to have some waterproofing function, but the chemistry is obscure and practicability perhaps doubtful. Examples of such materials are petroleum jelly, naphthalene, wax, certain celluloses and diluted coal tars and finally sodium silicate and aluminium powder.

Proprietary products which comprise any one of several materials from this group have to be judged on their proven merits. Justification may often appear obscure and no strict recommendations can be given.

Silicones, although widely used for the surface treatment of concrete, have not found much use as integral waterproofers. The cheaper silicones tend to cause excessive retardation when used in sufficient quantity to affect the properties of hardened concrete.[82,83] Methyl siliconates and polyhydrosiloxanes have been evaluated for improving the frost resistance of concrete, but the permeability was not found to be reduced. Research on these materials continues.[84]

15.8 Speciality admixtures

In addition to the main categories of admixture which constitute the bulk of those used in the concrete industry, there are several types which find occasional use in special applications. The following are the more important admixtures of this type.

15.8.1 POLYMER DISPERSIONS OR LATICES

The earliest attempts to modify the properties of cementitious compositions by the addition of natural rubber latex were only partially successful, due to stability problems which caused rapid coagulation of the rubber at the high pH of Portland cement pastes. With the development of synthetic rubbers and other organic polymers, achievement of the anticipated benefits is now a reality. This subject has been well reviewed.[85] These benefits include:

- improved tensile and flexural strength;
- improved bonding to steel and mature concrete surfaces;
- lower elastic modulus and hence reduced cracking tendency;
- lower permeability to water;
- reduced chloride diffusivity;
- improved durability (freeze–thaw, weathering, carbonation).

Due to their cost and relatively high dosage levels (typically 10 per cent latex solids by weight of cement), synthetic latices are rarely used in concrete, but are frequently used in renders, floor toppings and repair mortars.

Some of the earlier, cheaper polymer dispersions such as poly(vinyl acetate) (PVA), were found to hydrolyse at the high pH in mortar, and rapidly deteriorate under damp conditions. Although PVA is still widely used for internal applications where the mortar dries out permanently, new copolymers have been developed for more demanding situations, such as vinylacetate–ethylene, styrene–butyl acrylate, butyl acrylate–methylacrylate and styrene–butadiene. The acrylics are particularly useful for external application as they are transparent to UV radiation and therefore do not degrade on exposure to sunlight.[86]

All these copolymers are produced as ~50 per cent aqueous dispersions (solids in suspension), stabilised by suitable non-ionic surfactants. The latter allow a reduction in the mixing water when producing a mortar of a given workability, but can also lead to excessive air entrainment. This tendency can be minimised by the mixing technique employed and/or the addition of antifoam agents.

The action of the polymer latex is essentially the formation of an interpenetrating polymer network within the cement-based matrix. The film-forming properties of the polymer can only be realised by a partial drying out of the mortar which allows the dispersion to 'break' and the polymer particles to coalesce. In this regard the film-forming temperature should be below or close to ambient. Hence a period of dry curing is essential, after the initial damp curing of polymer-modified mortars, otherwise the desired properties will not be attained.[87]

Most synthetic latices have little effect on the hydration of the cement, although a modest acceleration of setting and early strength development occurs in most cases. Polymers for use as mortar or concrete admixtures are selected on the basis of several parameters which include film hardness, elongation at failure, particle size in aqueous dispersions and temperature of film formation (usually below ambient).

Both emulsions and dispersions of chemicals are often used to improve the bonding characteristics of mortars and concretes as well as to reduce permeability.

The composition of a typical styrene–butadiene (SBR) latex is shown in Table 15.11[88] and these materials may be used at high concentrations with respect to the cement – as high as 15–20 per cent. As a consequence, the properties of the modified material reflect the properties of the admixture. The marked improvement in using a slurry bond coat modified in this way is shown in Figure 15.60.[90]

15.8.2 THICKENING AGENTS/VISCOSITY MODIFIERS

This group of admixtures comprises a number of high molecular weight water-soluble polymers which modify the rheology of cementitious compositions. Natural gums, such as alginates and guar, have been largely superseded by cellulose ethers (methyl, hydroxyethyl and hydroxypropyl celluloses) and poly(ethylene oxide)s. These polymers can be produced in a wide range of both molecular weights and, in the case of cellulose ethers, of the degree of substitution of the basic cellulose skeleton.

Table 15.11 Typical properties of SBR latex designed for use with Portland cement[88]

Total solids	44–47% by weight
pH	10.5
Surface tension	0.03–0.05 N/m^2
Viscosity at 20°C (Brookfield LVT, spindle 2, 60 rpm)	0.004–0.01 N s/m^2
Specific gravity	1.01
Freeze–thaw stability	Withstands several freeze–thaw cycles, but inside storage above 0°C recommended
Particle size	~0.2 μm
Stabilisation	Non-ionic
Butadiene content	33–40% by weight of SBR polymer
Anti-oxidant	Yes
Bacteriocide	Present
Anti-foam	Usually present
Minimum film-forming temperature	1°–4°C
Shelf life (interior storage above 0°C)	Above 2 years, but agitate before use after prolonged storage, as creaming can occur

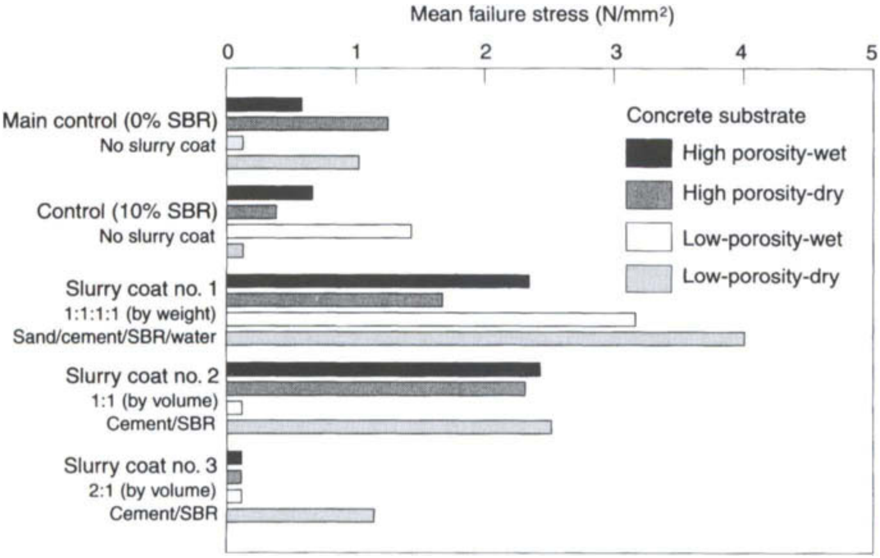


Fig. 15.60 The influence of various bonding primer coats on pull-off test results (source: Ref. 90).

All the polymers consist of long chains replete with hydrophilic groups (Figure 15.61) which cause the molecules to interact strongly with water and each other by hydrogen bonding. There are many equations that relate the size and shape of the molecules, the interactions with the solvent, and interactions between the polymer chains themselves. Suffice to say that

$$\eta \propto f(M) \tag{15.6}$$

where η = viscosity of the aqueous solution and M = molecular weight. Thus as M increases, so does η. Such solvent–molecular interaction can cause polymer chains to become very extended, thus encouraging entanglement (Figure 15.62).

Such molecules also have an affinity for the polar surfaces of cement and aggregate particles, hence the viscosity of the aqueous phase of cement paste is increased and there is a reduced tendency for water to separate from the solids. This property has resulted in the use of cellulose ethers as anti-bleed agents in grouts and concrete. Poly(ethylene oxide) has also been used as a pumping aid for concrete and mortars because its fluid retention properties are supplemented by increased lubricity, derived from the linked hydrocarbon chains preventing local turbulence and pressure loss.

As the molecular weight of the polymers increases, so does the viscosity contribution, assisted by interaction with the aqueous solvent. For instance, lignosulfonates are high molecular weight polyelectrolyte materials (molecular weight = 5000–200 000) but in water contract themselves to form little spheres, and solutions of high concentrations still have low viscosity (Figure 15.62). This is a consequence of the polymer–solvent interaction being relatively low.

Another application of thickening agents is in the production of cohesive concretes and grouts to be placed under water. Although cellulose ethers can be used alone to produce underwater concrete, there are difficulties in obtaining sufficient workability for the concrete to be self-levelling and self-compacting. Compound admixtures are therefore normally

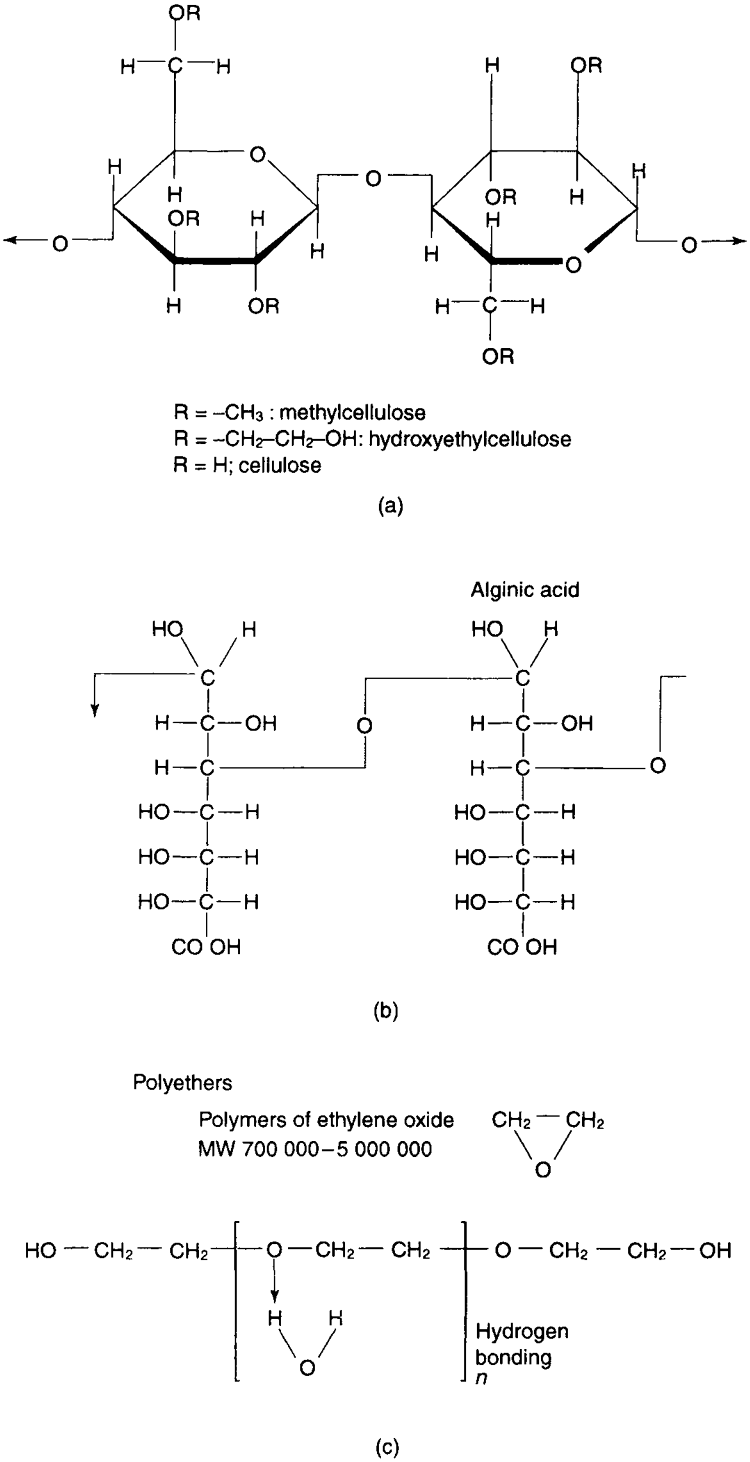


Fig. 15.61 Molecular structure of viscosity modifiers. (a) Cellulose ethers, (b) alginates and (c) poly(ethylene oxide)s.

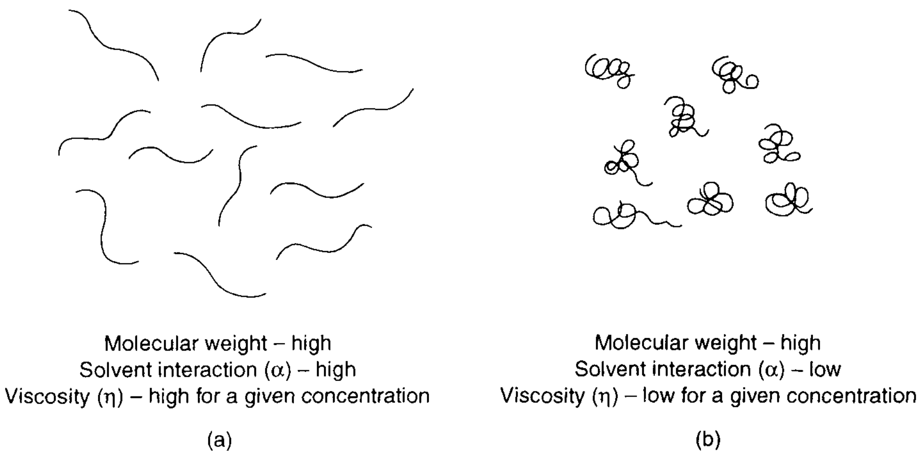


Fig. 15.62 Polymer–solvent interaction.

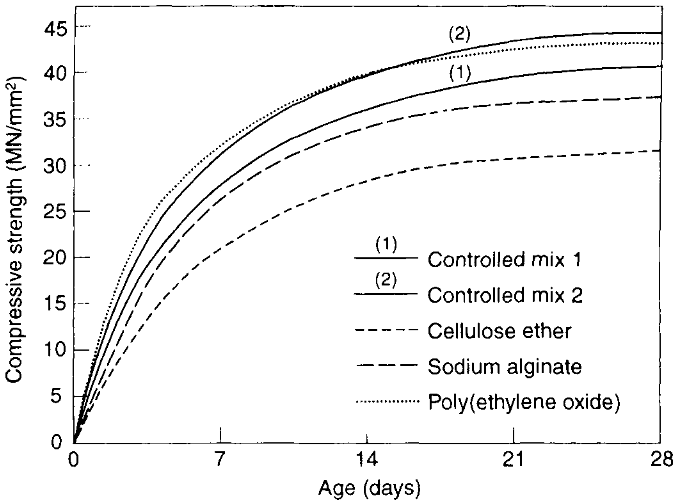


Fig. 15.63 Compressive strength results (source: Ref. 91).

employed for this purpose, incorporating a superplasticiser (preferably of the sulfonated melamine–formaldehyde type) together with an antifoam agent to prevent excessive air entrainment.[89]

The water-retention properties of these polymers have long been exploited in masonry mortars to ensure a good bond and to prevent premature drying out. More recently, the possibility of developing 'self-curing' concrete has been investigated, with a view to avoiding the need for wet curing or application of curing membranes (see below). The use of the anti-bleed tendency is apparent in aiding pumping of lean-mix concretes. The interstitial cement grout which tends to separate from the aggregate during pumping may be thickened and hence still function as the plug flow lubricant, thus aiding pumping. Whereas cellulose ethers and alginates tend to reduce strength somewhat, the polyox or poly(ethylene oxide) type of materials do not suffer from this problem.

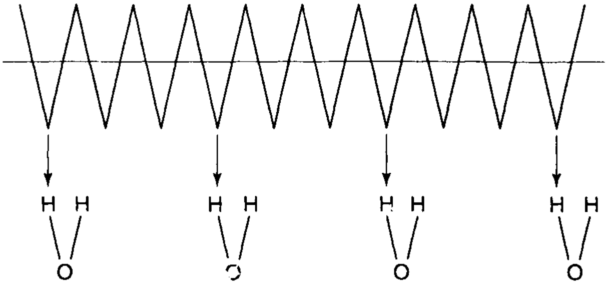


Fig. 15.64 Friction loss because long-chain poly(ethylene oxide) orients at a surface, thus reducing turbulence.

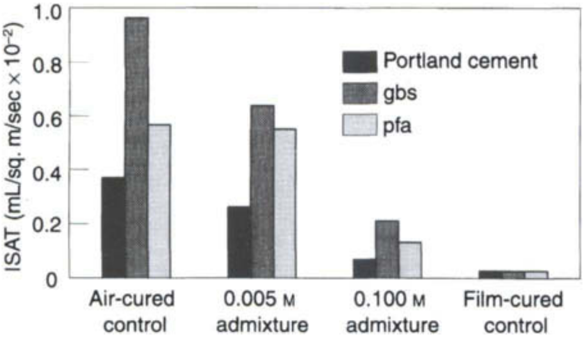


Fig. 15.65 Ten-minute initial surface absorption test (ISAT) readings for 150 mm concrete cubes at 28 days (source: Ref. 94).

Another interesting feature of the poly(ethylene oxide) polymer is that it imparts a water-retention capability to the concrete and thus gives strength in line with water-cured concretes even under conditions that are conducive to drying out (Figure 15.63).[91]

Polyethers are also interesting in that they orient at an air–water interface, forming a lubricating skin which induces laminar flow and prevents turbulence (Figure 15.64). This manifests itself as reduced friction which can be of application in both pumping and cement grouting.

It is desirable to prevent water loss while concrete is curing, and becomes even more important as the water/cement ratio reduces. However, most techniques require external application, e.g. wet hessian, curing membranes and plastic sheeting, and can be problematic.

Until recently, attempts to reduce water loss by controlling vapour pressure, thus reducing the tendency for evaporation have not succeeded. However, recent research[92–94] has shown that such control can be obtained using particular poly(ethylene glycol)s. The mechanism of their action would not seem to be due solely to reduction in vapour pressure but also involves enhanced hydrate formation and some pore blocking. Figures 15.65 and 15.66 show their comparative benefit.

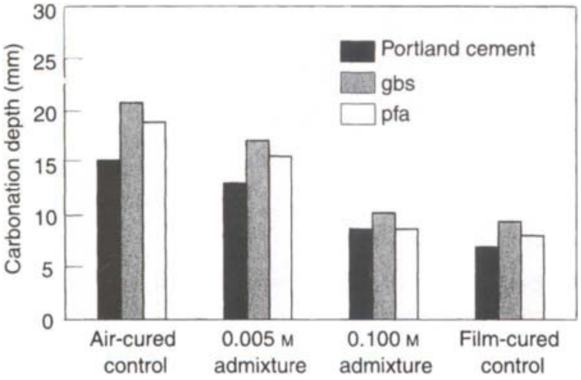


Fig. 15.66 Depth of carbonation after 2 weeks exposure to a carbonating environment (source: Ref. 94).

15.8.3 FOAMING AGENTS

In some circumstances, much larger volumes of air need to be incorporated into concrete or mortar than ordinary air-entraining admixtures can provide. Thus in the production of precast lightweight items or foamed mortars for filling trenches and cavities, up to 70 per cent air may be required. Powerful foaming agents have been produced for this purpose, some based on natural products such as hydrolysed protein and others on synthetic surfactants usually of the alkylarylsulfonate type, used in conjunction with a foam stabiliser. Foaming agents can be added directly to the mix, which is then subjected to vigorous agitation in order to entrain the required amount of air. More commonly, a preformed foam is introduced into the previously mixed mortar or concrete. The density and hence strength may be controlled by varying the proportion of foam added. This system is particularly useful for filling trenches and cavities on site. Densities in the range 800–1600 kg/m^3 can be obtained with sand–cement mortars, but for lower densities (300–700 kg/m^3) it is usual to use neat cement slurries.

An alternative method of producing lightweight precast items, such as blocks, is to add a small quantity of very fine aluminium powder to a mortar mix. Reaction of aluminium with the alkaline liquid phase produces tiny hydrogen bubbles, which in sufficient number expand, increasing the volume of mortar to give the required density before the material sets.

A dispersing agent, often of the calcium lignosulfonate type, is sometimes added with the aluminium powder to ensure uniform distribution throughout the mix and to assist in stabilising the bubbles.

15.8.4 EXPANDING AGENTS

These are used mainly in grouts and mortars to counteract 'shrinkage' that occurs after placing. Many are based on very fine flake aluminium, as used in lightweight block manufacture, but the dosage employed produces just sufficient volume expansion to replace any bleed or fluid loss before setting. Typically, 0.01 per cent of the cement weight will produce 1 per cent expansion of a neat grout at ambient temperature.

Other types are intended to provide a controlled expansion after setting to compensate for anticipated drying shrinkage. The admixture may depend on the oxidation of finely divided iron particles or incorporate an expansive calcium sulfoaluminate. The latter may be more accurately classified as a special cement, and is often marketed as a blend with Portland cement and anhydrite.

15.8.5 CORROSION INHIBITORS

Mention has already been made of steel reinforcement corrosion caused by chlorides introduced into concrete either intentionally (as, say, calcium chloride accelerator) or accidentally in contaminated aggregates or mixing water. A further hazard can arise from the diffusion of chloride ions into hardened concrete from an external source, as in the case of marine exposure or application of de-icing salts on roads in winter.

Although highly impervious and water-repellent concretes can be provided for such situations, prolonged contact with chloride salts will inevitably result in the diffusion of the ions through the concrete cover to the vicinity of the steel reinforcement. Eventually the concentration of chloride ions will depassivate the steel and corrosion may commence in the presence of oxygen.

To avoid this problem a number of chemicals have been investigated as possible corrosion inhibitors, including sodium nitrite, potassium chromate, sodium benzoate and stannous chloride. This earlier work has been reviewed by Berke and Weil.[95] Only sodium nitrite was found effectively to limit the corrosion of steel in the presence of chloride without also causing loss of strength.

Calcium nitrite became available in the 1970s as a stable solution containing up to 40 per cent dissolved solids and found immediate use as an accelerator. Various studies also confirmed that this chemical prevented pitting corrosion of steel exposed to chlorides in an alkaline environment.[96,97] The mechanism by which this protection occurs can be described as anodic inhibition.[98]

In contact with an alkaline solution, reactions at a steel surface convert iron to a series of hydrated oxides. In the absence of chloride or other destabilising ions, these oxides form a passive film only a few monolayers thick. On the microscopic scale there will be small areas devoid of these protective layers, and here chloride can react with Fe^{2+} ions to form a complex which then migrates from the steel surface, subsequently converting to a voluminous hydrate. Calcium nitrite prevents the continuation of this corrosion process by reacting with the ferrous ions formed initially by $Fe \rightarrow Fe^{2+} + 2e^-$ and converting them to the stable oxide γ-FeO·OH. Thus earlier active corrosion centres become blocked by a protective film.

Calcium nitrite will prevent pitting corrosion of steel reinforcement in concrete where the Cl^-/NO_2^- concentration ratio in the pore fluid is as high as 1.0–1.5, and Cl^-/OH^- ratios are in the range 0.27–0.57.[99,100] There is also evidence to show that the admixture is effective in protecting the steel in carbonated or cracked concrete where crack widths are <0.2 mm at the surface.[101,102]

15.8.6 WASH WATER SYSTEMS

These admixtures are employed to eliminate the wastage of material and water involved in the routine washing out of ready-mix concrete trucks. Instead of cleaning out residual concrete in the mixer/agitator drum, a retarder is added in sufficient quantity to prevent setting until the next batch of concrete is required.

The dosage is high with respect to the amount of concrete left in the drum, but insignificant when incorporated in the next full load. A measured volume of water is also required to ensure complete treatment of the residue in the drum, and this is then deducted from that calculated for the next batch.

These systems are of several types, three of which have been reviewed by Newman.[103] All are powerful retarders, and in some cases require an activator to ensure the normal setting of the first subsequent batch of concrete produced. The current systems are:

- A mixture of polyacrylate and hydroxylated polymers with standard retarders. Activation is normally brought about by dilution of the system when the first production batch is mixed, and the development of high pH.
- A formaldehyde-based chelating agent which effectively blocks all hydration processes, including pozzolanic reactions. It is necessary to add a thiocyanate-based activator to initiate normal hydration of cement in the next batch of concrete. This system can also be used to store unused loads of concrete in the truck, or to extend the 'shelf life' of freshly mixed wet shotcrete or gunite before spraying. In the latter case the activator is injected into the mixing chamber of the sprayer nozzle.
- A blend of citric and phosphoric acids used at high dosage. Retardation of the subsequent batch of concrete is prevented by adding an accelerator, usually calcium chloride or calcium nitrite (where concrete will be in contact with steel).

There is no evidence to indicate that any of these systems have a deleterious effect on the hardened concrete in which they become incorporated.

15.9 Conclusion

It is fair to say that a number of the advances made in concrete over the last 30 years have depended upon admixtures in order to be effective, for instance, frost-resistant concrete and mortars, high-workability mixes and self-levelling screeds. In addition, the benefits of supplementary hydraulic binders such as microfine silica fume and pulverised-fuel ashes require the use of admixtures in a synergistic way. It is likely that the on-going development of concrete, mortars and grouts will depend even more on the use of admixtures.

Such admixtures will also develop and there is already a trend to multi-functional materials. It is to be hoped that these developments will be based on sound science, although there will always be the unexpected and inventive occurrence highlighted by a pressing practical need. Table 15.12 gives a listing that is meant to be a prognosis for concrete into the third millennium. It is apparent that for concrete to achieve its potential there is a need to maintain the support for science underwriting the inventive flair often associated with admixtures. Such concrete potential could then be used with long-term confidence.

Table 15.12 Concrete into the third millennium

Option	Basic property	Attainability: + = now (within 10 years); − = in doubt	Science status: √ = satisfactory; × = unsatisfactory
Durability under service conditions	Water content, movement and control	+	√
	Controlled rheology – workability attainment/retention	+	√
	Porosity, water absorption, movement and control	+	×
	Setting, strength and density	+	×
	Protection of steel reinforcement	+/−	×
	Surface treatments	+	×
Manipulation of mechanical properties	Setting-strength/time response	+	×
	Strengths up to 250 MPa	+	×
	Improved fracture toughness ($F_E > 1000$ J/M)	−	×
Attainment of specified properties	Curing	+	×

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16

Concrete Aggregates

Ian Sims and Bev Brown

16.1 Introduction

The usefulness of mixing together stones, sand and some form of binder or cement to form 'concrete' has been recognised since Stone Age times.[1] The Romans developed a rather advanced appreciation of concrete technology, including the use of pozzolanas, experimentation with concrete reinforced using bronze bars and the introduction of lightweight and even air-entrained concrete. The stones and sand, or 'aggregates', were only included as bulking materials, but the writings of Vitruvius in *De Architectura*[2] demonstrate that the Romans recognised the influence of rock types and particle size distribution on the selection of aggregates for good quality concrete and mortars.

In more recent times it has become increasingly understood that the properties of aggregates can have an important bearing on the properties and durability of the concrete in which they are used, so that today the requirements for successful aggregates are closely specified and controlled. Concrete is the major structural engineering material of modern times and aggregates comprise around three-quarters by volume of concrete, so that the importance of the quality of those aggregates can hardly be overstated.

This chapter considers aggregates within the following sections in relation to natural aggregates:

- types and sources
- quarrying and processing
- classification and composition
- properties
- influence of aggregate on concrete properties.

This is complemented by a final section which addresses synthetic aggregates.

16.2 Types and sources of aggregates

16.2.1 CRUSHED ROCK AGGREGATE IN THE UK

Outcrops of hard and unweathered rock may be quarried to produce a material which is crushed and processed into aggregate for concrete. Many high-quality coarse aggregates are produced in this way, but fine aggregates (sands) comprising crushed rock may sometimes require particular processing or blending with other materials.

Sedimentary rocks

Limestones and some sandstones are quarried in the UK for use as concrete aggregate. Carboniferous limestone represents around 60 per cent of all crushed rock aggregate in the UK, being quarried mainly in the Mendips, in South Wales, in Derbyshire and farther north in the Pennines. Smaller amounts of Silurian, Devonian and Permian limestones are also quarried for aggregates. A certain amount of sandstone is quarried for aggregate in the UK, including greywackes in Wales, Scotland and Northern Ireland, sandstones in South Wales and northern England, and scattered exposures of orthoquartzites from older formations, such as the Cambrian quartzite at Hartshill, near Nuneaton.

Mudstones and other clay-bearing rocks are not generally suitable for use as aggregate, but in some countries highly compacted or slightly metamorphosed 'argillites' are used.

Igneous rocks

Many igneous rocks exposed in the UK would make excellent sources of crushed rock aggregate, but these tend to be geographically remote from the areas of greatest demand and are sometimes today also environmentally protected. Basalt and other basic or intermediate rocks, including dolerites and microdiorites, are common sources of crushed rock aggregate. The Devonian and Carboniferous basalts of the Midland Valley of Scotland, and the Tertiary basalt of Antrim in Northern Ireland (famous for the Giant's Causeway), are familiar sources of basalt aggregate in the UK. The Whin Sill of northern England, which gave rise to the commonly used term 'whinstone', is a well-known source of dolerite crushed aggregate.

Granites, microgranites and other similar rock types are other sources of crushed rock aggregate. One granite source, at Glensanda in western Scotland, has been developed as a 'mammoth quarry' to supply crushed rock aggregates by sea both to other parts of the UK and around the world, including Europe, the Middle East and North America.

Metamorphic rocks

In the UK metamorphic rocks only account for a very small proportion of the crushed rock aggregate production, but in some other parts of the world crushed gneiss, schist, phyllite, argillite, metaquartzite and other metamorphic rocks are quarried and used extensively for aggregate.

16.2.2 NATURAL SAND AND GRAVEL IN THE UK

Deposits of sand and gravel have mostly been accumulated in comparatively recent geological times by a variety of glacial, fluviatile and maritime processes. These 'drift' deposits are the principal sources of natural sand and gravel, although a small proportion of sand and gravel is obtained by quarrying into 'fossil' accumulations, or weakly cemented conglomerates, within the 'solid' geological formations.

Conglomerate 'solid' sources

In the UK about 10 per cent of the sand and gravel output of England and Wales is derived from a Triassic quartzite conglomerate known as the Bunter Pebble Beds, which outcrops in the West Midlands, and also as the Budleigh Salterton Pebble Beds in east Devon. The Bunter Pebble Beds can be up to 60 m thick in places and the ratio of gravel to sand is extremely variable.

There are occurrences of unconsolidated sand in the 'solid' stratigraphic sequence, being mainly marine and estuarine deposits in the Jurassic, Cretaceous and Tertiary ages.[3] However, these sands are typically 'soft' (i.e. building) sands, comprising fine, well-rounded and often well-sorted particles, and consequently they are not usually suitable for use in concrete.

Types of drift deposits

The superficial deposits of sand and gravel in the UK were mainly established during the Pleistocene Ice Age and were variously laid down under glacial or 'periglacial' conditions.

Rivers running in channels beneath an ice sheet or valley glacier, or along the edges of a glacier, can develop the sand and gravel features known as 'eskers' and 'kames'. However, the most widespread glacial sands and gravels are developed where sheets and streams of water emanated from beneath the retreating ice front. These 'outwash' sands and gravels are common in East Anglia and northern England and much of the so-called 'Plateau Gravels' (as shown on Geological Survey maps) are probably outwash sands and gravels (Figure 16.1).

The rivers at the southernmost extent of the ice front were much larger than their modern equivalents, cutting large valleys and carrying great quantities of eroded debris, including sand and gravel material. As the ice retreated and the rivers became smaller, the debris loads were deposited and the valleys were infilled. The subsequent terrestrial uplift upon removal of the ice mass caused the reduced rivers to cut new channels into the earlier infilled valleys, creating 'terraces' (Figure 16.2); climatic variations allowed the formation of several terraces in places, such as the Thames Valley. Indeed, the abundant sources of good sand and gravel aggregate in the Thames Valley are virtually all from floodplain or terrace gravel deposits. Another example of widely exploited terrace gravel is the Trent Valley in the East Midlands, where the materials tend to be dominated by quartzite particles derived from the Bunter Pebble Beds.

In the UK there are also some workable sources of beach and raised beach deposits. Other types of sand and gravel formation are encountered in different climatic conditions (section 16.2.3).

Crushed and partially crushed sands and gravels

The nominal maximum particle size of aggregate produced in the UK for use in concrete is usually 40 mm, but more commonly 20 mm is specified. However, many natural sand and gravel deposits can include cobbles and boulders in varying proportions and, where it is economic to do so, these oversized materials are often crushed to smaller sizes. Other sizes are produced in some European countries, with 31.5 mm or 22.4 mm being the nominal maximum sizes commonly produced.

In many cases this crushing and remixing with the natural material can produce an aggregate of improved overall particle shape, because a natural gravel or sand dominated by rounded particles becomes augmented by more angular or irregularly shaped particles (section 16.5.3). In other cases the natural particle size grading of a deposit may differ from the demand for the various aggregate sizes, so that relatively coarser sizes may be crushed to produce greater quantities of the smaller sizes.

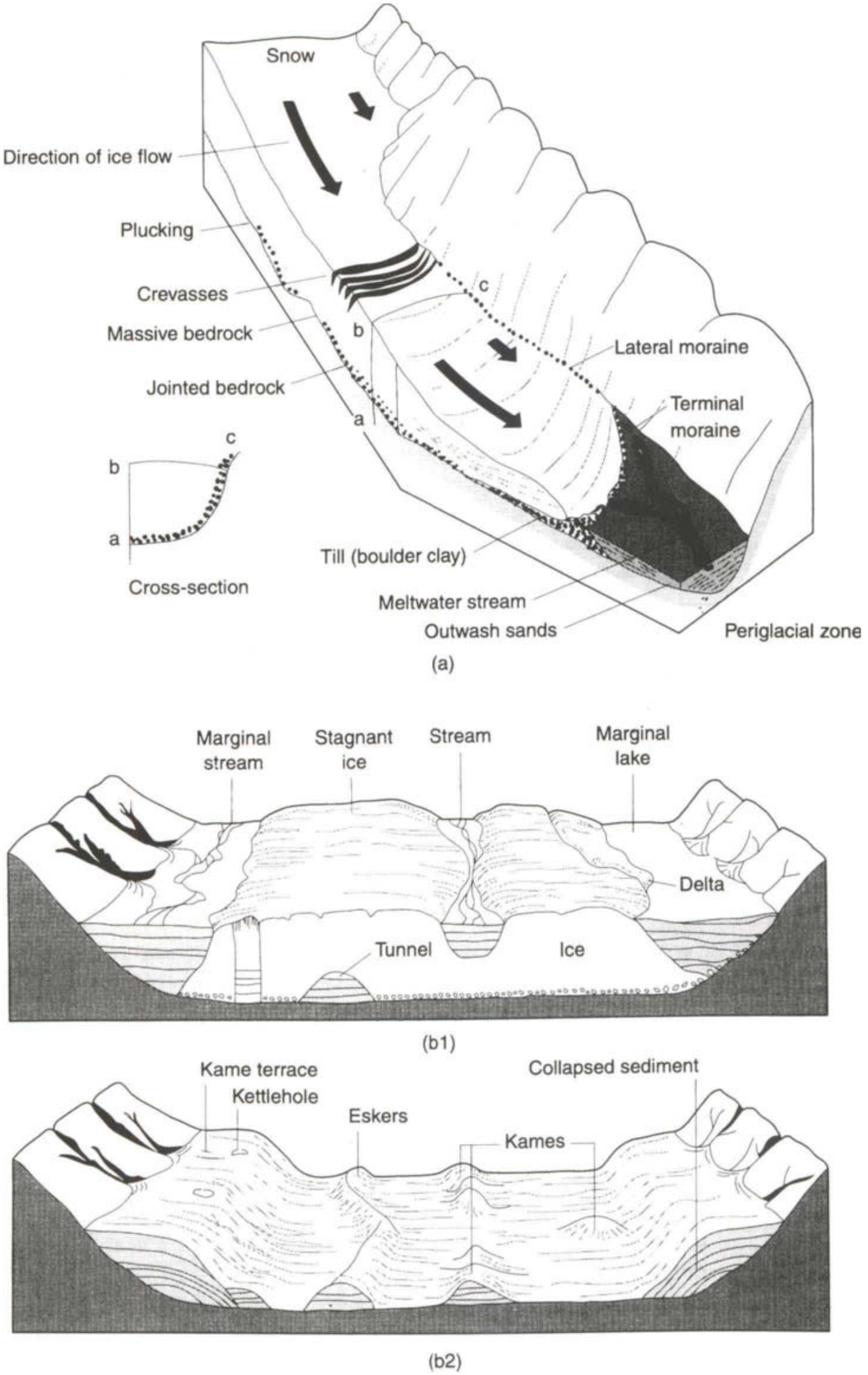

Fig. 16.1 The formation of some glacial deposits potentially useful as sources of aggregate (after Ref. 4). (a) Long-section through a valley glacier. (b) Cross-section through a glacier showing ice-contact stratified drift deposits: (b1) nearly motionless melting ice, (b2) after melting of ice and retreat of glacier.

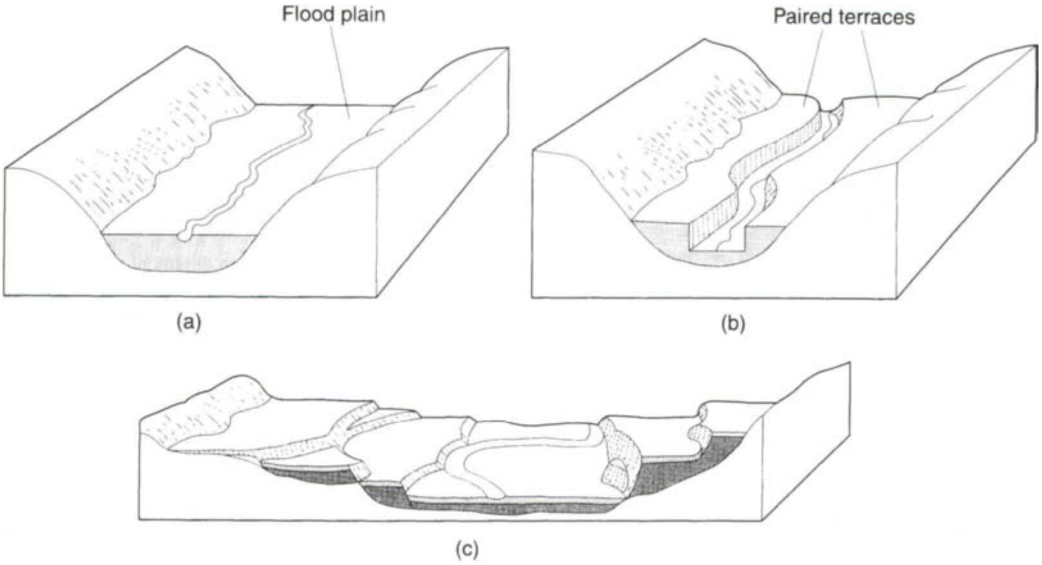

Fig. 16.2 The formation of river terraces (after Ref. 5). (a) Deposition of valley floor deposits including sand and gravel; (b) Later erosion of deposits leaving remnants of earlier flood plain as paired terraces; (c) Further periods of downward and lateral erosion leads to several terrace levels and sometimes unpaired terraces.

In all cases it is important in processing that the blending of natural and crushed materials is controllable, because the overall particle shape characteristics of an aggregate can influence the properties of concrete. Around Chichester, for example, the deposits contain large proportions of oversized flint material and are also low in sand content; consequently, they are routinely crushed and the separately processed natural and crushed aggregates are only reblended at the end of the processing chain when the proportions of crushed and uncrushed materials are controlled according to the purchaser's requirements.

Blended aggregates

It is not uncommon for fine aggregates (sands) from different sources to be combined together to produce a blended aggregate of superior properties to either of the separate materials. A crushed rock sand, for example, is often rather too coarse grained and of angular particle shape to be an ideal concreting sand, whereas natural sands can sometimes be excessively fine grained and of rounded particle shape; a blend of the two materials may produce a more satisfactory aggregate. It is much less common for coarse aggregates to be blended, except perhaps for architectural reasons, such as for use in 'exposed aggregate' or terrazzo concrete finishes.

Marine aggregates

As terrestrial sources of sand and gravel have been worked out and it has become environmentally less acceptable to quarry into rock exposures or to open new sand and gravel pits, so the use of sea-dredged or marine aggregates has steadily increased in the

UK and its use has been encouraged by the British Government.[6] Marine aggregates have been used in the UK since the 1920s, with a major expansion from the 1960s.[7,8] In the southeast of England, which is the largest concrete production area in the UK, marine aggregates have accounted for nearly 30 per cent of the sand and gravel consumed and in some county areas as high as 50 per cent. However, overall in the UK the proportion more realistically lies between 10 and 15 per cent.

The principal UK dredging areas at present are off the coast of eastern England between the Humber and Thames estuaries, in the English Channel east of the Isle of Wight, in the Bristol Channel and in Liverpool Bay (Figure 16.3). Dredging also occurs in the lower reaches of the Rhine and the North Sea.

During the Ice Age these areas of the Continental shelf would have been above sea level and thus subject to the same glacial depositional regimes as those which affected the present-day terrestrial areas; the postglacial rise in sea level caused these near-coastal regions to be submerged. The marine sands and gravels, therefore, are not substantially different in genesis to the glacial terrestrial deposits described earlier and they are compositionally related to the adjacent land-based materials. A geological account of the North Sea Quaternary deposits is given by Cameron *et al.*[9] In some places the offshore deposits may have been reworked to some extent by marine currents and possibly augmented by sediments emanating from modern estuaries.

It has sometimes been suggested that marine aggregates might be inferior to land-based aggregates, and in the 1960s this was the subject of much technical debate.[10] The only technically important differences between marine and land-based sands and gravels are the presences of sea shells and sea salts in marine aggregates. There is no evidence that

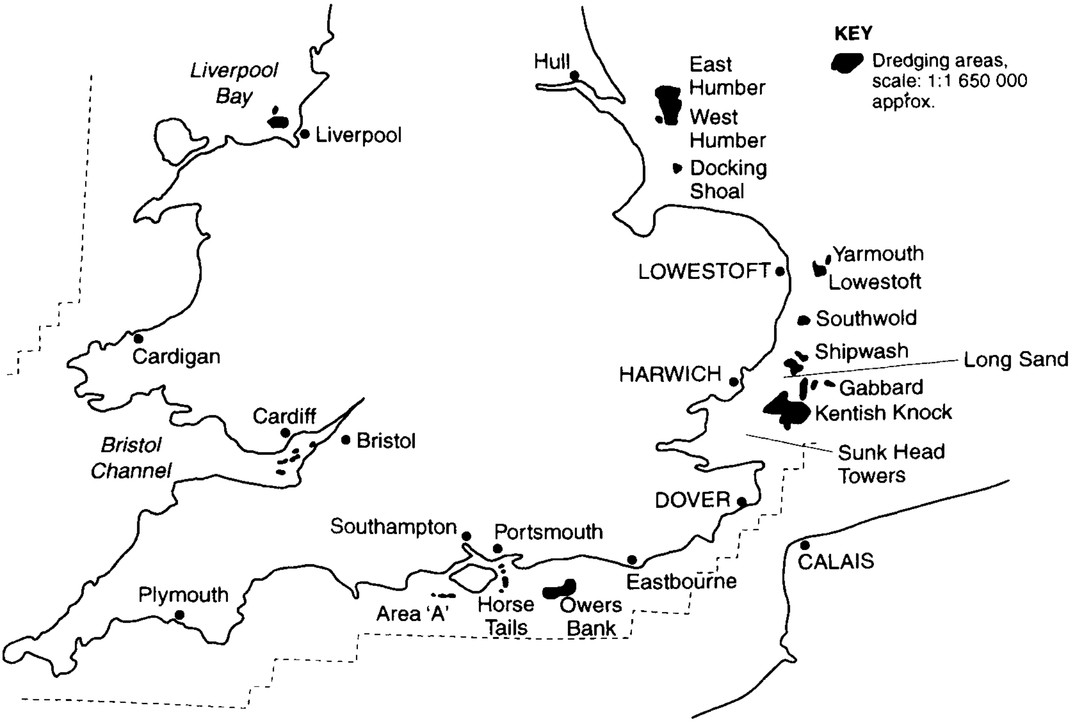

Fig. 16.3 Marine dredged sand and gravel licensed areas around part of the UK.

shells and shell fragments in the quantities normally present are injurious (section 16.4.4), although the allowable content is often controlled for coarse aggregates.[11,12]

Concerns which could arise from the presence of sea salts can be allayed by proper washing of aggregates.[13,14] Only in the case of prestressed or heat cured concrete do normal washing procedures need enhancement to ensure the required levels are met. Limits for the chloride ion content are normally expressed as a percentage by weight of cement in the concrete.[15] These requirements are further discussed in section 16.4.4.

In the broadest sense marine aggregates also include beach sands and those won from estuaries. Beach sands are often single-sized and need blending with other sands to produce a suitably graded material.

16.2.3 AGGREGATE OCCURRENCE IN OTHER AREAS OF THE WORLD

The types of aggregate source in the UK are reasonably representative of those found and exploited throughout the populous temperate climatic zones of the world. However, in recent decades much concrete construction has taken place in the arid and tropical climatic regions, and the materials available in such locations differ in both origin and properties from the traditional temperate zone aggregates.

Hot/dry climatic regions

Since the mid-1970s much has been written about construction materials in arid or desert regions, although most research has been directed towards the development areas along the Arabian Gulf and to a lesser extent the North African coastal belt.[16,17] Many good-quality crushed rock aggregates are produced from the igneous and metamorphic rocks forming the mountains of western Saudi Arabia and Oman. However, the extensive Tertiary carbonate rocks of the Gulf and North Africa are frequently less suitable aggregate sources, partly because of their inferior mechanical and physical properties and partly because of 'duricrust' formation in a climatic region where evaporation consistently exceeds precipitation. Duricrusts of 'calcrete' or 'dolocrete' are mechanically stronger than the underlying parent rock, but usually also contain unacceptable concentrations of potentially injurious sulfate and chloride salts.

Sands and gravels in desert regions are predominantly accumulated by 'flash flood' water action or by the action of wind; in the Gulf there are also recent marine sands in places along the coast (Figure 16.4). Flash floods or torrents deposit their sands and gravels in temporary valleys or 'wadis', and large alluvial fans can develop where such floods disgorge from mountain areas onto the flat coastal plain.

The coastal dunes are sometimes used for fine aggregates (sand), but the familiar dunes of the interior of deserts are usually unsuitable sources, as the sands are frequently too fine and too single-sized for use in concrete. The residual surface gravels, common in many flat desert areas, are the result of wind erosion and are sometimes the only nearby source of usable aggregate.[19]

Hot/wet climatic regions

The tropical regions are characterised by excessive depths and extents of chemical weathering of rock, and sometimes also by the presence of large rivers which have a prodigious capacity for erosion in the highlands and the transportation of debris in the

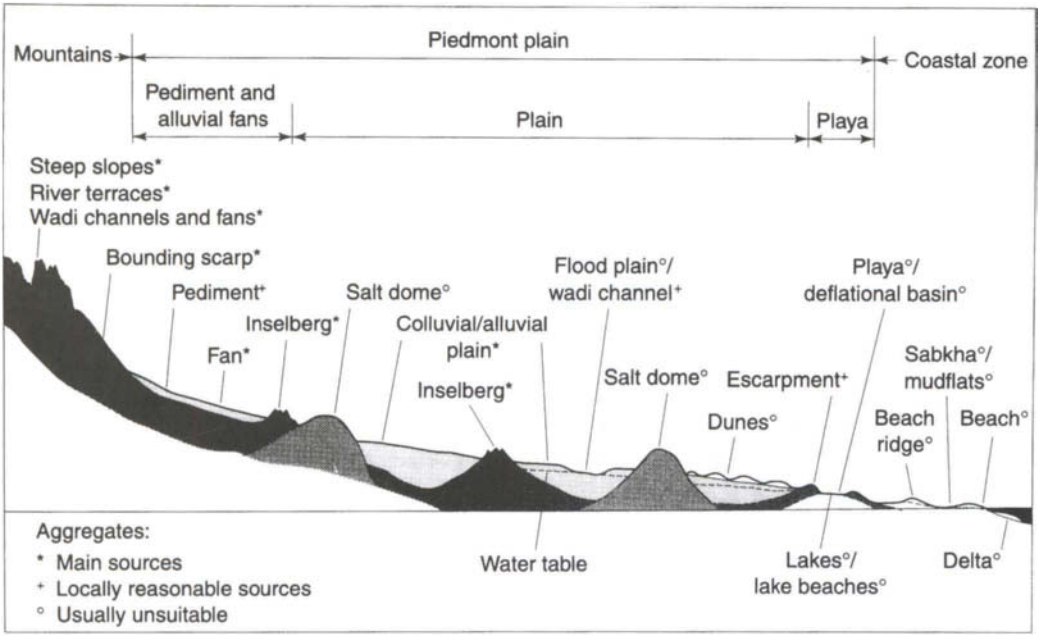

Fig. 16.4 Suitability of land form zones in 'hot drylands' for aggregates (from Ref. 18).

lowlands (Figure 16.5). Isolated hills or mountains of relatively fresh and hard rock may occasionally provide a source of good crushed rock aggregate. Elsewhere, the depth or variability of depth of chemical weathering makes hard rock sources inaccessible or difficult to quarry to produce a consistent product. A crushed rock aggregate from such a source will typically comprise a mixture of fresh and weathered rock particles.[21] In some places the zone of weathered rock may amount to a residual gravel material which might be usable as an aggregate.

In some tropical areas, particularly where chemical weathering affects igneous rocks, 'laterite' forms as the residual soil material. The development of a laterite duricrust (or 'ferricrete') can sometimes provide an acceptable source of crushed aggregate or, where erosion has occurred, a laterite gravel may be accumulated.

Tropical rivers are capable of transporting considerable quantities of debris from weathered rock sources in upland areas and these loads are deposited as gravels along the valleys and as alluvial fans where the rivers meet the coastal plains. The finer sand and silt are mostly deposited in the coastal belt and often in large delta areas. It is common for the gravel source to be abundant in oversized material, whereas the coastal plain sand sources are rich in silt and clay. In tropical costal regions there is also a considerable usage of coral and shell beach sands as concreting fine aggregate (sand).

16.2.4 SOURCE VARIABILITY

All sources of natural aggregate are subject to variation, some of which may be systematic and related to predictable geological structure or stratigraphy, whereas other variations may be more random and difficult or impossible to predict.

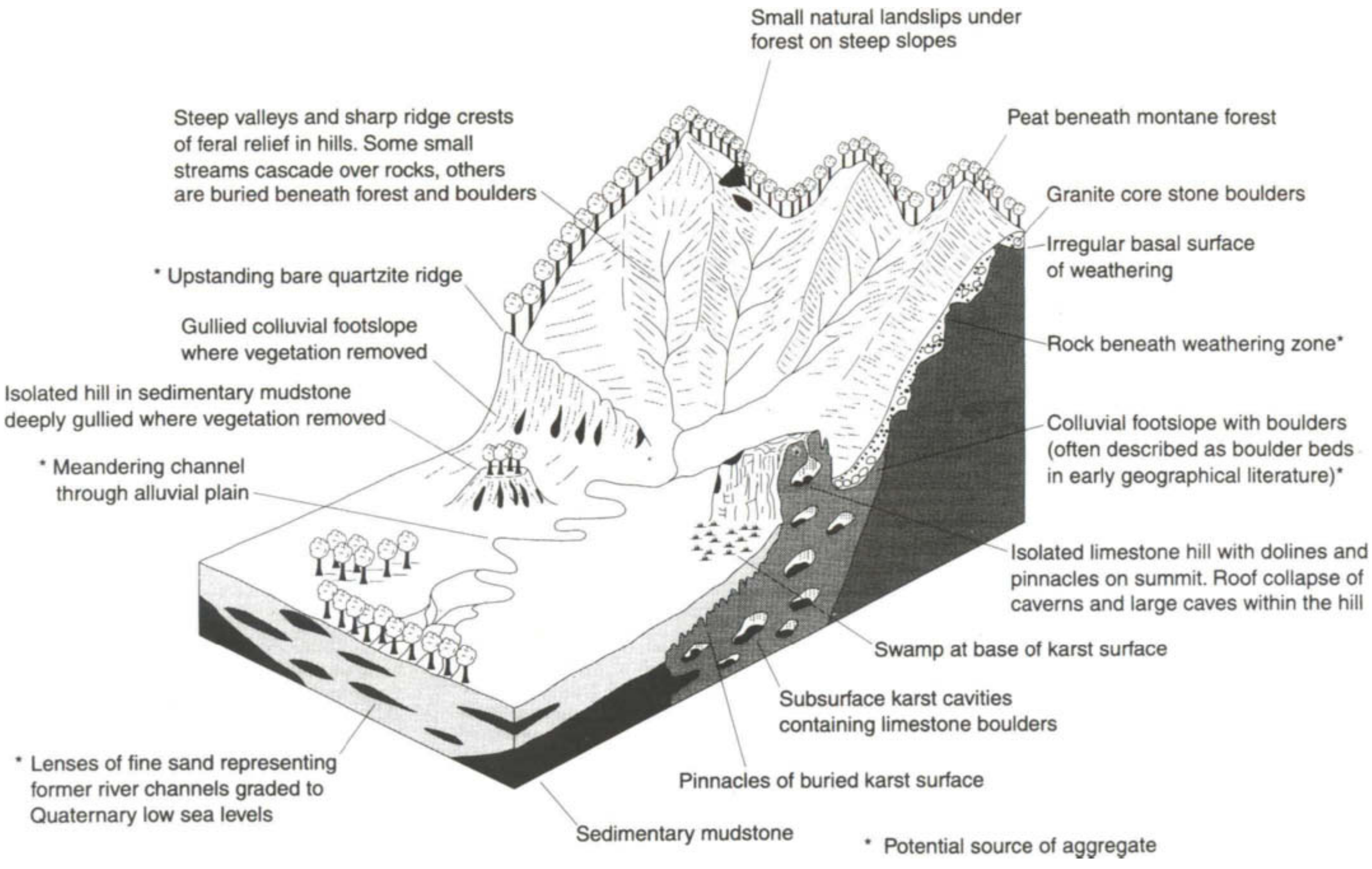

Fig. 16.5 Idealised diagram of the terrain in a humid tropical environment, showing some of the possible sources of material potentially suitable for use as aggregate (after Ref. 20).

Systematic variation

The material overlying the resource to be exploited for use as aggregate is known as 'overburden' and this can vary in both character and thickness. In some cases the overburden may be a thin soil layer, whereas in other cases the overburden may be a thick band of weathered rock or even a superincumbent stratum of less suitable material. For example, the granite sources of southwest England usually exhibit an appreciable overburden of weathered and partially weathered material, also the glacial gravels of East Anglia are often overlain by deposits of boulder clay.

The aggregate source may also vary systematically as exploitation proceeds, according to geological structure or stratigraphy. Igneous dykes and sills, for example, have definite limits beyond which they cannot be worked. Certain sedimentary strata may be worked preferentially, discarding the unsuitable layers above and below the useful material, or there may be layers of undesirable material which have to be avoided by selective quarrying. In Northern Ireland, for example, fossil soil horizons are interbedded with the basalt flows, and in southern Scotland thin layers of unsound mudstone are sometimes interbedded with more massive beds of usable greywacke sandstone. One large quarry in Libya, for example, exploits a horizontally bedded sequence of hard limestones, chalky weak limestones and unsound shaly siltstones; selective quarrying permitted an aggregate to be produced which comprised almost entirely hard limestone.

Random variation

Crushed rock aggregate sources for which the usable rock body or structure is continuous in the direction of quarrying may nevertheless be subject to random variations, caused by tectonic movements, minor igneous activity or local sedimentary features. Faults or local changes to the joint spacing pattern can affect the nature of quarrying and the condition of the rock material. Small igneous intrusions or mineral veins may introduce new constituents into the aggregate product. In sedimentary rock, small geological variations may occur, for example producing clay lenses or bands of chert nodules. There is a large number of ways in which a rock body worked for aggregates might exhibit unforeseeable variations, although experience usually demonstrates that some formations are more prone to such random variations than others.

Sand and gravel deposits are particularly liable to random variation, depending upon the mode of formation. However, it is usually possible to delineate the depth and extent of the particular deposit of sand and gravel being exploited, so that rapid stratigraphic changes in particle size and local incursions of gravelly channels, sandy layers or clay lenses become the main sources of physical variation. The methods of extraction of sand and gravel often ensure a thorough mixing of the material as quarrying proceeds, so that the final aggregate product can be surprisingly uniform despite considerable small-scale variability of the source deposit. The petrographic composition of sands and gravels can be extremely variable, both laterally and vertically, depending upon the diversity of their provenance and the depositional history of the material.

Weathering and alteration

It is important to distinguish between 'weathering', which is degradation of rock caused by climatic agencies such as wind, rain and frost, and 'alteration' which is the mineralogical modification of rock caused by secondary geological processes, especially hydrothermal activity. Weathering virtually always renders a rock material weaker and less durable in the engineering context than the comparable fresh rock, whereas alteration does not inevitably adversely affect the properties of the rock and in some cases could have improved them.

Weathering affects rock outcrops from the top downwards and may also affect exposed natural scarps or quarry faces. Such weathering is usually readily apparent to the field geologist, but altered rock may be less easily identified without microscopical examination (section 16.4.2). Weinert[22] for example, describes an altered dolerite in southern Africa which appeared to be hard and durable but which quickly degraded in use as road aggregate.

The interface between the upper weathered rock and the underlying fresh rock is known as the 'weathering profile' and this profile can vary both in shape and depth, especially in tropical climates (section 16.2.3). Penetration of the weathering profile into the rock mass may be facilitated by jointing, fracturing or other types of discontinuity. Alteration is much less predictable and may affect an entire rock body or instead be patchily developed, either randomly or in association with particular geological features; for example, alteration may occur along the margins of a fault zone or bordering a minor igneous intrusion.

Minor contamination

Apart from the comparatively large-scale variations already discussed, aggregate sources may contain constituents which only occur sporadically in minor or even trace proportions. In some cases such relatively minor contamination of aggregate can have a significant effect on concrete and the variable content may need to be monitored by petrographical and/or chemical analyses. The variable content of sodium chloride in marine aggregate would be an example; another example would be contamination by chlorides and also sulfates of some natural aggregate sources in the Middle East. Small amounts of some organic materials, such as humus or sugar, when present in aggregates can seriously interfere with the setting reactions of cement, as can trace proportions of certain types of metallic constituents, such as lead and zinc.

Minor contamination is especially problematic when the distribution is extremely variable within the aggregate source, because it may prove difficult to detect and avoid. Many of the flint gravel aggregates used in the southeast of England, for instance, are sporadically contaminated by 'reactive pyrite' which can cause unsightly staining of concrete surfaces.[23] These pyrite particles may represent only a fraction of 1 per cent of the overall aggregate, but they tend to be concentrated into particular horizons within the sand and gravel deposits and might not be easily detected unless weathering has affected the working face within the pit.

Other forms of contamination such as lignite may lead to discoloration when wet or pop-outs if present close to the surface of concrete. Since its density is lower than other solid constituents in concrete, there is a marked tendency for lignite to rise to the top surface. Very low levels of contamination, far less than 1 per cent of the total aggregate, can consequently have very significant effects on surface finishes of concrete floor slabs where the lignite concentrates in the surface layer. This makes sampling and testing for its presence extremely difficult, owing to the problem of detecting small quantities in realistic samples.

Humus and sugar-type materials are examples of contaminants which may affect the rate of hydration of cement in concrete, causing retardation effects.

Some clay minerals also adversely affect strength development and durability of concrete. These can appear in some aggregates because of inadequate washing and processing.

The concern over alkali–silica reactivity (ASR) (section 16.6.5) in the UK has also increased awareness of the importance of small-scale compositional variations in aggregates. Some types of reactive constituent, including chert and flint, but particularly opaline silica (which is rarely found in UK aggregate materials), can give rise to ASR expansion when present in aggregates in only very small proportions. A source of crushed diorite aggregate in Jersey, for example, is sporadically contaminated by minor veination which comprises chalcedony and opal in varying proportions. Recently, some crushed greywacke rocks in the UK have also been shown to be highly reactive.[24]

16.2.5 SYNTHETIC AGGREGATES

There is an increasing usage of artificial or synthetic aggregates for concrete, either as an economic alternative to natural aggregates or to achieve special concrete properties, such as lighter weight or improved thermal characteristics. These aggregates make use of wastes or by-products from other industries, or they may be manufactured by the treatment of rocks or other materials (Table 16.1).

16.2.6 SERVICE RECORD

Many aggregate sources, or source areas, have been exploited for aggregates for a long time and it is often assumed that 'a good service record' is a reliable guide to future aggregate quality from that source. Of course an apparently trouble-free record will understandably give reassurance to local users, but should not be regarded as an infallible guide to future production. The variations discussed earlier (section 16.2.4) ensure that few, if any, aggregate sources can guarantee to produce a uniform aggregate over an extended period of extraction. The quality may decline as more marginal materials become worked once the best reserves are exhausted or the working face has moved into a geologically different part of the resource. It is also difficult to ascertain that older concrete, in which aggregates were used with apparent success from a source under assessment, are reliably comparable in all relevant respects with the proposed concrete and the conditions to which it will be exposed.

16.3 Quarrying and processing

16.3.1 EXTRACTION PROCEDURES

General considerations

The extraction of land-based aggregates follows the general principles of all opencast mining and is described in greater detail elsewhere.[25,26] The methods and machinery used for extraction depend, *inter alia*, upon the extent and disposition of the usable resource, the nature of the material, particularly whether it is hard rock or natural sand and gravel, the thickness of the overburden and whether or not selective quarrying is necessary. The extent and disposition of the usable material, and the effect of any systematic variations (section 16.2.4) including overburden thickness,[27] will have been determined by normal geological surveying procedures including the placing and study of boreholes and

Table 16.1 A simplified classification of artificial aggregates, based upon the type of raw materials, the degree of any treatment and the uncompacted bulk density of the aggregate product

		Uncompacted bulk density (kg/m^3)			
		Ultra lightweight <300	Lightweight 300–1000	Dense (normal) 1000–1700	Extra dense (high density) >1700
Raw material	Treatment	Some examples with appropriate bulk density ranges[a]			
Natural	Untreated		Pumice 480–880	Colliery waste/spoil Slate waste China clay sand	Limonite, goethite 2100–2200 Magnetite, ilmenite 2600–2700 Barytes 2800 Haematite 3000
	Treated	Exfoliated vermiculite (Micafil) 60–160 Expanded perlite 80–320	Expanded clay/shale (Leca, Fibo/Liapor/Sintag) 380–720 Diatomite 450–800 Sintered colliery waste 550–900 Expanded slate (Liapor) 560–860		
Synthetic	Untreated				Ferrosilicon, ferrophosphorus 4300 Iron or steel shot 4800 Iron or steel fragments Lead shot 8000
	Treated	Expanded polystyrene 10–20 Foamed glass 240–260			
By-product or waste	Untreated		Wood particles 320–480 Furnace clinker or ‘cinders’ (Breeze) 720–1040 Furnace-bottom ash	Air-cooled blast-furnace slag 1000–1500 Steel slag 1600–1700 Non-ferrous slags Crushed concrete Crushed brick and tile	
	Treated		Foamed slag 560–960 Sintered pfa (Lytag) 770–960 Pelletised expanded slag (Pellite) 900 Sintered incinerator ash	Granulated blast-furnace slag Pulverised-fuel ash Sintered incinerator ash	Iron separated from slag 3800

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[a] The product names given in parentheses are included for guidance and do not necessarily represent the only commercially available forms in which the materials may be obtained; nor do the products necessarily continue to be available.

geophysical techniques.[27] The limit of extraction may be marked by pinching out or inaccessibility of the usable material, or simply by the geographical boundary of the area for which mineral rights have been obtained.[28]

A geotechnical review of the four main stages in the life of an aggregate quarry (exploration, planning and design, quarrying operations and closure after use) may be found in Ley and Stacey.[29]

Hard rock quarrying

The overburden is usually removed by an excavator or scraper and the removed material can then be used to backfill earlier quarried areas. The hard rock aggregate source itself is most commonly worked by drilling and blasting, or more rarely by mechanical ripping. The process of drilling and blasting is technically complex, to ensure that the exercise is done safely and also achieves the required quantity of broken rock at the foot of the working face, and which is fragmented into workable rock pieces without excessive microfracturing.[30]

The geological factors, including the presence and spacing of bedding places, joints and fractures and the rock types and fabric, are strong influences in the blasting performance of a rock mass and the techniques required to achieve the best results. Secondary blasting or some form of impact breaking are often required to reduce oversized rock fragments after primary blasting. The 'rippability' of a rock body, as an alternative to blasting, depends upon strength, fracture spacing and other factors, which can be assessed by geophysical or geotechnical techniques.[31,32]

Where the workable material is thick, the quarrying operation will usually have to be conducted according to a stepped bench pattern. After fragmentation the rock material is mechanically excavated for transport to the processing plant, at which stage it is possible for visibly unsuitable material to be rejected.

Working of sand and gravel

Once the overburden has been removed by processes similar to those used in hard rock quarrying, deposits of sand and gravel are usually extracted by a range of earth-moving plant (Figure 16.6). Some sand and gravel pits extract beneath the local water table and are 'wet pits', whereas others exploit wholly above the water and are 'dry pits'. Various types of dredger are commonly used for extraction in wet pits, or occasionally large excavators. In dry pits, a great variety of diggers or scrapers may be used, or very occasionally strong water jets known as 'monitors'. In the case of some deposits, wet pit working has the advantage that very fine or clay material can be washed out during the winning and the subsequent transportation of the material to the processing plant.

Dredging of marine aggregates

Just as land-based extraction can only be undertaken within areas for which mineral rights have been granted, so dredging for marine aggregates is also subject to very strict control.[33] Separate licences have to be obtained for both prospecting and extraction, and the granting of licences (by the Crown Estate Commissioners) is restricted according to the competing needs of the fishing industry, the presence of shipping lanes and other factors.

Fig. 16.6 General view of a sand and gravel pit in Essex, UK. The boulder clay overburden has been removed, the sand and gravel deposit is being worked using earth-moving plant and the base of the sand and gravel rests on London Clay.

Most UK marine aggregates are obtained using a fleet of 'suction hopper' dredging ships, which may be either anchor dredgers (with a forward leading dredger pipe) or trailer dredgers (with a trailing pipe which works 'under way'). Whichever type of dredger is used, the positioning is very precise and by maritime law the ship's log should be an accurate record of the geographical origin of any batch of sea-dredged aggregate. Petrographic monitoring[34] has demonstrated that the compositions of a marine gravel aggregate from a particular submarine bank can be surprisingly consistent. Greater detail of dredging, offloading and processing marine aggregates is given elsewhere.[14]

16.3.2 SELECTIVE QUARRYING

In response to systematic or random variations in the source (section 16.2.4), it may be necessary to work the rock or deposit selectively in order to obtain aggregate material of acceptable quality. The extent to which selective quarrying is economically feasible depends upon the demand for high-quality aggregates, the nature of alternative sources, local labour costs and other factors.

Fookes and Collis,[16] for example, have described a rock quarry in the Arabian Gulf in which the comparatively sound and uncontaminated limestone source graded upwards into a hard but salt-contaminated duricrust or 'caprock' of variable thickness and graded downwards into an unsound, leached and porous chalky limestone (Figure 16.7). Planned selective quarrying ensured that only the sound uncontaminated limestone was used for aggregate, but, in addition, secondary selection and rejection by simply trained personnel

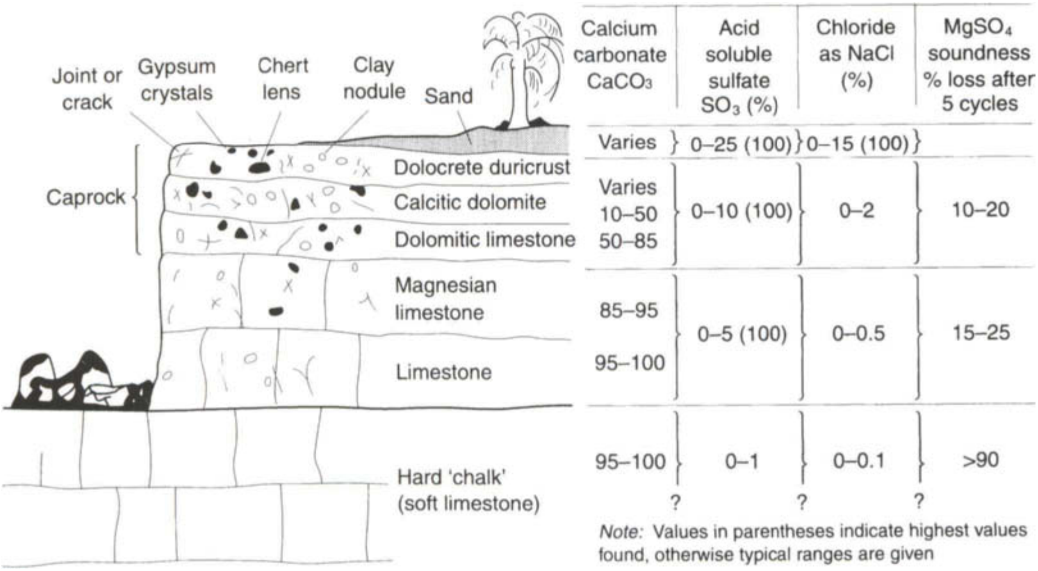

Fig. 16.7 Idealised profile through a limestone quarry in the Arabian Gulf, illustrating the development of a hard but chemically contaminated duricrust or 'caprock' (from Ref. 16).

was required to take account of random variations, including clay and chert modules which occur sporadically throughout the usable limestone layers.

In southern Scotland, selective quarrying has been exercised in order to minimise the mudstone content of an otherwise greywacke sandstone aggregate product, even employing petrographic monitoring on-site. Selective winning of a sand and gravel deposit can often be controlled by the extraction procedure itself; for example, dredgers in wet pits can become inoperable if the filters become blocked by excess quantities of clay and silt when unsuitable patches of material are randomly encountered. Fraser *et al.*[35] have described a practical selective extraction scheme for carbonate rock aggregates in Ontario, Canada.

16.3.3 'MAMMOTH' OR 'SUPER' QUARRIES

In the UK there has been a progressive change over the last few decades towards supplying the concrete industry's aggregate needs from a smaller number of larger quarries. A move to fewer quarries has social and environmental advantages and the development of larger quarries has economical advantages for the producer. Yeoman[36] was particularly responsible for pioneering the idea of the 'mammoth' or 'super' quarry, capable of replacing the production of perhaps as many as 200 small quarries. The location of such a mammoth quarry would need to ensure a suitably huge reserve of acceptable material and would also have to be served by a suitably economic means of transport. Large traditional quarries at Meldon in Devon and Penmaenmawr in North Wales, for example, are both served by the main railway system.

The massive development at Glensanda,[37] on the west coast of Scotland, exploits the huge Strontian Granite intrusion adjacent to deep sheltered water and is designed to export the aggregate output by sea to all parts of the UK and other parts of the world. Other mammoth quarries are being developed in the Yucatan Peninsula of Mexico, and on the east coast of Canada (Nova Scotia and Newfoundland). Further quarries of this type both in Europe and other parts of the world can be expected, although one review of the mammoth quarry concept has suggested that a coastal location is more important than quarry size.[38]

16.3.4 PROCESSING OF AGGREGATES

Design of processing plants

The objective of any concrete aggregate processing operation should be the production of good-quality, 'clean' coarse and fine materials in the normal range of sizes. The types of equipment used and the flow design of the plant is more or less completely dependent upon the nature and properties of the source raw material. Even after basic design, any plant will require commissioning trials, after which the experience gained will dictate both major and minor modifications to the process. The technology of aggregate processing is complicated and continually developing, and is more comprehensively covered elsewhere.[25,26] In general terms, however, processing consists of a reduction stage (always with crushed rock and sometimes with sand a gravel), a washing and beneficiation stage (as required) and a sizing stage.

Crushing and milling

Reduction of the broken rock material, or oversized gravel material, to an aggregate-sized product is achieved by various types of mechanical crusher. These operations may involve primary, secondary and even sometimes tertiary phases of crushing. There are many different types of crusher, such as jaw, gyratory, cone (or disc) and impact crushers (Figure 16.8), each of which has various advantages and disadvantages according to the properties of the material being crushed and the required shape of the aggregate particles produced.

It is common, but not invariable, for jaw or gyratory crushers to be utilised for primary crushing of large raw feed, and for cone crushers or impact breakers to be used for secondary reduction to the final aggregate sizes. The impact crushing machines can be particularly useful for producing acceptable particle shapes (section 16.5.3) from difficult materials, which might otherwise produce unduly flaky or elongated particles, but they may be vulnerable to abrasive wear and have traditionally been used mostly for crushing limestone.

Significance of quartz (free silica)

In any crushing operation, the raw material flow rate and the reduction ratio (ratio of feed size to product size) have obvious influences on the wear of crushing equipment. However, the hardness and fracture toughness of the rocks being crushed are unavoidable parameters in allowing for the wear of crushing plant. Traditionally, the assessment of hardness has been used as a crude guide to abrasiveness, although hardness alone is not in fact a reliable wear criterion.[40] Of the common rock-forming minerals, quartz alone is harder than normal steel, so that the average content of quartz (or 'free-silica') in the raw feed is some guide to the 'sliding' abrasiveness to be expected (fracture toughness is important to the 'impact' abrasiveness).

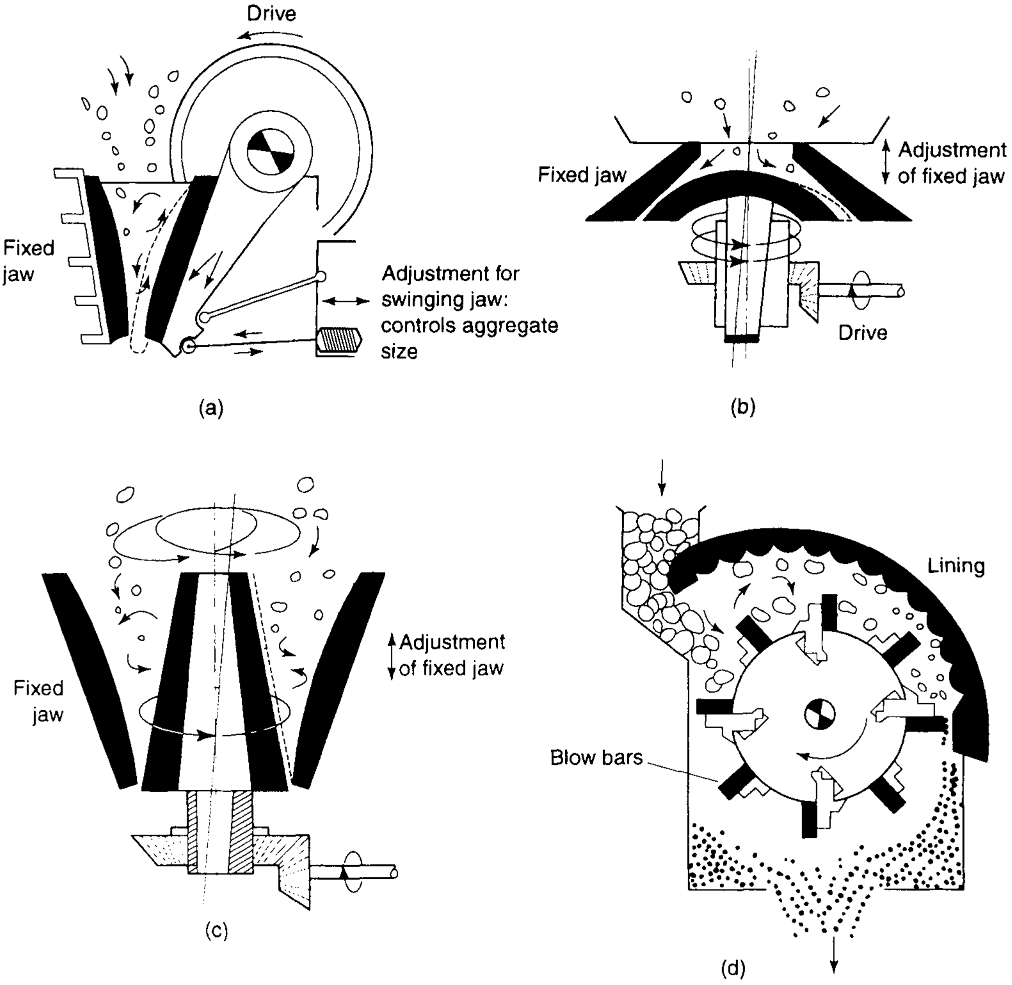

Fig. 16.8 Diagrams to illustrate the basic actions of some types of crusher: solid shading highlights the hardened wear-resistant elements (redrawn, adapted and modified from Ref. 39). (a) Single-toggle jaw crusher, (b) disc or gyrosphere crusher, (c) gyratory crusher, and (d) impact crusher.

Quantitative criteria for the relationship between quartz and wear are not easily available, but obviously the liability to high wear rates tends to increase with quartz content. Orchard[41] has suggested that free silica contents of less than 5 per cent will not cause trouble, whereas amounts above 20 per cent might become a problem. At a quarry in western Kenya a secondary impact crusher was included in the aggregate processing design on the basis of the incorrect information that the raw material was a quartz andesite, perhaps with a maximum quartz content of 10 per cent. In fact the material was mostly a dacite with quartz contents of up to 70 per cent and the machine's blow bars had to be replaced every third day during production, with obvious financial and contractual implications (in the limestone industry a set of blow bars will last for several months).

Washing and scrubbing

Sand and gravel materials, and more rarely crushed rock materials, are washed to remove clay or excessive proportions of silt. In more recent years, concrete aggregates have also been washed specifically to remove soluble salts (especially sodium chloride) which otherwise might induce or exacerbate the corrosion of steel reinforcement and other embedded metal or increase the risk of ASR.

Washing may be carried out by water jets during screening or by passing the raw feed through a washer barrel.[26] If the material contains less dispersive clay or more resistant clay lumps it may be necessary to employ more vigorous washing using a 'scrubber' or 'log washer'. Where it is important to minimise the sodium chloride content as well as removing fines, washing must be done using and regularly replenishing fresh water. Simple dewatering of marine aggregates or other aggregates washed using sea water will appreciably reduce the level of salt contamination, though not necessarily to a level which will avoid the need for any further washing.

Beneficiation

Additional processing to improve the quality of a product by selective removal of less desirable constituents is termed 'beneficiation' and is quite common in the metallic minerals industry. Beneficiation is employed only on a limited basis in the production of aggregates because of the relatively high plant and operating costs. Gravity and centrifugal separation plants are capable of successfully removing notably lightweight materials, such as coal, or notably heavyweight materials, such as iron ore particles. Some success has been claimed for the removal of unsound low-density chert from a crushed gravel aggregate.[42]

Discrete flakes of mica are frequently detrimental in fine aggregates for concrete (section 16.4.4) and could usefully be removed by beneficiation where uncontaminated sands are not available. Mica was formerly removed from some Cornish china clay sands, but principally to recover the mica for commercial sale rather than deliberately to beneficiate the sand aggregate.[43] Fookes and Marsh[44] have described some modified washing procedures for the reduction of mica content in Nepalese fine aggregates.

Screening and sorting

The separation of crushed aggregates, or sand and gravel, into different sizes is achieved by large sieves or industrial screens. Coarse screens known as 'grizzlies' or 'scalpers' are used to separate oversized or undersized materials from the raw feed as part of the crushing operation. Static, horizontal and cylindrical screens have been used, but today most plants are designed with inclined vibrating screens (Figure 16.9), some of which are primarily intended to discard undersized material and others of which are primarily intended to discard oversized material. A good overall design of a screening plant achieves clear and reliable separation of sizes (Figure 16.10). The further sizing of sand material, with particle sizes of 5 mm or less, is achieved by a process of 'classification' which is based upon the principle that coarse particles settle out from a water–sand slurry at a faster rate than fine particles.[45] Sand classification is more inefficient than coarse aggregate screening and differently graded products result which can be used for different purposes.

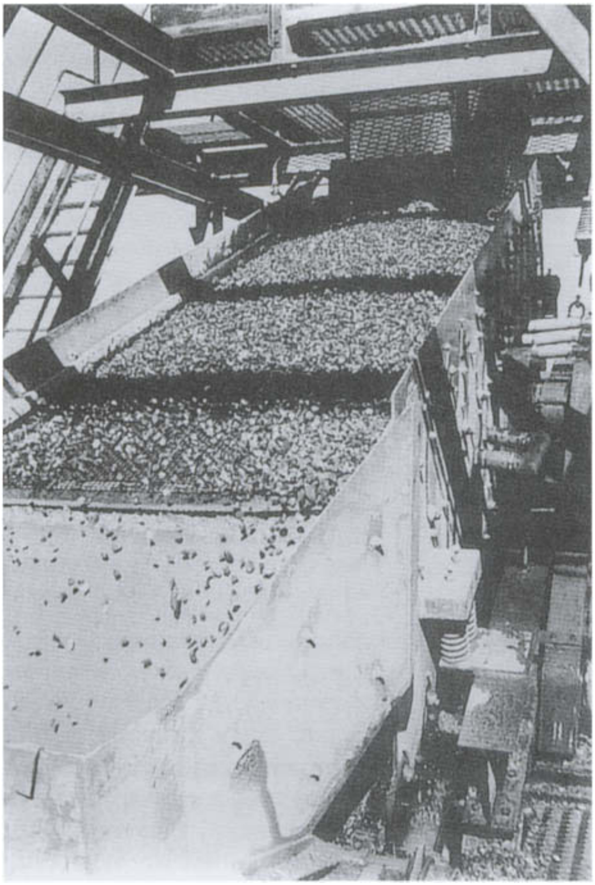

Fig. 16.9 Inclined vibrating screen, part of a coarse aggregate processing system.

16.3.5 TRANSPORTATION AND SUPPLY

In most cases, processed aggregates are transported from the quarry (or marine aggregates depot) to the construction site or precasting yard by road vehicles, although some larger quarries are served by direct rail links. Crushed limestone from Somerset is regularly transported to depots in London by rail. Where a precasting unit has been established adjacent to a quarry, direct supply may be effected by conveyor belt. In the case of some coastal quarries, the output can be conveyed by ship (section 16.3.3) either direct to the site or to a depot nearer to the main market; in this way, Irish dolerite aggregates have been brought into the Thames estuary by sea. Some recent large coastal construction projects have specified the use of shipborne aggregates to minimise the local nuisance caused by heavy vehicular traffic.

16.4 Classification and composition

16.4.1 PETROLOGICAL AND MINERALOGICAL TERMS

A mineral may be defined as 'a solid inorganic substance having a definite homogeneous chemical composition'.[46] Rocks are composed of mineral grains and the types and relative

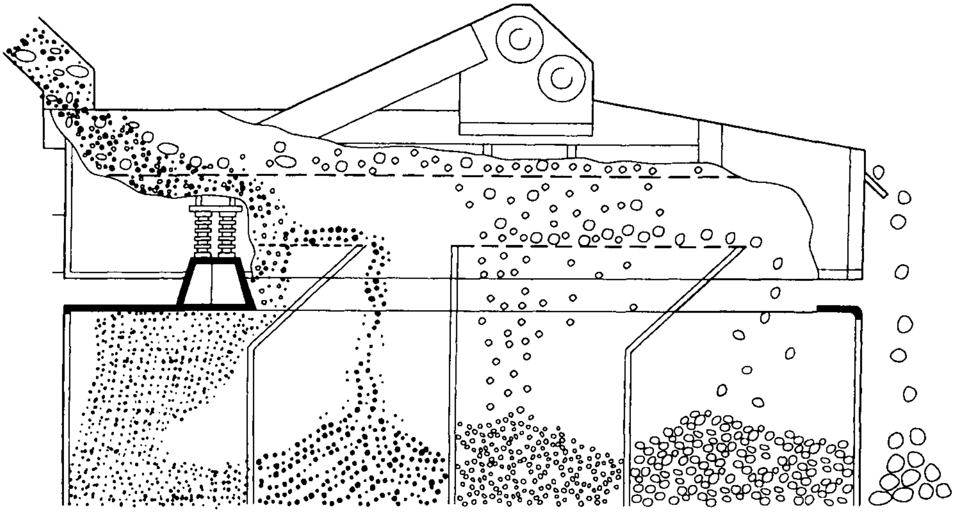

Fig. 16.10 Diagram to illustrate the action of a horizontal vibrating screen plant (from Ref. 39).

proportions of the minerals present in a rock are an important factor in petrological classification (petrology is the science of rocks); for example, granite is essentially composed of the minerals quartz, feldspar and mica. However, the mode of formation is another factor and leads to the major division of rock types into the groups: igneous, sedimentary and metamorphic. The composition of an aggregate may be described in terms of the petrological or mineralogical identities of the constituent particles; this is known as the 'petrographic composition'. The terms used in concrete aggregate petrography have been set out in ASTM C 294[47] and, to a lesser extent, in BS 812: Part 102: 1989.[48]

16.4.2 PETROGRAPHIC COMPOSITION OF AGGREGATES

Importance and usefulness

Particular physical and chemical properties of an aggregate can be controlled by the petrographic composition, the degree of weathering and the microtexture of the constituent rock and mineral particles. An informed petrographical examination therefore enables the suitability of an aggregate material to be evaluated for particular end uses. In some cases this may obviate the need for more extensive testing,[49] or it may direct attention to particular properties in need of further assessment. A petrographic understanding of the fundamental cause of an adverse aggregate property might enable an otherwise unusable source to be worked, or the raw material to be processed, in a way that will avoid or eliminate the undesirable constituent.

The usefulness of petrographic examination of concrete aggregates has been recognised and applied in North America for more than 40 years.[50] These petrographical techniques have been employed commercially in the UK for a little more than 20 years and more recently the approach has become more widely accepted within the industry with particular regard to ASR. Petrographical analysis might be expected to establish two main characteristics of an aggregate: the nature and properties of the constituent types of rock and mineral, and the presence and amount of any particular undesirable constituents usually present in subordinate or even trace proportions.

Methods of sampling and analysis

The importance of good sampling technique in the petrographic assessment of aggregates can hardly be overstated, because the results can only be as representative of the material under study as the samples subjected to examination.[25,51] The ideal number, size and disposition of the samples required truly to represent a resource, or a part of a resource, are controlled by statistical principles and depend substantially on the inherent variability of that resource, which might in practice be difficult to predict (section 16.2.4). Chapter 7 of Smith and Collis[25] gives some detailed guidance on such sampling principles.

In most cases it will be adequate at working sources to take samples from the stockpiles of processed aggregates or from an appropriate position on the processing plant; BS 812: Part 102: 1989 (BS EN 932-1: 1997)[48] gives guidance on the sampling of aggregate stockpiles. Where the assessment must cover future production for an appreciable period, or where there is a high degree of systematic or random variation apparent in the source, it might be necessary to take supplementary samples from selected positions on the working face of the quarry or pit.

Uncertainty will always remain about the resource material behind the working face, however uniform the aggregate appears to be and even after careful extrapolation of any systematic variations; for this reason, periodic resampling and repeat analyses may be appropriate. Borehole surveys and the use of modern geostatistics would be applicable prognostic techniques, but in many cases these might be prohibitively expensive.

The best-known standardised procedure for the petrographical examination of concrete aggregates is given in ASTM C 295.[52] This is a thorough technique which, among other things, requires sand and gravel materials to be sieved and then each separated size fraction to be examined separately, which for many applications produces unwarranted detail and can be expensive to perform. BS 812: Part 104: 1994[53] provides a procedure for the petrographical examination of aggregates, using macroscopical and optical microscopical techniques, in which the amount of sample to be examined is statistically controlled by the proportional importance of the constituents of greatest interest and the degree of precision required.

Composition

The petrographic composition of an aggregate has to be considered at two levels: the particulate level, in which composition is dependent upon the rock and discrete mineral identities of the particles which constitute the aggregates; and the intraparticulate level, in which the composition of the rocks and minerals themselves must be considered. In such a way, an aggregate first may be judged to comprise 80 per cent particles of granite and 20 per cent particles of dolerite (say from a dyke within the granite source); second, half of the dolerite may be found to contain quantities of clay-like minerals as the result of hydrothermal alteration. The useful expression of the composition might thus be 80 per cent granite, 10 per cent dolerite, and 10 per cent altered dolerite.

The engineering petrographer has to exercise informed judgement in avoiding detail of only nomenclatural interest and highlighting differences of possible engineering significance. The required determinative precision for any given constituent depends upon the effect, if any, of that material on the properties of concrete and the level of concentration at which the effect becomes measurable.

In Ontario, Canada, a 'petrographic number' (PN) technique has been developed over many years to express the quality of coarse aggregate, whereby the proportion of each rock constituent is multiplied by a factor, derived from experience of field performance and durability test results, and these values are summed to provide a PN for the aggregate.[54]

Weathering and alteration

Chemical weathering and alteration of rocks and minerals comprising aggregates leads to the formation of secondary and tertiary mineral replacement phases, or the voiding caused by chemical leaching. Attempts have been made to correlate the measured and characterised content of secondary alteration minerals with the strength and durability of certain rock materials.[55,56] In specific cases this method has been used as a basis for specification, notably for road aggregates in Victoria, Australia. Altered or severely leached materials are liable to be absorptive (section 16.5.5), but some weathered rocks may have become microporous, which is less easy to detect and yet may be unsound or susceptible to damage through freezing and thawing, depending on the pore sizes.

Microstructure and microtexture

The internal structure or fabric of a rock has a strong influence on the performance of that material as an aggregate particle. Laminated materials, for example, tend to produce 'flaky' particles (section 16.5.3), which might be prone to further splitting in service. The rock characteristics and the integrity of the granular interlock within the rock have effects upon the angularity, friability and strength of aggregate particles. However, it is probably the microstructure which has the most important textural influence on aggregate durability. In the case of microbrecciation this may be an adverse property which might not manifest itself prior to use in the absence of microscopical examination. A crushed trachyte in Scotland, for example, appeared to be fresh, hard and strong when quarried and satisfied all of the standard compliance tests, but failed badly in service as a road aggregate and in sulfate soundness tests carried out later. Subsequent petrographical examination revealed the presence of microbrecciation (Figure 16.11).

16.4.3 PETROLOGICAL CLASSIFICATION OF AGGREGATES

Purpose of classification

It is common with materials of diverse compositional complexity to use a simplified system by which they might be described; such a classification scheme facilitates the extrapolation of findings and experience with one material to other generally similar materials. In this way, many quarrymen's terms came into common usage to group together aggregates of supposedly similar character and performance: examples would include 'whinstone', 'elvan' and 'toadstone' (Table 16.2). British Standards concerned with aggregates have based classification systems on established geological terms since 1913 when the 'Trade Group' concept was introduced. Whatever the scheme of classification, it amounts to an artificial 'pigeonhole' approach to naturally variable material and thus it is fallible as a guide to engineering properties. Petrological classification has some limited usefulness as a consistent

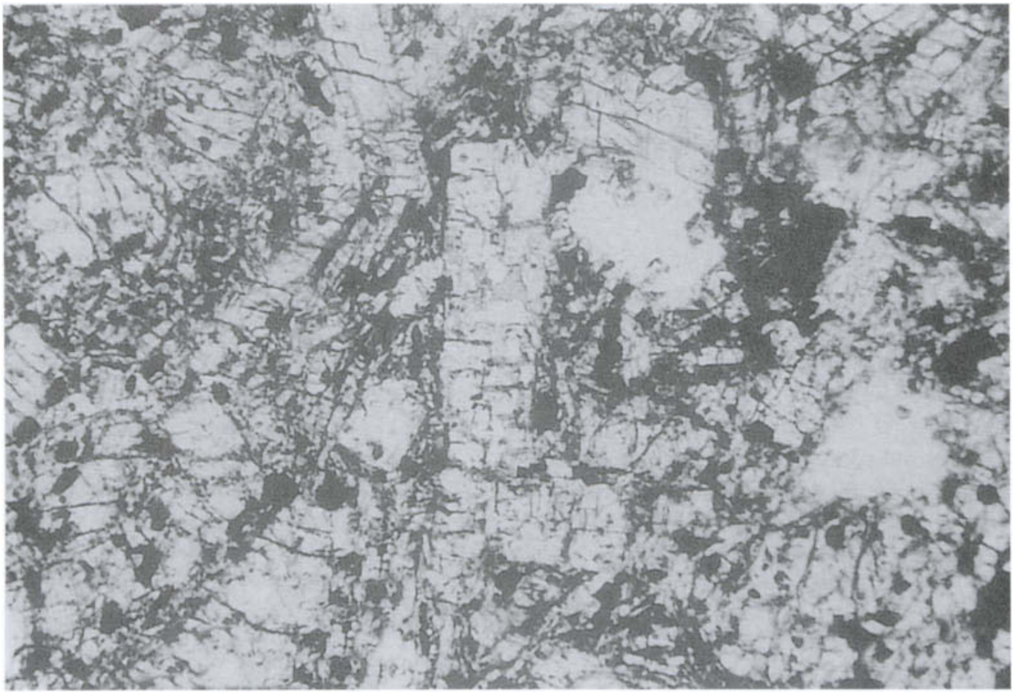

Fig. 16.11 Photomicrograph showing a potentially unsound trachyte aggregate particle, exhibiting extensive microbrecciation of feldspar crystals and haematite mineralisation. Plane polars, approximately × 120 magnification.

labelling technique, but should never be considered as a substitute for proper petrographical examination (section 16.4.2).

Standard classification schemes

A thorough review of the development history of various standardised aggregate classification schemes is to be found in Chapter 6 of Smith and Collis.[25] The Trade Group system was slightly modified in 1943 and was retained as the 'Petrological Group Classification' in BS 812: 1975.[57] The principal rock types used for aggregate in the UK were grouped into ten (plus an 'Artificial' group) under the title of the dominant rock type (e.g. Basalt Group, Granite Group, etc.). This 'Trade Group' system was found to be technically, contractually and practically unsatisfactory and was replaced in BS 812: Part 102: 1984 (now 1989)[48] by a more straightforward approach using established petrological terms. Both the 'Trade Group' system and the later petrological approach are biased towards crushed rock aggregates, making it difficult to apply to natural sand and gravel materials. Quartz, for example, is not included in the list, despite it being the dominant constituent of most UK sands.

CADAM system

The 'Classification and Description of Aggregate Materials' (CADAM) system was proposed in the 1985 Geological Society working party report on aggregates edited by Collis and Fox.[58] The proposal went beyond petrological classification and included the aggregate

Table 16.2 Some traditional names used to describe aggregates in the UK and their approximate petrological identities (modified and adapted from Ref. 25)

Traditional name	Petrological name/type	BS Type or petrological term
Blue elvan	Basic or intermediate intrusive/dyke	Dolerite
Brash	Sand and gravel	Sand and gravel
Cementstone	'Hydraulic' (argillaceous) limestone	Limestone
Clinkstone	Phonolite	Trachyte
Clunch	Sandy indurated clay	Hornfels
Cornstone	Impure limestone	Limestone
Crowstone	Hard gritstone	Gritstone
Elvan	Acid intrusive/dyke	Microgranite
Flagstone	Micaceous sandstone/fissile	Sandstone
Freestone	Sandstone or limestone/easily sawn in any direction	Sandstone and limestone
Ganister	Hard sandstone beneath coal seams	Sandstone
Greenstone	Altered igneous rocks (e.g. epidiorite)	Basalt, dolerite, etc.
Hassock	Loamy sand (in alternations with 'rag' - see below)	Sand
Hoggin	Sandy, clayey gravel	Gravel
Hornstone	Very hard rocks including chert, silicified tuffs and hornfels	Chert, tuff, hornfels
Mundic	Mining and processing waste from Cornish tin mines; typically metasediments with associated metal sulfides including pyrite (mundic is a Cornish word for pyrite)	Includes meta-shale, meta-sandstone, phyllite and slate
Pennant (sandstone and grit)	Sandstone	Sandstone and gritstone
Rag (ragstone)	Calcareous sandstone to sandy limestone (in alternations with 'hassock' - see above)	Sandstone and limestone
Thames ballast	Gravel/dredged, originally as ballast for ships	Gravel
Toadstone	Basaltic lavas, intrusives and tuffs (especially associated with limestones)	Basalt
Trap (traprock)	Igneous intrusive (not granite) or lava	Basalt
Whin (whinstone)	Dark compact igneous rocks	Dolerite and basalt
Grey whin	Moine siliceous granulite	Granulite

type (or 'form'), the mineralogical 'class' and petrological name (if known), and other geological data including age, colour, grain size and fissility. It was intended that CADAM should be 'an elementary system of description based on simple yet sound geological concepts'. The CADAM system has not been adopted by British Standards and, although the general idea has some merit as a standardised system for the basic labelling of aggregates, it was not pursued in the second edition of the Geological Society report edited by Smith and Collis.[25]

16.4.4 UNDESIRABLE CONSTITUENTS

The constituents of a proposed aggregate may comprise or include materials which could have an adverse effect on the properties of any concrete into which that aggregate was incorporated. With the exception of alkali-reactive constituents (section 16.6.5), these adverse effects generally will become more pronounced as the proportion of the undesirable constituent increases within the aggregate.

The undesirable constituents occur mostly as integral components of the aggregate, but occasionally they might represent secondary contamination of the source, or even of a stockpile. The adverse effects mainly include, (1) chemical interference with the setting of cement, (2) physical prevention of good bond between the aggregate and cement paste, (3) modification of the properties of the fresh concrete to the detriment of the durability or strength of the hardened material, (4) interaction between the cement paste and the aggregate which continues after hardening, sometimes causing expansion and cracking of the concrete, and (5) weakness and poor durability of the aggregate particles themselves.

Clay and altered rock particles

Clay minerals may be present in aggregates as very finely disseminated material (section 16.5.2), as persistent particle coatings, as discrete 'clay lumps', or as the result of geological alteration or weathering of rock components. Argillaceous rocks, being mainly composed of clay minerals, are rarely usable as aggregates for concrete, except for some metamorphosed varieties. Clay is unusually moisture sensitive, being mobilised by water and also having the capacity to absorb water into, or lose water from, the mineral structure with accompanying expansion or shrinkage. Clay therefore creates a water demand in a concrete mix, which in turn increases the water content when concrete workability is maintained and can lead to a weaker and more permeable hardened concrete.

Clay particle coatings obviously interfere with the aggregate–cement bond. Clay lumps, and altered rock particles containing clay or clay-like secondary minerals, are weak and vulnerable in themselves and can also cause damage by being able to expand on wetting or shrink on drying (section 16.6.6). West and Shakoor,[59] for example, have described some argillaceous carbonate aggregates from Indiana which cause pitting and pop-outs on concrete road surfaces exposed to winter conditions. Cole[60] has described a 'dimensionally unstable' basalt aggregate from Australia which contained secondary alteration minerals. Giovambattista and Traversa[61] reported on concrete bridges in Argentina which were damaged owing to the expansion and degradation of basalt aggregates containing smectite (montmorillonite).

Absorptive and microporous particles

There is no relationship between high aggregate absorption or porosity and impaired concrete strength and durability. Indeed some porous aggregates can have a beneficial influence, for example by acting as a water reservoir to assist later hydration of cement[62] or to reduce the disruptive expansion caused by alkali–silica reactivity.[63] Some porous aggregates may be vulnerable to freeze–thaw damage when occurring near to exposed concrete surfaces, including chalk[64] and Jurassic oolitic limestone.[65]

The presence of these or other soft and porous aggregates does not invariably lead to freeze–thaw damage, probably owing to the nature of the pores (section 16.5.5). Chalk when present in proportions up to 5 per cent and 10 per cent has been shown to reduce the concrete strength by some 19 per cent and 23 per cent, respectively.[66] Providing these strength reducing effects were accommodated, Norton[66] indicated that under one test regime freeze–thaw resistance was not significantly impaired. Collins[67,68] found that some oolitic and other porous aggregates stood up well to freeze–thaw conditions in field trials. These findings confirm that each aggregate needs individual assessment and that local experience may be a helpful guide.

In porous materials the pore size and the structure of the pore system appears to be more critical than the total pore volume. Microporous materials, in which ice formation can often take place more rapidly than water can migrate through the pore system, appear to be particularly frost susceptible. In this way, the microporous particles of flint 'cortex' present in the sands and gravels of southern England are liable to cause 'pop-outs' on exposed concrete surfaces (Figure 16.12; Table 16.3).

The water permeability of concrete aggregate particles in relation to water retaining structures is discussed in section 16.5.5 and permeability to carbon dioxide is important in reinforced concrete where the depth and rate of carbonation must be inhibited.[70]

Coal and lightweight particles

In some parts of the UK the natural sand and gravel aggregates contain variable proportions of coal and related materials, including carbonaceous shale. Coals are ranked according to the degree of carbon concentration and the lower ranks, such as bituminous coal and lignite, form weak and porous particles in concrete aggregate. Lignite, and more rarely

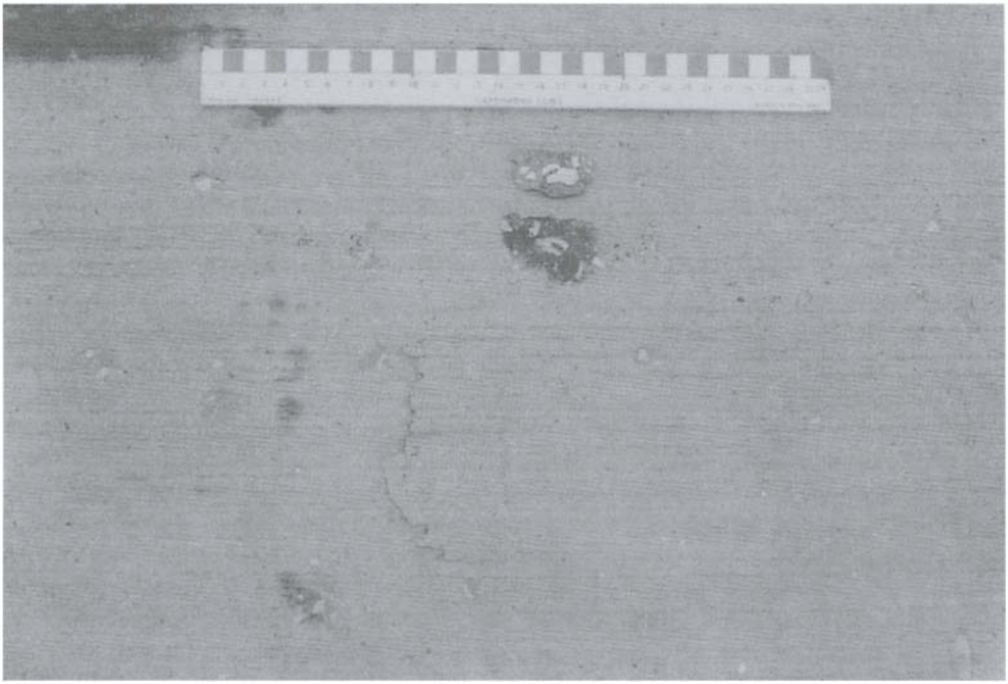

Fig. 16.12 Pop-outs and incipient pop-outs on a concrete pavement surface in the south of England, UK, caused by microporous flint cortex particles susceptible to freeze–thaw action.

Table 16.3 Comparison of two flint gravel coarse aggregates from southern England with different freeze–thaw performances, apparently related to the contrasting contents of microporous flint cortex materials

Freeze–thaw resistance[a]	Average (causes few pop-outs)				Poor (causes abundant pop-outs)			
Aggregate size (mm)	40	20	10	Overall[b]	40	20	10	Overall[b]
Composition of coarse aggregates								
Constituent	Approximate percentage[c]							
Microporous Flint Cortex, discrete particles	<1	13	37	10	20	39	60	24
					(18)	(13)	(14)	
Flint with attached cortex[d]	83	61	32	68	57	52	27	57
					(70)	(71)	(38)	
Flint without attached cortex	13	23	25	18	23	9	13	19
					(12)	(16)	(48)	
Others	4	3	6	4	–	–	<1	–
					(–)	(–)	(–)	
Freeze–thaw test results[e]								
Cumulative surface weight loss (mg/mm^2)				0.6				2.8
Depth of scaling (mm)				5.8				11.4
Area of scaling (%)				20				60

[a] Liability to form pop-outs on exposed pavement surfaces.

[b] Blend of 40, 20 and 10 mm sizes: in the case of the 'poor' aggregate, the blend was an equal mixture of crushed and uncrushed materials.

[c] Values in parentheses are for crushed gravel material.

[d] The attached cortex coatings were relatively thin for the 'average' aggregate and relatively thick for the 'poor' aggregate.

[e] RILEM tests[69] (with de-icing chemicals) on concrete made using the blended coarse aggregates, natural quartz sand and Portland cement.

bituminous coal, can also cause unsightly tarry staining on exposed concrete surfaces in the presence of water[71] or cause pitting in slabs subjected to wear. Pitting and associated staining of concrete roof tiles has occurred in some areas of the UK as the result of coal, carbonaceous shale and lignite particles in the sand aggregate.

Shell

Sea shells are considered by some commentators to be potentially deleterious owing to the presence of flaky or hollow shells. These could possibly affect the workability of concrete and weaken the concrete in the case of hollow shells being incompletely filled with mortar. BS 882: 1992[11] specifies limits for marine coarse aggregates based on earlier proposals by the Greater London Council.[72] However, Chapman and Roeder[73] found the important structural properties of concrete were not affected by significantly higher amounts of shell and that the original concerns were accordingly overstated.

Other weak or soft particles and coatings

There are many other types of material which can form weak or soft particles or coatings. In many parts of the Middle East, for example, wadi gravel aggregates mainly comprising igneous rock types frequently exhibit weak particle coatings of calcium carbonate or gypsum (Figure 16.13). Particles or coatings of iron oxides or hydrated iron oxides (ochres) are often soft and absorbent.

Organic matter

Apart from coal and related materials, water-soluble organic substances, such as humic acid and lignins found in decaying vegetation and other sources, are undesirable in concrete aggregates because these chemicals can retard or even prevent the normal setting and hardening of cement.[71] The presence of such organic matter is a potential problem with natural sand.[74,75] Whilst very unusual in UK aggregates, only very small proportions (say less than 0.1 per cent) are required for the retarding effect to be significant.[76]

Mica

The minerals muscovite mica and biotite mica are common constituents of many rock types, including granites, gneisses and sandstones, forming distinctive platy crystals. When

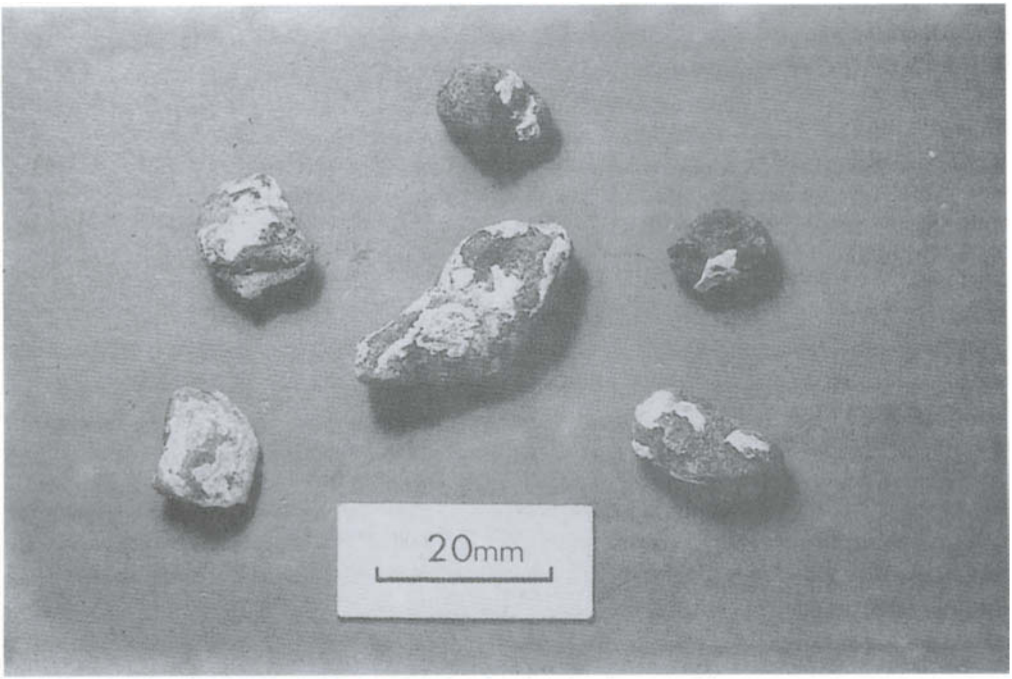

Fig. 16.13 Particles of wadi gravel coarse aggregate from the Arabian Gulf area. The particles comprise serpentinite and exhibit white partial coatings of calcite and gypsum.

mica occurs as discrete (or 'free') flaky grains in fine aggregates, it usually increases the water demand of concrete and also reduces the cohesiveness of the mix, which can adversely affect the final strength and durability of the hardened concrete. In one study of granite-derived sands from southwest England, Dewar[77] concluded that the compressive strength of a typical concrete mix may be reduced by as much as 5 per cent by the presence of 1 per cent by weight muscovite mica in the total aggregate.

In other studies, both Hoon *et al.*[78] using Indian materials and Forder,[79] again using southwest England materials, similarly demonstrated substantial strength reductions caused by mica addition; for example, 2 per cent mica in a 6:1 concrete mix caused a strength loss of 12–14 per cent at 28 days. Forder recorded a 1.3 per cent increase in water demand for each 1 per cent of muscovite mica added to the fine aggregate. Fookes and Revie,[80] carrying out a practical study of micaceous sand aggregates in Nepal, found that the greatest losses of workability and strength occurred with mica contents up to 2 per cent of total aggregate (Figure 16.14).

In particular cases, these disadvantageous effects of mica can be adequately compensated by slightly increasing the contents of cement and fine aggregate in the mix design or by using an admixture.[62,71]

Chlorides

Marine aggregates and some aggregates from coastal sources are likely to contain sodium chloride (common salt), although this can be reduced to minimal proportions by efficient washing. In the UK only a few aggregates from inland sources contain any significant

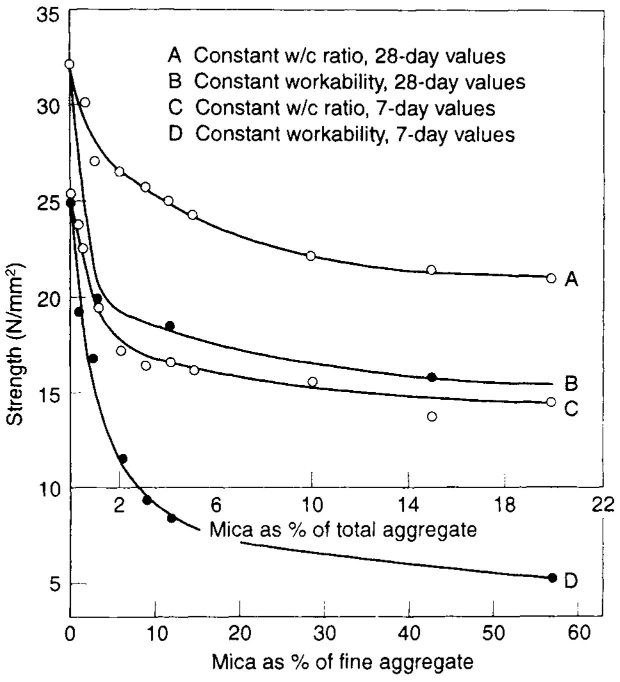

Fig. 16.14 Effects of increasing the muscovite mica content of aggregate on the water/cement ratio, workability and compressive strength of concrete (from Ref. 80).

amounts of chloride, but it is a serious problem in other parts of the world, especially in the Arabian Gulf.[16,81] In Ontario, Canada, rocks in the Niagara Escarpment have been found to contain relatively high amounts of chloride (up to 0.2 per cent), although some research has suggested that this chloride cannot be released into the concrete.[82]

Chlorides can promote or greatly exacerbate the corrosion of steel reinforcement or prestressing wires embedded in concrete (Figure 16.15) and, for this reason, BS 5328: Part 1: 1997[15] provides limits for the chloride contents permitted in concrete, whilst BS 882: 1992[11] gives related guidance limits for the chloride content of aggregates (Table 16.4).

Chlorides are not usually a hazard to unreinforced concrete, although they may enhance the rate of hardening, accentuate any tendency to efflorescence[71] and perhaps impair the sulfate-resisting properties of SRPC (sulfate-resisting Portland cement).[25] Also, sodium chloride incorporated into concrete increases the reactive alkali content as well as the chloride content and this may be important in the presence of an alkali-reactive aggregate combination.[83]

Sulfates

Portland cement contains a carefully controlled proportion of gypsum (hydrated calcium sulfate), which is added during manufacture as a retarding agent. Any additional amounts of sulfate present in the aggregate could lead to reaction with cement compounds and resultant expansion and disruption of the hardened concrete, especially if the sulfates are present as the readily soluble magnesium or sodium salts.

Fig. 16.15 Part of a concrete bridge deck in East Anglia, UK, exhibiting severe corrosion of the reinforcement steel promoted by chlorides: some of the steel has completely gone.

Table 16.4 Chloride contents permitted in British Standard

		Maximum total percentage chloride ion	
Type or use of concrete	Embedded metal	BS 5328: 1997[15] (by mass of cement)	BS 882: 1992[11] (by mass of aggregate)
Prestressed and heat cured	Yes	0.10	0.01
Made with cement complying with BS 4027	Yes	0.20	0.03
Made with cement complying with BS 4248	Yes or no	0.20	
Made with cement complying with BS 12, BS 146, BS 1370, BS 4246, BS 6588, BS 6110 or combinations with ggbs or pfa	Yes	0.40	0.05
Other concrete	No	No limit	No limit

BS 5328: 1997[15] recognises that it is the mobile sulfate from all constituents, including cement, after hardening of concrete that can cause these effects. No standard tests exist to measure this mobile sulfate and it is the acid-soluble sulfate that is measured. Accordingly, when setting limits, expert advice is necessary to avoid precluding satisfactory materials, such as some lightweight or blastfurnace slag aggregates and supersulfated cement.

In practice, few UK aggregates contain soluble sulfate salts, although some could contain small proportions of gypsum. Sulfates can be a very serious problem in aggregates in the Middle East.[16] Particles or coatings of coarsely crystallised gypsum can in some conditions give rise to concrete expansion as the result of internal sulfate attack.[84]

Pyrite and other metallic materials

Pyrite (iron disulfide, FeS_2) is a comparatively common aggregate constituent and the ability to oxidise in normal environmental conditions depends upon the structure and purity of the mineral. Certain 'reactive' forms of pyrite in aggregate can oxidise to brown iron hydroxide when occurring at or near to exposed concrete surfaces, causing areas of unsightly staining out of all proportion to the size of the reacting particle.[23] This is a problem with a number of sand and gravel sources in southern England, when the proportion of pyrite in the aggregates may only represent 1 per cent or less overall, although it can be locally more concentrated.

Crushed rock aggregates can also contain pyrite and related minerals and mostly these do not prove to be unstable in normal density concrete. However, Chinchón *et al.*[85] have described a crushed rock aggregate quarry in Spain in which the metamorphosed limestone and shale contain weathered pyrite and pyrrhotite ($Fe_{1-x}S$) and their expansive oxidation products (various complex sulfates).

Pyrite in some aggregates derived from tin mining waste has been involved in the general deterioration of low-grade concrete and concrete building blocks in Cornwall and parts of Devon in the UK.[86-88] However, this so-called 'mundic' problem ('mundic' is the old Cornish word for pyrite) also appears to involve moisture movement arising from clay and micaceous minerals in the slaty and phyllitic rocks. Guidance on the mundic problem has been prepared by the Royal Institution of Chartered Surveyors.[89]

Soluble lead, zinc and cadmium compounds can interfere dramatically with cement hydration, with zinc salts being up to 10 times more active than lead salts as retarders. Although only very small amounts of soluble lead and zinc salts are tolerable, in practice only a minority of these compounds are soluble and therefore a total upper limit for lead + zinc compounds of approximately 0.2 per cent by weight of aggregate has been suggested.[76] Lees,[90] however, states that 'the limits of soluble (heavy) metal have not been established' and suggests carrying out concrete strength development tests.

Alkali-reactive constituents

Certain types of siliceous rock and mineral aggregate constituents can react with alkali hydroxides in the concrete pore solution to form a gel product which can expand to cause cracking and other damage to the hardened concrete. These 'alkali–silica reactive' aggregate constituents can therefore be undesirable, but the possibility of reaction occurring and the magnitude of any resultant damage is dependent upon a combination of critical factors. Unlike the other 'undesirable constituents' dealt with in this section, sometimes, apparently paradoxically, small proportions of alkali–silica reactive constituents can be more injurious in concrete than larger proportions. This type of alkali–aggregate reactivity, and the other rarer varieties, is considered in more detail in section 16.6.5.

Releasable alkalis

The alkali hydroxides present in concrete pore solutions are mainly derived from Portland cement, which typically contains up to about 1 per cent total alkalis ($Na_2O + 0.658\,K_2O = Na_2Oeq$). Sometimes additional alkalis can be derived from the other constituents of concrete, including the aggregates, as well as from environmental sources. Many rock-forming minerals contain alkalis, but only a relatively small proportion of these alkalis are liable to be soluble or 'releasable' within concrete and in the UK their contribution is generally ignored.

However, in other countries, certain rock types in aggregate, such as granite and some volcanic rocks,[91] have been found to contain sufficient 'releasable alkalis' to enhance significantly the possibility of concrete expansion (Figure 16.16). The aggregate alkalis leachable by a saturated calcium hydroxide solution appear to correspond reasonably closely to those which are potentially releasable within concrete.[92]

16.5 Properties of natural aggregates

16.5.1 PARTICLE SIZE DISTRIBUTION (GRADING)

The overall particle size grading of aggregate is significant in ensuring the cohesion of concrete and the associated feasibility of achieving a satisfactorily high density by normal compaction methods. The influence of aggregate grading increases as the cement content decreases or as the required workability increases.[93] In practice, modern mix design techniques can enable successful concrete to be made using aggregates of almost any particle size distribution, but reasonable consistency of grading during a period of supply and construction remains essential. This approach is adopted in the draft European Standard

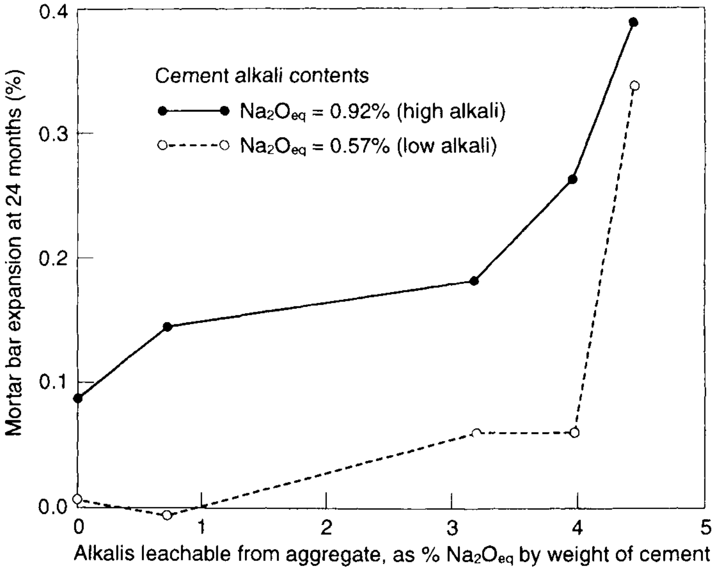

Fig. 16.16 Effects of alkalis leachable from an aggregate, by saturated calcium hydroxide solution at 38°C, on the expansion of ASTM C227 mortar bars at 24 months (data derived from Ref. 92). The aggregate was a natural sand comprising 45–50% quartz, 20–25% glassy to cryptocrystalline andesite to rhyolite, 10% feldspar, 5–10% granite and 5–10% quartzite, with traces of chert and sandstone. Variations in the aggregate alkali content were achieved by leaching for different periods up to 180 days, by which time virtually all the leachable alkalis had been extracted and this point is taken as zero on the abscissa of the graph.

for concrete aggregates, which requires suppliers to declare typical gradings and retain variation within given tolerances about this grading.[12]

In the UK it has hitherto been found convenient to standardise the 'acceptable' aggregate gradings in order to minimise the need for special mix design and to simplify monitoring for consistency. Grading of aggregates is usually established by sieve analysis, when the weight proportion passing each of a nest of sieves is computed and may be expressed graphically as a log-normal curve. A more detailed consideration of aggregate grading is given elsewhere.[94]

Coarse aggregates

Aggregates which are mainly retained on a 5 mm sieve are termed 'coarse' aggregates and, in the UK, standardised coarse aggregate gradings are specified in BS 882: 1992[11] and sometimes BS 63: 1987.[95,96] Alternative grading schemes are specified in BS 882: either 'graded' aggregates of nominal sizes 40–5 mm, 20–5 mm and 14–5 mm, or 'single-sized' aggregates of nominal sizes 40, 20, 14, 10 and 5 mm.

Except for the nominal maximum particle size, these grading limits incorporate generous tolerances for each sieve size to allow for natural material variation, imprecision in normal processing and also errors caused by sampling and testing.[97] The combination of single-sized coarse aggregates can permit a greater control to be exercised in the overall mix design and single sizes are thus sometimes preferred for high-quality structural concrete. This will, however, depend on the efficiency of processing and is not inevitably the case.

The draft European Standard[12] uses marginally different descriptions. Coarse aggregates are those mainly retained on a 4 mm sieve and aggregate sizes are described with the smaller sieve (*d* mm) before the larger sieve (*D* mm). For example, d/D as 4/20 in lieu of 20–5 mm graded in traditional BS parlance. This also allows for selection of a wider range of aggregate sizes to cover all European country requirements and traditions.

There are also some moves in Europe not only to provide general grading tolerances for all normal uses of concrete but also allow for alternative tighter tolerances for special uses or particular aggregates.

The use of 40 mm aggregates in the UK has become relatively rare and is mainly restricted to some pavement-quality concrete. The use of larger maximum aggregate sizes (e.g. 75 and 150 mm), or even 'plums' (individual large stones up to about 300 mm), is now rather unusual and confined to massive concrete placements where there is an essential need to minimise cement content and heat generation.[25]

Sands and fine aggregates

Aggregates which mainly pass a 5 mm sieve are termed 'sand' or 'fine' aggregates and, in the UK, standardised sand gradings are specified in BS 882: 1992.[11] For nearly 30 years from its introduction in the 1954 edition of BS 882, a four-zone system of fine aggregate grading limits was used in the UK. These zones were not related to performance and only represented a classification of many sand gradings already available in the UK (499 samples from 350 sources), with some deference to research carried out by the Building Research Station.[98] Experience of use revealed a number of shortcomings and widespread misunderstanding of this four-zone system, and a SAGA (Sand and Gravel Association) survey found that nearly 20 per cent of more than 16 000 results (from 526 sources) fell outside the zone system with 'failures' arising across nearly 90 per cent of the sources (Table 16.5).

Consequently, a new system comprising a wider overall grading envelope, plus three overlapping additional grading limits, was introduced into BS 882 in 1983 and survives in the 1992 edition. In the new system, a given fine aggregate will frequently comply with two of the three gradings termed 'C', 'M' or 'F' (coarse, medium or fine).

Generally, within the permitted standard limits, the grading of fine aggregate has a greater influence on the properties of concrete than that of coarse aggregate. At one end of the range, an unusually coarse sand tends to produce a 'harsh' mix of low workability

Table 16.5 Grading survey of 16 071 concreting sands from 526 UK sources, carried out by the Sand and Gravel Association in 1976–1977, showing that some 19% failed to comply with any one of the grading 'zones' specified in the 1954, 1965 and 1973 editions of BS 882; 87 per cent of the sources produced at least one 'failure' during the survey period (after Ref. 99)

Grading zone	1	2	3	4	Other grading (i.e. failure to comply)
Limits for per cent passing 600 μm sieve size	15–39	40–59	60–79	80–100	
Number of sieve analysis results	545	6775	4506	1186	3059
Percentage	3.4	42.2	28.0	7.4	19.0

and with a greater liability to 'bleeding' (segregation of water during mixing and/or placing of the concrete). At the other end, an unusually fine sand can significantly increase the water demand of a concrete mix, because of its much greater particle surface area, but concomitantly can improve cohesiveness. The overall grading of a sand can be improved by blending coarser and finer sands or fractions.

The draft European Standard for concreting aggregates[12] uses different descriptions and separates sand (fine aggregate) and coarse aggregate by a 4 mm sieve. The coarseness or fineness of sands is described by d/D sizes in mm of 0/1, 0/2 and 0/4. A further classification is provided based on either the percentage passing a 500 μm sieve (Table 16.6) or the fineness modulus, for coarse, medium and fine grading sands (C, M and F).

All-in aggregates

Coarse and fine aggregates which are supplied already combined are termed 'all-in' aggregates and, again, grading limits are specified in BS 882: 1992[11] for 40 and 20 mm nominal maximum sizes. All-in aggregates are not recommended for high-quality concrete and BS 5328: 1997[15] restricts their use to concrete strength grades of C15 or lower.

Gap-graded aggregates

Whatever the combined aggregate proportions, it is most usual to aim for a continuous grading, producing a relatively smooth, sigmoidal grading curve. However, it should be recognised that there is no one ideal grading since aggregates are processed from natural deposits and in practice ideal conditions do not exist. Thus completely smooth grading curves are rarely achieved and variations are accommodated in concrete mix design.

When there is a major deficiency of certain particle sizes, the aggregate is said to be 'gap-graded'. This may arise out of natural grading characteristics, for example with unusually fine sands, or the concrete may be deliberately designed to be gap-graded.[100] Although gap-grading can occasionally be beneficial for mixes of otherwise low workability, generally it appears that continuously graded and gap-graded aggregate combinations are equally usable for making good-quality concrete.[62,94] However the successful use of gap-graded concretes may require a greater degree of expertise.[25]

16.5.2 FINES (CLAY, SILT AND DUST) CONTENT

Tolerable limits

Most aggregates contain a proportion of 'fines' (previously referred to as 'clay, silt and dust'), which is defined in BS 812 as material passing a 75 μm sieve. In the future it is

Table 16.6 Guidance on the definition of coarseness and fineness of sands (fine aggregates) based on a draft European Standard for concreting aggregates[12]

Percentage passing the 500 μm sieve by mass		
C	M	F
5–45	30–70	55–100

probable that European practice will standardise on the 63 μm sieve (rather than the 75 μm sieve) as the defining maximum size. A certain amount of these fines is helpful in concrete, improving cohesiveness and preventing bleeding, and totally 'clean' aggregates are not normally desirable. However, excessive quantities of fines tend to increase the water demand of a concrete mix and can impair the aggregate cement paste bond, so that BS 882: 1992[11] specifies maximum limits for −75 μm material after washing and sieving,[101] which vary according to aggregate types and intended use. These limits appear to be somewhat arbitrary and it is quite frequently possible to design concrete mixes to accommodate appreciable contents of fines in the aggregate, particularly when using admixtures.

Importance of composition

The influence of −75 μm material on the properties of concrete depends crucially upon the nature of the fines. Natural sand and gravel aggregates can contain 'silt' (2 – 75 μm) and 'clay' (−2 μm) (see Ref. 102 for particle size definitions), whereas crushed rock aggregates can contain 'dust' of fracture (sometimes termed rock or mineral 'flour'). The dust in crushed aggregates is typically comparatively coarser and contains lesser amounts of clay minerals *per se* than the silt and clay-sized fines in natural aggregates, so that higher contents of fines are frequently permitted for crushed materials. Some types of crushed rocks continue to generate dust by self-attrition of the particles during handling, so that the dust content of the material at placement of the concrete might be significantly higher than that determined for a sample previously taken from the stockpile.

The 'clay' component of an aggregate fines may be 'clay-sized' material rather than being necessarily composed of clay minerals. This is an important distinction as clay minerals are unusually moisture sensitive and can be expected to produce more adverse effects in concrete than other clay-sized particles, especially in the case of the swelling clays such as smectites (montmorillonite) and some chlorites,[103] or the highly absorbent and plastic palygorskite (attapulgite in North America). Indeed, some research has indicated that the incorporation of non-clay fines into concrete can improve early strength without long-term detriment.[104,105]

In a study for the British Standards Institution, Pike[106] concluded that, 'a controlled content of mineral flour other than clay minerals may be tolerable (and occasionally useful) but clays are to be avoided; smectites are particularly harmful and their content shall be severely restricted'. Pike suggested that fines limits, for example those given in BS 882, perhaps could sometimes be relaxed if a test for harmful clay fines was available and he considered that a form of the methylene blue absorption method (section 16.5.9) might be appropriate in that respect. Ramirez *et al.*[107] have similarly proposed controls for calcareous sands based upon both fines content and methylene blue absorption. However, the strength performance effects for a particular methylene blue value vary depending upon the type of clay and the test is thus not definitive.[108]

16.5.3 PARTICLE SHAPE AND PARTICLE SURFACE TEXTURE

Flakiness and elongation indices

Aggregate particle shape characteristics and variations can affect the workability and strength of concrete.[39] The shapes of particles in concrete aggregates are best described following the principles long established for sedimentary rocks, with the two principal parameters being 'sphericity' and 'roundness' (Figure 16.17).

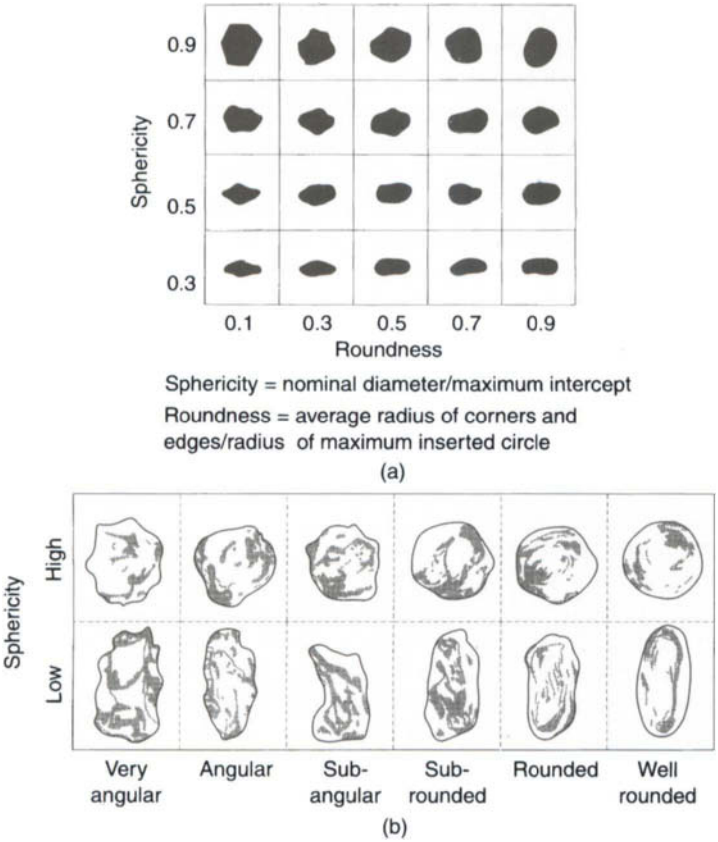

Fig. 16.17 Two comparable charts for the visual assessment of particle shape (from Refs 109, 110). (a) Derived from measurements of sphericity and roundness, (b) based upon morphological observations.

Although historically particle shape was considered important, modern concrete design procedures enable all but the most adverse shapes to be accommodated. BS 882 now only provides limits for flakiness (where particle thickness is small relative to other dimensions). Such aggregate particles could lead to either water gain under the aggregate, causing planes of weakness, or higher water demands and lower strength in concrete. BS 882: 1992[11] limits the flakiness index determined in accordance with BS 812: Section 105.1: 1989[110a] to 50 per cent for uncrushed gravel and 40 per cent for crushed rock or crushed gravel, with a warning that lower values may be specified for special circumstances such as pavement wearing surfaces.

Experience shows that certain particle shapes are associated with different aggregate types; for example, dune sands are typically well rounded, glacial sands and gravels often exhibit a useful mixture of rounded and irregular particle shapes, and crushed volcanic rock types often tend to produce angular and flaky aggregate particles.

Angularity

The void content of compacted aggregate is largely dependent upon the roundness (or angularity) of the component particles, so that the percentage of voids in a standardised test can be used as a quantitative measure of particle angularity.[111] A single-sized, well-rounded beach gravel produces a void content of 33 per cent and this has been established as the zero baseline for the 'angularity number', which is represented by the percentage of voids in excess of 33 per cent (i.e. angularity number = percentage voids − 33). In practice, angularity numbers can be obtained up to about 11 for the most angular crushed rock aggregate.

Modern advocates of concrete mix design use packing principles and measure the simpler uncompacted bulk density. This measurement incorporates both the effects of shape and grading.

Surface texture (roughness)

It is evident that particle surface texture has some influence on the strength of the aggregate–cement paste bond, but difficulty of measurement has meant that the property is rarely considered and almost never the subject of a specification requirement. A simple visual descriptive scheme was included in BS 812: Part 1: 1975[57] and various more objective and quantitative methods of surface roughness assessment have been suggested.[41,112,113] Procedures using Fourier and fractal methods for monitoring the shape, texture and roughness of aggregate particles in quantitative terms have been proposed.[114–116] However, none of these methods has been adopted for routine application.

16.5.4 PARTICLE DENSITY

Normal aggregates

Particle density, previously termed 'relative density' or 'specific gravity', is sometimes used as the basis of the broad classification of aggregates into 'normal', 'lightweight' or 'heavy' varieties. The particle density of aggregates is the ratio of the mass of a given volume of material (say a cubic metre) to the mass of the same volume of water, but different values are obtained in determination depending upon the allowance made for pores. Three types of value are generally recognised: oven dry, saturated surface-dried and apparent particle densities, in order of increasing numerical magnitude. Smith and Collis[25] highlight the difficulties which can be encountered when specifications make reference to the particle density of aggregates without stipulating the required basis of calculation.

The possible apparent particle density values for normal UK aggregates range between 2.4 and 3.0 $\mathrm{Mg/m^3}$ but the majority are in the narrow 2.5–2.7 band (Table 16.7). Aggregate particle density usually is not directly related to concrete performance in the materials sense, but might be relevant from a structural standpoint (e.g. gravity structures). It is, however, an essential property for concrete mix design and also for calculating the volume of concrete produced from a certain mass of materials (the yield). Unusually high or low aggregate densities can sometimes exacerbate segregation tendencies in normal concrete mixes.

Lightweight aggregates

Both natural and synthetic lightweight materials are deliberately used for concretes in which low density is a prime requirement. However, except for pumice and scoria, the majority of lightweight aggregates are synthetic. The dry densities of such lightweight concretes vary greatly according to aggregate type, from as low as 0.3 $\mathrm{Mg/m^3}$ for expanded vermiculite concrete, up to nearly 2.0 $\mathrm{Mg/m^3}$ for some slag aggregate concretes. There is

Table 16.7 Apparent particle densities for some UK aggregate types (after Refs. 94 and 117)

Aggregate type (crushed rock, and gravel where stated)	Average particle density, apparent basis (Mg/m^3)	Range of particle densities, apparent basis (Mg/m^3)
Basalt	2.80	2.6–3.0
Flint gravel	2.54	2.4–2.7
Granite	2.69	2.6–3.0
Hornfels	2.82	2.7–3.0
Limestone	2.66	2.5–2.8
Mixed igneous gravel	2.72	2.7–2.8
Rhyolite	2.73	2.6–2.9
Quartzite gravel	2.62	2.6–2.7
Sandstone	2.69	2.6–2.9

a general but not invariable tendency for compressive strength to be reduced as the concrete density is lowered, so that the very low-density concretes (say $< 1.0\,\mathrm{Mg/m^3}$) are principally used for insulation purposes (see section 16.7.2 for further information on synthetic lightweight aggregates).

Heavy aggregates

There are some specific applications for high-density concrete, notably for radiation shields but also for pipeline and other ballasting.[118,119] Natural heavy aggregates include barytes and haematite, whilst synthetic materials include iron and lead shot. The achievable concrete densities range from 3.0 up to more than $8.0\,\mathrm{Mg/m^3}$, depending upon the type of heavy aggregate used and the proportions of normal density aggregates with which the high-density aggregate might be combined (see section 16.7.4 for further information on synthetic heavy aggregates). There is a tendency for breakdown during mixing with some barytes aggregates and trials should be undertaken to assess any such effects on overall grading in the final concrete.

16.5.5 POROSITY AND ABSORPTION

The porosity and absorption of individual aggregate particles has been discussed in section 16.4.4. The overall porosity or absorptiveness of aggregates may depend either upon a consistent degree of particle porosity or represent an average value for a mixture of variously high and low absorption materials. In assessing the significance, if any, of a certain level of overall aggregate porosity or absorption, it is important to establish which of these causes pertains and this is usually apparent from the petrographic composition.

Natural aggregates in common usage in the UK exhibit water absorption values ranging from less than 1 up to some 5 per cent and, where this overall absorption arises from reasonably consistent particle absorption, such values are unlikely to be problematic in most concretes, providing the average values are known and can be taken into account in the mix design and batching. However, where the overall absorption value belies the presence of a minor proportion of highly absorptive particles among a majority of low-absorption particles, defects could occur at exposed concrete surfaces; in this way microporous flint cortex particles in flint gravel aggregates can cause pop-outs (section 16.4.4).

In determining the likelihood of pop-outs due to frost, it is important to consider the nature of the pores. If the pores are smaller than 4 μm in size they are likely to trap water, preventing drainage and leading to pressure build-ups under ice, resulting in frost damage.

In some circumstances it has been thought necessary to place an upper limit on aggregate absorption. BS 8007: 1987,[120] and BS 6349: 1984,[121] for example, each recommended a 3 per cent maximum aggregate absorption for water-retaining and maritime concrete structures, respectively, although the technical basis for these limits is uncertain. Indeed, Arnold and Littleton[122] found no significant increase in concrete water permeability with increasing aggregate absorption, up to 8 per cent maximum absorption investigated. In some special cases, porous aggregates have been found to be beneficial.[63]

16.5.6 BULK DENSITY

A given unit volume of aggregate has a lower overall or 'bulk' density than the 'particle density' (section 16.5.4) determined for that aggregate because of the voids that are present between aggregate particles. The bulk density value can be improved by compaction and obviously will be better for well-graded materials, but some void content will always remain. A moisture content will also reduce the bulk density, especially for fine aggregates, because of the tendency, termed 'bulking', for water to hold particles apart by surface tension.[62] Crushed aggregates tend to have lower bulk densities than natural sands and gravels, especially when uncompacted. The bulk density of fine aggregate is typically around 10 per cent greater than comparable coarse aggregate.[41]

The usefulness of bulk density as an aggregate characteristic has declined with the change from volume to weight batching of concrete, but has some value in concrete mix design as the aggregate void content or 'void ratio' (i.e. the ratio of voids to the volume of solid material) relates to the content of matrix required for the achievement of a dense concrete. Potentially, bulk density is an easily determined property capable of giving indirect comparative information about a range of other physical and mechanical characteristics of the aggregate, including grading and particle shape. The Quality Scheme for Ready Mixed Concrete requires its measurement for quality control purposes. Dewar[123] has also used the measurements of uncompacted bulk density in his method of mix design based on optimum packing principles.

16.5.7 STRENGTH AND TOUGHNESS

It is self-evident that aggregates for concrete need to be 'strong' in a general sense, because of the need to survive unchanged the processing, transportation, concrete mixing and placing stages, as well as performing the function of a bulking material in the hardened concrete. For this reason, 'soft' rocks, such as shale or chalk, are not contemplated for use as concrete aggregate and are thus not included in the list of rock names given in BS 812. Beyond this basic requirement for strength, it is only usually considered necessary for the aggregate strength to exceed that of the concrete of which it is to form part. In most cases, inherent aggregate strength does not greatly influence or limit the compressive or flexural strengths of concrete.[124]

By contrast, however, the wear resistance of concrete surfaces is in part dependent upon aggregate 'toughness',[125] a property broadly analogous to 'impact strength' and related to the basic material properties of tensile strength and modulus of elasticity. Limiting values are proposed for heavy-duty concrete floor finishes and pavement wearing surfaces in BS

882: 1992[11] using the 10 per cent fines or aggregate impact value tests, whilst future European Standards are likely to adopt the Los Angeles coefficient.

Compressive strength of rock

The mechanical properties of any aggregate are related to the inherent characteristics of the rock type or types comprising that aggregate. For crushed rock aggregates, a good measure of aggregate particle strength may be obtained by determination of the unconfined compressive (or 'crushing') strength of the source rock, using core tests (BS 812: 1967[126] – now withdrawn; ISRM[127]). Indirectly, and less reliably, the compressive strength of a rock can be assessed using point-load[128] or Schmidt rebound tests. Most rocks used for the normal production of concrete aggregate will exhibit compressive strengths in excess of 100 N/mm^2 and many varieties, including basalts and quartzites, may substantially exceed 200 N/mm^2.

Aggregate crushing value

A portion of 14–10 mm sized coarse aggregate particles is confined in a steel pot and subjected to a standard loading, after which the aggregate crushing value (ACV) is determined from the amount of fine material generated by crushing, expressed as a percentage of the original weight of the test portion. Lower values thus indicate aggregates which are more resistant to crushing. In the UK, the 10 per cent fines value test has become preferred to the ACV test which is no longer widely used.

Ten per cent fines value

Portions of 14–10 mm sized coarse aggregate particles (optionally dry or saturated) are confined in a steel pot and subjected to various loadings, after each of which the amount of fine material generated by crushing is determined; the 'ten per cent fines value' (BS 812: Part 111: 1990)[129] represents the applied load in kN required to produce 10 per cent fines by weight of the original test portion (an applied load which produces between 7.5 and 12.5 per cent fines is recalculated for the notional 10 per cent). Higher values in this test thus indicate aggregates which are more resistant to crushing. BS 882: 1992[11] provides limits for 10 per cent fines values, ranging from 50 kN minimum to 150 kN according to the type of concrete in which the aggregate is to be used.

Aggregate impact value

A small portion of 14–10 mm sized coarse aggregate particles is confined in a steel pot and subjected to 15 blows by a small hammer in a standardised test rig, after which the 'aggregate impact value' (AIV) is determined from the fine material generated, expressed as a percentage of the original weight of the test portion (BS 812: Part 112: 1990[130]). Lower values indicate aggregates which are tougher or more impact resistant and higher strength concrete aggregates will exhibit AIVs of less than about 20 per cent but very few will produce AIVs of less than 10 per cent. BS 882: 1992[11] provides limits for AIV, ranging from 45 per cent maximum to 25 per cent maximum according to the concrete surface wear expectation.

Each of these BS tests for aggregate strength and toughness (10 per cent fines value and AIV) is routinely carried out using dry material, but comparative retesting using saturated material can give information regarding aggregate soundness (section 16.5.9).

16.5.8 HARDNESS AND ABRASION RESISTANCE

The concept of 'hardness' is well known to geologists as a physical characteristic of minerals, usually assessed on the basis of scratch resistance with reference to the comparative scale of hardness devised in 1824 by the German mineralogist Friedrich Mohs (1772–1839). The 'hardness' of rocks may similarly be defined as the resistance to scratching, indentation or surface abrasion, and largely depends upon the 'microhardness' of the constituent mineral grains and the strength of the bond between those mineral grains. Although attempts have been made to quantify the measurement of rock or aggregate hardness, notably by adapting the Vickers' hardness apparatus used extensively in metallurgy[131] (Table 16.8) or by using scratch sclerometers, it is more usual for the resistance to abrasion or attrition to be assessed by a type of performance test and some of the more common procedures are described in the following sections.

Los Angeles abrasion value

Internationally, the most frequently used test for rock or aggregate abrasion resistance is probably that employing the Los Angeles apparatus[132,133] and this is the preferred test in the draft European Standard,[12] albeit using a slightly different apparatus. A test portion of rock lumps or coarse aggregate rotates for a standard number of revolutions in a steel drum together with a charge of steel balls, after which the difference between the original and final weights of the test portion (generated fines excluded) is expressed as a percentage of the original weight of the test portion.

Lower values of 'percentage wear' thus indicate rocks or aggregates which are more resistant to a combination of abrasion and impact. Most good concrete aggregates will exhibit 'Los Angeles abrasion values' of less than about 30–40 per cent, but few will produce values of less than about 15–20 per cent. ASTM C33[134] provides a limit of 50 per cent maximum for coarse aggregate for use in some types of concrete, according to wear expectation.

Aggregate abrasion value

BS 812: Part 113: 1990[135] includes a procedure for determining the 'aggregate abrasion value' (AAV), although in UK usage this test is primarily used for road aggregates and

Table 16.8 Mohs' scale of relative hardness and an approach to quantification using a relationship developed between the Mohs' hardness number and the Vickers' microhardness value (from Ref. 131)

Mineral	Mohs' hardness number	Computed Mohs' hardness number
Talc	1	1
Gypsum	2	1.8
Calcite	3	2.6
Fluorspar	4	3.2
Apatite	5	4.9
Orthoclase	6	5.6
Quartz	7	7.2
Topaz	8	7.8
Corundum	9	8.9
Diamond	10	Possibly 16.0

only rarely specified for concrete aggregates. However, for aggregates intended for use in concrete wearing surfaces (see also section 16.6.4), the test method is applicable and useful, although the criteria for assessing the results might need to be different from those accepted for bituminous-bound road aggregates. Inadequate resistance to abrasion can cause loss of the texture depth required for good skid resistance properties.

Test portions of selected representative coarse aggregate particles are mounted on to 'pad' specimens and pressed against a rotating steel lap charged with Leighton Buzzard (BS Standard) quartz sand for a standard number of revolutions. The 'aggregate abrasion value' (AAV) is determined from the average loss in weight of the pad specimens, adjusted according to the relative density of the aggregate material. Lower aggregate abrasion values indicate aggregates which are more resistant to abrasion and most good concrete aggregates will exhibit AAVs up to about 14 or 16. Higher values are not considered appropriate for road aggregates[136,137] in the UK, but it does not follow that a similar limitation applies equally to concrete aggregate.

Direct comparison between results obtained using the Los Angeles and AAV methods is not valid, because the former combines abrasive wear with impact, whereas the latter combines abrasive wear with constant pressure. However, it is reasonable to suppose that an aggregate which is sufficiently tough and wear resistant for successful use in concrete wearing surfaces ought to satisfy both test procedures.

Micro-Deval attrition

The micro-Deval test is used in some countries to measure the resistance of aggregate to abrasion and is one of the tests given in the draft European Standard.[12] The abrasion of 10/14 mm aggregate is produced by a charge of stainless steel balls in a rotating cylinder. The micro-Deval value is the percentage of material passing a 1.6 mm sieve after rotation for a fixed period. Variations of the test procedure enable the test to be undertaken in wet or dry conditions.

An evaluation of the micro-Deval test in Canada indicated a good correlation with the sulfate soundness test (section 16.5.9) and good within and inter-laboratory precision.[138]

Polished stone value

When considering road aggregates, the manner in which particles wear is as important as the quantitative amount of wear; a material which polishes with wear is not desirable for road surfaces. The 'polished stone value' (PSV) test is a uniquely British procedure devised by the Transport and Road Research Laboratory (TRRL) and now standardised in BS 812: Part 114: 1989.[139] The PSV test is of rather limited application to concrete aggregates but, arguably, may sometimes be of use when considering aggregate for a concrete wearing surface (see also section 16.6.4).

Test portions of selected representative coarse aggregate particles are mounted on the curved 'pad' specimens and subjected to wear in an accelerated polishing apparatus comprising a rubber wheel variously fed with water, corn emery and emery flour, after which the PSV is measured using a pendulum arc friction tester marked with an arbitrary scale. Because of the poor reproducibility of the test, the BS 812 method calls for use of a control sample, against which the results are 'corrected'.

High PSVs indicate aggregates with greater resistance to polishing and most good concrete aggregates, except non-silicified limestones, will exhibit PSVs of more than about

40 or 45, but very few will exceed a PSV of about 60. In the UK, bituminous-bound road aggregates are not usually considered suitable for use on main or secondary roads unless the PSV exceeds about 55 or 60,[140] but it cannot and should not be assumed that these values are in any way relevant to concrete aggregates.

16.5.9 SOUNDNESS AND PHYSICAL DURABILITY

The commonly used term 'durability' is actually rather difficult to use in relation to concrete aggregates, because it is a relative concept that needs to be qualified by the nature of the particular threat to the durability and which is also dependent upon the length of time for which duration is expected. The term 'soundness' is more specific, being 'the ability of aggregate to resist excessive changes in volume as a result of changes in physical conditions ... the physical causes of large or permanent volume changes of aggregate are freezing and thawing, thermal changes at temperatures above freezing, and alternating wetting and drying'.[94] Soundness or 'physical durability' is an important property of concrete aggregates, which can significantly affect the performance of a concrete in which they are incorporated. However, the difficulties in simulating natural exposure conditions or identifying any adequately reliable indicator tests have often caused this property of aggregate to be neglected.

Sulfate soundness

Internationally, the most widely used soundness test for rocks and aggregates is that using sodium or magnesium sulfate and standardised in ASTM C88.[141] This method was first devised in the early 1930s[142,143] and consists of subjecting a test portion of aggregate or rock pieces to cycles of alternate immersion in a saturated sulfate solution and drying, after which the test portion is washed, sieved and the weight loss computed. Tests alternatively using sodium sulfate or magnesium sulfate do not necessarily produce the same results for one aggregate and the latter is usually considered to be more aggressive, although exceptions have been reported.[144] Lower loss values indicate aggregates more resistant to the rigorous test conditions and most sound concrete aggregates will exhibit loss values of less than about 10 per cent.

Broadly similar test procedures have been specified in the UK by the Property Services Agency (PSA) for use with aggregates for airfield pavement works[145] and by the Scottish Development Department (SDD) for use with bituminous-bound road aggregates.[146] A magnesium sulfate soundness method was published as BS 812: Part 121 in 1989,[147] although it differs from ASTM C88 in being applied to a single size fraction and in citing the result as the proportion of sample retained rather than lost (a high value being a good result).

The usefulness of the sulfate soundness test as a reliable indicator of freeze–thaw or other forms of physical durability of aggregate has always been controversial and Bloem,[148] for example, emphasises the 'lack of justification for inflexible limits and the need for flexibility of interpretation'. One recent critical review of the sulfate soundness test was published by Rogers *et al.*[149]

According to Bloem,[148] whilst low loss values are usually indicative of good durability, high loss values should only place the aggregate 'in a questionable category until performance data become available'. Notwithstanding the uncertain efficacy of the sulfate soundess test, it has a long history of use and, in the absence of any more acceptable test method, its use may be supported in view of the importance of the property of soundness for concrete aggregates. The draft European Standard for concreting aggregates[12] proposes a range of limits from 35 per cent maximum loss to 18 per cent maximum loss depending on the exposure conditions and linked to the magnesium sulfate test.

Freeze–thaw soundness and frost susceptibility

The resistance of aggregate to freezing and thawing cycles and to freezing whilst wet is of importance for concretes with surfaces exposed to winter weather, especially if also subjected to de-icing chemicals. Because of the difficulty in devising tests which seek directly to reproduce the effects of freezing and thawing, the sulfate soundness test has frequently been relied upon for an indirect and perhaps unreliable assessment. A freezing and thawing soundness test for uncombined aggregates was briefly available in ASTM C137-38T,[150] but this was discontinued in 1944. However, a broadly similar procedure remains in the AASHTO test.[151] The Transport and Road Research Laboratory (TRRL) frost heave test,[152–154] which has recently been included in BS 812 as Part 124: 1989,[154a] is not appropriate for concrete aggregates as it is designed to simulate the mechanism of sub-base heave.

It is principally the pore structure within aggregate particles which determines freeze–thaw resistance, with generally a larger volume of smaller-diameter pores being more susceptible than a similar or lesser volume of larger diameter pores.[155,156] In practice it is frequently a content of clay mineral[61] or a related mineral, such as chlorite[157] or iddingsite,[60] within the aggregate particles which provides the vulnerable pore structure. Higgs,[157] however, found that rock texture was equally important: in some American volcanic rocks containing 20–30 per cent chlorite, only those in which the chlorite occurred as 'seams, clots and fissures' (SCF microstructure) exhibited poor freeze–thaw durability.

There is growing evidence that aggregates may be attacked and damaged by de-icing chemicals, whether or not they are susceptible to freeze–thaw damage.[158] In the UK there are some examples of damage to concrete pavement surfaces by freezing whilst wet, which have apparently been significantly worsened by de-icing chemicals and especially the varieties, such as urea, which are not corrosive to metals. The frost susceptibility of microporous particles of flint[159] has already been considered in section 16.4.4.

Staining tests

Selective stains have long been used in geology to assist in the identification of minerals.[160] Such techniques have some application to aggregates in helping to establish petrographic composition or detecting small proportions of undesirable constituents, including the differentiation of calcite and dolomite, the detection of sulfates[161] and the positive recognition of alkali–silica gel in tests.[162]

Arguably the potentially most useful staining techniques are those to identify clay minerals and, in particular, the smectite (montmorillonite) group of swelling clays, the presence of which is liable to cause an aggregate material to be unsound. Methods using nitrobenzene or benzidene have been used, but methylene blue absorption (MBA) is now the most commonly applied method and the results can often be correlated with X-ray diffraction determinations of smectite content.[163] The range of MBA values obtained varies for different rock types.[164] Taylor[165] and Pike[108] provide good reviews of MBA and indicate some of the shortcomings of the method.

Comparative mechanical testing

The standard tests for strength and toughness (section 16.5.7) are usually carried out using dried aggregate samples, but some less sound materials can suffer significant reductions in their strength properties when saturated. Consequently, information on soundness can be obtained using such 'modified' testing of saturated aggregate samples, particularly by comparing the results found for dry and saturated test portions from the same sample.[166] BS 812: Parts 111 and 112: 1990[129,130] now include modifications for evaluating aggregate impact and 10 per cent fines values in both the dry and wet conditions. Perry and Parsons[167] report a 65 per cent reduction in 10 per cent fines value on soaking for Carboniferous sandstone of 'low durability', but an overall limiting value is not yet apparent.

16.5.10 THERMAL EXPANSION AND CONDUCTIVITY

Thermal expansion

The coefficient of thermal expansion of neat cement paste ranges from around $11 \times 10^{-6}/°C$ to more than $20 \times 10^{-6}/°C$. Natural rocks used for aggregates exhibit a considerable range of thermal expansion coefficients, related generally to silica content (Table 16.9), but rarely exceed about $12 \times 10^{-6}/°C$ and can be as low as $4 \times 10^{-6}/°C$. The overall thermal expansion coefficient of concrete will be substantially influenced by the type of aggregate present, because of the volumetric proportion of concrete which comprises aggregate (around three-quarters typically).

Also, in many cases, there will be a significant difference in coefficient of thermal expansion between the cement paste and the aggregate, which might lead to damage as a result of differential expansion over extreme temperature ranges. Such differential thermal factors may be important when designing concrete mixes to withstand exceptional diurnal temperature ranges (e.g. desert areas), or to be particularly fire resistant, or to be particularly freeze-thaw resistant, or to be cured by accelerated or autoclaving techniques. Even in temperate climates, differential thermal factors might be important for large exposed road

Table 16.9 Coefficients of thermal expansion for some materials used as aggregate (after Refs 41 and 168)

Rock type	Coefficient of linear thermal expansion ($\times 10^{-6}/°C$)
Basalt/dolerite/gabbro	3.6–9.7
Granite	1.8–11.9
Sandstone	4.3–13.9
Dolomite	6.7–8.6
Limestone	0.9–12.2
Marble	1.1–16.0
Porphyry[a]	5.7–8.4
Quartzite	10.8
Flint/chert	7.4–13.1
Diorite/andesite	4.1–10.3

[a] Includes rhyolite, trachyte, microgranite, etc.

or airfield pavement surfaces. Venečanin[169] has highlighted potential problems with thermal incompatibility between some carbonate aggregates and other concrete constituents.

Thermal conductivity

The thermal conductivity of concrete is largely controlled by the thermal conductivity of the aggregate contained therein and this property varies greatly with rock type.[170] In practice, however, the property is usually only considered for mass concretes where the rate of heat dissipation needs to be controlled, so that thermal conductivity is rarely determined for aggregates. Quartz and quartzitic aggregates tend to exhibit the higher levels of thermal conductivity (say >3.0 W/m °C), whereas the basic igneous rocks and some limestones tend to exhibit comparatively lower values (say <1.5 W/m °C).

16.6 Influence of aggregate on concrete properties

16.6.1 GENERAL CONSIDERATIONS

Since aggregate forms such a dominant proportion of any concrete (typically around three-quarters by volume), it is inevitable that the composition and properties of aggregate will influence, but not necessarily dictate or control, the properties of the concrete into which it is incorporated. Sometimes these influences are immediately noticeable, such as when a fresh concrete is rendered difficult to mix or to finish, but in other cases such influences only become apparent with time, as with ASR, or in special circumstances, with aggregates which are less resistant to fire or chemical attack.

In many cases today, potentially adverse influences on the concrete, arising from the aggregate involved, can be ameliorated or even completely counteracted by careful mix design and/or by the judicial use of additions and admixtures. Consequently, although the properties of aggregates are nowadays rarely decisive in controlling the engineering qualities of concretes, an appreciation of the potential influences of the aggregate is one of the essential prerequisites for successful concrete mix design practice and in-service performance.

16.6.2 WORKABILITY OF FRESH CONCRETE

It is necessary that any fresh concrete can be quickly yet thoroughly mixed to ensure a reasonably uniform distribution of the various constituents and then successfully compacted into place so that the material becomes well consolidated and free of excessive air voids and other cavities. Additionally, the fresh concrete must be adequately cohesive to enable such mixing and compaction to be carried out without undue segregation of the constituents (including 'bleeding' of the mix water). The term 'workability' (sometimes the different concept 'consistence' is used, particularly for mortars) determines the ease of mixing, compaction and finishing without segregation and has been defined as 'the amount of useful internal work necessary to produce full compaction.'[93,94]

Aggregates can influence concrete workability in two principal ways: (1) by modifying the rheological properties, largely because of particle size, distribution and geometry, and (2) by affecting the lubricant water content required for achieving a required level of workability, again largely because of particle characteristics and also absorptivity.

Grading and fines content

The principles of grading aggregates for concrete were discussed in section 16.5.1. Evenly graded and well-shaped aggregates help to achieve high concrete densities and strengths for the minimum cement contents and also reduce the risks of segregation and bleeding. However, variations in the maximum aggregate particle size, the ratio of coarse to fine aggregate (sand) and the content of fine material influence the water content and hence the workability.

In general terms it is the specific surface area (ratio of total surface area to total particle volume) of an aggregate which controls the amount of water needed to wet and lubricate the mix, with the specific surface becoming less as the aggregate particle size increases.[171] Consequently, extending a graded aggregate to a higher maximum particle size lowers the water requirement for a given workability, or conversely allows greater workability for a given water content. However, this simple relationship does not necessarily apply equally to sizes coarser than about 40 mm, nor to particles finer than about 150 μm which appear to exhibit the effects of lubrication without being completely wetted.

The influence of grading and fines content on concrete workability varies with cement content and workability requirements. Broadly the influence of aggregate grading declines as the cement content increases, whilst raising the fines content can increasingly affect the cohesion of the concrete mix. The fines may also adversely affect concrete properties if this consists predominantly of clay, since this can both increase the quantity of water required for a given workability and impair the bond between aggregate and cement paste. The increase in water content varies with the type of clay, being least with kaolinite and increasing progressively with illite and palygorskite; the increase in water content is most pronounced with smectite.[104]

The presence of clay may also adversely affect setting/hardening times, strength and shrinkage. BS 882: 1992[11] provides some guidance on limits for fines and similar levels are identified in the draft European Standard for concreting aggregates.[12] The draft European Standard also provides an annex on test methods where fines values exceed the cited limits. A review of methods for assessing the variability of fines in sands used for concrete and mortar may be found in Pike,[108] which also details and evaluates the results of research in this field.

Particle shape and surface texture

The approaches to defining aggregate particle shape and surface texture were described in section 16.5.3. Interparticle friction, for a given size and grading of aggregate, is largely dependent upon particle shape and surface texture, with greater values of friction for angular rough crushed particles than for rounded smooth gravel particles.

The effects of particle shape and surface texture on workability are seemingly more pronounced for fine aggregates, in which particle geometry is more difficult to characterise, but it is generally recognised that natural sands make more workable concretes than crushed fine aggregates when the water content is held constant.

Concrete mix design is more complex than considering the individual effects of grading, particle shape and particle surface texture: it involves optimising the packing of solid materials with the minimum of water content. This has been recognised by Powers[172] and more recently Dewar[123] has presented a comprehensive design method incorporating these principles.

Aggregate constituents

The composition of an aggregate might affect workability in some circumstances. Low density, especially 'lightweight' aggregates, for example, tend to produce rather less workable concretes than normal-density aggregates. Aggregate water absorption (section 16.5.5) can have some influence on concrete workability, either by providing a reservoir of lubricating water to improve workability when saturated or by absorbing water from the concrete mix when dry or only partially saturated to reduce workability. Concrete mix design and batching should endeavour to make allowances for overall aggregate absorptivity and natural moisture content, so that workability variations are minimised. Also, Newman[173] found that the amount of water absorbed into aggregates during the concrete's plastic phase was rather less than the absorption value obtained in a 24 h immersion test (closer to a 30 min immersion value).

Certain types of constituent, notably clay material, in the forms of lumps, coatings, fines or as components of argillaceous or altered rocks, might be expected to absorb water more readily and could thus influence the workability more rapidly and with greater effect. Weak or unsound constituents which could break down during mixing would alter the aggregate grading and specific surface area, leading to some resultant detrimental effect on workability, although these constituents might need to be rather abundant for the effect to be noticeable. Discrete mica in a fine aggregate can have a detrimental effect on water demand and workability and this has been discussed in section 16.4.4.

16.6.3 CONCRETE STRENGTH

Although aggregate forms such a large proportion of any concrete, there are generally no simple relationships between the mechanical properties of aggregate and those of the resultant concrete,[174] with the probable exception of wear resistance (section 16.6.4). The Road Research Laboratory,[124] in the important book on concrete roads, states clearly, 'Provided that aggregates are stronger than the concrete of which they form part, their inherent strength is not likely to influence the strength of the concrete, either in crushing or in flexure'.

Aggregate strength and density

Most rock materials present in aggregates which are deemed suitable for use in concrete are appreciably stronger and tougher than concrete itself (Table 16.10), but there are few indications that the use of stronger aggregates leads to the possibility of stronger concrete. Kaplan,[176] for example, could establish 'no significant relationship' between aggregate crushing value and the compressive or flexural strengths of concrete for a wide variety of UK gravel and crushed rock aggregates. However, Kaplan's work did indicate a definite relationship between dynamic modulus of elasticity of aggregate and the strength of concrete (Figure 16.18). Kaplan suggested that, notwithstanding his findings, aggregates with lower strengths than used in his investigations might adversely affect the strength of concrete. Tighiouart *et al.*[177] found that, whilst the strength of the cement paste had the greatest influence on concrete strength and elasticity, the coarse aggregate controlled the *shape* of the stress–strain curves.

Research into weak or 'marginal' aggregates has shown that, whilst low-strength aggregates cannot be used to produce high-strength concrete, strengths comparable with

Table 16.10 Comparison of some physical, mechanical and soundness test results for materials used as aggregate, showing the range and (in bold) median values. A wide range of values can be expected for any particular rock type, so that some typical data are presented here for indicative purposes only. Median values are given only where the number of data points was deemed sufficient

Aggregate type (alphabetical order)[a]	Water absorption (%)	Unconfined compressive strength (UCS) (N/mm^2)[b]	Aggregate impact value (AIV) (%)	Aggregate crushing value (ACV) (%)	10% fines value (kN)	MgSO$_4$ soundness (% loss)[c]
Andesite/trachyte (16)	1.4–7.9	210–280	12–31	11–12	170–190	0–96
	3.0	–	**18**	–	**180**	**4**
Basalt (18)	0.4–5.4	160–310	10–22	11–58	160–350	0–16
	1.8	–	**18**	**19**	**220**	**2**
Blastfurnace slag (8)	2.0–4.8	90	15–33	33–42	55–210	–
	–	–	**28**	**34**	**85**	–
Flint/chert gravel (96)	0.4–7.6	200	16–24	14–31	160–320	0–6
	1.6	–	**20**	**16**	**260**	**3**
Gabbro/dolerite (10)	0.2–5.7	180–190	9–40	11–36	50–380	0–1
	0.6	–	**18**	**19**	**190**	**1**
Gneiss/granulite (5)	0.4–0.7	–	24–28	–	230	1–2
	0.6	–	–	–	–	**1**
Granite (27)	0.2–1.9	150–250	11–35	13–32	75–280	1–31
	0.6	–	**21**	**24**	**155**	**2**
Hornfels (–)	–	340–370	16–17	11–15	–	–
	–	–	–	–	–	–
Limestone/dolomite (58)	0.2–7.5	130–190	14–43	19–31	110–250	0–71
	1.6		**24**	**24**	**170**	**6**
Quartzite gravel (4)	0.7–1.2	280–390	13–22	16	140–250	–
	–	–	–	–	**195**	–
Sandstone (20)	0.3–31.0	190–260	10–58	12–31	100–350	0–100
	1.0	–	**18**	**15**	**200**	**4**
Serpentinite gravel (21)	0.5–6.6	–	17–23	–	150–260	3–17
	1.4	–	**21**	–	**240**	**8**
Slate (2)	1.8–3.0	–	20–22	19–22	140–170	–
	–	–	–	–	**155**	–

Based largely upon an analysis of worldwide test data provided by Mr D Hunt of Messrs Sandberg, London, UK. Also after Refs 41, 58, 94, 117, 175.

[a] Number of samples in the survey shown in parentheses for each aggregate type. Not all of the samples were tested for all of the properties shown.

[b] Tests carried out on 25 mm diameter × 25 mm length cylinder specimens.

[c] After 5 cycles of the ASTM C88 test.

those obtained using strong aggregates can frequently be produced with aggregates which are appreciably weaker than most current specifications permit.[65,178] For example, Collins[65] found that crushed oolitic limestone aggregate with 10 per cent fines values (section 16.5.7) as low as 35–55 kN in some cases could be used to produce 28-day concrete strengths of 20–40 N/mm^2 depending upon cement content (Figure 16.19). Collins[179,180] also showed that Carboniferous sandstones and magnesian limestones with similarly low 10 per cent fines values could produce similar or higher strengths. These data are summarised

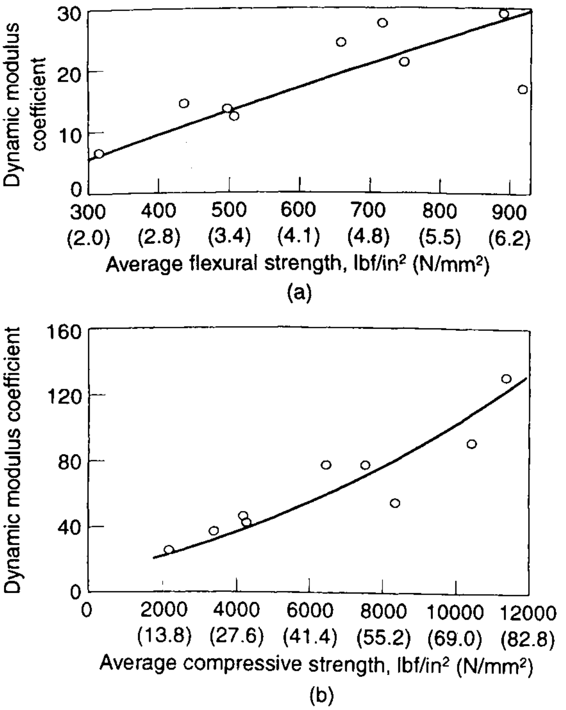

Fig. 16.18 Regression curves for the dynamic modulus of elasticity of aggregates and the flexural (a) and compressive (b) strengths of concretes made using similar aggregate materials (from Ref. 176).

by Brown,[181] adjusting strength data to a common workability and indicating that each aggregate source needs individual assessment.

Particle density (section 16.5.4) generally has little influence on concrete strength, although some lightweight or ultra-lightweight aggregates have very low strengths and these are reflected in the limited levels of concrete strength which are attainable.[182]

Grading and fines content

At any given age and set of conditions, concrete strength is principally controlled by the cement content and water/cement ratio of the mix and by the degree of compaction, which are interrelated factors. Aggregate grading and fines content influence the water/cement ratio and the workability (section 16.6.2), which in turn can affect compaction, so that indirectly these properties of aggregate have some influence over concrete strength.

Bloem and Gayner[174] demonstrated the rather complicated interrelationship between maximum coarse aggregate size, cement content, water/cement ratio and resultant compressive strength. For example, in the mixes of higher cement content, those made using 20 mm maximum sized aggregate produced higher strengths than those made with 40 mm aggregate. Similarly 10 mm aggregate gives higher strength than 20 mm aggregate at these higher cement content/higher strength levels, and for high-strength concretes 10 mm maximum aggregate sizes are often used.

Conversely, in the leaner mixes, those made using the larger maximum aggregate size yielded the higher strengths, because of the accompanying reduction in water/cement ratio

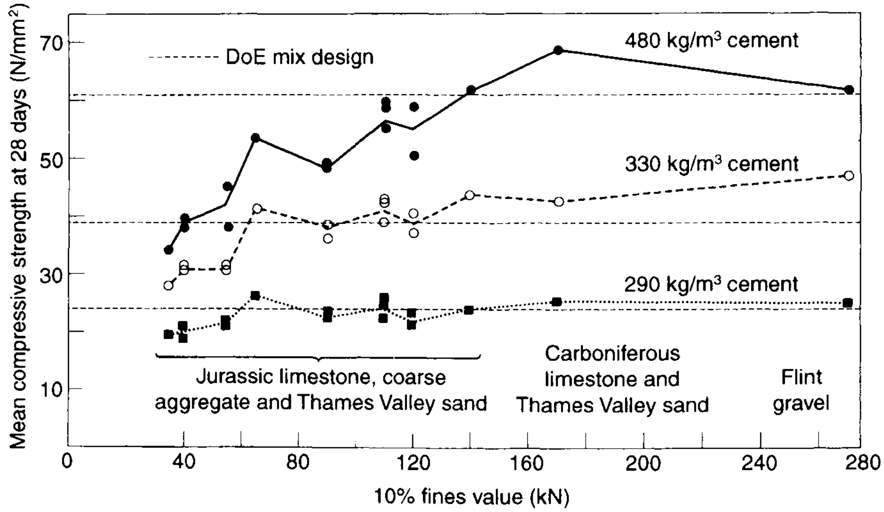

Fig. 16.19 Effect of 10 per cent fines value on concrete strength at 28 days, using three types of UK coarse aggregate (with Thames Valley sand in all cases) and three cement contents (from Ref. 65).

to achieve the same degree of workability. Earlier, Strange and Bryant[183] had found that larger aggregate particles precipitated the formation of microcracks in the concrete matrix at lower stresses than smaller aggregates, but that conversely larger aggregates better resisted the propagation of those microcracks.

It should be emphasised that the strength of the concrete matrix, that is, the 'mortar' between the coarse aggregate particles, is critical to the strength of the whole concrete, so that grading or other factors which affect only the mortar matrix may produce either positive or negative effects on overall strength.

The incorporation of fines can sometimes improve concrete strength (section 16.5.2). However, in one recent study of aggregates in use in Saudi Arabia, Ahmed and El-Kourd[184] found that increasing the content of $-75\,\mu\text{m}$ material in the fine aggregate linearly reduced concrete compressive strength when all other factors including workability (slump) were held constant. Ahmed and El-Kourd also reported that the concrete strength was less sensitive to increases in crushed rock fines than to increases in natural sand fines, which was presumably caused by the differing nature of the fines (section 16.5.2), although in this case the authors had not attempted to characterise the particle size distribution and composition of the respective fine materials.

Particle shape and bond strength

It has been noted already that aggregate particle shape influences water content and workability (section 16.6.2), which in turn will affect concrete strength. However, it appears that particle shape, perhaps together with particle surface texture, also has a direct influence on strength, because higher maximum concrete strengths are achievable with angular crushed rock aggregates than with rounded gravel aggregates.[185] The effect of particle shape seems to be more pronounced at the higher concrete strength levels.[176]

The strength and integrity of the bond between the concrete ('mortar') matrix and the coarse aggregate particles is a critical factor in determining concrete strength, especially flexural or tensile strength, and this bond appears largely to depend upon the surface texture and compositional character of the coarse aggregate, as well as the inherent strength of the 'mortar' matrix.

Kaplan[176] demonstrated a relationship between surface texture and strength (Figure 16.20) which becomes significant at higher strength levels. Perry and Gillott[186] showed that artificially roughening the surface of a previously smooth aggregate increased the compressive strength of the concrete, typically by some 10 per cent. In a comparative study of three crushed aggregates (andesite, dolomite and granite), Alexander *et al.*[187] found that the andesite produced a superior cement–aggregate bond owing to the fracture surfaces being 'topographically rougher and more complex'. Scholer[188] considered that rougher aggregate particle surfaces help to provide greater restraint to the drying shrinkage stresses within concrete that initiate the development of microcracking at aggregate–matrix interfaces.

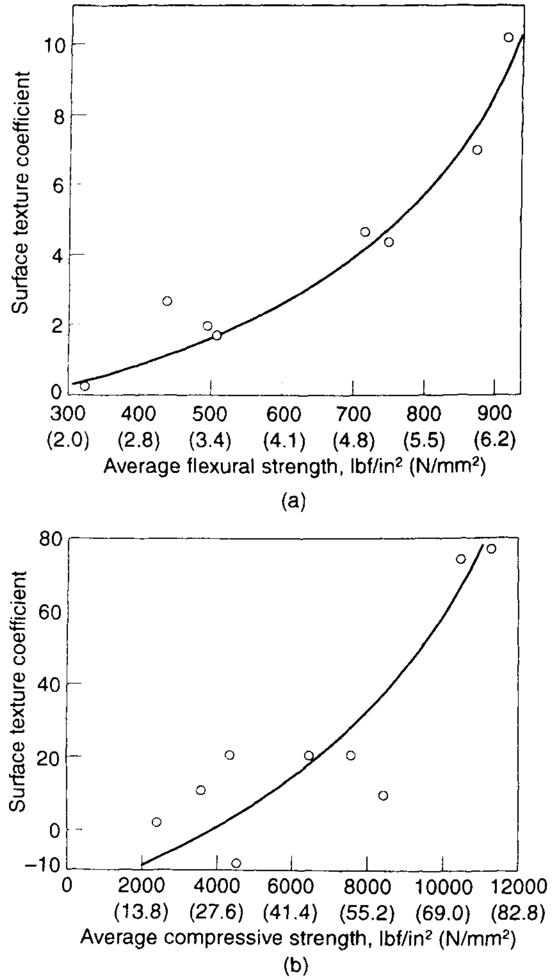

Fig. 16.20 Regression curves for the particle surface texture of aggregates, using the method of Wright,[112] and the flexural (a) and compressive (b) strengths of concrete made using similar aggregate materials (from Ref. 176).

Aggregate constituents

The potentially adverse influence of discrete mica on concrete strength has already been discussed (section 16.4.4). It is also apparent that some types of rock are particularly susceptible to the formation of flaky and elongated particles (section 16.5.3), which in turn can influence both workability and strength. In some parts of the world, coral coarse aggregates are used and are found to produce concrete with comparatively high tensile strengths, notwithstanding the potential problems of particle weakness, absorption and corrugated (rugose) shape.[189]

In particular, aggregate composition can affect the nature and strength of the crucial bond with cement. Just as roughening the surface texture probably improves the intimacy of contact between the aggregate and the binder, enabling a mechanical key to be established, so a degree of aggregate porosity should assist in the achievement of a strong aggregate–cement bond. Thus, whilst the smoothness of the particles in a natural gravel seem likely to inhibit bond, Newman[173] reported that the particles in such a gravel can exhibit an outer weathered 'patina' layer which is absorbent.

In other cases, the bond might be strengthened by a degree of chemical interaction between the cement phases and some aggregate constituents. The disruptive form of alkali–silica reaction (ASR) is now well known (section 16.6.5), but it is probable that in many other cases, some non-disruptive interaction can occur between caustic cement and siliceous aggregates which adds strength to the bond. It is known that some forms of cement–aggregate reaction involving carbonate materials are beneficial to the bond strength rather than deleteriously expansive.[190,191]

16.6.4 CONCRETE WEAR RESISTANCE

In many cases concrete durability is threatened by natural weathering or even by chemical attack (section 16.6.8), but only in certain locations or applications is concrete subjected to mechanical wear, including abrasion, attrition and erosion of concrete surfaces. In such places, clearly it is the quality and properties of the exposed surface layer of concrete which govern the resistance to wear, so that factors associated with the nature of placing, finishing and curing of the concrete play an important part, irrespective of the inherent properties of the concrete material and its constituents, which are also important.

It is sometimes maintained that wear-resistant concrete requires the use of strong aggregates with good abrasion resistance characteristics. Murdock and Brook,[39] for example, advise that the 'best insurance' against abrasion of concrete is 'good dense concrete made with a hard tough aggregate'. BS 882: 1992[11] continues to specify superior values of 10 per cent fines and aggregate impact for pavement wearing surfaces, and even more so for heavy-duty floors. The UK Department of Transport[192] specifies, for pavement-quality concretes containing limestone sand, limits on the acid-soluble material to maximise skidding resistance.

Research has shown that concrete compressive strength grade is the most meaningful parameter, assuming a high quality of concrete placement and finish, although the use of larger coarse aggregate sizes is also beneficial. For example, research by the Road Research Laboratory[124] into the resistance of concrete road surfaces to tank traffic indicated that, for concretes with compressive strengths greater than about 40 N/mm^2, the type of aggregate had little effect (Figure 16.21). At lower strengths, however, the type of aggregate had a pronounced effect, with flint gravel concrete failing badly because of debonding, and

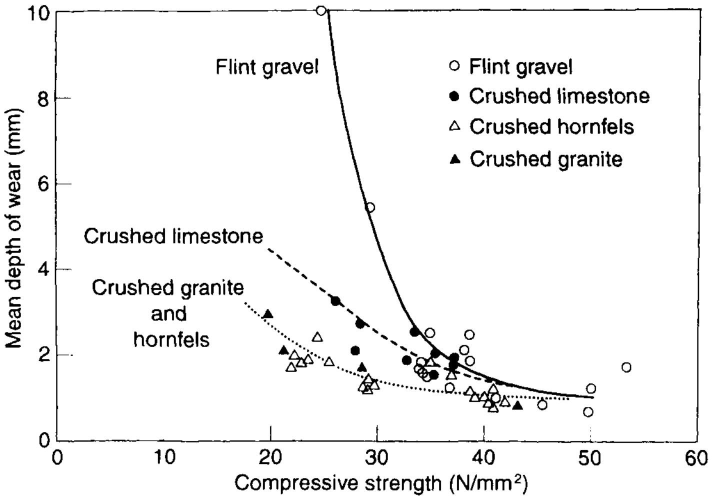

Fig. 16.21 Effect of different aggregate types on the relationship between the compressive strength of concrete and the wear resistance as measured using the Road Research Laboratory wartime tank-wear testing machine (metricated from the imperial original, after Ref. 124). The concrete mix proportions were 1:1½:3 by weight and the load on the wearing element was 3000 lb (1361 kg).

otherwise the harder and stronger granite and hornfels aggregates wearing away more slowly than the limestone aggregates.

In practice, a wear-resistant concrete is probably most reliably achieved by the combined use of a high-strength grade concrete mix and an aggregate exhibiting the appropriate grading and mechanical properties.[193] In certain cases, such as some concrete road pavements, the abrasion and polished stone values (section 16.5.8) of the coarse aggregates might be considered to be important parameters.

Metallic and other synthetic fine aggregates are sometimes incorporated into a concrete wearing surface, particularly floors exposed to heavy trafficking, although their true effectiveness is uncertain, especially if the overall quality of the floor finish is poor. Cast iron particles are widely used and, although such material is not as hard as the quartz particles in most natural sand aggregates, it is less brittle and might help to resist impact wear. On the other hand, staining and disruption caused by rusting can be problematic. Silicon carbide ('Carborundum'), steel slag and even industrial synthetic corundum have also been used. Such materials can be harder than quartz sand particles, but are not necessarily impact resistant and might only be beneficial to prevent polishing where floors are subjected to unusually heavy foot trafficking.

16.6.5 ALKALI-AGGREGATE REACTIVITY

Reaction between cement and aggregates that causes cracking within hardened concrete was first described in the USA by Stanton.[194,195] Since that time 'alkali-aggregate reactivity' (AAR) has been found to occur around the world in two main forms: 'alkali-silica reactivity' (ASR), which is by far the more common, and 'alkali-carbonate reactivity' (ACR). A possible third type of AAR, 'alkali-silicate reactivity', has been described but is now recognised as a more complex form of ASR.

The whole subject of AAR has generated extensive research, the many findings of which are presented in BRE Digest 330,[196,197] books by Hobbs,[198] Swamy[199] and West,[200] as well as the proceedings of the series of international conferences on AAR, of which the most recent was held in Melbourne, Australia.[201] A thorough review of ASR research was prepared as part of the Strategic Highway Research Program in the USA.[202] It now seems that in most cases AAR might not impair structural performance to the extent that was hitherto assumed.[203,204] This section refers mainly to the influence of aggregates on AAR.

Alkali–silica reaction

ASR is a chemical reaction within concrete between specific siliceous constituents which sometimes occur in the aggregate material and the alkali hydroxides released during the hydration of Portland cement. The reaction product is an alkali–silicate gel which displays a variable capacity for swelling caused by the absorption of further moisture. Such swelling within hardened concrete can cause cracking and overall expansion (Figure 16.22).

Fig. 16.22 Expansion, cracking and displacement of concrete caused by alkali–silica reactivity (ASR), affecting part of a bridge abutment in south-west England, UK. The reactive constituent was chert in the coarser fractions of the sand.

In nearly all ASR cases, the alkali hydroxides (often termed simply 'alkalis') are predominantly derived from the Portland cement binder, but it is now recognised that additional alkalis can sometimes be contributed by the other constituents, such as the aggregates (see section 16.4.4 on Releasable alkalis) and pfa (pulverised-fuel ash) or slag additions.[205] Also, in certain environmental circumstances, additional alkalis can be derived from an external source, such as sea water or de-icing chemicals.[206 208]

The reactivity of silica largely depends upon the degree of atomic disorder and internal surface area[209] with the greatest reactivity for a natural material being exhibited by opal (a hydrous and highly disordered form of cristobalite). Other potentially reactive forms of silica include cristobalite, tridymite, chalcedony, microcrystalline and cryptocrystalline quartz (which occur for example in chert), possibly strained or recrystallised quartz, and siliceous volcanic glass or the 'devitrified' derivative. Recent work by Xhang *et al.*[210] using transmission electron microscopy has suggested that, in reactive rocks containing quartz (such as chalcedony and chert), a high dislocation density in the quartz atomic structure is an important factor.

The reactivity of quartzitic rocks containing strained quartz grains may be related to the additional presence of fine-grained and recrystallised quartz at the grain boundaries. Procedures for assessing the stability of these quartz textures have been described by Smith and Dunham[211] and Wigum.[212] Measurement of the 'undulatory extinction angle' of quartz[42] is no longer considered to be a useful assessment criterion.[211,213,214]

Many studies have been carried out in Japan in recent years into the reactivity of some volcanic rocks, particularly andesites with glass contents of rhyolitic composition and devitrified andesites which contain cristobalite and tridymite.[215]

These reactive materials can form discrete aggregate particles or might occur as components within other rocks forming aggregate particles. The first example of ASR in the British Isles was identified in Jersey in the early 1970s[216] and involved opal and chalcedony within a crushed granodiorite coarse aggregate. Most of the ASR since identified on the UK mainland[217] has involved chert (or the Cretaceous form known as 'flint') (Figure 16.23), frequently forming the coarser sand particles when the coarse aggregate is a non-reactive material such as crushed limestone or granite. Some crushed greywackes in the UK have been found to be alkali–silica reactive and this reactivity appears to be caused by the presence of microcrystalline quartz in the rock matrix.[24]

A major research programme into the reactivity of UK sands, gravels and volcanic rocks has recently been carried out by the Building Research Establishment.[218] In a parallel programme, the source of flint reactivity was investigated by Scott,[219] who identified exceptionally small microquartz crystallites in the regions between discontinuities within the microquartz crystals forming the main part of the flint. The Mineral Industry Research Organisation (MIRO) has also sponsored an important programme of ASR expansion testing for selected UK aggregate combinations.[220,221]

Alkali–carbonate and other reactions

Swenson[222] identified a Canadian carbonate aggregate from Kingston, Ontario, which caused cracking in concrete in a way which appeared analogous to ASR. The rock was found to be an argillaceous (illitic) dolomitic limestone and expansion in concrete was suggested to occur because of swelling of the illite constituent following de-dolomitisation by the cement alkalis.[223,224] Later work in China has demonstrated that de-dolomitisation alone is

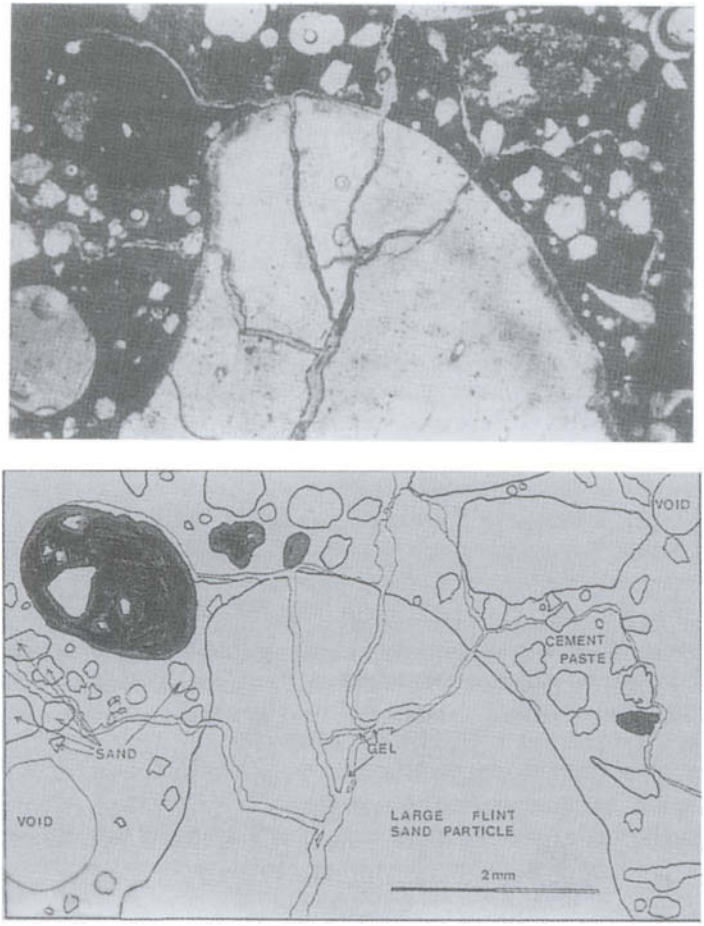

Fig. 16.23 Thin-section photomicrograph and corresponding drawing showing an alkali–silica reaction site associated with a flint coarse sand particle in a concrete in the UK. (Figure courtesy of Transport Research Laboratory, Crowthorne, UK.)

sufficient to explain the expansion of carbonate aggregates.[225–227] These findings have been supported by work in other parts of the world.[228,229]

A number of different types of alkali–carbonate reaction (ACR) have been identified, not all of which cause expansion.[190]

The deleterious reactions involving carbonate aggregates appear to be rare on a world scale, having been mainly described from Canada,[42,230] the Middle East,[231] North Africa[232] and China.[226] No cases of ACR have so far been confirmed in the UK.

In 1973 Gillott *et al.*[233] characterised a new type of 'alkali–silicate' reaction involving aggregates from Nova Scotia, in which layered phyllosilicate minerals within a variety of rocks (including phyllites, greywackes and argillites) expanded as the result of alkali attack and water absorption. Other examples of AAR have been likened to the suggested Nova Scotia mechanism, notably the Malmesbury hornfels in South Africa[234] and even some greywacke aggregates in the UK. However, it is now generally accepted that these 'alkali–silicate' reactions are just more complicated variants of ASR.[217,235]

Eglinton *et al.*[236] have described a different form of 'alkali–aggregate' reaction from Trinidad, in which natural sand and gravel aggregate particles had become coated with an organic–iron substance during tropical weathering. This organic–iron complex was remobilised by higher levels of cement alkalis, giving rise to staining of the concrete, retardation of the hydration of surrounding cement and surface pop-outs.

Aggregate composition and the 'pessimum'

It is now possible to recognise the types of rocks and minerals which are either potentially alkali-reactive in themselves or might contain reactive components, so that petrography can be used to evaluate the composition of aggregates for concrete in respect of AAR.[237] However, there is no simple relationship between the proportion of any given reactive constituent in an aggregate and the magnitude of any resultant AAR and expansion. In some cases, for example with some metaquartzites and some glassy volcanic rocks, the amount of concrete expansion caused by ASR increases progressively as the proportion of reactive constituent increases in the aggregate.

In many other cases, however, a limited or 'pessimum' range of reactive constituent concentrations in the total aggregate yields the greatest resultant concrete expansions, with the amount of expansion being curtailed if the content of reactive material in the aggregates is either reduced or increased from the pessimum (Figure 16.24). Hobbs[198,245] provides an explanation for pessimum behaviour based upon the balance between the available reactive silica content and the concentration of alkalis, also noting that the pessimum effect is most pronounced for the rapid-reacting types of silica such as opal.

In the UK it seems that expansive ASR involving chert (or flint) mainly occurs when the chert content of the total aggregate is in the range 3–54 per cent.[218] This probably explains why reaction has predominantly occurred when flint sand is combined with non-flint coarse aggregate. Concretes made using flint gravel and sand aggregates, when the flint content typically exceeds about 60 per cent, including some contribution from the sand, appear to be largely unaffected. Some investigations, however, have indicated that such a pessimum behaviour for UK flint aggregates might not obtain if the concrete alkali content is raised above the normal range arising from the cement, for example by the action of de-icing salts.[207] Also, whilst considerable evidence is now available generally to corroborate this pessimum behaviour of flint aggregates, Rayment and Haynes[246,247] have identified occasional anomalies, suggesting that consideration should additionally be given to the porosity of flint aggregates.

Careful attention is needed in determining if ASR is the cause of damage in concrete. A British Cement Association working party produced guidance to assist in diagnosis.[248]

Methods of testing and assessment

The testing of aggregates for AAR potential continues to be indicative rather than definitive.[49] One review of the available standard and other proposed test methods has been carried out by Grattan-Bellew.[249] Broadly speaking, the various methods of assessment may be categorised as (1) visual procedures for recognising rock and mineral materials known to be potentially reactive, (2) chemical procedures for identifying the presence of reactive constituents, and (3) expansion test procedures for accelerating and quantifying the physical consequences of reaction.

A standard procedure for visual (or petrographical) examination of aggregates has been

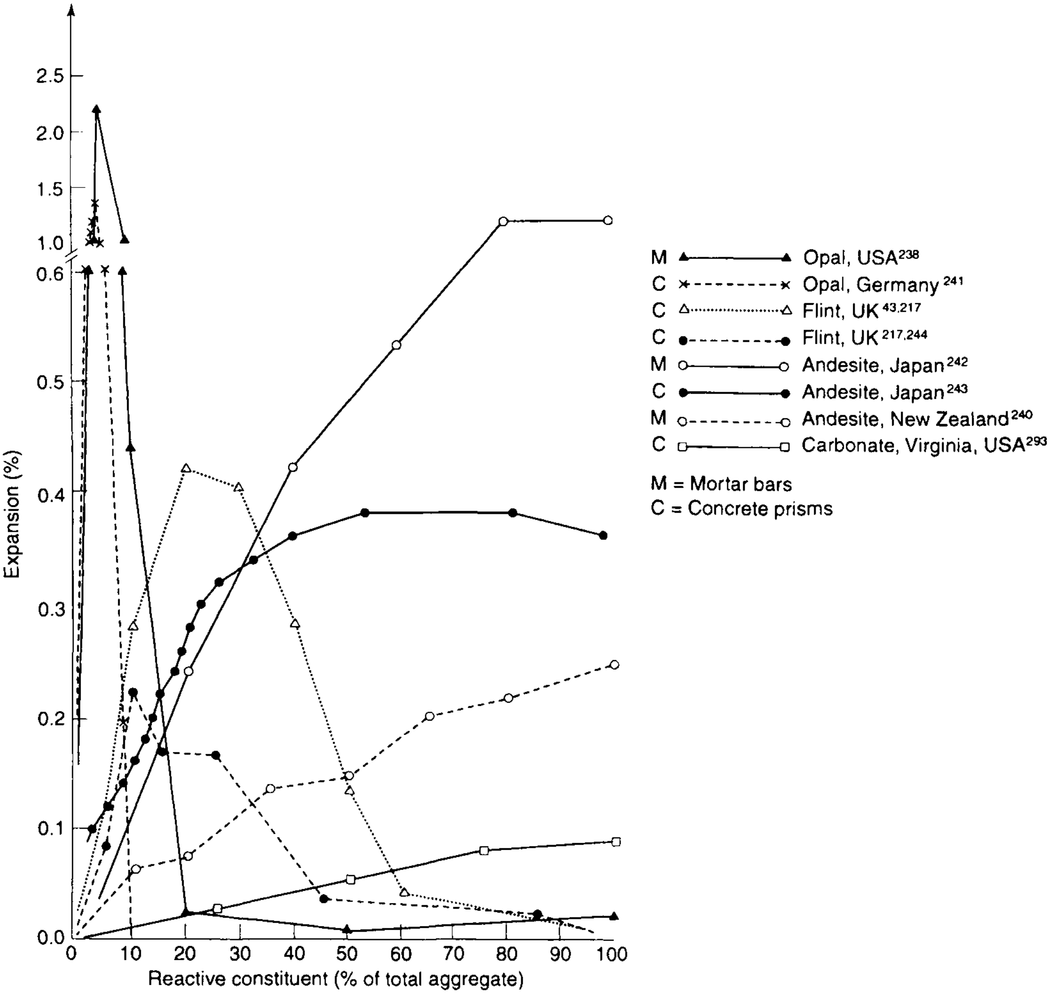

Fig. 16.24 Relationships between the proportion of reactive constituent in aggregates and the expansion of mortar-bar or concrete prism specimens for a selection of different types of aggregate material (after Refs 43, 217, 238–244). Some types of reactive constituent, such as opals and flints, usually exhibit a 'pessimum' behaviour, whereas other materials, such as andesites and quartzites, often show a positive correlation between increasing proportion and increasing expansion.

available in the USA since the 1950s (ASTM C295-90[52]) but it is only recently that BSI has developed a method (BS 812: Part 104: 1994[53]). The visual approach is effective as a screening procedure, providing the samples are representative and the compositional analysis adequately precise.[237]

The chemical tests for ASR include the well-known ASTM C289-94[250] method, which is an effective screening test for some aggregates but which is insensitive to pessimum behaviour, and the UK 'gel-pat' test[251] which has now been developed by BSI for use as an opal detection aid for the petrographer.

The ASTM C 227-90 'mortar bar' expansion test[252] was long considered to be the most reliable method of assessment, but in the UK and elsewhere the conventional mortar bar test has been found to be unreliable for predicting expansive aggregate combinations and various forms of concrete prism test have become preferred.[253] [256] No universally accepted criteria for interpreting the results of the BS/DD 218: 1995 concrete prism test method[255] have yet been agreed, but a classification system has been proposed (Table 16.11).

Table 16.11 Suggested criteria for interpretation of the concrete prism test.[255] Applies to low and normal reactivity UK aggregates (from Ref. 197)

Per cent expansion (up to 12 months)[b]	Classification for the aggregate combination tested[c]	Aggregate type as defined by BRE Digest 330[197] [a]	Notes	Some examples from the British Isles
>0.20	Expansive	Normally reactive	Exhibited by combinations known to have been involved in cases of actual damage to concretes	Limestone coarse aggregates with chert/flint-bearing sand
0.10–0.20	Possibly expansive	Normally reactive	Includes combinations which have sometimes been involved in cases of actual damage to concrete structures, but also include some widely used combinations with no record to date of causing damage to concrete	Quartzitic gravels/sands from the English Midlands and some crushed rock containing microcrystalline quartz
0.05–0.10	Probably non-expansive	Low reactivity	Combinations in this range have rarely been associated with actual cases of damage to concrete structures. However, these might be considered unsuitable in extreme conditions	Some of the quartzitic gravel sands from the English Midlands
⩽0.05	Non-expansive	Low reactivity	Combinations which have no record of causing damage to concrete	Crushed limestone and igneous rock aggregates.[d] Most chert/flint bearing coarse/fine combinations with >60% chert/flint contents

[a] The Digest places crushed greywacke, together with recycled aggregates, into a 'high reactivity' type. In the concrete prism test, some greywackes exhibit delayed expansion, which gives a misleadingly low result at 12 months.

[b] Occasionally expansion in the test might not have reached its ultimate expansion at 12 months.

[c] If the concrete alkali content and environmental factors are also conducive to ASR: see Concrete Society Technical Report No. 30.[83]

[d] Except when contaminated by opaline and/or microcrystalline quartz.

In Canada, until recently, different limits had been suggested for ACR and 'slow/late expanding' alkali–silicate/silica reactions (for which separate concrete prism tests were provided, using storage conditions of 23°C at 100 per cent RH (relative humidity) and 38°C at 100 per cent RH, respectively), with two sets of limits according to the exposure classification. On the basis of further research, however, the matter was simplified in the 1994 version of the Candian Standard,[253,254] which includes just one concrete prism test method (38°C at 100 per cent RH) and specifies a single maximum limit (0.04 per cent at 1 year) for all aggregate types.

In respect of the conventional mortar bar and concrete prism tests, the long period of testing required (up to 6 or 12 months) makes the procedures difficult to apply for quality compliance purposes. Therefore, a number of ultra-accelerated expansion tests have been devised, notably in South Africa,[257] China[258] and Japan.[259] In particular, the South African (NBRI) accelerated mortar bar test appears to be gaining worldwide support and a version of the method has been standardised as ASTM C 1260-94.[260]

The RILEM technical committee on AAR aggregate testing (TC-106) has developed procedures for both the concrete prism and accelerated mortar bar methods[261] and versions of these seem likely to be adopted in due course for the European Standard. RILEM TC-106 has also discontinued work on the traditional mortar bar and chemical tests.

Tests for ASR are not necessarily appropriate for assessing alkali–carbonate reactivity (ACR). A direct expansion test using small cylindrical specimens prepared from the carbonate rock has been described for many years in ASTM C 586.[262] A concrete prism expansion test for carbonate aggregate has been used in Canada for some time[253,254] and more recently a concrete prism test, which uses the alkali content and mix proportions intended for the project in question, has been published as ASTM C 1105.[263] However, experienced petrographical examination coupled with chemical analysis can often characterise the carbonate rock sufficiently to establish whether or not there is a risk of expansive ACR without the need for lengthy testing.

Minimising the risk of ASR

Three essential factors are required for damage to concrete to be caused by ASR: (1) sufficient moisture, (2) sufficiently high alkalis and (3) a critical amount of reactive silica in the aggregate. Chatterji[264] has suggested that the presence of calcium hydroxide is a further essential condition for ASR to occur and this view has recently been supported by Diamond.[265] Measures to minimise the risk of ASR are mostly based on eliminating one or more of these three or four essential factors.

In the UK, for example, guidance has been issued by the Concrete Society,[83] which differentiates between 'general concrete construction' and 'particularly vulnerable construction' for which certain preventative measures are considered unsuitable. Controlling moisture availability is very difficult and generally only permanently dry internal concretes are considered to be free from the risk of ASR. Maintaining a sufficiently low concentration of alkalis in the concrete is frequently the preferred option, variously by reducing cement content, by using a 'low-alkali' cement or by diluting the 'reactive' alkali content using mineral additions such as pfa or ggbs (ground granulated blastfurnace slag). Controlling the alkali content may not be effective, however, when additional external alkalis are available or when alkali concentrations can occur as the result of moisture migration.[266,267]

There has been controversy over the 'reactive' alkali contribution of pfa and ggbs. In the UK, for example, the BRE[196] and the DoT[268] have each indicated that 50 per cent and 17 per cent, respectively, of the acid soluble alkalis in ggbs and pfa should be regarded as being 'reactive' in calculating the overall concrete reactive alkali content. Some work by Moir and Lumley[269] has even suggested that the 50 per cent level for ggbs might be too low, although their research was conducted using a specially manufactured reactive aggregate. However, other studies have indicated that these materials and some other pozzolanas can be effective at suppressing ASR expansion irrespective of concrete alkali content.[270-272]

The position is confusing and the actual contributions are likely to be dependent on a range of factors. In order to circumvent this complexity and simplify practical application for users, consideration has been given in the UK to providing 'safe' alkali limits linked to the Portland cement content in concrete alone.[197] Sibbick and Page[273] found that the alkali 'threshold' level at which appreciable expansion and microcracking commenced in the concrete prism test varied for different types of UK aggregate and this has been corroborated by later work.

Although it is not yet possible to cite a particular concrete alkali limit for each type of aggregate, the 1997 edition of BRE Digest 330[197] introduced a new system for categorising the recommended alkali limits on the basis of aggregate and cement types. In this approach, the aggregate is deemed to be of 'low', 'normal' or 'high' reactivity and the Portland cement component of the cement on its own is deemed to be of 'low', 'moderate' or 'high' alkali content. This appraisal of aggregate and cement categories is used to provide a matrix of limits for alkali contents in the concrete for a wide range of conditions.

The selection of non-reactive aggregate combinations can be variously based upon permitting the presence of only rock and mineral constituents considered unlikely to be reactive, prohibiting or controlling the content of reactive or potentially reactive constituents, and possibly by carrying out a concrete expansion test. The UK Concrete Society guidelines[83] proscribe the presence of detectable opal and then restrict the content of rock and mineral constituents other than those listed, on the basis of UK materials and experience, as unlikely to be reactive.

16.6.6 CONCRETE DRYING SHRINKAGE AND WETTING EXPANSION

The setting of cement involves an irreversible reduction in volume which causes all unmodified concretes to be subjected to internal shrinkage stresses as drying proceeds. The magnitude of such concrete drying shrinkage is controlled by many factors, including cement type, environmental conditions, curing arrangements, the properties of any additions or admixtures and, above all, the mix water content.

The principal effect of the aggregate component is to restrain the cement paste contraction, thus dissipating the shrinkage stresses throughout the concrete mass and helping to reduce the likelihood of cracking. Properties of the aggregate which tend to increase the concrete water demand (sections 16.6.2 and 16.6.3) might also cause those aggregates to be less effective at preventing excessive shrinkage. Increasing the aggregate/cement ratio of concrete will reduce the propensity for shrinkage, concomitantly by reducing the volume of contracting cement paste and by increasing the volume of restraining aggregate particles. In general, aggregates exhibiting a high modulus of elasticity (greater 'stiffness') and rough particle surface textures are likely to offer more restraint to concrete shrinkage.[274]

Composition and absorption

It has been known for many years that the magnitude of concrete shrinkage can vary substantially with different types of aggregate,[275] often being broadly related to absorptivity

Table 16.12 Some indicative values of concrete drying shrinkage and wetting expansion for different types of aggregate (after Refs 276, 277)

Aggregate type	Water absorption (%)	Drying shrinkage of concrete (%)	Wetting expansion of concrete (%)
Granite	0.2	0.030	0.022
Quartz	0.3	0.032	–
Limestone	0.2	0.041	–
Dolerite	1.5	0.047	0.036
Granite	0.8	0.047	–
Meta-sandstone	1.0	0.052	0.035
Quartz dolerite	1.3	0.054	0.040
Andesite	1.4	0.054	0.045
Olivine basalt	1.3	0.060	0.050
Olivine dolerite	1.4	0.060	0.053
Basalt	1.6	0.065	0.054
Slate	1.3	0.068	–
Mudstone/greywacke	1.0	0.081	0.070
Sandstone	5.0	0.116	–

and 'compressibility' (or modulus of elasticity) (Table 16.12). Quartz, granite and limestone aggregates are frequently associated with low concrete shrinkage, whereas sandstone and some basic igneous rock aggregates are more likely to cause or permit comparatively greater shrinkage.

Some aggregate materials, notably those containing integral clay and some related minerals, are capable of substantial moisture movements themselves, thus contributing to the initial drying shrinkage of concrete, and also facilitating excessive and sometimes damaging, largely reversible, movements of hardened concrete exposed to variable wetting and drying conditions. Excessive drying shrinkage of concrete caused by aggregate shrinkage can create a fairly distinctive pattern of microcracking (Figure 16.25), although it is important to recognise that even concretes which have not suffered undue drying shrinkage are liable to exhibit some degree of microcracking. This in turn weakens the concrete and increases the permeability, making it less effective in protecting steel reinforcement and itself more vulnerable to damage by frost (since shrinkable aggregates are also liable to be frost susceptible the concrete degradation could be rapid in such cases) and other agencies.

Clay minerals may be present as matrix materials in the rocks, as in some sandstones or argillaceous limestones, or as the secondary product of rock weathering, or as the secondary product of the geological alteration of rock. A sandstone aggregate from South Africa has been reported to exhibit excessive shrinkage in concrete[278] and was found by Roper *et al.*[279] to contain montmorillonite (smectite), which exhibits swelling characteristics in addition to the degree of moisture movement associated with the other types of clay mineral. The 'mundic' deterioration of concrete blocks in Cornwall, UK, is probably caused in part by moisture movement of the slaty and phyllitic rocks in the mining waste aggregates (see Pyrite and other metallic minerals in section 16.4.4).

The high shrinkage exhibited by many glacial gravel aggregates from central and southern Scotland was found to be associated with greywacke, mudstone and sometimes altered dolerites and basalts.[280] Cole and Beresford[281] have described weathered basalt materials from Australia that exhibit sometimes considerable moisture instability associated with

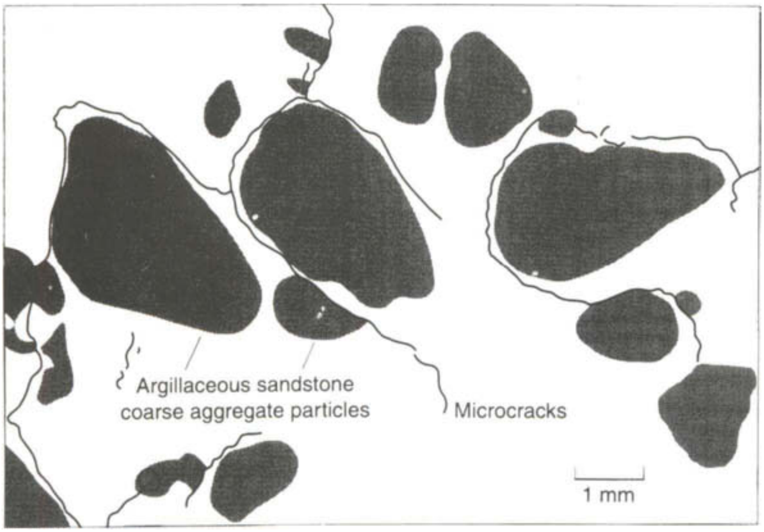

Fig. 16.25 Drawing taken from a ground section of concrete containing shrinkable coarse aggregate, illustrating a typical microcrack development, magnification × 14 (from Ref. 279).

smectites and interlayered chlorite-smectites, although the instability of some rocks was apparently more associated with the presence of a fine cracking system caused by the weathering, rather than with the presence of clay minerals.[60]

Comparative test for shrinkage

Following concrete performance problems associated with the use of some crushed dolerite aggregates (Figure 16.26), the Scottish Building Research Station carried out research[276,280,282] which identified a range of shrinkable aggregate types in Scotland and culminated in the publication of Digest 35,[283,284] now withdrawn. The Digest included a concrete drying shrinkage test procedure and recommendations for the use limitations for four levels of concrete shrinkage. This has subsequently been superseded by BRE Digest 357,[285] which refers to the BS 812: Part 120: 1989 test,[286] which is a modified version of the original Digest 35 test.

Because the concrete mix proportions are standardised in the test, the procedure is essentially a comparative measure of aggregate shrinkage. Results have indicated flint gravel and crushed granite concretes frequently to exhibit very low shrinkage of less than 0.03 per cent, many other aggregate materials occur in the middle range of values whilst, exceptionally, some highly altered basic igneous rocks and some gravels containing argillaceous rocks can produce very high concrete shrinkage of more than 0.08 per cent (even greater than 0.1 per cent on rare occasions).

Unusually for a BS test method, BS 812: Part 120: 1995[286] includes an appendix on the classification of aggregate shrinkage, in which materials are simply divided into two categories: 'A' for shrinkage values up to 0.075 per cent, considered generally suitable for all concrete uses, and 'B' for values greater than 0.075 per cent, for which usage is limited. It is likely that any corresponding requirements in a future Europen Standard for concreting aggregates will be similarly both optional and simplified.

Fig. 16.26 Cracking of concretes caused by shrinkable aggregates. Further deterioration would occur as the result of freeze–thaw action facilitated by the shrinkage cracking. In the view shown, the shrinkage cracks are highlighted by white deposits of calcium carbonate, which have resulted from leaching of the cement paste by water percolating through the crack system. (Photograph courtesy of D. Palmer, retired, British Cement Association.)

16.6.7 CONCRETE FREEZE–THAW RESISTANCE

Freeze–thaw damage to concrete surfaces is associated with the freezing of concrete which is critically saturated with water. In practice, the fatigue resulting from repeated cycles of freezing and thawing is more liable to cause damage than the occasional freezing whilst wet; de-icing chemicals can also exacerbate the damage. Freezing and thawing of concrete can cause cracking parallel to the exposed surface, surface 'pop-outs', 'durability cracking' (or 'D-cracking'), surface spalling and surface scaling. A number of good reviews have provided concise accounts of the main theories which have endeavoured to explain the complicated mechanisms leading to freeze–thaw damage in concrete, although the definite causes remain uncertain.[287–291] The aggregates can affect freeze–thaw durability either directly, by being themselves frost susceptible (see also sections 16.4.4 and 16.5.9), or indirectly, by influencing the properties of the hardened concrete.

Aggregate constituents and composition

Aggregate particles are thought to be directly associated with the occurrence of pop-outs, D-cracking and sometimes surface spalling. Those clay-bearing rock constituents which are prone to high shrinkage (section 16.6.6) are similarly liable to be susceptible to freeze–thaw action when critically saturated. West and Shakoor,[59] for example, have described argillaceous carbonate aggregates from Indiana, USA, which have caused pitting and pop-outs of concrete pavement surfaces in service.

Other constituents susceptible to freeze–thaw action are weak and/or absorptive materials, including some limestones (including chalk), friable sandstone, some iron oxide materials, coal and related material and a wide range of weathered and/or altered rocks. According to Stark,[292] nearly all the rock types known to be associated with D-cracking (fine closely spaced surface cracks which occur parallel and adjacent to joints, larger cracks and free edges) are of sedimentary origin, including limestones, cherts and shales.

The microstructure of the individual aggregate particles might also be important in some cases, although Higgs[157] described some chlorite-bearing altered volcanic rock materials which were only freeze–thaw unsound when the chlorite occurred in a certain texture, and Stark[292] illustrated a fractured carbonate aggregate which was judged to be 'a source of distress in D-cracking' (Figure 16.27). A range of factors will determine whether a 'susceptible' aggregate causes any concrete deterioration in practice, even when the environmental conditions would be generally conducive to freeze–thaw action. Verbeck and Landgren,[293] for example, found that for a given type of aggregate there is a 'critical particle size' below which freeze–thaw cycles cannot destroy the particle.

Microporosity and soundness

Although frost-susceptible aggregate constituents tend also to be water-absorptive, the pore size distribution and pore structure frequently determines whether or not, and to what degree, a particular absorptive material can become critically saturated and will thus be damaged, or will cause damage, as a result of freeze–thaw cycles. In general terms, materials exhibiting a large volume of relatively small-sized pores (i.e. high microporosity) are more likely to be susceptible to damage than materials exhibiting either a large volume of large voids or a small volume of small voids; the ease with which moisture can be absorbed and then lost is also important.

Stark[292] described studies comparing the vacuum absorption and adsorption values, in which it was found that aggregates with absorption values ranging from less than 1 per cent up to more than 8 per cent could be durable, depending upon the adsorption. He also found that materials capable of causing pop-outs as well as D-cracking exhibited the highest values of both absorption and adsorption. Kaneuji *et al.*[155] used mercury intrusion porosimetry to relate total pore volume to median pore diameter and thus to calculate an 'EDF' (expected durability factor). Such an approach might be practicable for reasonably homogeneous crushed rock aggregates providing field trials can establish a reliable maximum EDF level (Figure 16.28).

It is more difficult to assess natural aggregates of mixed composition, such as the flint gravels of southern England, which contain variable proportions of frost-susceptible particles of microporous flint 'cortex'.[159] Quantitative petrography[34] can be a useful guide and some UK authorities also now specify water absorption maxima for both individual flint coarse aggregate sizes and the total coarse aggregate combination.[294] Neither the sulfate soundness tests (section 16.5.9 and 16.6.8) nor the direct freeze–thaw soundness test[151] appear to be particularly helpful in identifying or evaluating microporous frost-susceptible materials, although these methods are probably more reliable for physically weak and/or clay-bearing aggregates. Some success has been reported in Ontario, Canada, for the combination of an unconfined freeze–thaw test and determinations of water absorption.[54]

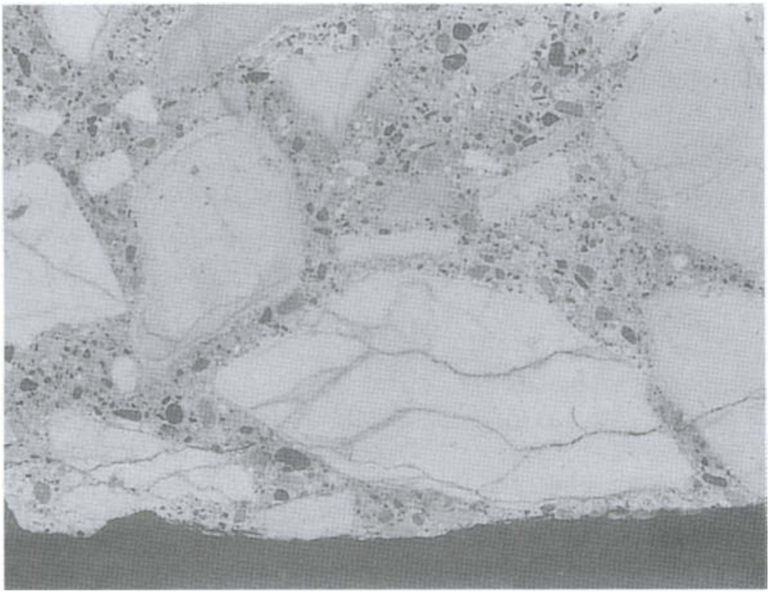

Fig. 16.27 Fractured carbonate aggregate particles in concrete judged to be a source of distress in D-cracking (from Ref. 292).

The draft European Standard for concreting aggregates[12] provides a combination of options drawn from the above types of tests. It suggests petrographical assessment to identify weak materials or a limit of 1 per cent for water absorption, but acknowledges that aggregates with higher values may be satisfactory. In the event that the water absorption exceeds 1 per cent, aggregates are assessed using a freeze–thaw test (CEN/prEN 1367-1[295]) or a magnesium sulfate soundness test (BS EN 1367-2[295a]). Four classifications are

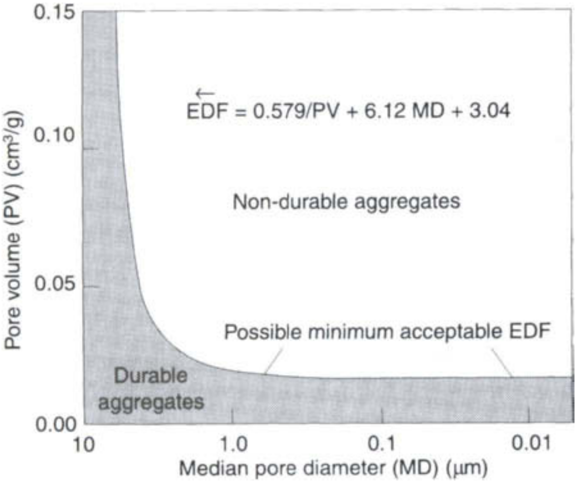

Fig. 16.28 A classification of durable and non-durable aggregates using an 'expected durability factor' (EDF) based upon total pore volume and median pore diameter (from Ref. 155).

given, depending upon the environmental exposure conditions. Acceptance is also permitted on the basis of service history without testing, although this option should be applied with caution in view of the difficulty of ensuring that such previous experience is both reliable and adequately comparable with the aggregate and site under consideration.

Technical literature provides a large number of freeze–thaw tests and further developments in this area can be expected. The most widely used tests currently are ASTM C 666-92[296] and ASTM C 672-92,[297] and a Swedish modified RILEM test.[69,298] A further development is the BRITE cube test[299] which, together with the Swedish test, is being assessed by a CEN working group as a possible draft European test method.

Other properties

Apart from the occasional presence of frost-susceptible coarse aggregate, the freeze–thaw durability of concrete depends upon the quality of the surface finish, which is strongly dependent upon the adequacy and type of curing, and the inherent resistance of the 'mortar' matrix. The freeze–thaw properties of the mortar matrix are largely controlled by the cement type and content, the water content, the presence and type of any admixtures, the degree of compaction and the amount and degree of dispersion of any entrained air. Any aggregate properties which influence these matrix properties, especially the water content, will indirectly affect the freeze–thaw durability.

Effect of de-icing chemicals

Experience has shown that freeze–thaw damage to concrete is exacerbated by the use of de-icing chemicals (Figure 16.29). It is variously considered[300] that de-icing chemicals can impart a thermal shock to the concrete layers immediately beneath the surface by rapid thawing on the surface itself, that the presence of salts helps to maintain critical saturation of either or both of the concrete and the aggregates, and that the pre-existence of de-icing salts at the time of freezing tends to multiply the number of freeze–thaw cycles endured by the concrete. In addition, Gillott[158] has shown that some aggregates, especially limestones, are themselves attacked by de-icing chemicals (such as sodium and calcium chlorides). The concentration of the salt solution resulting from the use of de-icer has been found to be important with, for example, sodium chloride concentrations of about 3 or 5 per cent being much more damaging than either weaker or stronger solutions.[301,302]

16.6.8 CHEMICAL RESISTANCE OF CONCRETE

The ability of concrete to resist chemical attack is primarily dependent upon the properties of the hydraulic binder, including the cement type, the presence and type of any mineral additions, the water/cement ratio and the degree of compaction. Aggregate properties only rarely directly influence the overall chemical resistance of concrete. Tuthill[303] has claimed that 'if the paste can be made resistant, the concrete will be resistant and serviceable, if the aggregate otherwise makes serviceable concrete'. Of course, as with other properties considered in this section, the aggregate might sometimes adversely influence the water/cement ratio and thereby the water content, thus making the concrete more permeable and hence less resistant to a range of durability threats. Aggregate absorptivity seems usually to have little effect on the overall permeability of concrete, being encapsulated by cement paste, but in some cases an aggregate comprising porous particles might cause the exposed concrete surface layer to be more easily penetrated by aggressive solutions or gases.

Fig. 16.29 Scaling of a concrete surface in the central reservation between two road carriageways in the English West Midlands caused by freeze–thaw damage involving a weak and porous oolitic limestone aggregate. The freeze–thaw damage had been greatly worsened in those areas most subjected to the wheel-splashed accumulation of water and de-icing salt.

Environment and aggregate composition

Most concretes are not exposed to exceptionally aggressive chemical conditions. Therefore, since the majority of aggregates which satisfy the normal physical requirements are no more chemically vulnerable than the concrete paste itself, special aggregate selection for different types of exposure has not generally been considered necessary.

There are some instances of particularly aggressive conditions, in which certain types of aggregate might be considered unsuitable. One apparently obvious example would be the susceptibility of limestone aggregate to dissolution in an acidic environment, as encountered with some natural moorland waters or in industrial situations (Figure 16.30). However, it has also been reported that limestone aggregate can help to reduce the severity of damage to concrete in sewers by neutralising the acids.[304] Also, Hughes and Guest[305] found that in some situations limestone aggregate concrete was preferable since it eroded more smoothly and created less debris than a comparable siliceous aggregate concrete.

Siliceous aggregates, by contrast, are more vulnerable to highly alkaline environments and, for example, localised ASR (section 16.6.5) has been found in concretes exposed to industrial processes involving strongly caustic solutions. Useful reviews of some of the environments likely to cause chemical attacks on concrete are to be found in an American Concrete Institute guide,[193] Plum and Hammersley[306] and Harrison.[307]

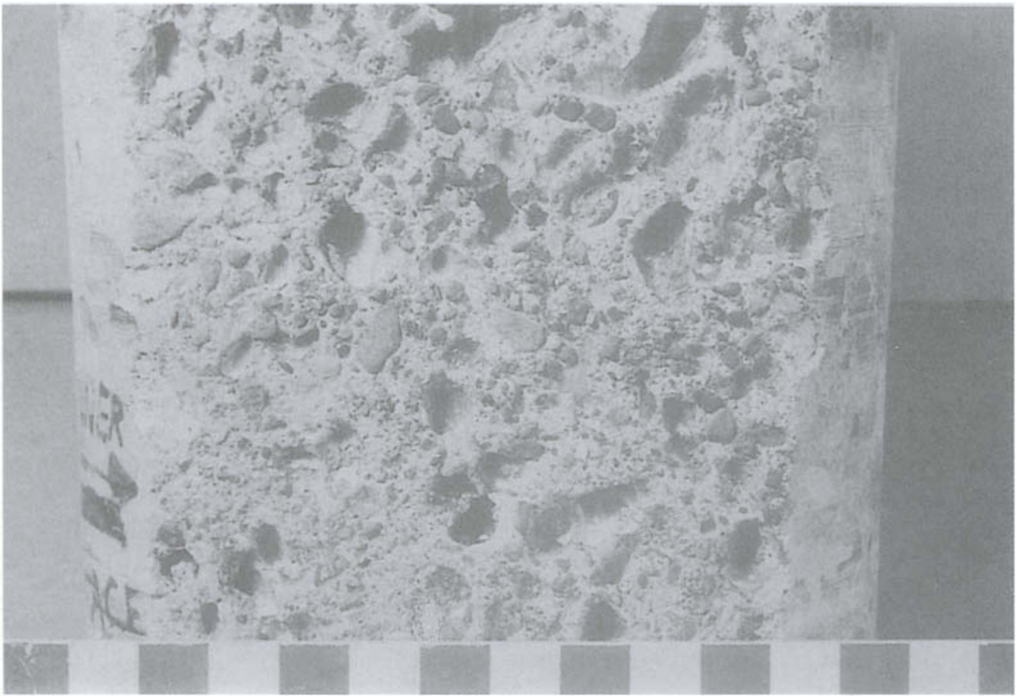

Fig. 16.30 Sample of a concrete surface from northern England, UK, exposed in service to a flow of slightly acidic water, showing the preferential dissolution of limestone aggregate particles. (Scale is in centimetres.)

Sulfate actions

Sulfate attack is one of the most damaging causes of concrete deterioration, causing either softening and decay of the concrete matrix (the 'acid' type of sulfate attack) or expansive cracking and other disruption associated with the formation of ettringite (calcium sulfoaluminate hydrate) and other reaction products within the hardened concrete. Good summaries of sulfate attack are given by Figg[308] and Eglinton;[309] more extensive treatments may be found in Swenson[310] and an American Concrete Institute publication.[311]

These reactions largely involve the cement paste, rather than the aggregates, and are not further considered in this chapter. However, in some unusual circumstances, the sulfate action may derive from a constituent of the aggregate, or the aggregate itself might be vulnerable to attack. Aggregates which are contaminated by sulfate minerals can cause 'internal' sulfate attack, and many such materials have given rise to problems in the Middle East.[16,81,312] Particles of gypsum present in natural sands from Bahrain, for example, were observed by Hussen[312] to react within concrete, forming calcium hydroxide (portlandite) and ettringite. Samarai,[313] in experiments in Iraq using powdered gypsum in mortar bars, produced unacceptably high expansions with Portland cement concrete mixtures containing total sulfate contents in excess of 5 per cent by weight of cement.

French and Crammond[314] identified the cause of expansion of concrete and mortar made with serpentinite wadi aggregates from the United Arab Emirates as being internal sulfate attack involving contamination of the aggregate by up to 5 per cent coarsely crystalline gypsum (Figure 16.31), and later work by Crammond[84] found that up to 2.5

Fig. 16.31 Scanning electron photomicrograph of internal sulfate attack in concrete from the Arabian Gulf area (from Ref. 314). The view shows the interface between a gypsum particle (top, out of view) and the cement paste (bottom); portlandite crystals have developed (top half) with associated acicular crystals of ettringite.

per cent coarsely crystalline gypsum (or about 6 per cent total sulfate by weight of cement) could be tolerated for Portland cement concrete (Figure 16.32).

In rare cases, pyrite (iron disulfide) in aggregate can decompose in concrete in a complicated series of reactions with cement to form gypsum, ettringite and other compounds with accompanying expansion.[315] Other aggregates may themselves be vulnerable to sulfate attack: Braga Reis,[316] for example, has described expansive ettringite formation as the result of reactions between sulfates and kaolinised feldspar in a weathered granite aggregate.

In a small number of documented cases worldwide,[317–320] a particular form of sulfate attack has been reported where concrete had been designed to resist sulfates. In these limited cases a different reaction product, thaumasite ($CaSiO_3{\cdot}CaCO_3{\cdot}CaSO_4{\cdot}15H_2O$) had been formed instead of the gypsum ($CaSO_4{\cdot}2H_2O$) and ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$) associated with normal sulfate attack. Laboratory studies have shown that in certain circumstances in the presence of carbonate ions the silicate hydrates can also be attacked and thaumasite is the predominant reaction product formed.

The reaction appears to require consistently wet and cold conditions, but this and any other contributing factors remain to be defined. In its worst case, thaumasite formation can cause concrete to decay into a mush-like form losing its strength. It occurs as needle-like

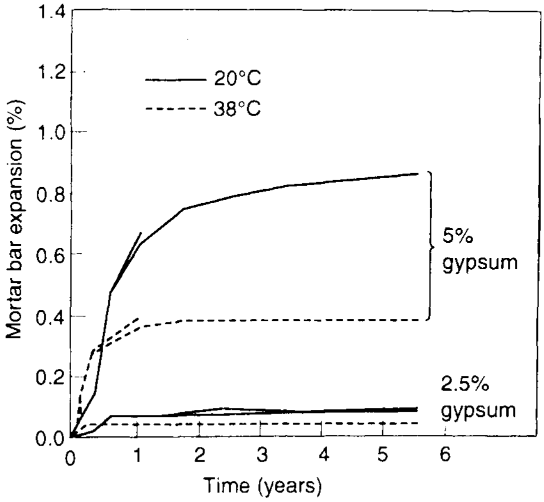

Fig. 16.32 Effect of coarsely crystalline gypsum in aggregate on the expansion of mortar made using ordinary Portland cement containing 14% tricalcium aluminate (C_3A). Appreciable expansion overall with 5% gypsum, especially at the lower temperature of 20°C. (Building Research Establishment: Crown copyright 1990.)

crystals, similar in appearance to ettringite. Analytical methods to determine sulfate contents of concrete are unable to distinguish between the two different forms of attack, ettringite and thaumasite. Differentiation between these two forms requires microscopical, X-ray diffraction or spectroscopic methods.

Crammond and Halliwell[320] highlight the role of finely divided carbonate filler in promoting the thaumasite type of sulfate action, indicating that aggregate type can sometimes have an influence over the occurrence of that form of damage to concrete.

Salt weathering and soundness

In addition to purely chemical actions, concretes and some aggregates can be damaged by expansive salt crystallisation within pores, in a mechanism analogous to the salt weathering of rock which occurs in desert regions.[321] It is reasonable to suppose that the sulfate soundness test (section 16.5.9) is a measure of the resistance of aggregates to such salt weathering. The damage to concrete and some aggregates by de-icing salts might, in part, be caused by a similar process. Gillott[158,289,300] has demonstrated the ways in which the microtextures of various aggregate materials, especially carbonate rocks, can be damaged by treatment with magnesium sulfate solutions.

16.6.9 CONCRETE RESISTANCE TO THERMAL CYCLING AND FIRE

It was explained in section 16.5.10 that the thermal properties of aggregates can substantially affect those of the concretes in which they are used. When hardened concrete is exposed to extreme temperatures (high or low), the often considerable differences in coefficient of thermal expansion between the aggregates and the cement paste can cause disruption. Such extremes can be experienced in some special applications (e.g. chimney linings), in certain climatic regions of the world and when concrete surfaces are subjected to fire. Refractory and cryogenic concretes need to be made with particular materials and are outside the scope of this chapter.

Tensile stresses can develop within concrete, caused by thermal incompatibility of the aggregates and the cement paste, if the diurnal or seasonal changes in temperature are large, or if the coefficients of thermal expansion of these components differ too much.[169,322] One study of concrete made using limestone aggregates in the Arabian Gulf[323] found losses in compressive and flexural strengths of 27 per cent and 32 per cent respectively, and a four- to six-fold increase in permeability, after repeated thermal cycling between 20 and 80°C. The resistance of concrete to such thermal cycling depends critically upon the thermal properties of the aggregate (Table 16.9), which vary widely both between different rock types and also within any one rock variety.[170,324]

Some rock-forming minerals also exhibit thermal anisotropy, expanding more in some directions than in others, which can sometimes accentuate the differential stresses arising from temperature changes. Senior and Franklin[325] also found that hysteresis during thermal cycling can cause irreversible 'growth' or shrinkage of certain rock aggregates, and suggested that the combination of aggregate–mortar thermal incompatibility, aggregate anisotropic thermal expansion and 'growth' of aggregate might be particularly damaging to concrete.

Fire damage to exposed concrete surfaces is an extreme case of thermal cycling, whereby very high temperatures can be reached in places and cooling is often achieved very rapidly by cold-water quenching. Lightweight aggregates (artificial and natural) generally appear to exhibit the best heat resistance, followed in order by fine-grained igneous rocks (e.g. basalt), carbonate rocks and siliceous aggregates.[326] Carbonate aggregates can start to decompose at high temperatures (> 660°C), and perhaps also expansively react with calcium hydroxide in the cement,[327] with dolomitic varieties being the more vulnerable, but in compensation these effects also tend to insulate and thus protect the concrete at greater depths beneath the surface.

Siliceous aggregates perform poorly at high temperatures, partly because quartz has a higher coefficient of thermal expansion than most other constituents, and partly because the spontaneous inversion to alpha-quartz at 573°C involves a volume increase. It is well known that many aggregates develop a pinkish coloration after heating to about 300°C, caused by the oxidation of traces of iron, and this feature is commonly used in the assessment of concrete fire damage.[328] Flint aggregates also exhibit a marked shattering at temperatures above about 500°C, believed to be caused partly by the inversion of the quartz forming the rock and partly because of the expulsion of the small content of combined water.[329]

16.7 Synthetic aggregates

Brief mention of synthetic aggregates was made in section 16.2.5 and a classification of such materials was provided in Table 16.1.

16.7.1 TERMINOLOGY

Synthetic and artificial aggregates

The terms 'synthetic' and 'artificial' are each used to describe aggregates which are not 'natural' in the way that crushed rocks or sands and gravels are natural geological materials. Both synthetic and artificial aggregate terms imply human-made materials, whether by-products of some other industry or deliberately manufactured. Arguably the term 'synthetic' further implies a product of like nature to a natural equivalent, whereas in fact some manufactured aggregates exhibit particular properties not readily matched in nature. In practice the terms synthetic and artificial aggregates are used synonymously, with BS 6543: 1990[330] and many others preferring the overall term 'artificial'.

By-products and manufactured aggregates

Many artificial aggregates are either controlled by-products of industrial processes, such as the various slags, or uncontrolled waste materials resulting from other industrial processes, such as clinkers and ashes. Another important source of waste material is the mineral extractive industry, including the extractions of coal and china clay. Some of the by-products or wastes can be, or need to be, reprocessed in order to manufacture materials which are suitable for use as aggregate for concrete or which exhibit special properties. Additionally, some naturally occurring materials, such as perlite or vermiculite, also can be processed to produce aggregates exhibiting special properties.

Demolition waste is being recycled to produce concrete aggregates. A RILEM technical committee (TC-121) has proposed a classification of such aggregates,[331] which is summarised in Table 16.13.

Other waste materials, such as domestic refuse and sewage subject to appropriate processing by incinerators or sintering have also been proposed as potential 'artificial' aggregates. The production of such sintered concrete aggregates has been piloted in laboratory scale conditions for domestic refuse,[332] colliery spoil[333] and clay-bearing silts.[334]

Lightweight and high-density aggregates

The bulk density of artificial aggregates is frequently used as the basis for classification of the diverse types of material available. Harrison[335] proposed that 'lightweight' aggregates were those that exhibited a bulk density of 1000 kg/m^3 or less, whereas 'extra-dense' (or 'high-density') aggregates exhibit a bulk density in excess of 1700 kg/m^3; materials in the bulk density range 1000–1700 kg/m^3 are 'dense' and would correspond to the values found with natural aggregates. Harrison also defined an 'ultra-lightweight' category for aggregates with a bulk density of less than 300 kg/m^3.

Table 16.1 is a classification based upon the raw material source and degree of manufacture on the one hand, and the bulk density on the other.[336] There is no particular critical change in material properties at these values and they merely assist in providing some form of description. Indeed, the classification between lightweight and normal density aggregate in the draft European Standard[12] for concreting aggregates uses a particle density of 2.0 Mg/m^3 and again this merely for convenience.

Mineral additions and fillers

A number of by-product or waste materials, including some slags, are intentionally ground to cement-like fineness and used as mineral additions for concrete; other by-product fine powders (e.g. pulverised-fuel ash) or naturally occurring fine-grained materials are similarly used for concrete. Some of these materials exhibit hydraulic properties or are pozzolanic in the presence of Portland cement and might be classed as binders rather than aggregates. However, since the majority of the volume of these materials usually remains unreacted within a hardened concrete, it is appropriate that some consideration should be given herein to their dual role as very fine aggregates or fillers.

Table 16.13 Composition and use of recycled aggregates (Based on Ref. 331)

Type of aggregate	1	2	3
Composition	Mainly derived from masonry (brick)	Mainly derived from concrete	80% natural aggregate < 10% Type 1 up to 20% Type 2
Maximum strength	C16/20	C30/37	C50/60
Foreign material, e.g. glass, bitumen, soft material (%)	⩽5	⩽1	⩽1
Total organic material (%)	⩽1	⩽0.5	⩽0.5

16.7.2 LIGHTWEIGHT SYNTHETIC AGGREGATES

Density data on the various types of lightweight synthetic aggregate are included in Table 16.1.

Expanded clay, shale and slate

Bricks are produced by the drying and firing of clay or shale raw material, forming a sintered porous structure. Similarly, the drying and sintering of pelletised clay or shale can produce a usable aggregate, but more especially if the raw material is capable of being 'bloated'. Some forms of clay or shale contain organic or mineral matter which can release gases on heating, leading in the appropriate conditions to bloating or expansion of the pelletised particles.[335] 'Lightweight expanded clay aggregate' ('Leca') is produced in this manner.

Colliery spoil and Coal Measures shales have been crushed, pelletised and expanded using a sinterstrand. As an alternative to pelletising, hardened sintered products may be crushed to produce a more angular material; however, the nearly spherical pellets tend to form a dense outer coating over the cellular interior, so that water absorption is reduced (at least initially) and the coated aggregate enhances the concrete workability. Slate wastes have been used to produce expanded lightweight aggregates (e.g. Liapor).

Expanded polystyrene, expanded perlite and vermiculite

Mix details and material behaviour of polystyrene aggregate is discussed by Perry *et al.*[337] Apart from this rarely used material, expanded perlite and exfoliated vermiculite constitute the only ultra-lightweight aggregates and are widely used for insulating purposes. Perlite is a natural volcanic glass of rhyolitic composition which expands on rapid heating to the point of incipient fusion owing to the evolution of steam, yielding aggregate bulk densities in the range 80–240 kg/m^3.[338] Vermiculite is a laminated mica-like natural mineral, which expands on heating by up to 300 times its original volume owing to exfoliation of the constituent laminae, yielding very low aggregate bulk densities in the range 65–200 kg/m^3.[338]

Foamed blastfurnace slag

Molten blastfurnace slag (section 16.7.3) is discharged into a pond through water jets and the generation of steam and gases within the rapidly cooling slag causes foaming and the formation of a uniformly porous grey material. The rapid quenching ensures that none of the unstable compounds associated with air-cooled slag can form.[339] Foamed or expanded blastfurnace slag aggregate is specified for concrete in BS. 3797: 1990.[340] Recently, production of foamed slag has tended to become superseded by pelletised slag.[341,343]

Clinker, cinders and breeze

Furnace clinker, known as 'cinders' in the USA, was the fused or sintered residue from the burning of lump coal in high-temperature industrial furnaces and particularly in the boilers of early electricity power stations. Clinker was the first synthetic aggregate to be used, but production has now ceased in the UK as the new coal-burning power stations use pulverised fuel, which produces a residue of 25 per cent furnace-bottom ash and 75 per cent pulverised-fuel ash (section 16.7.5).

Apart from the often extremely vesicular texture of the clinker particles, the material was frequently and variably contaminated by unburned coal, sulfurous compounds, hard-burned quicklime, periclase, anhydrite, refractory fragments, shaly particles and iron pyrites. Some forms of unburned coal were unsound and capable of causing expansion if wetted (Figure 16.33). The content of coal was controlled by the loss-on-ignition limits now given in BS 3797: 1990,[340] although a pat test is still needed to detect clinker unsoundness. The quicklime, periclase, anhydrite and perhaps the shale could slowly hydrate and cause 'popping and spalling' of clinker concretes.[344]

Reviews of the unsoundness of some clinker aggregates are included in Short and Kinniburgh[345] and Crammond and Currie.[346] Some recent structural damage to concrete blockwork in Northern Ireland was attributed to the hydration and carbonation of hard-burned lime in clinker aggregates which had complied with the only BS requirements, for loss-on-ignition and sulfate content (then BS 1165: 1985[347]).

The corrosion threat posed by the sulfurous compounds generally precluded the use of clinker in reinforced concrete, although it was frequently used in buildings for lightweight infill concrete between steel joists or for encasement concrete around steel stanchions. 'Breeze' was the name given to a less well-burned variety of furnace clinker and for a while it was a very widely used low-cost aggregate in the concrete block industry.

Sintered pulverised-fuel ash

Sintered pfa (or 'Lytag') has been one of the most widely used synthetic aggregates in the UK over the last 30 years. Pellets are formed of pfa and water and then fired on a sinterstrand, sometimes with 7–8 per cent added ground coal as a fuel. Little 'bloating' occurs, but the low density derives from the hollow nature of the pfa 'cenospheres' (section 16.7.5) themselves and to the cavities left between the sintered pfa particles. The siliceous and glassy nature of sintered pfa raised questions about ASR potential, and a brief study by Sims and Bladon[348] found some evidence of reaction but no resultant expansion. It is possible that such highly porous aggregates can accommodate the products of reaction so that no disruption of the concrete is caused, and this type of aggregate is now classified as unlikely to cause ASR damage.[83]

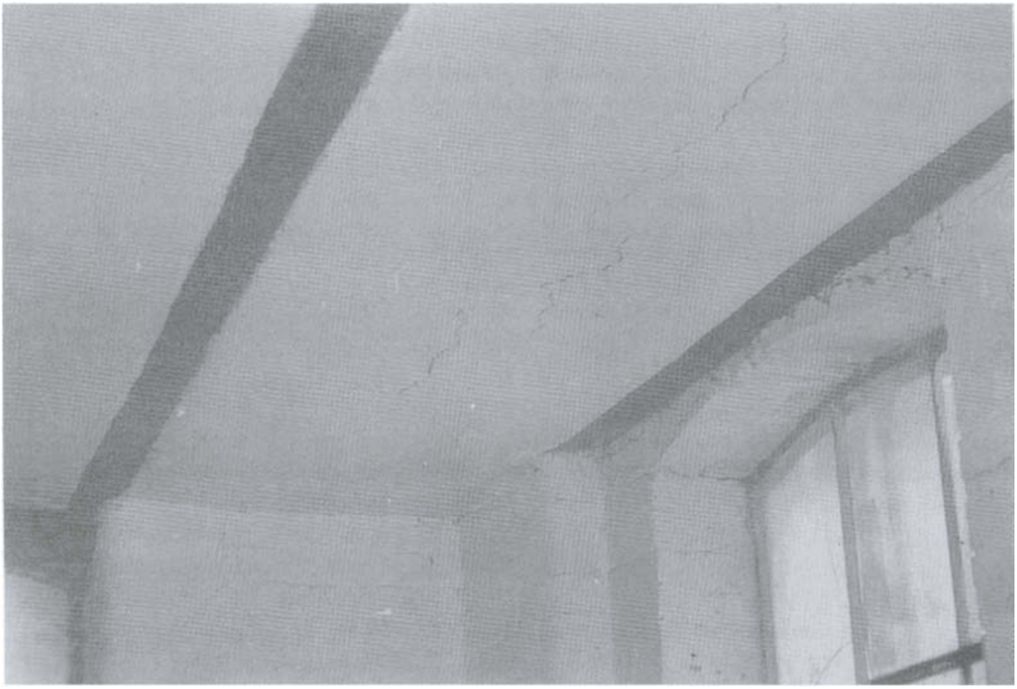

Fig. 16.33 Expansion and cracking of a flat concrete roof slab caused by unsound clinker aggregate. The view shows the ceiling on the underside of the recently water-penetrated roof slab in an early 20th century warehouse building in London, UK.

16.7.3 NORMAL-DENSITY SYNTHETIC AGGREGATES

Natural wastes from extractive industry

Colliery spoil tips have been considered as a potential source of aggregate, but so far the unburned material has generally not been used for concrete in the UK. The spoil material mainly consists of Coal Measures shales and 'seat earths' associated with the coal seams and can be extremely variable, with contamination by potentially detrimental constituents including coal, sulfates, clay minerals, mica and pyrite. Gutt *et al.*[339] considered that some untreated colliery spoils might be usable as a lower grade aggregate for concrete 'for undemanding applications'.

By-product sand waste of the china clay industry in southwest England has long been used for fine aggregates, although they might not be suitable for higher quality concrete without some processing to remove mica. The china clay sands tend to be rather single-sized, but can be screened to produce BS 882: 1992[11] gradings. Crompton[349] investigated the performance of a normal granite coarse aggregate with a natural quartzite sand against the use of a china clay sand. Although slightly reduced strengths were found, strengths up to 65 N/mm^2 were obtained when using the china clay sand.

Typically, high mica contents can cause difficulties (section 16.4.4), but according to BS 6543: 1990[330] these might be overcome by increases in cement content. Residual particles of partially kaolinised feldspar might sometimes present soundness and durability problems.

Gutt *et al.*[339] suggest that the china clay sands are particularly useful for the production of white concrete.

The efficient extraction processes used in obtaining ores leads to tailings being in the finer fractions. Such aggregates have been used satisfactorily in the UK from the fluorspar recovery industry and Rai *et al.*[350] also reported on the potential of tailings from zinc, iron and copper extraction. Obviously such aggregates would need careful examination to check for the presence of organic substances, minerals or remnant soluble ores which could affect the appearance or performance of concrete in which they were to be incorporated.

Blastfurnace slags

A by-product of the iron-making process, blastfurnace slags result from the fusion of fluxing stone (limestone or dolomite) with gangue (siliceous and aluminous) residues from the iron ore, and coke ash.[343,351] The chemical composition is dominated by lime, silica and alumina (Table 16.14), with smaller amounts of magnesia, sulfur and iron. The equilibrium mineralogical compositions are usually in the melilite field,[353] although small relative increases in the lime component can move the composition into the adjacent merwinite or even dicalcium silicate fields (Figure 16.34).

A range of slag textures is formed by differing cooling regimes and the resultant slag types exhibit varying properties. Air-cooled slag, which is allowed to solidify slowly in ladles or pits, is by far the most abundant and is a grey, compact, rock-like material which is almost wholly crystalline. More than 80 per cent of the UK production of air-cooled slag is consumed in road aggregate uses other than concrete. Although studies have shown the material to be satisfactory for use in concrete[355] and BS 1047: 1983[356] provides a specification for suitability, it is rarely used for this purpose in the UK.

Potential problems with air-cooled blastfurnace slag concern the occasional presence of metastable crystals of the beta form of dicalcium silicate (larnite), which can convert at atmospheric temperatures to the gamma form with an accompanying increase in volume leading to disintegration of the slag.

A microscopical test for this 'lime unsoundness' is included in BS 1047: 1983[356] (Figure 16.35). Tests to ensure freedom from dicalcium silicate and iron disintegration are included in both BS 1047: 1983 and a CEN method (prEN 1744-1[357]).

The other principal slag types are lightweight foamed or pelletised (section 16.7.2), and granulated slag, which is glassy because of rapid quenching and is mostly ground for use as a cementitious addition (section 16.7.5).

Steel slags

Steel-making slags are often strong and dense with good wearing characteristics. However, compositions and textures vary considerably, and unstable compounds, including free lime and periclase (MgO), are commonly present, so that steel slags are rarely considered suitable for use as concrete aggregate.[330,339,341] Montgomery and Wang[358] have claimed an 'instant-chilled' variety of steel slag to be suitable for use in concrete, although their programme does not seem to have included any mineralogical analysis or durability testing.

Table 16.14 Some typical chemical compositions of blastfurnace slags (per cent) (after Refs 330, 343, 352)

Reference	1	2	3	4	5	6	7
SiO_2	31–36	34.8	34.9	33.5	33.2	37.1	38.4
Al_2O_3	9–20	14.5	11.3	15.9	10.8	8.8	8.8
TiO_2	0.8	0.5	0.6	0.4	–	0.3	0.4
Fe_2O_3	0.5	0.4	1.3	0.4	0.6	1.9	0.6
MnO	–	0.8	0.4	0.2	–	0.7	1.4
MgO	4–15	6.2	7.8	9.4	12.5	11.5	18.6
CaO	33–45	40.7	42.9	38.9	41.6	40.0	32.3
Na_2O	0.7	0.3	0.4	0.2	0.4	0.4	0.2
K_2O	0.8	0.9	0.5	0.5	0.5	0.4	0.7
P_2O_5	0.6	<0.1	–	–	–	–	–
S (total)	0.8–2	1.2	1.2	1.3	0.5	2.0	1.0
SO_3	0.5	–	–	–	–	–	–

1. BS 6543: 1985.[330] 2. Average of 11 analyses of granulated slag from Scunthorpe, UK. 3. Average of two analyses of granulated slag from Dunkerque, France. 4. Average of 3 analyses of pelletised slag from Redcar, UK. 5. Granulated slag from Atlantic Cement Company's 'Newcem'. 6. Standard pelletised slag cement, Hamilton, Ontario. 7. Algoma granulated slag, Sault Ste. Marie, Ontario.

Non-ferrous slags

Non-ferrous slags have little significant use as aggregate for concrete, although some phosphorus slags appear to be usable,[341] and Rossouw *et al.*[359] have indicated the conditional suitability for use in concrete of several types of metallurgical slag.

Recycled concrete

A significant proportion of demolition rubble comprises concrete and attention has been directed for some time towards its processing for use as a low-cost and environment-friendly aggregate for new concrete, especially in construction areas where good natural aggregates are expensive or in limited supply.[360-362]

The physical and mechanical properties of concretes made with recycled concrete aggregate appear generally inferior to those of comparable concretes made using natural aggregates,[363,364] but nevertheless might be adequate and economical for many applications. Tavakoli and Soroushian[365] found that the qualities of the original concrete being recycled exercised control over the qualities achievable in the new concrete, but concluded that it was feasible to use recycled concrete aggregate to produce high-quality new concrete. RILEM[331] has produced a draft specification for concrete with recycled aggregates.

In some circumstances, it seems, the freeze–thaw performance of concrete can be improved with the use of recycled concrete aggregates.[361,366] It is of course essential that any recycled concrete proposed for use as aggregate is not significantly contaminated with organic matter, such as oil or bitumen, or with salts, such as chlorides or sulfates. Also, the occurrence of alkali-reactivity in the recycled concrete or the presence of high alkali levels could be detrimental to the new concrete.

Processing is necessary to separate concrete from other demolition wastes and reinforcement. Some authorities recommend limiting the percentage of recycled concrete aggregates which

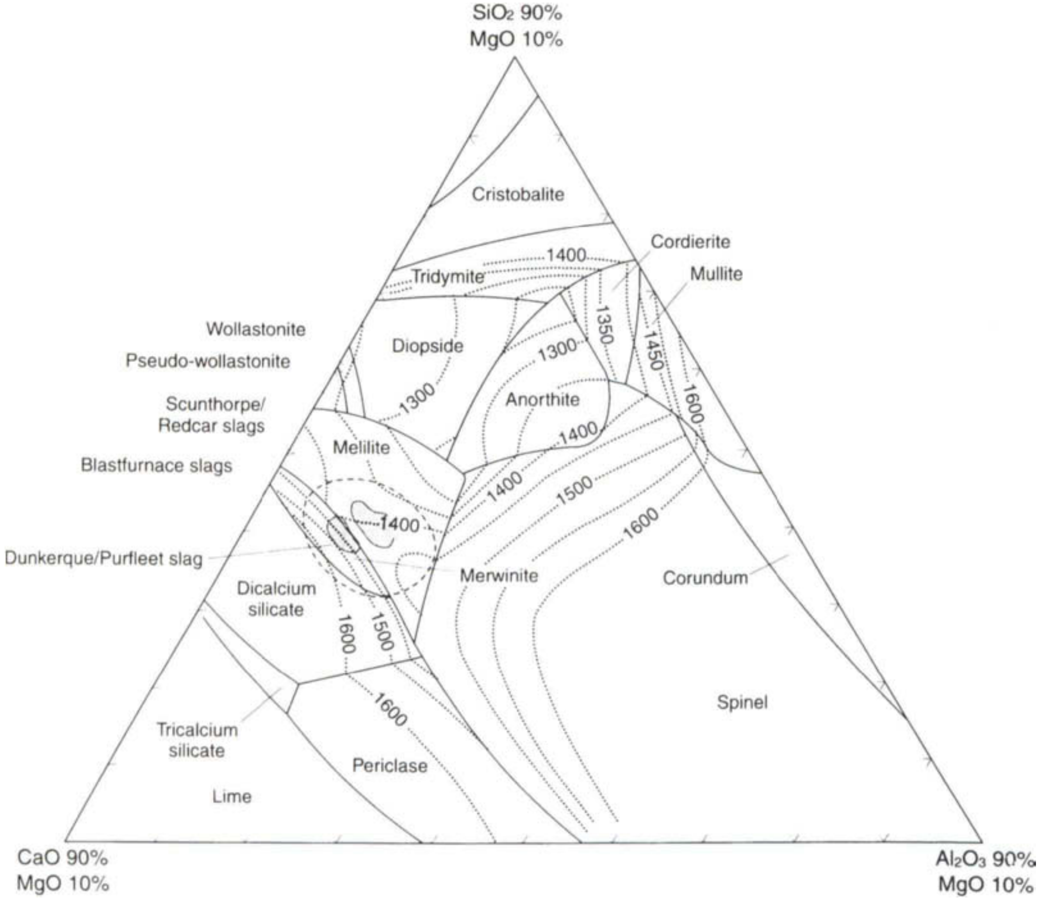

Fig. 16.34 Section through the CaO–SiO_2–Al_2O_3–MgO system at 10% MgO, showing the approximate position of the blastfurnace slag field (after Ref. 354). Of the two UK sources of ground granulated blastfurnace slag, that at Scunthorpe produces a melilitic slag and that at Purfleet (grinding a slag from Dunkerque) produces a merwinitic slag.

can be used in order to minimise the changes in concrete design and properties. Additionally, the use of finer fractions less than 2 mm can lead to harsh and high water demand mixes with significant strength reductions. One pilot project in the use of recycled concrete aggregate within the UK has been undertaken by the BRE in construction of their energy efficient office building in 1996, which successfully used 100 per cent recycled concrete coarse aggregate, although significant increases in water content as a result required an enhanced compensating cement content.

A comprehensive review of recycled concrete is given by Hansen.[367]

Brick and other materials

Crushed clay brick material has been used as aggregate in concrete since at least Roman times.[368,369] In modern times brick aggregate is used in some refractory concretes and

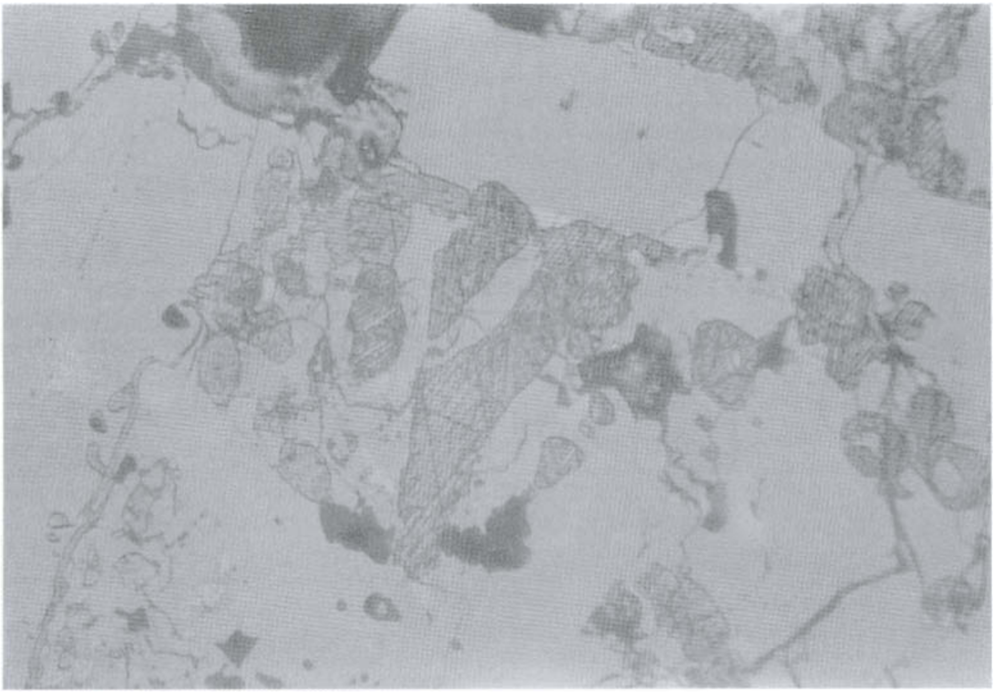

Fig. 16.35 Photomicrograph of a polished specimen of blastfurnace slag in reflected light and after etching with dilute magnesium sulfate solution. The presence of striated crystals of beta-dicalcium silicate (larnite) indicates 'lime unsoundness' according to the BS1047 test method. Approximately × 100 magnification.

sometimes as a medium-weight aggregate for structural concrete. Brick aggregates are often used for making concrete in Bangladesh, where there is a shortage of naturally occurring usable aggregate materials.[189]

One study has shown that crushed brick aggregate concrete has a modulus of elasticity in general about 30 per cent lower than normal-weight concrete but 40 per cent higher than lightweight concrete, with the tensile strength being around 11 per cent greater for the crushed brick aggregate concrete.[370] Suitable brick waste would of course need to be largely free from soluble salts or any associated gypsum plaster material.

Control of crushed brick masonry when used in concrete is heavily affected by variation in its absorption and density. Strengths are reduced relative to natural aggregate concrete and very significantly reduced if both coarse and fine masonry aggregates are used.

In Iran, owing to the inefficiency of brick-producing kilns, about 1 per cent of bricks are produced as very hard-burned bricks with distorted or bloated shapes. This material is referred to as 'clinker brick' and proposals have been made for its use as a concreting aggregate when crushed. Khaloo provides a review of the properties in concrete.[371]

Other possible materials include sintered domestic refuse incinerator ash[332] and other waste materials. Since recent legislation in various countries, including the UK and other European countries, has implemented taxes on landfill, there is likely to be an increased interest in the re-use and recycling of waste materials. This is likely to result in a range of new material options including those for concreting aggregates. For example, in the USA, plastics aggregate has been used in a concept house built in Massachusetts in 1989. The researchers into such aggregates consider polybutylene terephthalate as having the greatest potential. This material has high mechanical strength, low moisture absorption and good dimensional stability. Although the cost is high and data on long-term performance are unavailable, the recycling of plastics and further research may in due course lead to an acceptable material for particular purposes.

Another potential material proposed in the UK is derived from the sintering of a combination of sewage and pfa.

Arising from the landfill legislation, re-use of foundry sands is also a possibility, subject to ensuring these sands are free from resins or heavy-metal contaminants originating within the foundry processes for which they were first used. The use of these materials may be possible as a partial sand fraction subject to this aspect of cleanliness.

16.7.4 HIGH-DENSITY SYNTHETIC AGGREGATES

High-density concretes have a number of specialised uses, including the construction of radiation shields and for ballasting pipelines and offshore oil platforms. The high density of such concrete is achieved by using high-density aggregates, and mostly these are natural materials, especially barytes, but also magnetite, haematite and other forms of iron ore. Concrete densities in excess of 3500 kg/m^3 can be achieved with barytes, but according to Neville[94] barytes concrete is not resistant to weathering. Concretes made using some iron ore aggregates can reach densities of nearly 4000 kg/m^3 and have been used, for example, for concretes associated with North Sea oil pipelines and platforms.[118,119] Even higher densities can be achieved with some high-density synthetic aggregates,[118,119] including iron or steel shot, iron or steel fragments, lead shot, ferrosilicon and ferrophosphorous, but the large differences in particle density of the concrete components can lead to segregation and special concrete placement techniques may be needed.[94]

16.7.5 MINERAL ADDITIONS AND FILLERS

In addition to coarse aggregate, fine aggregate (sand) and cement, it is now common for concrete mixes to contain mineral additions of cement fineness (or finer in the case of microsilica and metakaolin), often as a pozzolanic and/or hydraulic cement replacement material but sometimes as a filler. These materials can substantially modify the properties of concrete and are thus of great importance in concrete mix design, but they are not 'aggregate' in the usually accepted sense and therefore will only be briefly described in this chapter.

Ground granulated blastfurnace slag (ggbs)

Granulated (and pelletised) blastfurnace slag is produced by the rapid quenching of molten blastfurnace slag as it passes through water sprays, followed by water granulation or pelletisation over a spinning drum.[343] The granulate material produced is largely glassy, with typically at least 95 per cent being glass exhibiting a composition close to that of the bulk composition, and the balance being crystals of either melilite or merwinite (section 16.7.3) with some oldhamite and native iron.[352] Pelletised material is generally similar in composition but characterised by a much higher content of vesicles (gas bubbles). These granulated or pelletised materials are ground to cement fineness for use either as a separate constituent material in concrete or for intergrinding with cement clinker in the manufacture of Portland blastfurnace or high-slag blastfurnace cements.

The potential benefits of using ggbs in concrete have been summarised by the Concrete Society[372] and by Dewar and Anderson.[62] These include cost reduction, temperature reduction in large pours, improved resistance to sulfate attack and other durability threats and the inhibition of expansion caused by alkali-reactivity. The features or properties most responsible for variations in the performance of ggbs have been the subject of controversy and are reviewed by Hooton.[343] In the UK, ggbs is specified by BS 6699: 1992,[373] from which the earlier microscopical method for measuring the content of glassy particles[354] has been excluded in favour of an X-ray diffraction procedure for estimating glass (i.e. non-crystalline material) content.

Pulverised-fuel ash (pfa)

Pulverised bituminous coal (pulverised-fuel) is burned at some electricity power stations, producing pulverised-fuel ash, about 20–25 per cent of which becomes fused together like clinker and is known as 'furnace-bottom ash' (section 16.7.2) whilst the remaining 75–80 per cent is a fine pfa dust or 'fly ash' collected from the combustion gases.[374] [376]

The chemical composition of this fly ash or pfa is dependent upon the 'rank' of coal burned and also the nature of the clay impurities in the coal, but all are dominated by silica (45–50 per cent) and alumina (25–30 per cent). The 'Class C' types (ASTM C 618-96[377]) are produced from sub-bituminous coal (or even lignite) and can be relatively high in calcium content (>10 per cent), whereas the 'Class F' types are produced from bituminous coals and are low in calcium content (<10 per cent): UK production is currently only of Class F pfa.

Most pfa is dominated (45–70 per cent) by aluminosilicate glass,[378] principally in the form of solid spheroidal particles less than 20 μm in diameter[379] and occasionally forming hollow 'cenospheres'.[380] Hubbard *et al.*[378] found that the crystalline component of UK pfa variably consists of mullite, haematite, quartz and magnetite, with about 5–10 per cent unburned coal. The product from any one power station was found to be relatively consistent and the variations between stations was largely correlated to the clay impurities in the coal used, aluminosilicate glass being generated by the fusion of illite and mullite being formed by the recrystallisation of kaolinite. McCarthy *et al.*[381] reported a different and wider variety of crystalline phases for Class C pfa from western USA, perhaps accounting for Class C materials being cementitious as well as pozzolanic, whereas Class F ashes are only normally pozzolanic.[379]

The use and potential benefits of pfa in concrete have been reviewed by many authors.[62,372,374,375,382,383] In the UK, pfa for use in concrete is specified in BS 3892: 1993,[384] which includes controls over particle size and water demand, and also a strength factor which has replaced the earlier test for pozzolanicity.

Microsilica (silica fume)

Silicon, ferrosilicon and other silicon alloys are produced by reducing quartz, with coal and iron or other ores at very high temperatures (2000°C) in electric arc furnaces.[385] Some silicon gas (or 'fume') is produced in the process and reaches the top of the furnace with other combustion gases, where it becomes oxidised to silica by the air and then condenses as submicroscopic particles and agglomerated particles (0.1–0.5 μm) of amorphous silica.

This material is usually known as condensed silica fume (csf) or 'microsilica', and consists of an ultrafine silica (85–96 per cent) powder between 50 and 100 times finer than cement or pfa.[386]

Microsilica for use in concrete derives from the manufacture of ferrosilicon alloys and is processed into micropellets or slurries to facilitate handling. World supplies of microsilica are limited with total production probably being between 1 and 1.5 million tonnes, 80 per cent of which is produced in USA, USSR, Norway and Japan.[387] The UK currently imports modest quantities of microsilica for use in concrete. In Iceland blended microsilica–cement is used routinely as a precaution against ASR.[388]

The potential benefits of using microsilica either as a cement replacement material or as an addition to improve concrete properties have been reviewed by Malhotra and Carette,[387] Sellevold and Nilsen[389] and Durning and Hicks.[390] The disadvantages of using microsilica would probably include the health hazards involved with fine dust materials and the increased cost of the concrete. It has also become apparent that microsilica is typically incompletely dispersed, so that the formation of agglomerates causes the mean particle size to be in the range 1–50 μm, rather than the 0.1–0.2 μm range frequently cited.[391] Exceptionally coarse agglomerations of microsilica have the potential to behave as alkali–silica reactive aggregate particles and examples of resultant damage to concrete have been reported.[392]

Metakaolin

Metakaolin is a pozzolanic material and its use dates back to 1962 when it was incorporated in concrete for Jupia Dam in Brazil. Metakaolin is manufactured for use and is formed when china clay, the mineral kaolinite, is heated to between 600 and 800°C. It seems that metakaolin has significant potential as a beneficial addition for concrete.[393,394]

Because metakaolin is a very reactive pozzolana (Table 16.15), the calcium hydroxide content of concrete can be virtually eliminated by its incorporation.[396] A range of concrete property improvements have been recorded, including improved resistance to the penetration of chlorides, freeze–thaw resistance and reduced shrinkage;[397] improved sulfate resistance[398] and resistance to acids;[399] improved strength[400] and abrasion resistance;[401] effectiveness in the suppression of ASR expansion; and also improvements in finish characteristics and the elimination of efflorescence.

Diatomite and other pozzolans

Pozzolanas, or simply 'pozzolans', may be defined as 'materials which, though not cementitious in themselves, contain constituents which will combine with lime at ordinary temperatures in the presence of water to form stable insoluble compounds possessing cementing properties'. Artificial pozzolanas include pfa (see above), burned clay and shale (including some brick), moler (burned diatomaceous earth) and 'rice husk ash'.[379]

The natural pozzolanas are mainly volcanic dust and ash materials, the term 'pozzolana' being derived from the Roman source of zeolitic tuff at Pozzuoli in the foothills of Mount Vesuvius. Other well-known sources of natural pozzolana include the Santorin earth of Greece and the trachytic 'tuffstein' (ground to 'trass') from the Rhineland and Bavaria. Suitable volcanic deposits are also exploited in many other places including the USA, former USSR, Japan and New Zealand.

Table 16.15 Reactivity of pozzolans using the Chapelle test (Ref. 395)

Pozzolan	Pozzolanic reactivity (mg $Ca(OH)_2$ consumed per g of pozzolan)
ggbs	40
Microsilica	427
pfa	875
Metakaolin	1050

The other main group of natural pozzolanas consists of diatomaceous earth (or 'diatomite' when consolidated or artificially hardened and dried), which is mainly composed of diatom fossil remains of opaline silica. The USA is the largest producer (about 30 per cent of the world total), with Romania, former USSR and France also being major sources.[402] The properties and potential benefits of using natural pozzolanas in concretes have been reviewed by Mehta.[403]

16.8 Conclusion

This chapter has reviewed the types and sources of aggregates, their classification, their composition and an outline of their processing. Significant properties of aggregates and their effects on concrete have also been identified. In practice, experience has been gained with a large number of both natural and artificial aggregates and the extent of their general acceptability for use in concrete is already well known. However, the technology related to aggregates and their use continues to develop and the effects of aggregates on concrete properties should be regularly reviewed for suitability in the end-use product. In particular, caution is necessary in selecting aggregates for new uses and from new sources. Hopefully this chapter will assist in these appraisals.

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