I. Soroka

PORTLAND CEMENT PASTE & CONCRETE

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Preface

This book describes and explains the properties and behaviour of Portland cement paste and concrete with respect to their composition and physical structure. The intention is to provide civil and structural engineers, architects and other users of concrete with a better insight into these aspects, and consequently to help them to understand and cope with practical problems which may arise in the daily use of concrete. In addition, the book is intended for use as an advanced textbook on cement and concrete for students of civil engineering or architecture.

First, Portland cement is discussed with particular reference to the effect of its composition and some manufacturing factors on its properties, and the resultant properties of the paste and concrete. Then the hydration process and structure formation of the hardened paste are described, and the factors affecting these processes are explained. The physical structure of the hardened paste is presented in some detail together with the suggested models. The properties of the hardened paste and its behaviour are explained with respect to these models. Finally, concrete properties and behaviour are dealt with at some length. Essentially this is done by considering the effect of the aggregate on the properties of the paste. The effect of some technical factors on the properties of concrete are briefly considered with some emphasis on the effect of steam curing and autoclave treatment.

A number of topics included in this book are usually dealt with in some detail in publications addressed to non-engineers, such as chemists, physicists, etc., and have hitherto only been partially discussed in the available books on concrete. The book, although not claiming to be comprehensive, tries to provide a systematic and comprehensive treatment of these topics in terms which are familiar to its potential readers, namely, civil and structural engineers, architects, etc. It is believed that, in this respect, and in its more basic treatment of the subject, the book differs from apparently similar books.

Haifa, July, 1978 I.S.

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1 Chemical and mineralogical composition

1.1 Introduction

Cements, in a general sense, are adhesive materials which are capable of bonding together fragments or particles of solid matter into a compact whole. This definition covers a wide variety of materials, but for engineering purposes it is generally restricted to 'calcareous cements', i.e. those which contain compounds of lime as their principal constituent or, sometimes, certain allied compounds of magnesium.

Cements may be classified into two groups.

(1) *Non-hydraulic cements* are those which are either not able to set and harden in water (e.g. non-hydraulic lime) or which are not stable in water (e.g. plaster of Paris).

(2) *Hydraulic cements* are able to set and harden in water, and give a solid product which is stable in water. Portland cement is, by far, the most important and widely used hydraulic cement. The following text deals essentially with the properties of Portland cement as well as with the properties and behaviour of Portland cement paste and concrete.

1.2 Chemical composition

Portland cement, by definition (BS 12), is a cementive material which is obtained by

> intimately mixing together calcareous or other lime-bearing material with, if required, argillaceous and/or other silica, alumina, or iron oxide-bearing materials, burning them at a clinkering temperature and grinding the resulting clinker.

A few per cent of gypsum is added during grinding to regulate the setting time of the cement. Accordingly, Portland cement consists mainly of lime (CaO), silica

(SiO_2), alumina ($A\ell_2O_3$), and iron oxide (Fe_2O_3). The combined content of the four oxides is approximately 90% of the cement weight and they are generally referred to as the 'major oxides'. The remaining 10% consists of magnesia (MgO), alkali oxides (Na_2O and K_2O), titania (TiO_2), phosphorus pentoxide (P_2O_5), and gypsum. These are referred to as 'minor constituents'.

There has been a gradual change of the composition of Portland cements over the years. This change has been mainly reflected in the increase in lime content, and in the slight decrease in silica content. The specific composition of the cement depends on the type involved and on the specific composition of the raw materials used in its production. An idea of the composition of present-day Portland cements can be obtained from the approximate limits given in Table 1.1.

Table 1.1 Approximate oxide composition limits of Portland cement[1]

Oxide	*Composition* (wt %)
CaO	60-67
SiO_2	17-25
$A\ell_2O_3$	3-8
Fe_2O_3	0.5-6.0
MgO	0.1-5.5
$Na_2O + K_2O$	0.5-1.3
TiO_2	0.1-0.4
P_2O_5	0.1-0.2
SO_3	1-3

Composition limits for Portland cement in the system $CaO\text{-}A\ell_2O_3\text{-}SiO_2$ are given in Figure 1.1.[2] In this figure iron oxide is considered together with the alumina and the sum of the lime, alumina, silica, and iron oxide made up to 100%. Accordingly, the limits in Figure 1.1 are some 10% higher than those given in Table 1.1.

Most modern cements have a high lime content and their composition falls in that area covered by Portland cement with a lime content exceeding 65%. Cements having a lower lime content, e.g. cements whose composition falls within the Portland cement zone but on the low lime side of the 65% CaO line, are slow to harden for reasons which are explained later. On the other hand, on the high side, the maximum lime content is limited by the need to avoid free lime in the cement. As will be shown later, the presence of such lime may cause volume instability (unsoundness) in the hardened cement paste.

The alumina and iron oxide act as a flux and lower the burning temperature of the cement. The minimum content of these oxides is mainly determined by the need to avoid difficulties associated with high clinkering temperatures rather

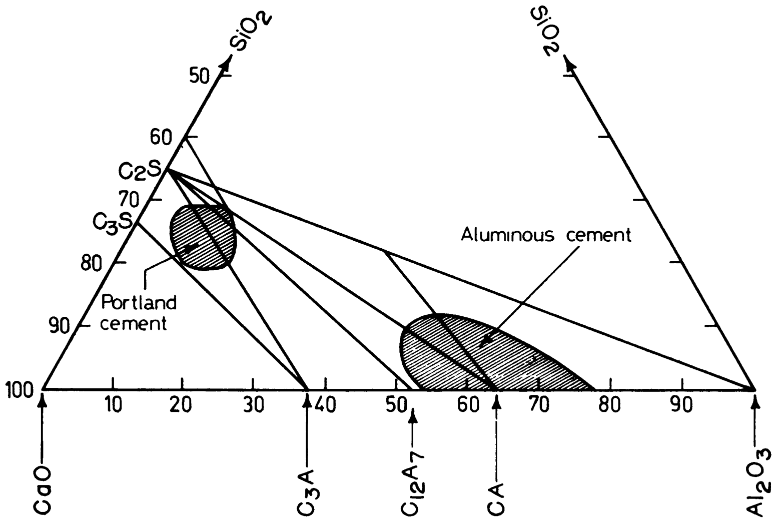

Figure 1.1 *Composition limits of Portland cements in the system* CaO-$A\ell_2O_3$-SiO_2 (*after Lea*[2])

than from any composition requirements. White Portland cements are characterized by a very low iron oxide content (0.5%), and their composition lies, therefore, in the low-alumina region of the Portland cement zone. The maximum content of alumina and iron oxide is determined by the need to control the rapidity of the setting of the cement. Cements with a SiO_2/R_2O_3 ratio lower than 1.5* begin to show rapid setting which can no longer be controlled by the addition of gypsum. This is particularly the case when the decrease in the SiO_2/R_2O_3 ratio is due to the increase in the alumina content. This difference in the effect of alumina and iron oxide is discussed in some detail later.

To sum up, it may be stated that the composition of most modern cements falls within the triangle C_3S-C_2S-C_3A in the Portland cement zone (Figure 1.1). The composition of earlier cements fell within the triangle C_2S-C_3A-$C_{12}A_7$ or, at most, within the triangle C_2S-$C_{12}A_7$-CA.[2]

1.3 Mineralogical composition: major constituents

The cement is a heterogeneous substance made up of several fine-grained minerals which are formed during the clinkering process. This was first observed by Le Chatelier at the end of the nineteenth century,[3] and somewhat later, but independently, by Törnebohm.[4] In addition to an isotropic colourless glass, Törnebohm identified in the cement clinker four minerals which he named alite,

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*The notation R_2O_3 refers to the combined amount of alumina and iron oxide.

belite, felite, and celite. These names are still used. Later work has shown that alite is essentially tricalcium silicate (C_3S), belite and felite are two forms of dicalcium silicate (βC_2S and αC_2S respectively), and celite is a C_6A_2F-C_6AF_2 solid solution. The isotropic matter is glass and the calcium aluminates C_3A and $C_{12}A_7$*.

As already mentioned, the cement is a mixture of fine-grained minerals. The separation of these minerals, by chemical or mechanical means, is rather difficult, if not impossible. Consequently, the determination of the chemical composition of these minerals and their content in the cement clinker have presented some difficulties. High-temperature phase equilibrium studies have proved to be very valuable, and have provided many data. The method usually employed in these studies is known as the 'quench method'. A certain mix, having any desired composition, is prepared and heated until chemical reaction between the components is complete. A small portion of the resulting product is then heated at a desired constant temperature, for a period long enough to allow equilibrium to be attained. When equilibrium is attained, the sample is cooled rapidly by dropping it into water or mercury. The rapid cooling 'freezes' the equilibrium, and the minerals present in the quenched sample can be identified from their refractive indices and other optical properties. The systematic determination of the minerals present in quenched samples, prepared from different mix proportions at different temperatures, gives the 'phase diagram' of the system studied. The phase diagram for the system CaO-SiO_2, for example, is presented in Figure 1.2.[5]

It is evident that by establishing phase diagrams of systems with oxide compositions of Portland cement, the identity of the cement minerals can be established, and the cement composition may be determined. In this respect, the most important system is CaO-SiO_2-$A\ell_2O_3$ which was first studied by Rankin and Wright at the Geophysical Laboratories of the National Bureau of Standards, Washington.[6] This study was followed by similar ones of the ternary systems CaO-$A\ell_2O_3$-Fe_2O_3 and CaO-SiO_2-Fe_2O_3, and of the quaternary system CaO-$A\ell_2O_3$-SiO_2-Fe_2O_3†. On the basis of these studies, and some others, it may be concluded that clinkering a mixture of CaO, SiO_2, $A\ell_2O_3$ and Fe_2O_3 of a Portland cement composition would result, if equilibrium were attained, in the formation of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and a ferrite phase often close in composition to C_4AF. Studies using optical methods, X-ray diffraction techniques, etc., have confirmed these conclusions and it is accepted that cement mainly consists of the four compounds C_3S, C_2S, C_3A, and C_4AF. The combined content of the four compounds is approximately 90% of the cement weight. Hence these four are referred to as 'major compounds' or 'major constituents'.

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*In cement chemistry it is usual to describe each oxide by a single letter, namely, $CaO = C$, $SiO_2 = S$, $A\ell_2O_3 = A$, $Fe_2O_3 = F$, and $H_2O = H$. Accordingly, for example, tricalcium silicate ($3CaO \cdot SiO_2$) is written as C_3S.

†A detailed discussion of the systems is presented in reference 1, pp. 28–81.

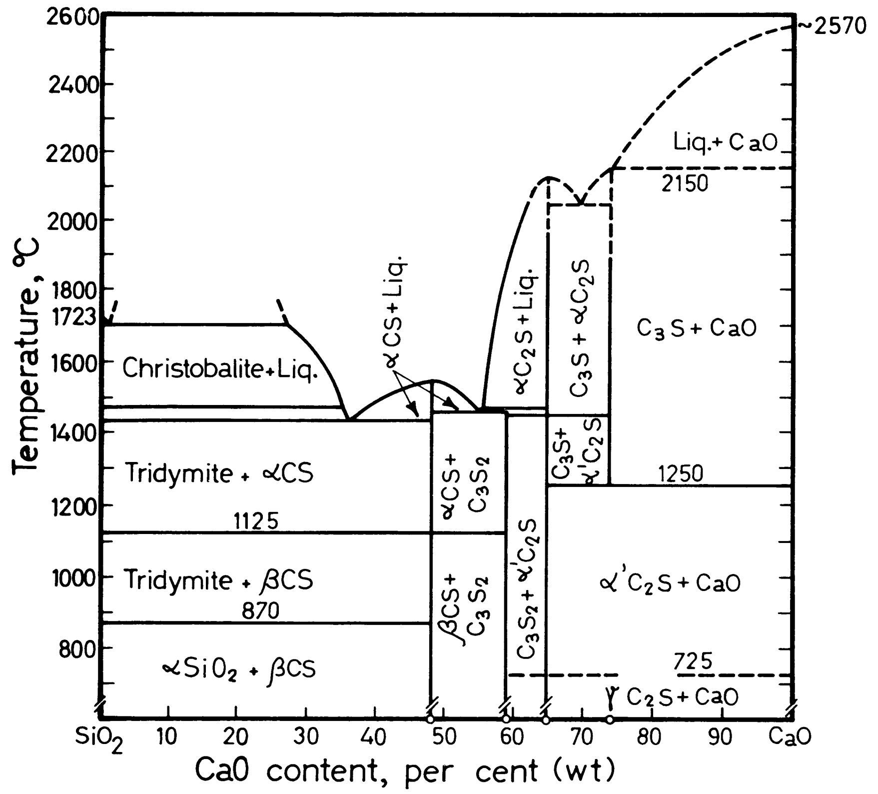


Figure 1.2 *Phase diagram for the system* CaO-SiO_2 (*after Lea*[5])

The four major constituents of Portland cement clinker can be identified in the photomicrograph of a polished clinker which is presented in Figure 1.3. The C_3S phase is angular and dark grey in colour whereas C_2S is rounded and striated, and is a lighter colour. The interstitial material is composed of the white ferrite phase (C_4AF) and the angular C_3A (light grey). It will be seen later that the possibility of identifying the different phases by their shape and colour, facilitates the determination of the compound composition of the cement clinker by optical methods.

In the preceding discussion, the composition of the cement constituents was represented in a simple way as made up of oxides. Alternatively, the compounds may be represented as salts of silicic or aluminosilicic acids.[7] Hence, dicalcium silicate, for example, can be represented as $2CaO{\cdot}SiO_2$, i.e. as a combination of two separate oxides, or as Ca_2SiO_4, i.e. as the calcium salt of orthosilicic acid H_4SiO_4. Both methods are used by mineralogists, though neither represents the correct structure of the silicates. The silicate molecules have been found to consist of a long chain, sometimes extending indefinitely, of silicon-oxygen groups in which an oxygen atom always forms the link between two silicon atoms. The metal atoms in the molecule appear to be linked to oxygen atoms

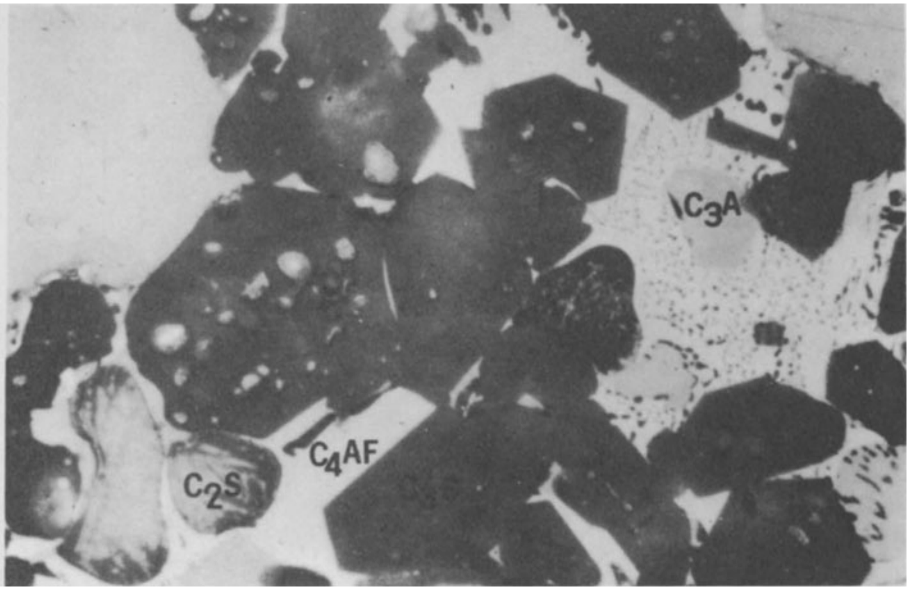
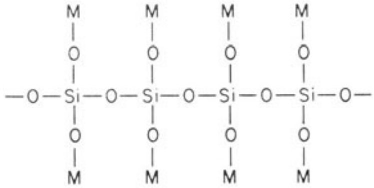


Figure 1.3 *Photomicrograph showing the four major constituents of Portland cement clinker (courtesy of W. Gutt, Building Research Station, Garston, UK)*



$$\begin{array}{ccccccccccccc} & & M & & & & M & & & & M & & & & M & & \\ & & | & & & & | & & & & | & & & & | & & \\ & & O & & & & O & & & & O & & & & O & & \\ & & | & & & & | & & & & | & & & & | & & \\ -O- & & Si & & -O- & & Si & & -O- & & Si & & -O- & & Si & & -O- \\ & & | & & & & | & & & & | & & & & | & & \\ & & O & & & & O & & & & O & & & & O & & \\ & & | & & & & | & & & & | & & & & | & & \\ & & M & & & & M & & & & M & & & & M & & \end{array}$$

Figure 1.4 *Schematic description of the silicate chain*

which have only one link to silicon. In some cases an aluminium atom may replace a silicon atom. A schematic description of the silicate chain is given in Figure 1.4.

The silicon-oxygen groups exist only in the solid state and do not form free ions. That is, the silicates cannot be regarded as salts because they do not dissociate in water to give positive and negative ions. Consequently, as already mentioned, both methods of representation fail to describe correctly the silicate structure. Describing the silicates as the sum of a number of oxides, however, remains the most convenient method of representing their composition, and this way of representation is used throughout this text.

Finally, it should be pointed out that none of the major compounds exist in the cement in their pure form, and all four contain small amounts of other oxides in solid solution. The presence of such impurities affects the properties of the compounds and causes the cement's calculated compound composition to deviate from the true one. These considerations are dealt with later in the text.

1.4 Properties of the major constituents*

1.4.1 Tricalcium silicate (C_3S)

C_3S is unstable at temperatures below 1250°C, and it can be seen from the phase diagram of the system CaO-SiO_2 (Figure 1.2) that below this temperature it breaks down to C_2S and CaO. This breakdown, however, is very slow and below 700°C C_3S exists indefinitely. There are six forms of C_3S, namely, three triclinic, two monoclinic, and one trigonal form. The monoclinic form is the one that usually occurs in Portland cement†.

The properties of C_3S are similar to those of Portland cement. On the addition of water setting takes place and the paste hardens within a few hours. The resulting solid gains strength mainly during the first week, and its 'final' compressive strength reaches the order of a few tens N/mm^2 (Figures 1.5 and 1.6). As will be

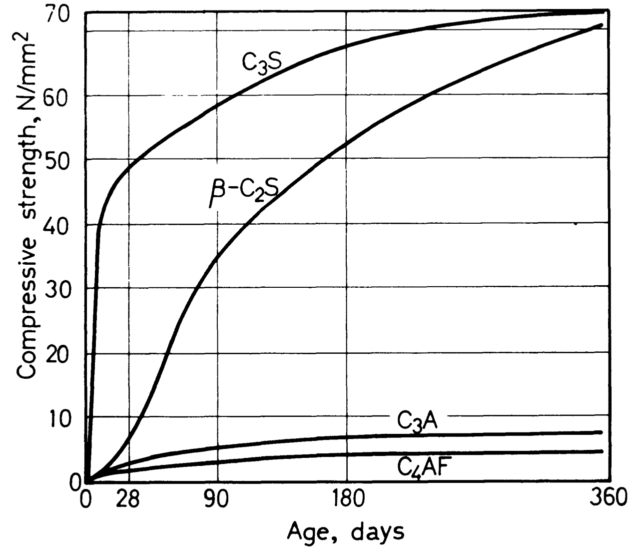


Figure 1.5 *Compressive strength of the major constituents of Portland cement (after Bogue and Lerch*^{10}*)*

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*For physical properties of the major compounds see reference 8.

†For a detailed discussion see reference 9.

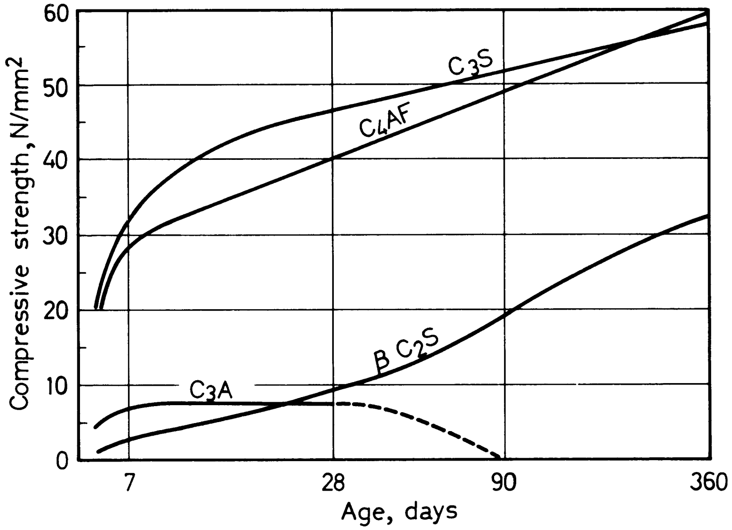

Figure 1.6 *Compressive strength of the major constituents of Portland cement (after Mironov and Malinina*[11]*)*

seen later, setting and hardening of the C_3S, and indeed of all the constituents of the cement, involves a hydration process. The hydration is exothermic and in the case of C_3S the amount of the heat liberated (i.e. heat of hydration) is about 500 J/g.

As pointed out earlier, the major compounds do not occur in the cement in their pure forms but contain small amounts of other oxides in solid solution. Accordingly, the alite is an impure form of C_3S which contains a few per cent of $A\ell_2O_3$, Fe_2O_3, MgO, Na_2O, and K_2O. The presence of impurities affects the properties of the C_3S, and the properties of the pure form are not identical, therefore, with those of alite. The effect of impurities on strength is demonstrated in Table 1.2, which presents the strength of mortars made of different types

Table 1.2 Compressive strength of different types of alite[12]

Form and composition of the alite	*Compressive strength*, N/mm²		
	1 day	3 days	28 days
Pure C_3S (triclinic)*	9	21	24
Pure C_3S (triclinic)	12	18	23
$C_{154}M_2S_{52}$ (triclinic)	9	19	23
$C_{150}M_5S_{52}$ (monoclinic)	16	25	28
$C_{54}S_{16}MA$ (monoclinic)	12	30	35

*Without gypsum; all others contained four per cent of the alite weight of gypsum.

of alite.[12] It may be noted that the compressive strength of C_3S is also affected by the presence of gypsum. Gypsum also affects the tensile strength of C_3S,[13] improves the plasticity of its paste, and affects its setting time. The exact nature of the latter effect, however, is not clear because both retardation and acceleration of the set have been reported.

The alite content in ordinary Portland cement* ranges from 35% to 55% with the average being about 45%.

1.4.2 Dicalcium silicate (C_2S)

There exist four forms of C_2S. αC_2S is stable only above 1420-1447°C and changes reversibly on cooling to the α' form. $\alpha' C_2S$ is stable in the temperature range 800-1447°C, but on cooling persists down to about 650-670°C where it changes reversibly to the β from.[14] Pure βC_2S inverts on cooling, at about 520°C, to the γ form. The presence of impurities, however, affects the rate of inversion which may be delayed or restrained indefinitely. This effect of impurities explains the presence of the β form in Portland cement and its stability at room temperature.

Unlike the α and γ forms, βC_2S possesses cementive properties. On addition of water, βC_2S hydrates liberating a comparatively small amount of heat, i.e. about 250 J/g. The hardened paste gains strength steadily and slowly for weeks and months (Figures 1.5 and 1.6), reaching a final strength which may be of the same order as that of C_3S (Figure 1.5). Figure 1.6, however, indicates that the strength of the βC_2S may be much lower than that of C_3S. This difference in strength may be attributed to the different type of materials used to stabilise the βC_2S. It is clearly evident from the data of Table 1.3 that the type of stabiliser used affects considerably the strength of βC_2S.[15]

The belite in Portland cement is an impure form of βC_2S which contains a few per cent of aluminium and ferric oxides and alkali oxides (Table 1.8). The belite content in ordinary Portland cement varies from 15% to 35% with an average of about 25%.

Table 1.3 Effect of stabiliser on compressive strength of β-dicalcium silicate[15,*]

Stabiliser	*Compressive strength*, N/mm^2		
	7 days	28 days	180 days
Fe_2O_3	1.5	2.4	10.6
B_2O_3	2.8	5.0	16.7
$Ca_3(PO_4)_2$	3.8	9.7	24.9

*$\frac{1}{2}$ inch cubes made of 1:3 mortar.

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*For the various types of Portland cement see Chapter Seven.

1.4.3 Tricalcium aluminate (C_3A)

In its pure form tricalcium aluminate reacts with water almost instantaneously giving a flash set accompanied by the evolution of a large quantity of heat, i.e. about 850 J/g. Normal setting may be achieved in mixes with a high water content by the addition of 15% gypsum. In moist air most of the strength is developed within a day or two, but the strength, as such, is comparatively low (Figures 1.5 and 1.6). In water the set paste disintegrates (Figure 1.6), and C_3A may not be regarded, therefore, as a hydraulic cement.

In Portland cement the tricalcium aluminate occurs as an impure form (Table 1.8). Its content in ordinary Portland cement varies from 7% to 15%.

1.4.4 Tetracalcium aluminoferrite (C_4AF)

C_4AF reacts with water rapidly and setting occurs within minutes. The heat evolution on hydration is approximately 420 J/g. The strength of the set paste is uncertain. According to Figure 1.5 it is rather low, whereas according to Figure 1.6 it is high and reaches the strength of C_3S.

In Portland cement the ferrite phase (celite) occurs as a solid solution, the composition of which varies from about C_6A_2F to about C_6AF_2, with the median value being fairly close to C_4AF. The celite content in ordinary Portland cement ranges from 5% to 10% with an average of approximately 8%.

1.4.5 Summary

The properties of the four major constituents are summarised in Table 1.4, in which the strength properties are based on the data of Bogue (Figure 1.5). It should be noted that these data do not necessarily agree with those of others, in particular, with respect to the strength of the ferrite phase (Figure 1.6).

Table 1.4 emphasises the differences in the properties of the four constituents. These differences are made use of in producing different types of Portland cement. This aspect is discussed in some detail in Chapter 7.

1.5 Minor constituents

1.5.1 Gypsum ($CaSO_4 \cdot 2H_2O$)

As has already been mentioned, gypsum is added during grinding of the clinker in order to regulate the setting time of the cement. There is an optimum gypsum content which imparts to the cement maximum strength and minimum shrinkage, and this optimum depends on the alkali oxides and C_3A contents of the cement and on its fineness. On the other hand, the gypsum content must be limited because an excess may cause cracking and deterioration in the set cement. This adverse effect is due to the formation of ettringite ($3C_3A \cdot 3CaSO_4 \cdot 31\ H_2O$)

Table 1.4 *Properties of the major constituents of Portland cement*

Compound	Alite	Belite		Celite
Approximate chemical composition	Tricalcium silicate, $3CaO{\cdot}SiO_2$ (C_3S)	Dicalcium silicate, $2CaO{\cdot}SiO_2$ (C_2S)	Tricalcium aluminate, $3CaO{\cdot}A\ell_2O_3$ (C_3A)	Tetracalcium aluminoferrite, $4CaO{\cdot}Fe_2O_3{\cdot}A\ell_2O_3$ (C_4AF)
Rate of hydration	Rapid (hours)	Slow (days)	Instantaneous	Very rapid (minutes)
Strength development	Rapid (days)	Slow (weeks)	Very rapid (one day)	Very rapid (one day)
Ultimate strength	High: tens N/mm^2	Probably high: tens N/mm^2	Low: few N/mm^2	Low: few N/mm^2
*Heat of hydration**	Medium: ~ 500 J/g	Low: ~ 250 J/g	Very high: ~ 850 J/g	Medium: ~ 420 J/g
Remarks	Characteristic constituent of Portland cements		Unstable in water, sensitive to sulphate attack	Imparts to the cement its characteristic grey colour

*See Tables 7.1–7.3.

resulting from reaction between C_3A and gypsum. The formation of ettringite involves volume increase because of its comparatively low density, i.e. 1.73 g/cm^3 as compared with an average of about 2.5 g/cm^3 for the other hydration products. When only a small amount of gypsum is added the reaction takes place mainly when the paste is plastic and the volume increase, therefore, does not cause any damage. When greater amounts are added, the formation of the ettringite and the associated volume increase take place to an appreciable extent in the hardened paste and may cause cracking and damage. Consequently, cement standards specify a maximum SO_3 content which is, in accordance with BS 12, 2,5% for cements having a tricalcium aluminate content of 7% or less, and 3% for cements having a tricalcium aluminate content greater than 7%. In this respect, it should be noted that the above limitations apply to the total SO_3 content, i.e. to the combined amount originating both from the raw materials and from the added gypsum. The amount of SO_3 originating from the raw materials is usually 0.1% to 0.5%.

1.5.2 Free lime (CaO)

The presence of free (uncombined) lime in the cement may occur when the raw materials used in the manufacturing process contain more lime than can combine with the acidic oxides SiO_2, $A\ell_2O_3$, and Fe_2O_3. Alternatively, free lime may occur when the amount of lime in the raw materials is not excessive, but when its reactions with the acidic oxides are not complete after the clinkering process.

The maximum amount of lime in the raw materials can be determined in such a way that virtually no free lime should occur in a properly clinkered cement. To this end a few formulae have been suggested, such as that proposed by Lea and Parker:[16]

$$CaO \leqslant 2.80\ SiO_2 + 1.18\ A\ell_2O_3 + 0.65\ Fe_2O_3.$$

Here, use is made of a 'lime saturation factor' (LSF) which is defined as the ratio of the actual lime content in the cement (corrected for the amount combined as gypsum) to the maximum content which may be allowed without producing free lime. That is, to avoid free lime in the cement the lime saturation factor must not exceed unity. Accordingly BS 12 specifies that this factor shall not be greater than 1.02* and not less than 0.66, when calculated by the formula:

$$LSF = \frac{CaO - 0.7\ SO_3}{2.8\ SiO_2 + 1.2\ A\ell_2O_3 + 0.65\ Fe_2O_3}$$

which is based on the previously mentioned formula of Lea and Parker.[16]

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*The value 1.02 is specified rather than unity to allow a small tolerance in the maximum lime content.

The reactions taking place during the burning of cements are essentially solid-solid reactions, and it is only in the final stages of the burning that any liquid is formed through which reactions occur. Under solid-solid conditions the reactions proceed slowly and are conditional on physical contact between the solid particles. In order to allow the reactions to be completed during the burning, the raw materials are finely ground and intimately mixed. Nevertheless, even under carefully controlled conditions complete reaction is not fully achieved and a small amount of free lime, usually less than 1%, is always present in Portland cements*.

It will be seen later that $Ca(OH)_2$ is formed when the alite and the belite hydrate. The adsorption of moisture on storage causes some hydration, and the presence of $Ca(OH)_2$ in cement should, therefore, always be considered. In determining the quality of the cement, the presence of free lime as CaO is the important factor. The CaO present in the cement is formed when $CaCO_3$ dissociates on burning of the raw materials. The burning of the cement is carried out at temperatures which are much higher than the dissociation temperature of $CaCO_3$, about 900°C. Consequently, the CaO is 'hard burnt' and, as such, is very slow to hydrate. Furthermore, the lime formed on burning is intercrystallised with other minerals and is, therefore, not readily accessible to water. Consequently, with such lime, the hydration will take place after the cement has set. Since the hydrated (slaked) lime occupies a larger volume than the free CaO, hydration causes an expansion of the set cement which, in turn, may cause cracking and deterioration. Cements which exhibit such expansion are said to be 'unsound' and the phenomenon is known as 'unsoundness due to lime'.

It is evident that free lime in the cement should be limited and that this limitation should apply to the CaO only. It is not possible to distinguish between the CaO and the $Ca(OH)_2$ by means of chemical analysis, and for this special methods are required†. Moreover, it is rather difficult to specify a quantitative limit for the free lime because the adverse effect depends not only on its content, but also on its particle size and distribution in the cement. Consequently, the cement standards, including BS 12, do not specify a maximum free lime content

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*The efficiency of the burning process is indicated from the 'insoluble residue' content which is that part of the cement which is insoluble in hydrochloric acid (HCl) (see BS 12, Appendix B). Unlike the cement constituents, most of the clay minerals present in the raw materials are insoluble in hydrochloric acid. Hence, the insoluble residue is the amount of such minerals present in the cement and measures, therefore, the efficiency of its burning. In accordance with BS 12 the insoluble residue should not exceed 1.5% (Table 7.6).

†The $Ca(OH)_2$ content in the cement can be estimated from the amount of combined water in the $Ca(OH)_2$. The combined water of calcium hydroxide is lost almost entirely on heating between 350 and 550°C. In this temperature range some other compounds present in the set cement lose water. This amount, however, can be allowed for, and the loss of water from the cement over the range of 350–550°C may be used as a measure of the $Ca(OH)_2$ content.[17] This content is then subtracted from the total free lime content to give the free lime present as CaO.

but rather specify the soundness of the cement as measured by its expansion, or by its cracking due to accelerated slaking of the free lime. The relevant test prescribed in BS 12 is the one developed by Le Chatelier. In this test the lateral expansion of a cylinder, made of a standard paste, is determined after heating in boiling water for one hour at an age of 24 hours. The apparatus used for conducting the Le Chatelier test is shown in Figure 1.7. It consists of a small split cylinder forming a mould 30 mm internal diameter and 30 mm high. On either side of the split are 165 mm long indicators with pointed ends. The cylinder is placed on a glass plate, filled with a paste of standard consistence, which is made from the cement to be tested, and then covered with another glass plate. The whole assembly is placed for 24 hours in water at 18.9 ± 1.1°C and the distance between the indicators recorded. The mould is then placed in water which is heated to 100°C in 25 to 30 min, and kept boiling for one hour. After cooling the distance between the two indicators is measured again. The difference between the two measurements represents the expansion of the cement. In accordance with BS 12 this difference should not exceed 10 mm.

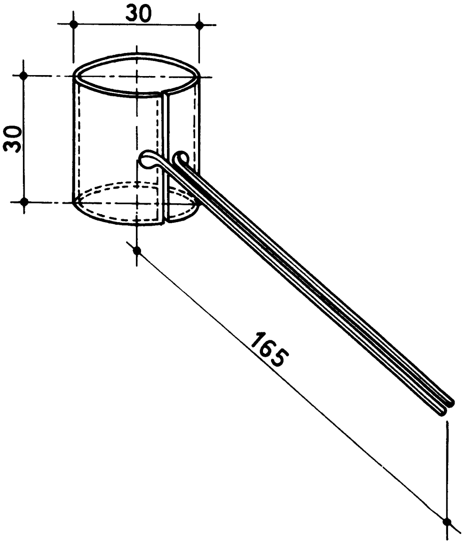

Figure 1.7 *Le Chatelier apparatus, after BS 12* (*dimensions in* mm)

In the USA the soundness is determined from the expansion of 1 inch x 1 inch prisms, made of a paste of a standard consistence, which are treated in an autoclave for 3 hours at 295 p.s.i. (ASTM C151). In Germany (DIN 1164) the test is made by observing possible cracking of round cake-like specimens cured in cold water (18-21°C) to the age of 28 days, or in boiling water for 24 hours.

1.5.3 Magnesia (MgO)

The raw materials for the cements usually contain a certain amount of $MgCO_3$ which on burning dissociates to magnesium oxide (magnesia) and carbon dioxide. The magnesia does not combine with the major oxides. Some of it is taken up in solid solution in the clinker minerals, and the remainder crystallises as periclase (MgO). The hydration of periclase, similar to that of the CaO, involves volume increase and the presence of the magnesia may cause unsoundness. At the burning temperature of the cement the magnesia is dead burnt and reacts with water very slowly over a period of years at ordinary temperatures. As a result of this very slow hydration, short-term tests, such as the Le Chatelier and the German 'cake' tests, are not suitable for determining unsoundness due to the presence of MgO. In the autoclave test (ASTM C151), however, the conditions bring about the hydration of both CaO and MgO and the expansion measured in this test represents unsoundness due to the combined effects of both magnesia and lime.

The magnesia content is limited to 4% by BS 12 (Table 7.6), and similar limitations are specified by other standards (Table 7.7). It should be pointed out that the magnesia content as such is not a good indication of potential unsoundness. As has been pointed out some MgO is held in solid solution by the clinker minerals and the remainder crystallises as periclase. Only the presence of periclase may cause unsoundness. Moreover, the degree of unsoundness depends on crystal size because the smaller crystals tend to hydrate more rapidly or without setting up excessive internal pressure.[18] The size of the crystals depends, in turn, on the cooling rate of the clinker. The periclase crystallises from the liquid phase and the more quickly the clinker is cooled, the smaller are the periclase crystals. Hence, a higher MgO content may be tolerated in cements made from rapidly-cooled clinkers. It is obvious, however, that for practical reasons the cooling rate of the clinker cannot be considered in the standards which specify a single maximum value for the total MgO content.

1.5.4 Alkali oxides (K_2O, Na_2O)

The alkali oxides are introduced into the cement through the raw materials and their content varies from 0.5% to 1.3% (Table 1.1). On burning, the alkali oxides combine, usually, with sulphur trioxide (SO_3) giving a solid solution of sodium-potassium sulphate which tends to have the approximate composition $3K_2SO_4 \cdot Na_2SO_4$. The SO_3 content in the clinker (0.1-0.5%) is generally not sufficient to satisfy all the alkali oxides and the excess is taken up in solid solution: K_2O mainly by C_2S to give an approximate composition $KC_{23}S_2$ and Na_2O mainly by C_3A to give an approximate composition NC_8A.

The presence of the alkali oxides in the cement assumes practical importance when alkali-reactive aggregates are used in concrete production. Such aggregates contain a reactive form of silica which combines with the alkali oxides released from the cement. This reaction results in the formation of alkali-silica gel and involves expansive forces which, in turn, may cause cracking and deterioration of the concrete. This adverse effect may be avoided by the use of 'low-alkali' cements, i.e. cements in which the total alkalis content, R_2O, calculated as equivalent to Na_2O, does not exceed 0.6%*.

1.5.5 Titanium oxide (TiO_2)

Titania (TiO_2) occurs in the cement to a small extent and its content varies from 0.1% to 0.4%. The titania is introduced into the cement through the clay or the shale used in its manufacture.

1.5.6 Phosphorus pentoxide (P_2O_5)

The P_2O_5 is usually introduced into the cement through the limestone used in its manufacture. Generally the P_2O_5 content in the cement does not exceed 0.2%. Its presence slows the cement hardening because it breaks down the C_3S to C_2S, which contains the P_2O_5 in solid solution, and CaO. Larger amounts of P_2O_5 may cause unsoundness because free lime is formed. This latter effect may be partly overcome by reducing the lime content in the raw materials. Accordingly, sound cements, having a P_2O_5 content of 2.0% or 2.5%, can be produced.[19]

1.6 Potential compound composition by the Bogue Method

Assuming that the cement consists of C_3S, C_2S, C_3A, and a ferrite phase close to C_4AF, its compound composition can be readily calculated on the basis of its oxide composition. The oxide composition, in turn, can be determined by means of conventional chemical methods such as the ones prescribed in ASTM C114. For reasons which are discussed later, the preceding assumption is not entirely correct, and the composition determined deviates from the 'true' composition of the cement. Hence, the calculated composition is referred to as the 'potential' composition.

It can be shown[20] that, assuming the cement consists of C_3S, C_2S, C_3A, and C_4AF, the content of these compounds in the cement is given by the following equations:

$$C_3S = 4.071\ CaO - (7.600\ SiO_2 + 6.718\ A\ell_2O_3 + 1.430\ Fe_2O_3 + 2.852\ SO_3) \tag{1.1}$$

$$C_2S = 2.867\ SiO_2 - 0.7544\ C_3S \tag{1.2}$$

$$C_3A = 2.650\ A\ell_2O_3 - 1.692\ Fe_2O_3 \tag{1.3}$$

$$C_4AF = 3.043\ Fe_2O_3 \tag{1.4}$$

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*The molar ratio Na_2O/K_2O equals 0.658. Hence, the total alkali content, R_2O, calculated as equivalent to Na_2O, $R_2O = Na_2O + 0.658\ K_2O$. This calculation assumes that equal concentrations of NaOH and KOH are equal in their effect. This may not necessarily be correct.

in which CaO, SiO_2, $A\ell_2O_3$, Fe_2O_3, and SO_3 represent the corresponding oxide contents as determined by chemical analysis. The CaO content, however, must be corrected to allow for free lime. The free lime content generally varies from 0.5% to 1%, and if not determined in the chemical analysis, its value may be estimated.

Equations (1.1)-(1.4) are applicable to the more common cases when the $A\ell_2O_3/Fe_2O_3$ ratio is equal to, or greater than, 0.64, and the composition of the ferrite phase can be assumed to be C_4AF. In cements low in alumina, where the A/F ratio is less than 0.64, this latter assumption is no longer valid, and for such cements it is assumed that the ferrite phase consists of $C_4AF + C_2F$ and that the cement contains no C_3A. Accordingly, the following equations are used in calculating the compound composition:

$$C_3S = 4.071\ CaO - (7.600\ SiO_2 + 4.479\ A\ell_2O_3 + 2.859\ Fe_2O_3 + 2.852\ SO_3) \tag{1.5}$$

$$C_2S = 2.867\ SiO_2 - 0.7544\ C_3S \tag{1.6}$$

$$C_3A = 0 \tag{1.7}$$

$$C_4AF + CF_2 = 2.100\ A\ell_2O_3 + 1.702\ Fe_2O_3 \tag{1.8}$$

The potential compound composition calculated in accordance with the preceding equations, is sometimes referred to as the 'Bogue composition' after R. H. Bogue, the first person to suggest this method of calculation.[20] The use of this method is illustrated in the following worked example which considers a cement of the following oxide composition:

Oxide	*Content*, wt %
CaO	64.4
SiO_2	20.0
$A\ell_2O_3$	5.8
Fe_2O_3	3.2
SO_3	2.6
MgO	1.8
Na_2O	0.4
K_2O	0.3
Loss on ignition	1.8
Total	100.3

The A/F ratio in the cement in question is 5.8/3.2 = 1.81, i.e. it is greater than 0.64 and therefore equations (1.1)-(1.4) are to be used. Assuming a free lime content of 0.8%, the corrected CaO content is 64.4 – 0.8 = 63.6%, and the C_3S content is given by [equation (1.1)]:

$$C_3S = 4.071 \times 63.6 - (7.600 \times 20.0 + 6.718 \times 5.8 + 1.430 \times 3.2 + 2.852 \times 2.6) = 56.0\%$$

the C_2S content by [equation (1.2)]:

$$C_2S = 2.867 \times 20.0 - 0.7544 \times 56.0 = 15.1\%$$

the C_3A content [equation (1.3)] by:

$$C_3A = 2.650 \times 5.8 - 1.692 \times 3.2 = 10.0\%$$

and the C_4AF content [equation (1.4)] by:

$$C_4AF = 3.043 \times 3.2 = 7.9\%$$

The total of the four major compounds equals 90.8%. The remaining percentage comprises the minor oxides and gypsum. The gypsum content equals $1.7 \times SO_3$, i.e. $1.7 \times 2.6 = 4.4\%$ for the given conditions. Adding the free lime content (0.8%), the magnesia (1.8%), the alkali oxides (0.7%), and the loss on ignition (1.8%), gives the expected total of 100.3%.

Table 1.5 Effect of oxide composition on compound composition of Portland cement[21]

Cement	*Oxide composition*, wt %				*Compound composition*, wt %			
	CaO	SiO_2	Al_2O_3	Fe_2O_3	C_3S	C_2S	C_3A	C_4AF
1	66.0	20.0	7.0	3.0	65.0	8.0	14.0	9.0
2	63.0	22.0	7.7	3.3	33.0	38.0	15.0	10.0
3	66.0	20.0	5.5	4.5	73.0	2.0	7.0	14.0

Table 1.5 presents the potential compound composition of three different cements.[21] It can be seen that the compound composition is sensitive to slight variations in oxide composition. The CaO content of cement 2, for example, is 3% lower than that of cement 1 and the contents of its remaining oxides are correspondingly somewhat higher. These small differences result, however, in considerable differences in compound composition: the C_3S content of cement 2 is approximately half of that of cement 1 and its C_2S content is almost five times higher. Cements 1 and 3 have the same lime and silica contents with cement 3 having slightly lower alumina, and somewhat higher Fe_2O_3 contents. Again, the resulting compound composition varies considerably: the C_3A content of cement 3 is half of that of cement 1 and its C_2S content is only one quarter that of 1. In other words, the cement composition may be changed considerably by changing the oxide composition, i.e. by changing the mix proportions of the raw materials. Cements of different composition have different properties and, accordingly, different types of Portland cement can be manufactured. The different types of Portland cement are discussed in some detail in Chapter 7.

1.7 Factors influencing the compound content

It was pointed out earlier that the calculated Bogue composition is not the true composition of the cement and that it is referred to as 'potential' composition. The Bogue method assumes that a state of chemical equilibrium is reached on burning of the raw materials, that this equilibrium is maintained during cooling, and that the cement is entirely crystalline, i.e. that no glass remains in the clinker after cooling. It further assumes that the four major compounds have exact compositions of C_3S, C_2S, C_3A, and C_4AF. None of these assumptions is entirely correct and this causes deviation of the calculated composition from the true composition of the cement.

1.7.1 Cooling of the clinker

The content of liquid phase at the clinkering temperature of the cement (1400-1500°C) is 20 to 30%. In calculating Bogue composition it is assumed that the liquid phase crystallises completely and that the equilibrium which is reached at the clinkering temperature is maintained during cooling. Rapid cooling, such as usually occurs in cement manufacture, may cause the liquid to crystallise independently of the solids already existing and the assumed state of equilibrium will not be maintained. Such an independent crystallisation and the presence of glass in the cement clinker both affect compound composition. For example, in the limiting case, when the whole liquid phase solidifies to a glass, the clinker contains no C_3A and C_4AF because at clinkering temperature both the $A\ell_2O_3$ and the Fe_2O_3 are present in the liquid. Slower cooling allows crystallisation of the C_3A and C_4AF phases, and thereby reduces the glass content in the clinker. In other words, the ratio of the glass content to the C_3A and the C_4AF contents depends on the cooling rate, and the slower the rate, the higher are the C_3A and the C_4AF contents at the expense of the glass. In this respect it was observed that cements produced from slowly-cooled clinkers tended to set more rapidly, and exhibited poorer sulphate-resistance properties than cements which were produced from rapidly-cooled clinkers. It will be seen later that such properties are, indeed, characteristic of cements having a high C_3A content.

The effect of cooling rate on clinker composition is demonstrated in Table 1.6. This table compares Bogue potential composition of a given clinker to its calculated composition assuming that (a) the whole liquid phase is solidified to glass and (b) the liquid phase crystallises independently of the solids already existing in the clinker. The calculations were made by the method developed by Lea and Parker, the details of which can be found elsewhere.[22]

It is not clear what are the actual cooling conditions during cement manufacture, and there exists some difference of opinion with respect to the presence of glass in the clinker.[23-25] In any case, it may be concluded that the equilibrium

Table 1.6 Effect of cooling conditions on compound composition of Portland cement clinker[22,*]

Compound	*Content*, wt %		
	Complete crystallisation (Bogue composition)	Complete solidification of liquid phase	Independent crystallisation of liquid phase
C_3S	57.5	59.6	59.6
C_2S	22.6	15.6	21.0
C_3A	10.8	0	9.8
C_4AF	9.1	0	9.1
$C_{12}A_7$	0	0	0.5
Glass	0	24.8	0

*Oxide composition: CaO 68.0%, SiO_2 23.0%, $A\ell_2O_3$ 6.0% and Fe_2O_3 3.0%.

state is probably not maintained during cooling and the true compound composition differs therefore from the composition which is calculated on the basis of complete equilibrium.

1.7.2 Composition of the ferrite phase

The composition of the ferrite phase, depending on the A/F ratio, can vary from C_6A_2F to C_6AF_2.[25,26] The assumption that the ferrite phase is C_4AF may be essentially correct for many cements but may contribute, in some others, to deviation of the calculated composition from the true composition of the cement.

The effect of the ferrite phase composition on the cement compound composition is illustrated in Table 1.7.[27] The Bogue composition of the cement in question was calculated assuming, as usual, that the composition of the ferrite phase was C_4AF. This is compared with the results of a modified Bogue method,

Table 1.7 Comparison of cement compound composition calculated by Bogue's original and modified methods[27,*]

Compound	*Bogue original*	*Bogue modified*
C_3S	49.9	46.0
C_2S	20.1	23.1
C_3A	0.9	5.7
Ferrite phase	19.6	15.7

*Cement oxide composition: CaO 65.51%, SiO_2 20.15%, $A\ell_2O_3$ 4.47%, and Fe_2O_3 6.44%.

i.e. with the results of the same calculation but taking the true composition of the ferrite phase, which was $C_4A_{0.72}F_{1.28}$. It is evident from Table 1.7 that the calculated compound composition depends on the assumed composition of the ferrite phase, in particular with respect to the C_3A and the ferrite phase contents, and that any failure to allow for the true composition of this phase will cause the calculated composition to deviate from the true composition of the cement.

1.7.3 Composition of major compounds

In calculating Bogue composition it is assumed that the four major compounds have the exact compositions, C_3S, C_2S, C_3A, and C_4AF. This is not entirely correct because all four occur in the cement as solid solutions containing certain impurities. In other words, the true compositions of the compounds differ from the ones assumed in the calculation and this, again, causes the results to deviate from the true values.

The impurity content in the major clinker compounds can be determined by means of electron microprobe analysis,* and available relevant data are summarised in Table 1.8.[28]

Table 1.8 Solubility range in the major clinker compounds[28]

Compound	*Content*, wt %						
	$A\ell_2O_3$	Fe_2O_3	MgO	SiO_2	Na_2O	K_2O	TiO_2
C_3S	0.7-1.7	0.4-1.6	0.3-1.0		0.1-0.3	0.1-0.3	0.1-0.4
C_2S	1.1-2.6	0.7-2.2	0.2-0.6		0.2-1.0	0.3-1.0	0.1-0.3
C_3A		4.4-6.0	0.4-1.0	2.1-4.2	0.3-1.7	0.4-1.1	0.1-0.6
Ferrite phase			0.4-3.2	1.2-6.0	0.0-0.5	0.0-0.1	0.9-2.6

The effect of impurities on the composition of the major compounds, and that of the A/F ratio on the composition of the ferrite phase, are allowed for in the method developed by Midgley for calculating the compound composition of Portland cement clinker.[29] Considering available data, Midgley proposed a series of equations which relate the minor oxide contents of the parent clinker to the contents of the relevant oxides in each of the four major compounds, assuming certain upper limits of solubility for each oxide in these compounds. He further assumed that the oxides Na_2O, K_2O, TiO_2, P_2O_5, and MgO occur as free oxides,

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*In this method, a polished surface or thin section is made conducting by evaporating onto it a carbon or metal film. The surface is then made a target for a focussed beam of electrons which excite a small area of approximately 1 μm in diameter. This, in turn, causes the emission of X-rays which are characteristic of the elements present in the irradiated area. The identification of these elements can be achieved by analysis of the emitted X-rays by use of a suitable spectrometer.

and that each contains 0.1% of all the others as impurities. On the basis of these equations and assumptions, the following 9 x 9 matrix is solved to give the content of the alite a, the belite b, the tricalcium aluminate c, the ferrite phase f, and the content of the free minor oxides Na_2O n, K_2O k, TiO_2 t, P_2O_5 p and MgO m:

$$\begin{bmatrix} C \\ S \\ A \\ F \\ N \\ K \\ T \\ P \\ M \end{bmatrix} = \begin{bmatrix} \\ \\ \\ \\ m_{ij} \\ \\ \\ \\ \\ \end{bmatrix} \times \begin{bmatrix} a \\ b \\ c \\ f \\ n \\ k \\ t \\ p \\ m \end{bmatrix}$$

where C, S, A etc., are the relevant oxide contents as determined from a chemical analysis. The CaO content, however, is corrected to allow for free lime and CaO in calcium sulphate. The matrix coefficient m_{ij} is the oxide, i, content in the phase j. For example, m_{11} is the CaO content in the alite, m_{12} in the belite, m_{13} in the tricalcium aluminate etc. Similarly, m_{21} is the SiO_2 content in the alite, m_{22} in the belite, etc.*

Table 1.9 Comparison of cement clinker composition determined by different methods[29]

Compound	*Oxide composition*, wt %					
	CaO 64.08%, $A\ell_2O_3$ 4.23% SiO_2 23.06%, Fe_2O_3 6.33%			CaO 66.69%, $A\ell_2O_3$ 6.28% SiO_2 20.98%, Fe_2O_3 2.97%		
	Compound composition, wt %					
	Bogue	X-Ray	Midgley	Bogue	X-Ray	Midgley
Alite	46.27	41.6	47.94	59.12	48.4	70.53
Belite	31.26	31.1	33.40	15.56	23.9	8.10
C_3A	0.47	3.8	3.50	11.60	15.7	10.62
Ferrite	19.24	14.4	14.16	9.03	7.0	8.05

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*Actually the matrix is solved twice. The first solution produces small quantities of free Na_2O and K_2O. It is usually assumed, however, that alkali oxides in the cement are not free but combined as sulphates. Accordingly, the apparent free alkali oxides are assumed to combine with the sulphate present in the clinker. The remaining sulphate (if any) is calculated as calcium sulphate and a new value for CaO is determined accordingly. The matrix is then solved again to give the composition of the cement clinker.

It is apparent that the reliability of the proposed method depends on establishing the true composition of the compounds and the resulting matrix coefficients. That is, although in principle the proposed method may be considered more reliable than the Bogue method, this is not necessarily the case because quantitative data on the impurity contents in the cement constituents are not complete as yet. It seems, however, that the method is preferable for cements in which the C_3A content is less than 3.5%. To some extent this is apparent from Table 1.9[29] which compares the composition of two cements, one high and one low in C_3A, when determined by the Bogue method, X-ray diffraction, and by the method proposed by Midgley. It will be shown later that X-ray diffraction is considered more reliable for determining the C_3A and the ferrite phase contents. It can be seen that the contents of these phases, as determined by the method of Midgley, are similar to those determined by X-ray diffraction when the cement of low C_3A is considered.

1.8 Determination of compound composition by direct methods

1.8.1 Optical microscopy

It was shown earlier (Figure 1.3) that it is possible to identify the clinker constituents on polished surfaces under the microscope. This possibility allows the quantitative determination of the composition of the clinker by what is generally known as the Rosiwal, or Delesse-Rosiwal, method. In this the content of each constituent on the surface is estimated by measuring the intercepts made by each compound on a series of equally spaced lines. The measurement is usually done by placing a thin section of the clinker on the stage of a recording micrometer which, in turn, is attached to the stage of a microscope. The micrometer is fitted with a few screws, to each of which a compound is assigned. The section is then moved across the field of vision by turning the screws, each screw being used to traverse across the particular compound to which it was assigned. The screws have graduated micrometer heads and record the total distance traversed across each compound. The measurement is repeated for a series of parallel equidistant traverses which cover the entire surface. The content of each compound is given by the total of the distances traversed across the compound in question, on the premise that the linear measurements are directly proportional to the volumes of the grains. This method gives volume percentages of the constituents and conversion to weight percentage is necessary for comparison with other methods.

The preceding method may be subject to considerable error because it is difficult to locate accurately the limits of each individual grain. At present therefore, the 'point counting' method is preferred. This is also a less time consuming method. The regular spacing between traverses is retained, but the individual traverses are broken up into a series of equally spaced points. At each point the compound is identified and counted. To this end the stage is provided with suitable keys which are connected to mechanical or electrical counters. Again, each key is assigned to a different compound. On pressing a key, the relevant compound is counted and the stage is moved a fixed distance along the traverse line. When the line is run, the counting is continued along equally spaced traverses covering the entire section. The content of each compound is given by the number of times it is identified, adopting the fundamental premise that this number is directly proportional to volume of the compound in question.

1.8.2 X-Ray diffraction

In recent years quantitative determination of the cement composition by X-Ray diffraction has gained wide use. It is based on the fact that, in a mixture, the measured intensity of a diffraction peak is directly proportional to the content of the substance producing it. This may be expressed by the equation

$$I_1/I_0 = aW_1/W_0$$

where I_1 is the intensity of a given peak of one constituent and W_1 is its weight percentage. I_0 and W_0 similarly relate to a second constituent and a is a constant. The constant a can be determined from the slope of the line which is obtained by measuring the intensity ratios I_1/I_0 for a number of mixes with different W_1/W_0 ratios.

If a known material, an 'internal standard', is added in a given amount to the mixture of minerals of unknown proportions, the following series of equations may be written:

$$\begin{aligned}
I_1/I_0 &= a_{11}X_1 + a_{12}X_2 + \ldots a_{1n}X_n \\
I_2/I_0 &= a_{21}X_1 + a_{22}X_2 + \ldots a_{2n}X_n \\
&\bullet \\
&\bullet \\
&\bullet \\
I_n/I_0 &= a_{n1}X_1 + a_{n2}X_2 + \ldots a_{nn}X_n
\end{aligned}$$

in which I_0 is the intensity of a characteristic peak of the internal standard and $I_1, I_2 \ldots I_n$ are the intensities of the characteristic peaks of the remaining constituents of the mixture. $X_1, X_2 \ldots X_n$ are the constituent contents in relation to the known content, W_0, of the internal standard. The constants, a_{ij}, may be determined from the intensity ratios I_i/I_0 measured for mixtures with different $X_i = W_i/W_0$ ratios. The constants a_{ij} being known, n diffraction peaks are to be measured to solve the n equations for the n weight ratios X_i.

The application of X-ray diffractometry in practice involves certain difficulties. In a mixture of several minerals, for example, there exists a minimum content for each mineral which can be measured, and below this minimum the mineral in question cannot be detected. Also very high resolution X-ray spectrometers may break down what seems to be a single strong reflection into a series of closely spaced weaker ones, giving rise to another difficulty because such breakdowns occur with the impure forms of C_3S and C_2S present in the clinker. Moreover, the position of these reflections depends on the nature of the impurities which the mineral contains. Additional difficulties may arise when the reflections from different minerals coincide or overlap. Nevertheless, by use of X-ray diffractometry the content of C_3S can be determined to within ± 2-5%, that of C_2S to within ± 5-9%, that of C_3A to within ± 0.5-1.5%, and that of the ferrite phase to within 0.5-2%.[30] The A/F ratio in the ferrite phase can be determined by X-ray diffraction from the change in the spacing of a selected diffraction line.

1.9 Summary and concluding remarks

Portland cement is a hydraulic cement produced by clinkering a mixture of raw materials containing lime (CaO), silica (SiO_2), alumina ($A\ell_2O_3$), and iron oxide (Fe_2O_3). The four major constituents of the cement are essentially tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and a ferrite phase close in composition to C_4AF. In the cement all four occur as impure forms containing a few per cent of various impurities in solid solution. The C_3S in the cement is known as alite, the C_2S as belite and the ferrite phase as celite. The compound composition of Portland cement varies and depends on the type in question (see Chapter 7). The average content of the alite in ordinary Portland cement is about 45%, of the belite 25%, of the tricalcium aluminate 12%, and of the celite 8%. Their combined total content is approximately 90% and, accordingly, they are referred to as 'major compounds' or 'major constituents'. The remaining 10% is the 'minor constituents', gypsum (about 5%), the alkali oxides Na_2O and K_2O (1%), and magnesia (2%). The properties of the four major compounds are summarised in Table 1.4.

A few methods for determining the cement compound composition exist. None of these is entirely free from error. At present it is generally accepted that the microscopic 'point counting' method is preferable for determining the silicates content[31] whereas X-ray diffractometry is preferable for determining tricalcium aluminate, the ferrite phase, the free lime, and the magnesia contents.[32,33] Apparently, best results are obtainable with the 'combined method' which combines chemical analysis and X-ray diffractometry. For engineering purposes, however, the Bogue method is quite satisfactory. Indeed, this method is used almost exclusively in engineering applications while the others are used mainly for scientific purposes.

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2 Setting and hardening

2.1 Introduction

Mixing cement with water produces a plastic workable paste. For some time these characteristics of the paste remain virtually unchanged, and this period of time is known as the 'dormant period'. At a certain stage, however, the paste begins to stiffen to such a degree that, although still soft, it becomes unworkable. This is known as the 'initial set' and the time required for the paste to reach this stage as the 'initial setting time'. The 'setting' period follows, in which the paste continues to stiffen until a stage is reached when it may be regarded as a rigid solid. This is known as the 'final set' and the time required for the paste to reach this stage as the 'final setting time'. The resulting solid is known as the 'hardened cement paste' or, sometimes, as the 'cement stone'. With time the hardened paste continues to harden and gain strength, a process known as 'hardening'. The various stages of setting and hardening are shown in Figure 2.1.

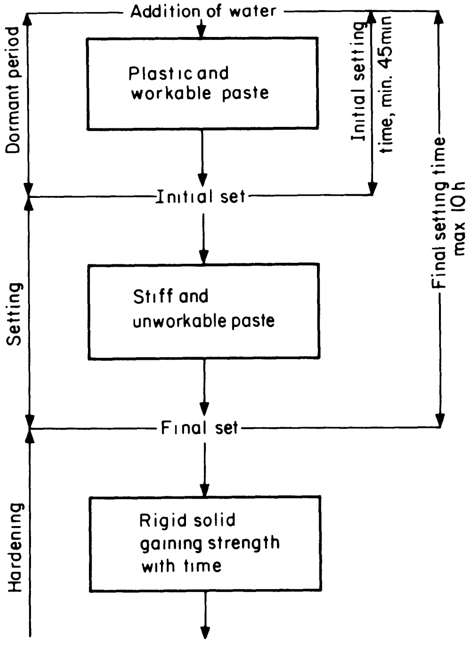

Figure 2.1 *Schematic description of setting and hardening of a cement paste*

The initial and final setting times are of practical importance. The initial setting time determines the length of time in which cement mixes (concrete) remain plastic and workable, i.e. the length of time during which practical use can be made of such mixes. Accordingly, a minimum of 45 minutes is specified in most standards for ordinary Portland cement (BS 12, ASTM C150, DIN 1164). The final setting time, on the other hand, should not be too long in order to allow construction work to continue within a reasonable time after casting the concrete. Accordingly, a maximum of 10 hours is specified in BS 12, and eight hours in ASTM C150.

The initial and final setting times are determined, almost universally (BS 12, ASTM C191, DIN 1164) by the apparatus known as the Vicat needle which measures the resistance of a paste of a standard consistence to the penetration of a needle under a total load of 300 g (Figure 2.2).

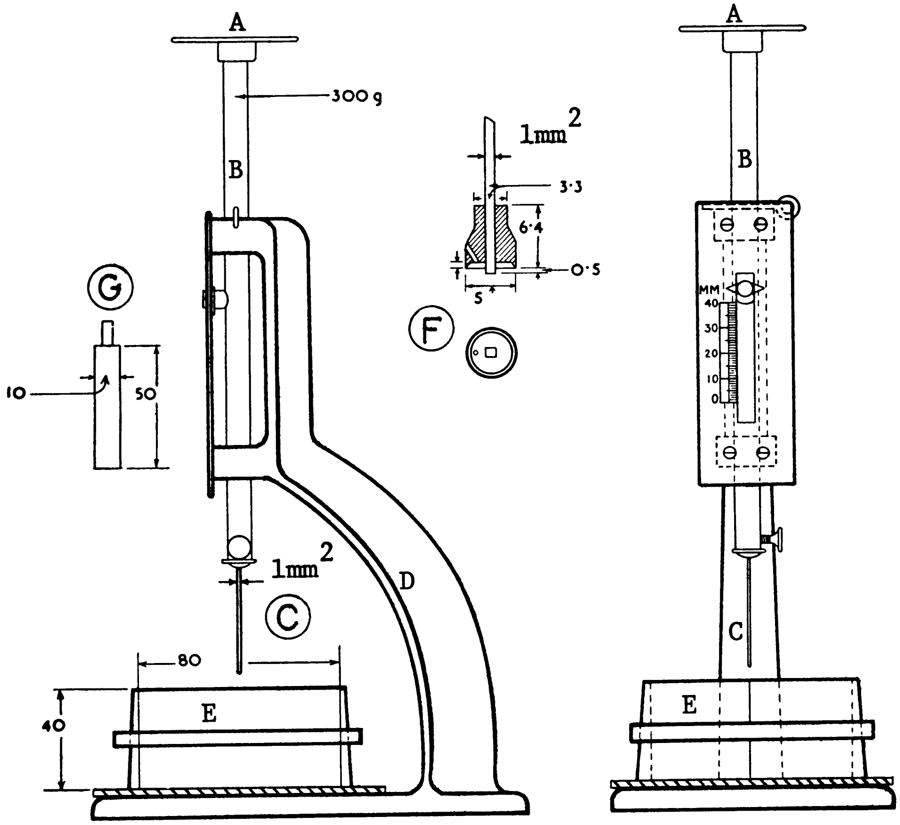

Figure 2.2 *Vicat apparatus for determining the standard consistence and setting times of Portland cement in accordance with BS 12 1971 (dimensions in* mm)

The standard consistence is determined by means of needle G, which is 10 mm in diameter. The paste is placed in the round mould E, and the needle is brought gently into contact with the surface of the paste. The needle is then released, and the depth of its penetration into the paste is measured on the scale. A paste into which the needle penetrates to a depth of 5 to 7 mm from the bottom of the mould is defined as a paste of 'standard consistence'. The amount of water required to produce a standard consistence varies and depends on the specific properties of the cement, particularly its fineness. However, a value of 25-26% of the cement weight may be considered as usual.

The initial set is determined by needle C, which has a cross sectional area of 1 mm^2. Again, the needle is released after being brought into contact with the surface of the paste. This process is repeated until the needle does not penetrate beyond about 5 mm from the bottom of the mould. The period between the addition of water to the anhydrous cement and the time at which the needle ceases to penetrate the paste beyond 5 mm, is defined as the 'initial setting time'.

Final setting time is determined with the aid of needle F. This needle, which is 1 mm^2 in cross section, projects $\frac{1}{2}$ mm from the centre of a circular cutting edge 5 mm in diameter. When the paste is soft, both the needle and the cutting edge make impressions on the surface when released; the 'final set' is said to be attained when only the needle makes such an impression. The period between the time the water was added to the cement and the time the final set is attained is defined as the 'final setting time'.

2.2 Hydration of the cement[1-5]

Setting and hardening are brought about by the hydration of the cement constituents. The physical aspects of this process are dealt with later in the text; the following is limited to a discussion of the chemical reactions involved in the hydration process, and of the nature of the hydration products.

Generally speaking, the hydration of the cement may involve either a 'through solution' mechanism or direct topochemical (solid state) reactions. In the first mechanism the reactants dissolve to produce ions in solution. The ions then combine and the resulting products precipitate out. In cement, due to the low solubility of its constituents, hydrolysis rather than dissolution is considered to be significant.

In the second mechanism the reactions take place directly at the surface of the solid without the cement constituents going into solution. Hence, reference is made to topochemical or solid-state reactions. In the hydration of cement both mechanisms are probably involved. It seems that the through-solution mechanism predominates in the early stages of hydration whereas the second mechanism operates during the later stages.

As cement is made up of several compounds, its hydration involves a number of chemical reactions which take place simultaneously. The products produced by hydration of the individual compounds are, in many cases but not always, similar to those resulting from their hydration as part of the cement. It is convenient, therefore, to consider first the hydration of the individual compounds and then the hydration of the cement as a whole.

2.2.1 Calcium silicates (C_2S and C_3S)

In water the calcium silicates undergo hydrolysis, the products being calcium hydroxide and a less basic calcium silicate hydrate, i.e. a hydrate in which the C/S ratio is lower than in the anhydrous silicate. It is generally assumed that on complete hydration, a hydrate, having the approximate composition $C_3S_2H_3$ is formed; the reactions may be approximately represented by the following equations:

for tricalcium silicate,

$$2(3CaO{\cdot}SiO_2) + 6H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + 3Ca(OH)_2$$

and for the dicalcium silicate,

$$2(2CaO{\cdot}SiO_2) + 4H_2O \rightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + Ca(OH)_2$$

The resulting hydrate is poorly crystallised and produces a porous solid which may be defined as a rigid gel. This gel is sometimes referred to as 'tobermorite gel' after a naturally occurring mineral of seemingly similar structure. However, the use of this name has been strongly criticised[6,7] because the similarity in structure is rather weak and not always clear. Moreover, the chemical composition of the calcium silicate hydrates varies and depends on age, temperature, and water/solid ratio. It is preferable, therefore, to refer to these hydrates more generally as 'calcium silicate hydrate' (CSH), i.e. a name which does not imply any particular composition or structure. More specific forms of CSH are denoted CSH(I) and CSH(II). The first is poorly-crystalline foils or platelets which have a C/S molar ratio of 0.8-1.5. The second has a fibrous structure with a C/S molar ratio of 1.5-2.0

The hydration of the alite and the belite in the cement is essentially similar to the hydration of pure C_3S and C_2S. At the very early stage $C_3S{\cdot}aq$ and $C_2S{\cdot}aq$ are formed changing, within a few hours, to less basic hydrates having the C/S molar ratio of approximately 1.5. The ratio increases with time reaching 1.8, and sometimes 2-3,[7] depending on the type of the cement involved, the hydration temperature, and the water/cement ratio. The presence of impurities in the alite and the belite affects the composition and properties of their hydration products. Nevertheless, it may be generally assumed that their hydration products are a CSH gel of average composition $C_3S_2H_3$ and $Ca(OH)_2$. The alite and belite make up approximately 70% of the cement, so the set cement will consist mainly of their hydration products and its properties will be determined accordingly.

The presence of $Ca(OH)_2$ makes cement pastes highly alkaline (pH 12.5 and this explains why such pastes are very sensitive to acid attack and why they provide good protection to embedded steel against corrosion.* The latter property is valuable in the use of steel as reinforcement for concrete, and therefore, very important from an engineering point of view.

It follows from the hydration equations that the $Ca(OH)_2$ produced amounts to 40% and 18% of the total hydration products of the C_3S and C_2S, respectively. In other words, the hydration products of C_3S are richer in $Ca(OH)_2$ than those of C_2S. This difference in the amount of $Ca(OH)_2$ produced affects the specific surface area of the hydration products, and is reflected later in the discussion on selective hydration. From the same equations it may be noted that on hydration the C_3S and C_2S combine with 24% and 21% water, respectively.

2.2.2 Tricalcium aluminate (C_3A)

In the presence of an excess of water, the hydration of C_3A produces hexagonal plate crystals consisting essentially of the hydrates C_4AH_{19} and C_2AH_8. These hydrates are metastable and with time transform into a less soluble and more stable hydrate of the composition C_3AH_6 which belongs to the cubic crystal system. C_3AH_6 is formed directly at room temperatures in pastes with a low water/solid ratio. Under such conditions, owing to the considerable heat evolution (Table 1.4), the temperature of the paste rises further favouring the formation of C_3AH_6.

In cement, C_3A hydrates differently because of the presence of gypsum. It is now generally accepted that the immediate reaction between C_3A and gypsum results in needle-like crystals of a high-sulphate calcium sulphoaluminate known as ettringite ($3CaO\cdot A\ell_2O_3\cdot 3CaSO_4\cdot 31H_2O$). The ettringite continues to form, provided that sufficient sulphate ions are present in the solution, i.e. generally during the first 24 hours after the addition of water to the cement. When the sulphate ions have been removed, further hydration of C_3A results in the conversion of ettringite into a low-sulphate sulphoaluminate ($3CaO\cdot A\ell_2O_3\cdot CaSO_4\cdot 12H_2O$) sometimes referred to as monosulphate, or into hexagonal plate solid solution of $C_4A\bar{S}H_{12}$ and C_4AH_{13}. The limiting composition of the solid solution being reached, the remaining C_3A hydrates to produce C_4AH_{19}. Depending on temperature, the C_4AH_{19} may convert to cubic C_3AH_6 or, by taking up silica, to a hydrogarnet.†

As a simple approximation, the final hydration product of C_3A may be assumed to be the stable hydrate C_3AH_6 and the reaction may be represented by the following equation:

$$3CaO\cdot A\ell_2O_3 + 6H_2O \rightarrow 3CaO\cdot A\ell_2O_3\cdot 6H_2O$$

---

*Environments in which the pH exceeds 11 protect steel against corrosion.

†Garnets are a group of minerals which crystallise in the cubic system.

Gypsum is added to the cement in order to delay its setting. The tricalcium aluminate reacts with water almost instantaneously and, in the absence of gypsum, may cause rapid setting of the cement as a whole. The delaying effect of gypsum is attributed to the formation of an ettringite layer on the surface of the tricalcium aluminate grains. This layer retards further hydration of the C_3A and causes the setting of the cement to be mainly dependent on the hydration of the calcium silicates. The ettringite layer, however, does not completely prevent hydration of the tricalcium aluminate. With time, as a result of a diffusion process, ettringite is formed directly on the surface of the C_3A grains. The formation of ettringite involves expansion forces which result from the

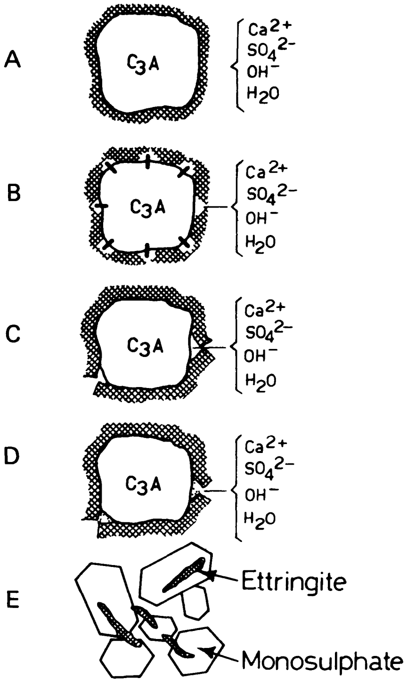

Figure 2.3 Schematic description of retarded setting caused by sulphates (after Stein[8] *and Schwiete, et al.*[9]*).* A *First stage: a thin layer of ettringite is formed on the* C_3A *grains;* B *second stage: formation of ettringite directly on the* C_3A *grains produces crystallisation pressure;* C *third stage: bursting of the ettringite layer caused by the pressure of crystallisation;* D *fourth stage: burst section is sealed by newly formed ettringite;* E *fifth stage: insufficient sulphate ions to allow formation of ettringite; on further hydration of the* C_3A*, ettringite converts to monosulphate.*

increase in the volume of the solids. The expansion forces cause the ettringite layer to burst and the hydration of C_3A to be resumed. The burst section, however, is subsequently sealed by newly formed ettringite and the hydration is retarded again. The process is repeated until insufficient sulphate ions are available in the solution for the formation of ettringite, and further hydration of the C_3A results in the conversion of the ettringite into monosulphate. A schematic description of this retarding effect is presented in Figure 2.3.

2.2.3 Ferrite phase

Apparently in the early stages the ferrite phase reacts with gypsum and $Ca(OH)_2$ to produce needle-like crystals of a solid solution consisting of high-sulphate sulphoaluminate and sulphoferrite. Assuming the composition of the ferrite phase to be C_4AF, the hydration reaction may be represented by the following equation:

$$4CaO \cdot A\ell_2O_3 \cdot Fe_2O_3 + CaSO_4 \cdot 2H_2O + Ca(OH)_2 \rightarrow$$
$$3CaO(A\ell_2O_3, Fe_2O_3) \cdot 3CaSO_4 \cdot aq$$

In a similar way as happened with ettringite, the resulting solid solution converts, when sulphate ions are exhausted, into a low-sulphate aluminoferrite solid solution $3CaO(A\ell_2O_3, Fe_2O_3) \cdot CaSO_4 \cdot aq$ and/or into a solid solution phase in which sulphate ions are replaced by hydroxide ions, i.e. $3CaO(A\ell_2O_3, Fe_2O_3) \cdot Ca(SO_4, (OH)_2) \cdot aq$.

2.3 Development of structure in cement paste

As a result of the hydrolysis of the calcium silicates, a super-saturated solution of $Ca(OH)_2$ is formed when water is added to the cement. Sulphate and alkali metal ions, as well as small amounts of silica, alumina, and ferric oxide, are also present in the solution. $Ca(OH)_2$ and ettringite precipitate out and a dense CSH gel coating is formed on the cement grains. This coating, and the ettringite coating on the C_3A grains (Figure 2.3), retards further hydration and explains the existence of a 'dormant period', i.e. a period of relative inactivity lasting 1-2 hours, during which the paste remains plastic and workable.

The end of the dormant period and the initial set (Figure 2.1) are attributable to the break up of the CSH coating and the resulting continuation of the hydration process. According to Powers,[10] the force causing break up of the coating is an osmotic pressure brought about by the difference between the ion concentration in the solution at the gel-cement interface and that in the solution outside the coating. According to Kalousek[3] the coating disintegrates simply because of the decomposition of the unstable hydrate. In any case, the rupture or the disintegration of the gel coating exposes the cement grains, hydration is resumed and setting takes place.

The volume of the hydration products is more than twice that of the anhydrous cement. Consequently, as the hydration proceeds, the hydration products gradually fill in the spaces between the cement grains. Points of contact are formed causing stiffening of the paste. At some later stage, the concentration of hydration products and the resulting concentration of points of contact, restrict the mobility of the cement grains to such an extent that the paste becomes rigid, i.e. final set is attained.

A schematic diagram representing the hydration process, and the resulting formation of the paste structure, is shown in Figure 2.4.[11] The cement grains are shown in this figure by the shaded areas, the $Ca(OH)_2$ crystals by the hexa-

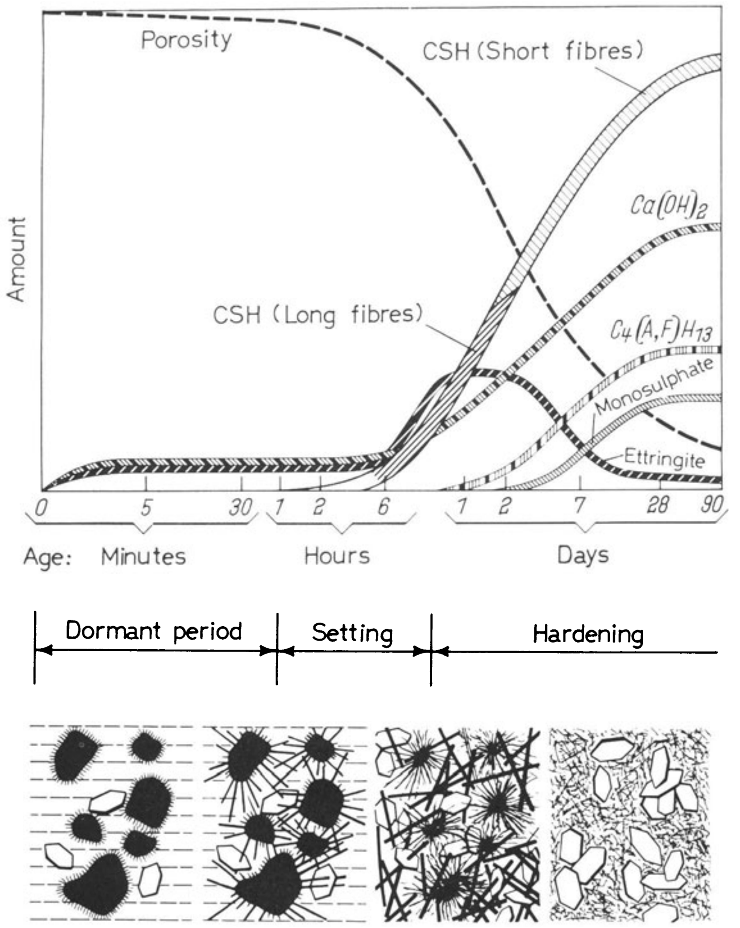

Figure 2.4 Schematic description of the hydration and structure development in cement paste (after Locher and Richartz[11])

gonal shapes, the ettringite needles by the heavy short lines and the CSH particles by the thin short ones. It can be seen that during the dormant period the cement grains are separate and the hydration products are mainly $Ca(OH)_2$ and ettringite After an hour, CSH gel begins to form, with its particles having the shape of long fibres. Intergrowing causes stiffening while the increase in the volume of the solids decreases the porosity of the paste (see dotted curve at the top of Figure 2.4).

After 24 hours the sulphate ions are depleted, alumina and iron oxide containing phases such as $4CaO(A\ell_2O_3, Fe_2O_3)\cdot aq$ begin to form, and the ettringite is converted into monosulphate. The calcium silicates continue to hydrate giving, at this later stage, CSH particles having the shape of short fibres. Again, the hydration products continue to fill pores, and the porosity of the set paste is decreased further.

The preceding description is, of course, schematic. A more detailed discussion of the structure of the set paste, including the nature of the inter-particle bond, is given later.

2.4 Factors affecting the rate of hydration

The rate of hydration of Portland cement depends on many factors, and the properties of hardened paste depend, to an appreciable extent, on its degree of hydration. Consequently, all the factors which affect the rate of hydration, necessarily affect the properties of the paste. The relation between degree of hydration and paste properties is discussed later. The following discussion is limited to those factors which affect the rate of hydration only.

2.4.1 Age of paste

With the exception of the dormant period, the rate of hydration is maximum at early ages. The rate decreases with time until a stage is reached when virtually no further hydration takes place (Figure 2.5). Hydration is conditional, of course,

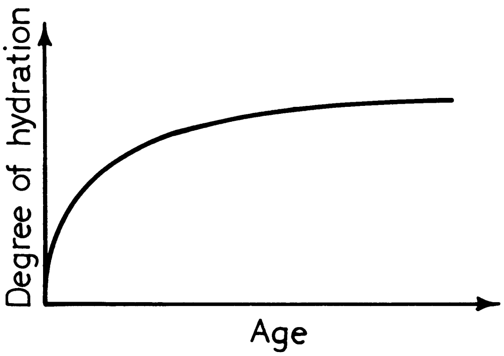

Figure 2.5 *Degree of hydration plotted against age of a cement paste*

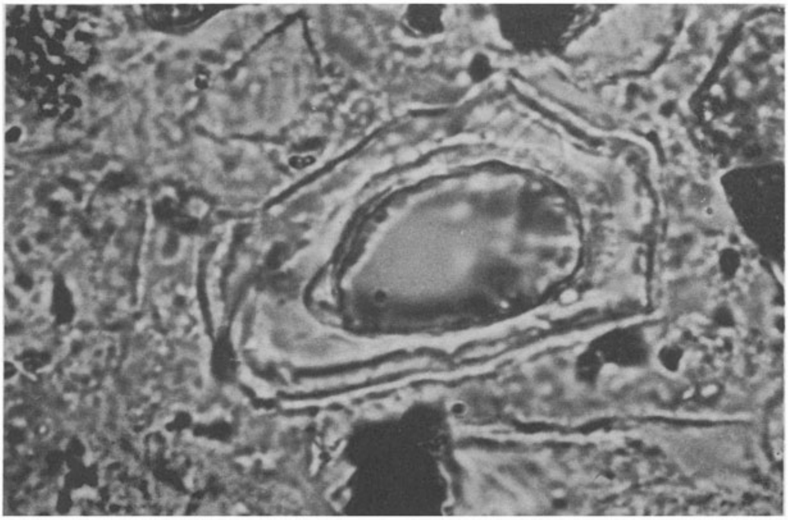

Figure 2.6 *Thin section of Portland cement paste seen under an optical microscope showing reaction rim on* C_3S *grain* (*courtesy of K. Pettifer, Building Research Station, Garston, UK*)

on the presence of water. Nevertheless, even when sufficient water is present (i.e. with paste immersed in water), hydration stops after a time, although an appreciable amount of unhydrated cement is left in the paste, an amount which may exceed 50% of the original weight of the anydrous cement. The decrease in the hydration rate may be attributed to the formation of a dense layer of CSH gel around the cement grains (Figure 2.6). In the presence of such a layer, further hydration involves the diffusion of water through the layer. The rate of diffusion is controlled by, among other factors, the thickness of the layer; the greater the thickness, the slower the diffusion rate. Moreover, it is to be expected that, at a certain thickness, diffusion and the resulting hydration will stop completely. Theoretical calculations indicate that hydration is expected to stop when the thickness of the layer reaches 25 μm.[12] Accordingly, an unhydrated core is always left inside cement grains which have a diameter greater than 50 μm. Various measurements have indicated that the depth of hydration may be even lower. In one case it was found to be 6-9 μm at an age of five months,[13,14] and in another, only 8 μm at an age of one year.[14] This small depth of hydration partly explains the restriction imposed on the coarseness of cement by the relevant standards. These standards usually specify a minimum specific surface area, thereby reducing the amount of the cement which is liable to be left unhydrated. The size of the cement grains in ordinary Portland cement ranges from 5 to 55 μm.

2.4.2 Cement composition

The rate of hydration of the individual cement constituents varies considerably (Table 1.4). C_3A, for example, reacts with water almost instantaneously and most of its hydration takes place within 24 hours. C_2S, on the other hand, reacts with water rather slowly and its hydration continues for weeks or months. In the early stages the rate of hydration of the compounds in the cement is essentially the same as the rate for the separate compounds. This conclusion may be drawn from Figure 2.7 which shows the hydration with time of the compounds in a particular Portland cement.[15] It can be seen that after 24 hours approximately 65% of the C_3A is hydrated as compared to only 15% of the C_2S. It may be concluded, therefore, that during this early stage the hydration is selective, i.e. the degree of hydration of the cement is determined by the rate of hydration of the individual compounds. Such a selective hydration is to be expected because, at this stage, the water is virtually in direct contact with all of the cement constituents. Consequently, each of the constituents hydrates independently of the others at its characteristic rate. At later stages, however, a layer of CSH gel is formed around the cement grains. As the thickness of this layer increases, the rate of hydration becomes increasingly dependent on the rate of water diffusion through the layer and less on the rates of hydration of the individual compounds.

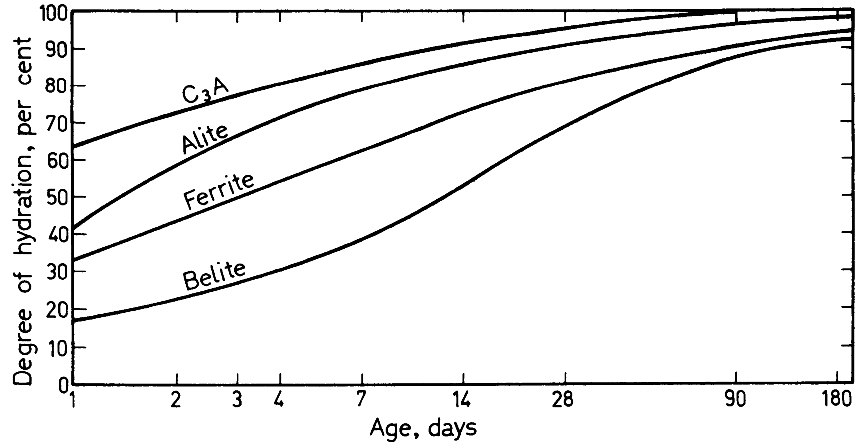

Figure 2.7 Rates of hydration of the various compounds in a Portland cement[15]

Under such conditions, it may be expected that hydration will penetrate the cement grains at an equal rate, implying, in turn, that all of the cement constituents will hydrate at an equal fractional rate, i.e. when a cement is, say, 50% hydrated, each one of its constituents is also 50% hydrated.

Hydration at equal fractional rates was first indicated by the work of Powers and Brownyard,[16] in which the relation between gel specific surface area and the degree of cement hydration was found to be linear (Figure 3.8). Such a relation, however, is not to be expected if the hydration of the cement is selective. Hydration of C_3S and C_2S produces the same hydration products. The hydration of C_3S, however, produces a greater amount of $Ca(OH)_2$ than that of C_2S. The $Ca(OH)_2$ crystals are large enough to be easily visible through an optical microscope whereas the gel particles are of colloid dimensions. In other words, the specific surface area of the hydration products is determined by their gel content. The hydration of C_2S produces less $Ca(OH)_2$ than that of C_3S, hence the specific surface area of its hydration products is larger than that of the C_3S products. Assuming selective hydration, and noting that the rate of hydration of C_3S is significantly greater than that of C_2S, the ratio between the gel specific surface area and the degree of hydration must increase with time, i.e. with increased amount of hydrated C_2S. That the ratio remains virtually unchanged implies, therefore, hydration at equal fractional rates.

The preceding conclusion is partly supported by experimental data relating the heat of hydration of a cement to its degree of hydration.[17] As the heat of hydration of the individual cement constituents varies (Table 1.4), a non-linear relation is to be expected between the two parameters if selective hydration takes place. In some cements, however (types I and III in ASTM C150), but not necessarily in others (types II and IV), a linear relation has been established between the heat evolved and the degree of hydration implying that hydration proceeds at equal fractional rates. In this context, it may be noted (from Figure 2.7) that after a few days the curves become more or less parallel supporting the same conclusion. Accordingly, it seems that selective hydration is limited to the early stages, and that at later stages the hydration proceeds at equal fractional rates. In turn, this implies that at later stages the composition of the paste remains essentially the same.

2.4.3 Fineness of the cement

The rate of hydration increases with fineness of the cement. The more fine the particles, the greater the surface area of the cement which is exposed to water and, consequently, the higher the rate of hydration, particularly at early ages. This effect of fineness is made use of in the production of rapid-hardening Portland cement (see Chapter 7).

*2.4.4 Water/cement ratio**

Experimental data relating the degree of hydration to the *W/C* ratio are presented in Figure 2.8.[18] The degree of hydration in the figure is given as the ratio of weight of chemically combined water to weight of anhydrous cement. Such a presentation assumes that the composition of the cement paste remains unchanged throughout the hydration. This is probably not correct at early ages when the hydration is selective. At later ages, however, when hydration at equal

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*The water/cement ratio (*W/C*) is defined as the weight ratio of mixing water to cement.

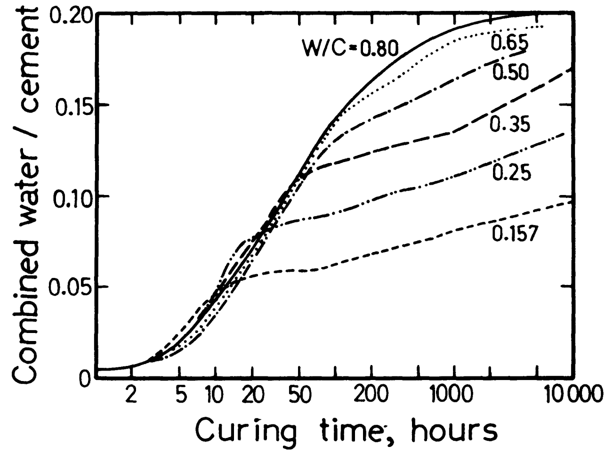

Figure 2.8 *Effect of W/C ratio on the hydration of Portland cement (after Taplin*[18]*)*

fractional rates becomes operative, such an assumption can be made, and indeed, is made by various authorities.

From Figure 2.8 it may be seen that initially the *W/C* ratio does not significantly affect the rate of hydration, and the different curves almost coincide. Later, however, the rate of hydration decreases, and this decrease takes place earlier the lower is the *W/C* ratio. Consequently, the lower the *W/C* ratio, the lower the degree of hydration and the average rate of hydration. This effect of the *W/C* ratio may be attributed to the decrease in the space available for the hydration products at lower *W/C* ratios.

2.4.5 Temperature

The rate of hydration increases with temperature, provided that the rise in temperature does not cause drying of the paste. Such drying slows down hydration and may stop it completely in extreme cases. The following discussion is limited to conditions where drying-out is eliminated by immersion of the paste in hot water or by exposure of it to hot water vapour.*

The expected acceleration in the hydration rate with temperature is demonstrated in Figures 2.9 and 2.10.[19,20] It can be seen, however, that this effect occurs mainly at early ages. Ultimately the same degree of hydration is reached whatever the curing temperature (Figure 2.10). In other words, temperature

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*The exposure of cement products to warm water vapour is often used in concrete technology to accelerate hardening. When such treatment is carried out at atmospheric pressure the vapour temperature cannot exceed 100°C. This form of treatment is known as 'steam curing at atmospheric pressure'. Curing at higher temperatures must be carried out under pressure in autoclaves and is known, accordingly, as 'steam curing under pressure' (see Chapters 10 and 11).

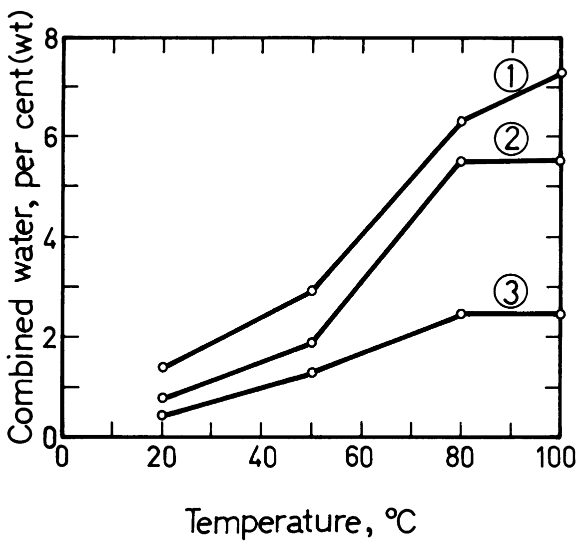

Figure 2.9 *Effect of temperature on the degree of hydration at an age of three hours (after Odler and Gebauer[19]). 1, Portland cement produced in a rotary kiln; 2, Portland cement produced in a vertical kiln; 3, Portland blast furnace slag cement*

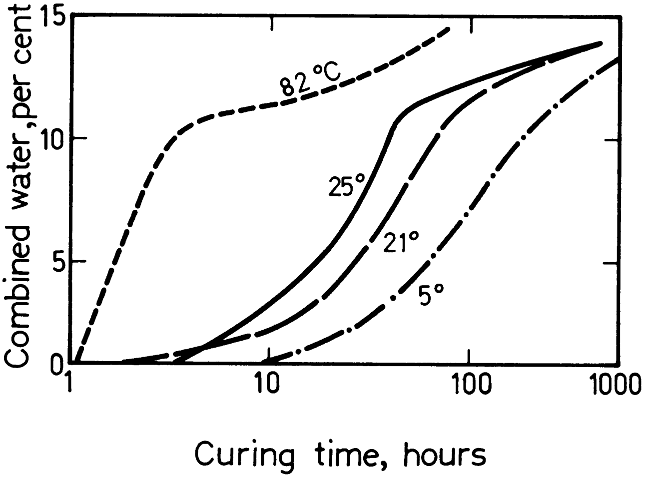

Figure 2.10 *Effect of temperature on the degree of hydration as a function of curing time (after Taplin[20])*

affects the rate of hydration but not the final amount. The degree of hydration is controlled by the density and thickness of the CSH layer which encapsulates the cement grains. This layer retards hydration and when it attains a certain thickness, it prevents hydration from taking place altogether. The fact that the ultimate degree of hydration is independent of temperature, implies that temperature does not affect the thickness or density of the CSH gel layer. Other opinions about this have been expressed and these are discussed in Chapter 4.

2.4.6 Admixtures

It was mentioned earlier that gypsum retards the setting of cement. Some other materials exist which retard the setting of cement and others which accelerate it. These are known as 'retarders' and 'accelerators', respectively. The effect of retarders and accelerators is not limited to setting times and, in most cases, the cement rate of hydration is also affected, i.e. the retarders and accelerators generally decrease and increase the rate of hydration, respectively.

Calcium chloride ($CaC\ell_2$) is probably the most common accelerator. Sodium chloride ($NaC\ell$) is another accelerator, but its use is rather limited. Most common retarders are based on sugars or on soluble salts of zinc. Sugar is of special interest because even very small additions may inhibit setting completely. Another group of retarders includes the lignosulphonic acids and their salts and yet another group includes the hydroxylated carboxylic acids and their salts. The latter may be used to decrease the amount of water required to obtain a cement mix of a given consistence and, accordingly, they are also known as 'water reducing agents'.

Retarders and accelerators generally work through their effect on the hydration of the C_3A of the cement. As discussed earlier, the rapid setting of cement which contains no gypsum is a result of the almost instantaneous setting of C_3A. In such a cement the alumina passes into solution and combines with silica to give a gel, poor in lime, which stiffens the mix. In the presence of gypsum ettringite is formed and coats the C_3A grains. The formation of this coating retards the hydration of C_3A (Figure 2.3), and setting is delayed until the calcium silicates start to hydrate.

Similarly, setting may be delayed by reducing the solubility of the alumina.[22] Such a reduction will limit the formation of the lime-poor gel, and thereby delay setting even when the cement does not contain gypsum. Lime, for example, retards the setting of such cements provided the cements are low in alkali oxides. In solutions of low alkali concentration, the solubility of the lime increases and in solutions of high lime concentration the solubility of the alumina decreases. On the other hand, in solutions of high alkali concentration, the solubility of the lime decreases and that of the alumina, therefore, increases. Hence, in cements rich in alkali oxides the lime does not retard setting.[21]

Some admixtures may act as both retarders and accelerators. The addition of $CaC\ell_2$ to the cement results in the formation of a double sulphoaluminate salt. In concentrations lower than 1%, the presence of $CaC\ell_2$ does not affect the solubility of the alumina which remains low. Hence, in small amounts $CaC\ell_2$ acts as a retarder. At higher concentrations, the solubility of the alumina is increased and $CaC\ell_2$ acts, therefore, as an accelerator.[23] That is, the accelerating effect due to the increased solubility outweighs the retarding effect brought about by the precipitation of the double salt.

With organic retarders, such as calcium lignosulphonate, an adsorption theory has been suggested to describe the mechanism involved.[24] According to this theory, molecules of the retarder are adsorbed onto the surface of the cement grains and form a layer which retards hydration.

Finally, fillers (i.e. finely powdered minerals) may have an accelerating effect on cement hydration by acting as crystallisation nuclei (seeds). Generally speaking, the structure of such fillers should be the same as that of the crystallising phase, or closely resemble it, so that epitaxial growth can occur.* Ground limestone and dolomite are such fillers.[25]

2.5 Summary and concluding remarks

On addition of water the cement constituents hydrate giving mainly hydrates of calcium silicate (CSH gel) and calcium hydroxide, with the remaining products being aluminates and ferrites. The hydration involves increase in the volume of the solids bringing about the stiffening of the water–cement system (i.e. of the cement paste), and its subsequent hardening. Further hydration decreases the porosity of the hardened paste, and thereby its strength is increased. The stiffening of the paste and its subsequent solidification is known as 'setting', and the gain in strength of the set paste with time as 'hardening'.

The following factors affect the rate of the cement hydration.

1. *Age* The hydration rate is a maximum at early ages, gradually decreasing with time until, at a certain stage, it stops completely.
2. *Cement composition* Selective hydration, which depends on the hydration rate of the individual compounds, takes place only at early stages. Indeed, during these stages, the rate of hydration is greater in cements rich in C_3S and C_3A. At later stages, however, the hydration proceeds at equal fractional rates regardless of the hydration rates of the individual compounds.
3. *Cement fineness* The hydration rate of the cement increases with its fineness, particularly at early ages. The ultimate degree of hydration is not affected, however, by the fineness of the cement.
4. *Water/cement ratio* At early ages the W/C ratio hardly affects the rate of hydration. The lower the W/C ratio, however, the sooner the rate of hydration begins to decrease. Consequently, the average rate of hydration, and the ultimate degree of hydration, both decrease with decrease in the W/C ratio.

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*Epitaxial or oriented growth is the growing of crystals of one material in a particular orientation on the face of a crystal of another material.

5. *Temperature* The rate of hydration increases with temperature, particularly at early ages. However, the ultimate degree of hydration is apparently not affected by curing temperature.
6. *Admixtures* Admixtures based on sugars and lignosulphonic acid and its salts, retard hydration; others, such as $CaC\ell_2$, accelerate hydration. These additives are known as 'retarders' and 'accelerators' respectively.

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3 Structure of the hardened paste

3.1 Introduction

Microscopic examination of the hardened cement paste reveals the CSH gel to be an undifferentiated amorphous mass in which unhydrated cement grains, hexagonal crystals of calcium hydroxide, and occasionally small numbers of hexagonal or cubic crystals of aluminate and of sulphoaluminate are embedded. Pores, either filled with water or empty, are also detectable in the mass. As already mentioned, this amorphous mass is a rigid gel, i.e. a solid made up of small particles of colloidal dimensions. The particles are mainly hydrates of calcium silicate with some aluminates and ferrites. The hydrates of the calcium silicate are poorly crystallised and their structure is characterised by a high degree of disorder. Accordingly, these hydrates are sometimes described as 'crystallites' or 'quasi-crystallites'.[1,2]

The properties of the hardened paste are primarily determined by its structure rather than by its exact chemical composition. A few models have been suggested to describe the structure of the hardened paste and to explain its behaviour. In developing these models, sorption studies have played an important role. Hence, the subject of sorption, including sorption isotherms, is discussed before the description of the models.

3.2 Adsorption isotherms and the BET method

The term 'adsorption' is used to describe a state in which there exists, on a surface of a liquid or a solid, an average molecular concentration of any material higher than the molecular concentration of the same material in a free state at the same pressure and temperature. Cement studies are generally limited to adsorption of gases or water vapour. Hence, the following discussion is limited to the adsorption of gases on solids.

All gases below their critical temperature (i.e. vapours) tend to be adsorbed as the result of physical interaction between the molecules of the gas and the molecules in the surface of the solid. This type of adsorption is known as physical adsorption or van der Waals' adsorption because the forces involved in the process are collectively known as van der Waals' forces. The physical adsorption is non-specific and reversible, i.e. desorption occurs on lowering of the vapour pressure or increasing the temperature. Chemical adsorption (sometimes chemisorption), on the other hand, is specific and occurs only between certain combinations of materials. The energy involved in chemical adsorption is large enough to suggest that full chemical bonding occurs. Consequently, a gas that is chemically adsorbed may be difficult to remove, and desorption may be accompanied by chemical changes. In cement, only physical adsorption is usually involved and, therefore, only this type of adsorption is further considered.

The amount of adsorbed gas increases with the increase in vapour pressure and decrease in temperature. However, the thickness of the adsorbed layer does not exceed a few molecules and the amount of the adsorbed gas is very minute indeed. Consequently, in solids with a small specific surface area it is impossible to measure the amount of adsorbed gas. In solids of very high specific surface area, however, like the CSH gel, the amount is high enough to be measured. Accordingly, in sorption studies, the relationship between the amount of gas adsorbed and its relative vapour pressure is determined at constant temperature. The resulting curve is known as an adsorption isotherm. Adsorption isotherms may be of different forms. The one which characterises the hardened cement paste, sometimes known as an 'S' isotherm, is described schematically in Figure 3.1.

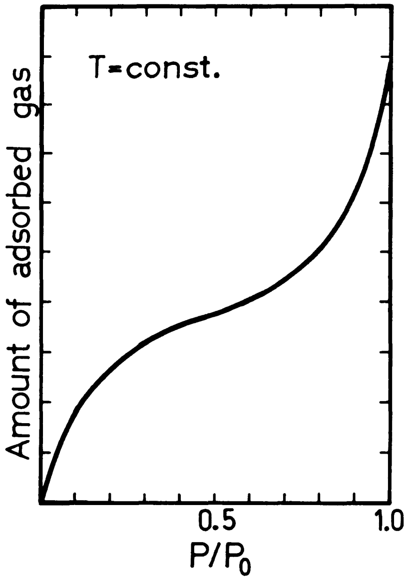

Figure 3.1 *Adsorption isotherm for hardened cement paste* (P_0 *is the saturation vapour pressure*)

The amount of adsorbed vapour is clearly related to the specific surface area of the solid. In the study of hardened paste, the latter is usually determined by the BET method, named after Brunauer, Emmett, and Teller who developed this method in 1938.[3] A detailed description of this method and its mathematical representation are outside the scope of the present discussion. The resulting equation, however, gives the following relation between the volume, V, of the adsorbed gas and the vapour pressure, P:

$$\frac{P}{(P_0 - P)V} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \times \frac{P}{P_0},$$

where V_m is the volume of the adsorbed gas when the entire surface of the adsorbent is covered with a complete mono-molecular layer, and C is a constant which depends on the specific test conditions.

It can be seen that plotting $P/(P_0 - P)V$ against P/P_0 should result in a straight line of slope $(C - 1)/V_m C$, and intercept $1/V_m C$ (Figure 3.2). This plot can be established from adsorption experiments in which the volume of the adsorbed gas, V, is determined at different vapour pressures P/P_0. With the slope and intercept known, V_m can be determined, and the total area of the adsorbent, A, can be calculated from the equation:

$$A = \frac{V_m}{V_0} N\sigma_0,$$

where V_0 is the volume of one gram-mole of the adsorbed gas at STP (i.e. 24 400 cm^3), N is Avogadro's number (i.e. 6.023×10^{23} mol^{-1}), and σ_0 is the area covered by a single molecule of the adsorbed gas. The specific surface area of the solid is then determined by dividing the total area, A, by the weight of the sample studied.

The BET equation is only valid within the pressure range $P/P_0 = 0.05$-0.30, but this limitation may be overcome by the use of modified equations. The

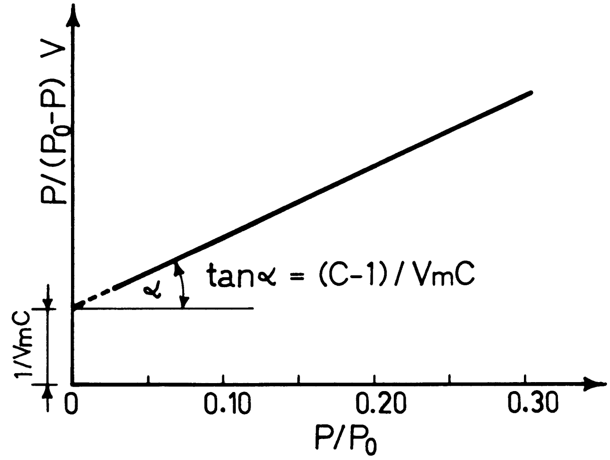

Figure 3.2 *Graphical representation of the BET equation*[3] study of the hardened paste, however, is usually limited to a pressure range where the BET equation may be considered valid. Hence, a discussion of the modified equations is not presented here.

3.3 Powers' model

Adsorption isotherms for hardened cement pastes have been determined in many studies, but the use of such isotherms in studying the microstructure of the paste was not extensive until they were first successfully employed by Powers and Brownyard at the Laboratories of the Portland Cement Association (PCA), Chicago. Their work produced a considerable body of data[9] which later formed the basis of the model proposed by Powers to describe the microstructure of the hardened cement paste, and to explain its properties and behaviour.[4–6] A schematic description of the model is presented in Figure 3.3.

According to Powers' model the cement gel is a rigid substance made up of colloid-size particles, and has a characteristic porosity of 28%. The average width of the pores involved is 15 Å and they are known as 'gel pores'. Much bigger pores, known as 'capillary pores', form another component of the hardened paste. These are the remains of the original water-filled spaces that have not become filled with gel. As will be seen later, the volume of the capillary pores depends on the original W/C ratio and the degree of the cement hydration. The remaining components, not shown in Figure 3.3 are unhydrated cement grains, calcium hydroxide crystals and air voids.

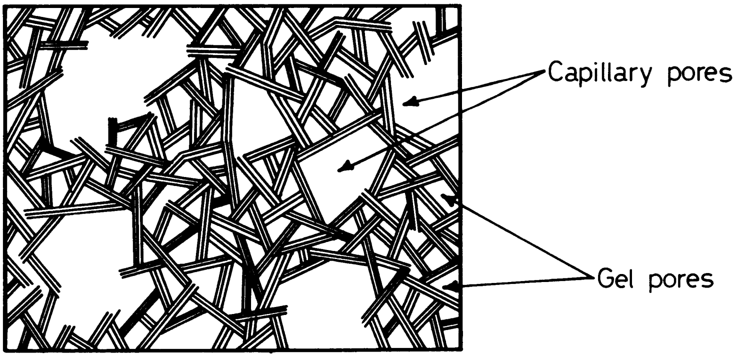

Figure 3.3 *Schematic description of the structure of the cement gel (after Powers*[5]*)*

It may be noted that Powers' model classifies the pores in the hardened paste into two distinct groups which differ significantly in their size. This classification is sometimes criticised on the basis that the pore-size distribution in the paste is continuous. The model has also been criticised for other reasons which are discussed later. Nevertheless, many of its features, such as those relating to the colloidal nature of the hydration products, the porous nature of the gel, and the important role of water in determining the behaviour of the paste, are generally recognised and accepted.

3.3.1 Water in the hardened paste

The water in the hardened paste was classified by Powers and Brownyard as follows:

1. Water which is combined in the hydrated cement compounds and as such is part of the solid. Such water has been referred to as 'chemically-bound water', 'combined water' or 'non-evaporatable water'.
2. Adsorbed water which is held by surface forces on the gel particles. Such water has been referred to as 'gel water'.
3. Free water which is present in the pores beyond the range of the surface forces of the solids in the paste. Such water has been referred to as 'capillary water'.

In practice this division of water in the paste is somewhat arbitrary. In drying crystalline hydrates, a vapour pressure against water content curve is characterised by distinct breaks by which the differently held water may be identified. In the hardened paste, however, due to its heterogeneity and the nature of the gel structure, the curve is continuous (Figure 3.1), and gives no indication by which, say, gel water can be distinguished from chemically bound water or capillary water. Moreover, on heating at 105°C not only gel and capillary water are lost, but also some water of hydration, such as part of the combined water in the calcium sulphoaluminates and in the hexagonal tetracalcium aluminate hydrate.

Powers and Brownyard assumed that on drying to a constant weight over magnesium perchlorate hydrate [$Mg(C\ell O_4)_2 \cdot 2\text{-}4\,H_2O$] at 23°C, capillary and gel water are completely lost whereas the combined water is fully retained in the paste. Accordingly, the gel and capillary water were collectively named 'evaporatable water'. The retained water was assumed to be the combined water and was named 'non-evaporatable water'. It follows that the amount of the non-evaporatable water is given by the weight loss of the dried paste on heating at 1000°C.

It is evident that such classification into evaporatable and non-evaporatable water is somewhat arbitrary being dependent on the method of drying. More intensive drying (i.e. at reduced vapour pressure) will increase the amount of evaporatable water at the expense of the non-evaporatable part, and vice versa. This is indicated in Table 3.1.[10]

It may be noted that, according to the preceding classification, the porosity of the paste is given by its evaporatable water content in a saturated surface-dry condition, i.e. the porosity of the paste is given by the difference in weight between the saturated and the dry paste. This assumption, which constitutes a premise of Powers' model, may be questioned and, indeed, has been questioned

Table 3.1 Effect of drying method on the amount of water retained in hardened Portland cement paste[10]

Drying agent or method	*Vapour pressure,* mmHg at 25°C	*Relative amount of water retained*
$Mg(C\ell O_4)_2 \cdot 2\text{–}4\ H_2O$*	0.008	1.0
P_2O_5	0.000 02	0.8
Conc. H_2SO_4	<0.003	1.0
Ice at – 79°C*	0.000 5	0.9
Heating at 50°C	–	1.2
Heating at 105°C	–	0.9

*Drying over $Mg(C\ell O_4)_2 \cdot 2\text{–}4\ H_2O$ is sometimes referred to as p-drying and over ice as d-drying.

recently. The implication of this will be discussed later when the other models are presented.

The amount of chemically bound water is related to cement composition and age of the paste, as well as to W/C ratio. The chemically bound water, W_n, is generally related to the cement potential composition by the following equation:[11]

$$W_n/C = a_1(C_3S) + a_2(C_2S) + a_3(C_3A) + a_4(C_4AF) \qquad (3.1)$$

where C is the cement content and C_3S, C_2S etc., are the calculated fractional contents of the tricalcium silicate, dicalcium silicate, etc., respectively. The parameters a_i, which give the amount of water bound to each component relative to its weight, have been determined experimentally and are summarised in Table 3.2.[11] Assuming, for example, that a cement has the composition 47% C_3S, 25% C_2S, 12% C_3A, and 8% C_4AF, the W_n/C ratio after 13 years of hydration will be:

Table 3.2 The coefficients a_i of equation (3.1) (*after Kantro and Copeland*[11])

a_i	*W/C ratio*				
	0.4	0.4	0.6	0.8	0.4
	1 year	6½ years			13 years
a_1	0.228	0.234	0.238	0.234	0.230
a_2	0.168	0.178	0.198	0.197	0.196
a_3	0.429	0.504	0.477	0.509	0.522
a_4	0.132	0.158	0.142	0.184	0.109

$$
\begin{aligned}
0.230 \times 0.47 &= 0.1081\\
0.196 \times 0.25 &= 0.0490\\
0.522 \times 0.12 &= 0.0626\\
0.109 \times 0.08 &= \underline{0.0087}\\
&\ 0.2284 \approx 0.23.
\end{aligned}
$$

This value, 23% of the cement weight, is generally assumed to be valid for well matured pastes of ordinary Portland cement.

3.3.2 Adsorption isotherms for cement pastes

Powers and Brownyard, using water vapour, obtained adsorption isotherms for different cement pastes and these isotherms were later used by Powers in developing his model. Some of the isotherms are presented and discussed here to explain the model.

Figure 3.4 presents adsorption isotherms determined for the same paste at different ages. In this figure the total water content is considered, i.e. evaporatable and non-evaporatable water. Hence, the water content in the dry paste (i.e. at $P/P_0 = 0$) equals the amount of chemically bound water. It can be seen that

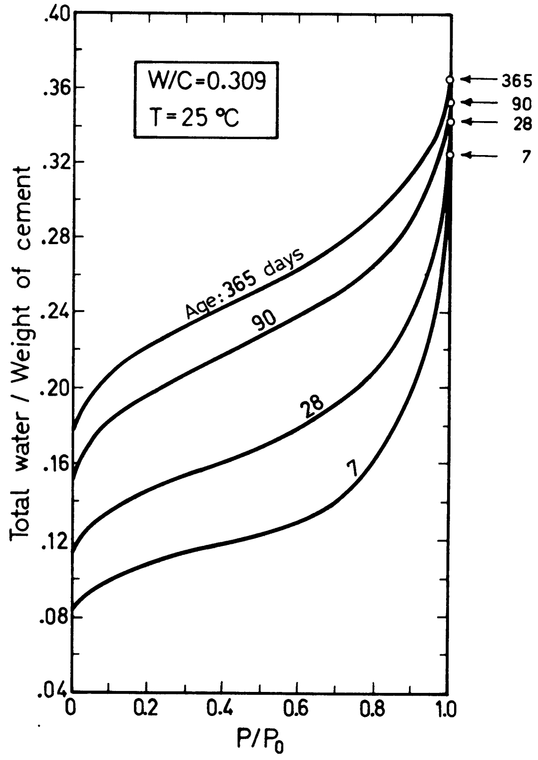

Figure 3.4 *Adsorption isotherms for a cement paste at different ages (after Powers and Brownyard*[9]*)* this amount increases with age implying, of course, that the degree of hydration increases with time.

On hydration, Portland cement combines with 23% of its own weight of water. In Figure 3.4 the combined water at 365 days is only 17% of the original weight of the anhydrous cement. That is, under the conditions of Figure 3.4, only 74% (17/23 = 0.74) of the cement hydrated. As pointed out earlier, complete hydration is not to be expected due to the formation of a gel layer around the cement grains, which prevents further hydration.

Figure 3.5 presents the same data as Figure 3.4. In this figure, however, the water content in the paste is evaporatable water only. It can be seen that the amount of evaporatable water increases with age, but that near saturation (i.e. $P/P_0 > 0.9$) the trend is reversed. The evaporatable water at saturation ($P/P_0 = 1$) is a measure of the porosity of the paste, and it may be concluded that porosity decreases with age.

The pastes in question differ only with respect to their degree of hydration and the degree of hydration increases with age (Figure 3.4). It is implied, therefore, that the density of the paste increases with increase in the degree of hydration. Again, this is a well known finding which will be further discussed later.

The question arises as to why, in the lower pressure range, the water content in the younger pastes, which are of higher porosity, is lower than that in the more mature counterparts. The vapour pressure of water in capillaries is lower than that of water in a free state. This phenomenon is discussed in some detail in Chapter 5 but, generally speaking, the smaller the diameter of the capillaries the lower the vapour pressure. Consequently, at the low pressure range, the smaller pores remain filled with water whereas the larger ones are empty. In other words, in the lower pressure range only gel pores, which are much smaller

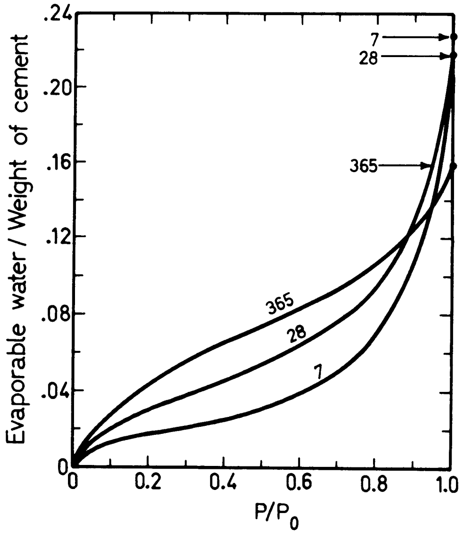

Figure 3.5 Adsorption isotherms for a cement paste at different ages (after Powers and Brownyard[9])

than the capillary pores, are filled with water. The gel content of the paste and the associated volume of gel pores are higher the greater the degree of hydration. Since the degree of hydration is greater in the older than in the younger pastes, the gel content in the former is higher. Hence, in such pastes the volume of gel pores and the resulting water content are greater than in their younger counterparts.

Figure 3.6 presents adsorption isotherms for hardened pastes at the same degree of hydration (combined water about 15% of the cement weight) but prepared with different *W/C* ratios. It can be seen that the porosity of the paste (i.e. water content at $P/P_0 = 1$) increases with *W/C* ratio. Some important properties of the paste, such as strength and durability, are determined to an appreciable extent by its porosity. As the porosity is related to the *W/C* ratio, the latter must affect the properties of the paste. This effect of the *W/C* ratio is of practical importance and is made use of in the control of concrete quality.

In the pressure range below about $P/P_0 = 0.45$, the three isotherms of Figure 3.6 converge, and the same curve holds for the three pastes. In this range the water content is determined by the volume of gel pores which, in

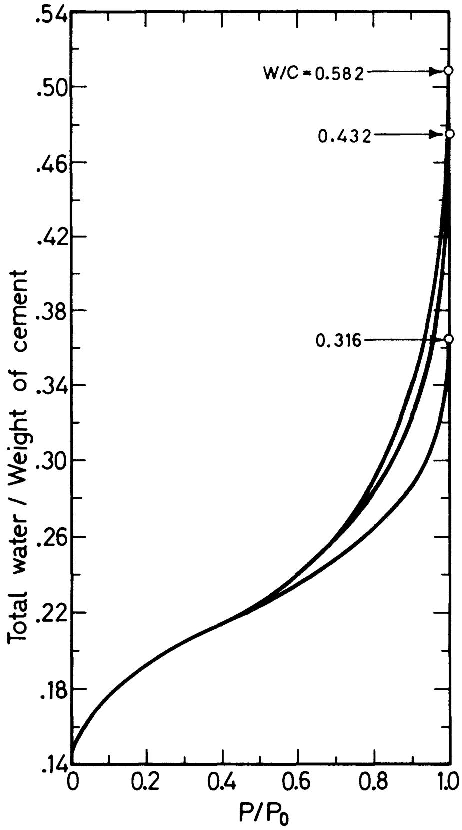

Figure 3.6 Adsorption isotherms for hardened pastes of different W/C ratios and the same degree of hydration (after Powers and Brownyard[9])

turn, is determined by the degree of hydration. The pastes in question are of the same degree of hydration. Hence, the pastes have the same volume of gel pores and, consequently, the same water content. This explanation assumes that the gel has a characteristic porosity which is independent of *W/C* ratio and age. According to Powers the gel does have such a characteristic porosity, 28%.

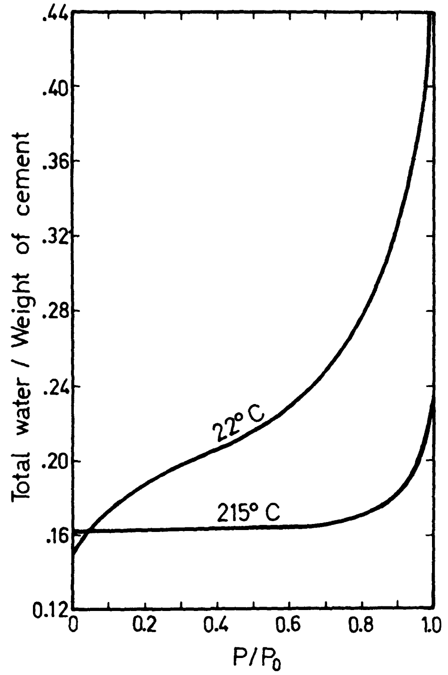

Figure 3.7 *Adsorption isotherms for cement pastes of the same degree of hydration but cured differently (after Powers and Brownyard*[9]*)*

It should be noted that the convergence of the isotherms in Figure 3.6 below P/P_0 = 0.45 is not conditional only on the pastes having the same degree of hydration. This is reflected in Figure 3.7 which presents isotherms for two pastes of the same degree of hydration (16% combined water) which were cured differently. The first was treated in an autoclave for 6 hours at 215°C and the second was immersed in water at 22°C for 28 days. It can be seen that the respective isotherms are completely different. This difference may be attributed to the different structure of the pastes. It was concluded from Figure 3.6 that below P/P_0 = 0.45 only the gel pores are filled with water and that the capillary pores are empty. Accordingly, it can be concluded from Figure 3.7 that no pores of the size of gel pores in a normally cured paste are present in paste treated in an autoclave. Moreover, the size of the pores in the latter paste is so much greater that virtually all pores are empty at pressures below P/P_0 = 0.8 (Figure 3.7). In any case, the data imply that the assumption of a characteristic gel porosity is limited to normally cured pastes.

3.3.3 Specific surface area of hydration products

Using the BET method, Powers determined the specific surface area of the hydration products from water vapour adsorption data.[5] Results for four cements are summarised in Table 3.3.

The hydration of C_3S results in a smaller amount of gel than that of C_2S. Hence, an increase in the specific surface area of the hydration products is to be expected with increase in the C_2S content in the cement at the expanse of C_3S. Such a tendency is suggested in the data of Table 3.3. The specific surface areas of the hydration products of cements 3 and 4 are, the highest and the lowest respectively, as would be expected from their C_3S and C_2S contents. On the other hand, the specific surface area of the hydration products of cement 1 is higher than would be expected from its C_2S content. Also, because hydration of both C_3S and C_2S produces a gel of the same composition, no great difference is to be expected in the specific surface area of the gels of the different cements.*

Table 3.3 Specific surface area of Portland cement gel and its hydration products (after Powers[5])

Cement No.	*Cement composition*, wt %				*Specific surface area* m^2/g	
	C_3S	C_2S	C_3A	C_4AF	Hydration products	Gel only*
1	45.0	25.8	13.3	6.7	219	267
2	48.5	27.9	4.6	12.9	200	240
3	28.3	57.5	2.2	6.0	227	255
4	60.6	11.6	10.3	7.8	193	235
Average					210	249

*Calcium hydroxide excluded.

It is rather difficult to determine from the data of Table 3.3 the relationship, if any, between cement composition and the specific surface area of its hydration products and, accordingly, Powers concluded that the specific surface area of the cement gel is not affected very much by differences in cement composition.[5] In any case, taking the average value, the very high specific surface area of the hydration products (calcium hydroxide excluded) is a reflection of their collodial size and justifies the definition of the resulting solid as a rigid gel. Quantitative treatment of this aspect is presented in section 3.3.9.

In discussing hydration it was stated that, at later stages at least, the specific surface area of the hydration products is independent of the degree of hydration and consequently (at these stages) hydration at equal fractional rates may be

---

*Gel specific surface area is usually determined from the CSH content because the specific surface area of the aluminate hydrates is much lower, i.e. approximately 20 m^2/g.[2]

assumed. Relevant data are presented in Figure 3.8 which shows the relation between V_m and the degree of hydration measured by the amount of the combined water, W_n. W_m is the amount of water required to cover the surface of the solids with a monomolecular layer, and is a measure of the surface area of the paste. Hence, the relation between surface area and the degree of hydration is linear and is given by the expression $V_m = kW_n$. The constant k depends on the type of cement and method of drying. p-Drying results in $k = 0.255$ and d-drying in $k = 0.32$. The linear nature of this relation implies that the composition of the paste remains unchanged as hydration proceeds. In turn, this implies, as already pointed out, that hydration proceeds at equal fractional rates.

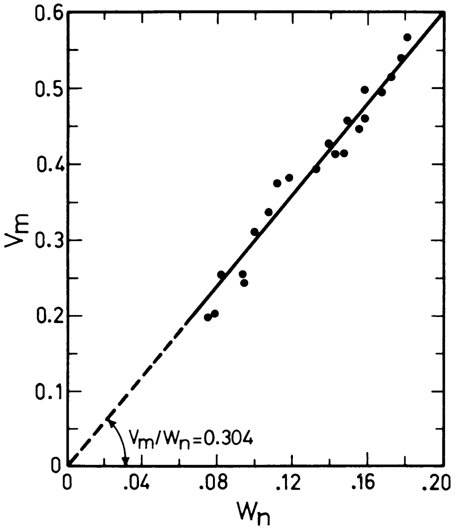

Figure 3.8 V_m *plotted against combined water* W_n *(after Powers and Brownyard*[9]*)*

Table 3.4 Effect of curing temperature on specific surface area and strength of cement paste (after Ludwig and Pence[12]*)*

Pressure	*Temp., °C*	*Combined water/cement ratio*	*Specific surface area of dry paste,* m²/g	*Compressive strength,* N/mm²
Atmospheric	27	0.142	103.4	26.4
	66	0.162	122.6	42.3
20 N/mm²	93	0.152	74.7	35.1
	127	0.139	30.3	8.8
	160	0.139	9.4	9.2

Treatment in an autoclave affects the specific surface area of the hydration products. It was shown previously (Figure 3.7) that such treatment results in a coarser structure containing no gel-size pores. It is to be expected, therefore, that the specific surface area of such pastes will be lower than that of normally cured pastes. This conclusion is clearly confirmed by the data in Table 3.4.[12]

3.3.4 Size of gel pores

Adsorption may be expressed by the number of monomolecular layers of water which cover the gel surface, i.e. by W/V_m where W is the total amount of adsorbed water and V_m is as previously defined. The isotherms in Figure 3.9 show such data.

It was shown previously (Figure 3.6) that at pressures below $P/P_0 = 0.45$ only the gel pores are filled with water and at this pressure therefore the amount of adsorbed water is determined by the gel content of the paste. Hence, in this range, adsorption is the same for pastes of equal degrees of hydration, i.e. of equal gel content.

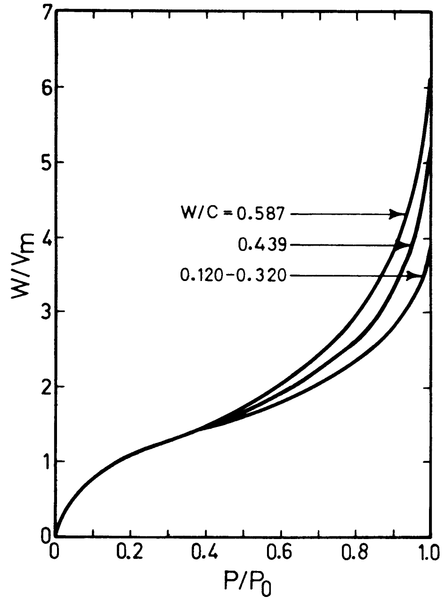

Figure 3.9 *Thickness of the adsorbed water layer for cement pastes of different W/C ratios (after Powers and Brownyard[9])*

The adsorption results in Figure 3.9 are given in terms of W/V_m, i.e. the thickness of the water layer covering the surface of the gel. The thickness is directly related to the amount of adsorbed water, W, and indirectly to the specific surface area of the gel. Assuming that the specific surface area remains unchanged, the amount of adsorbed water and gel surface area change at the same rate as hydration proceeds, and the ratio between them (i.e. the thickness of the adsorbed layer) remains constant. In other words, at the lower pressure range, the thickness of the adsorbed layer is independent of the degree of hydration and at any given pressure the thickness of the layer will be the same in all pastes regardless of their *W/C* ratio and degree of hydration.

The preceding conclusion is confirmed by the data in Figure 3.9. This figure presents adsorption isotherms at 180 days for two pastes prepared with a *W/C* ratio of 0.439 and 0.587. The third isotherm in Figure 3.9 is based on the combined 90 days data of ten pastes prepared with different *W/C* ratios, from 0.12 to 0.32. As expected, the same curves hold for all the pastes up to $P/P_0 = 0.45$. The difference in the curves in the higher pressure range is attributable to the difference in the capillary pore contents of the different pastes. Accordingly, in the high pressure range, the same isotherm will hold for different pastes, provided that the pastes do not contain capillary pores. This is the case with the third isotherm which represents ten pastes of different *W/C* ratios. It is implied, therefore, that the isotherm in question represents pastes with no capillary pores, and consequently water adsorption at $P/P_0 = 1$ is a measure of the volume of the gel pores only. According to Figure 3.9 this volume equals to 4 V_m, being modified later to 3 V_m.[5,13] Accordingly, the average width of gel pores is 6 V_m , i.e. equal to the thickness of six monomolecular water layers. Assuming that the specific volume of adsorbed water is 0.9 cm^3/g, and taking the diameter of a water molecule in a free state as 3.4 Å, the average width of the gel pores is $6 \times 0.9 \times 3.4 =$ 18 Å. Further research has indicated this width to be only 15 Å.[14]

3.3.5 Density of the hydration products

The absolute volume of the solids in the hardened paste equals the combined volume of the hydration products, and that of the unhydrated cement. Hence, the dry paste with the corresponding volume being dependent also on the water specific volume. Assuming that the specific volume of the adsorbed water is evaporatable water is given by the difference in the weights of the saturated and the dry paste with the corresponding volume being dependent also on their specific volumes. Assuming that the specific volume of the adsorbed water is different from that of water in a free state, the specific volume of the evaporatable water varies and depends on the ratio of the adsorbed to the free water content. To avoid the difficulties brought about by this variation, Powers and Brownyard used a helium pycnometer to determine the volume of the solids in the paste. The degree of hydration was determined from the amount of combined water. The degree of hydration being known, the weight and the volume of the unhydrated cement could be calculated. The volume of the hydration products is the difference between the volume of the solids and the volume of the unhydrated cement and, accordingly, the specific weight and volume of the hydration products can be calculated. Using this procedure the density of the hydration products was found to be 2.44 g/cm^3 (i.e. specific volume of

$1/2.44 = 0.41\ \text{cm}^3/\text{g}$), and virtually independent of the type of cement. In determining the preceding value, p-drying was employed. Drying over ice resulted in a density of $2.51\ \text{g/cm}^3$. Others have reported density values from 2.43 to $2.59\ \text{g/cm}^3$.[15]

3.3.6 Specific volume of combined water-intrinsic shrinkage

On hydration, cement combines with 23% of its own weight of water. The specific volume of the cement is $0.32\ \text{cm}^3/\text{g}$, and that of the hydration products $1/2.51 = 0.398\ \text{cm}^3/\text{g}$. Hence,

$$1\ \text{g cement} + 0.23\ \text{g water} \rightarrow 1.23\ \text{g of hydration products},$$

and the corresponding volumes involved are

$$0.32\ \text{cm}^3\ \text{cement} + 0.23\ \text{cm}^3\ \text{water} \rightarrow 1.23 \times 0.398 = 0.490\ \text{cm}^3\ \text{of hydration products}$$

The combined volume of the reacting cement and water equals $0.32 + 0.23 = 0.55\ \text{cm}^3$. That is, the volume of the resulting hydration products is $0.06\ \text{cm}^3$ smaller than that of the reacting cement and water. Accordingly, the decrease in the original volume of the cement + water system is $0.06/0.23 \approx 25\%$ of the volume of the combined water. Alternatively, the combined water may be assumed to have a hypothetical specific volume of $0.75\ \text{cm}^3/\text{g}$. The reduction in the volume of the solids usually increases the porosity of the paste and is not reflected in its bulk dimensions. This phenomenon is known as 'chemical' or 'intrinsic' shrinkage.

3.3.7 Porosity of the gel

It was shown that the volume of the gel pores equals $3V_\text{m}$, and that $V_\text{m} = kW_\text{n}$ where $k = 0.32$ for a paste dried over ice. Assuming that the specific volume of the gel water is $0.90\ \text{cm}^3/\text{g}$, then the volume of the gel pores, V_gp, is given by

$$V_\text{gp} = 3 \times 0.9 \times 0.32\ W_\text{n} = 0.86\ W_\text{n}$$

In ordinary Portland cement $W_\text{n} = 0.23C$, hence,

$$V_\text{gp} = 0.86 \times 0.23C = 0.198C,$$

or the pore volume per one gram of cement is

$$V_\text{gp}/C = 0.198\ \text{cm}^3/\text{g}.$$

The volume of the hydration products per gram of cement equals $0.490\ \text{cm}^3$ therefore the total volume of the gel equals $0.490 + 0.198 = 0.688\ \text{cm}^3$. Accordingly, gel porosity is $0.198 \times 100/0.688 \approx 28\%$.

3.3.8 Gel to cement volume ratio

Hydration of one gram of cement produces 0.49 cm^3 of hydration products. Since the porosity of the gel is 28%, the volume of the produced gel will be $0.49/0.72 = 0.688\ \text{cm}^3$, and the ratio of the gel volume to that of the anhydrous cement will be $0.688/0.32 \approx 2.2$. In other words, the volume of the gel is 2.2 times the original volume of the cement; this increase in volume implies that paste porosity decreases as hydration proceeds. Moreover, in order to allow complete hydration, the space between the cement grains must exceed 1.2 times the volume of the grains, V_c. The volume of this space is determined by the amount of mixing water, W_0. Hence, we can write $W_0 \geqslant V_c$.

Assuming that the specific weight of the cement is 3.12 g/cm^3, we obtain $V_c = C/3.12$. Substituting this value of V_c into the preceding inequality, we obtain $W_0 \geqslant 1.2\ C/3.12$, and the minimum water/cement ratio which is required to allow complete hydration is given by

$$W_0/C = 1.2/3.12 = 0.38.$$

It is rather uncertain whether hydration would stop because of lack of space for the hydration products to form and, in any case, hydration stops at earlier stages due to the increased thickness of the gel layer surrounding the cement grains. The preceding calculation was based on the assumption that gel porosity remains constant and equal to 28%. It may be argued that in paste of lower W/C ratio, when the space available for the hydration products is limited, the resulting volume constraint would bring about a denser gel, and hydration would continue to a greater extent than would be expected from the preceding considerations. This argument is partly supported by test data relating to cement pastes which were made with a low W/C ratio of 0.2.[16] In these tests the ratio of the volume of the gel to that of the cement was 1.555 only, corresponding to a gel with zero porosity ($0.49/0.32 \approx 1.555$) or, alternatively, to a gel of some porosity but made up of hydration products having a higher density than those formed under normal conditions.

3.3.9 Size of gel particles

The specific surface area of the cement gel is, say, 200 m^2/g and the density of the hydration products is 2.51 g/cm^3. Assuming that the cement combines with 23% of its weight of water, the hydration of one gram of cement produces 1.23 g hydration products having a specific volume of 0.398 cm^3/g. Accordingly, the specific surface area per gram of hydration products is $200/1.23 = 160\ \text{m}^2/\text{g}$.

The specific surface area of the hydration products is, by definition, the sum of the surface areas of all the particles contained in one gram or, alternatively, in 0.398 cm^3. Assuming the particles to be spheres of diameter d, and denoting by N the number of particles contained in 0.398 cm^3, the following equations may be written:

$$\pi d^2 N = 1.6 \times 10^6 \tag{3.2}$$

$$\tfrac{1}{6}\pi d^3 N = 0.398 \tag{3.3}$$

and hence $d \approx 150$ Å.

The gel particles are, of course, not spheres but, in general, have the form of rolled or crumpled thin sheets. However, regardless of their true shape, the calculations imply that at least one of their dimensions is smaller than 150 Å. A colloid, by definition, has at least one dimension smaller than 1000 Å. Hence, the particles in question are clearly of colloidal size and the use of the term gel to describe the hydration products is, therefore, justified.

3.3.10 Summary of Powers' model

A schematic diagram showing Powers' model is given in Figure 3.3. According to this model the cement gel is a rigid substance made up of colloid-size particles, and has a characteristic porosity of 28%. The average width of the pores involved is 15 Å and these are known as 'gel pores'. Much bigger pores, known as 'capillary pores', are also present in the hardened paste. These are the remains of the original water-filled space that has not become filled with gel. The other components, not shown in Figure 3.3, are unhydrated cement grains, crystals of calcium hydroxide, and air voids. This model is essentially based on water-vapour isotherms and on a somewhat arbitrary classification of the types of water held in the paste. The exact particle shape and the nature of its structure are hardly considered in the model.

Powers' model has been criticised on several grounds, particularly with respect to the interpretation of the water-vapour adsorption isotherms. Nevertheless, some features of the model, such as those relating to the colloidal nature of the hydration products, the porous structure of the gel, and the importance of the role played by the water in determining the behaviour of the paste, are generally recognised and accepted.

3.4 Ishai's Model

This model was developed mainly to explain volume changes in the paste due to variations in its moisture content (swelling and shrinkage) and due to continuous loading (creep). The model is essentially based on work carried out at Technion, Israel Institute of Technology. It was first suggested in general terms in 1962[17] and a more detailed and comprehensive description appeared in 1965.[18] The model is based on Powers', the main difference between the two being in the classification of the water held in the hardened paste. Ishai's model distinguishes four types of evaporatable water as compared to the two types in Powers' model (Figure 3.10).

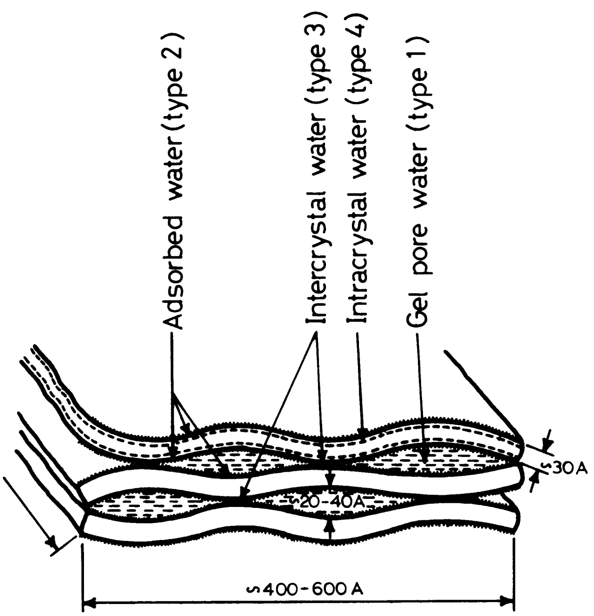

Figure 3.10 *Schematic description of the cement gel* (*after Ishai*[18])

1. Water present in gel and capillary pores outside the range of surface forces, i.e. at a distance greater than 10-20 Å from the surfaces of the solids.
2. Water which is adsorbed on the surface of the crystallites in layers 1-2 molecules deep, i.e. 4-8 Å thick.
3. Adsorbed water which is confined between adjacent crystallite surfaces in narrow spaces, the width of which does not exceed 8 Å (i.e. two molecules). This type of intercrystalline water is subjected to two sets of forces, and consequently is adsorbed more strongly than types 1 and 2.
4. A water layer, one molecule thick, which is between layers of CSH crystallites. This type of intracrystalline (zeolitic) water is strongly bound to the solid and cannot be removed during normal drying.

It may be noted that type 1 is actually the capillary water of Powers and types 2 and 3 are the gel water subdivided in accordance with the number of sets of forces which act upon it. It should be pointed out that Figure 3.10 may appear to contradict the proposed definition of type 1 (capillary) water. The width of the pores in the figure is 20 to 40 Å whereas, to be outside the range of surface forces, the water must be at a distance exceeding 10-20 Å from the surface of the solids. Hence, the pores in question can hardly contain type 1 water.

The intracrystalline (zeolitic) water (type 4) is not considered in Powers' model. The presence of such water in the cement paste was suggested by Kalousek as long ago as 1955.[19]

3.5 Feldman and Sereda's model

According to Powers' model, the pore content of the cement paste equals the volume of the evaporatable water. However, the layer structure of the gel particles may suggest that part of the evaporatable water is interlayer (zeolitic) water which may be regarded as part of the solid. If such were the case, the pore content of the paste would not be equal to the volume of the evaporatable water, but would be less, and all calculations based on the former premise would be incorrect. The possible presence of zeolitic water and some of the resulting implications were discussed by Kalousek in 1955 who stated

> the very large surface 'areas' of cement pastes obtained by vapour adsorption are not true areas. Water apparently enters the lattice of some of the hydrous calcium silicates, perhaps similarly, as it does in zeolites or certain clays and other minerals.

The presence of interlayer water, and the importance of this type of water in explaining the properties and behaviour of the cement paste, are two of the main features of Feldman and Sereda's model. Note that Ishai's model (Figure 3.10) also includes interlayer water as part of the evaporatable water held in the cement paste. The importance of this type of water is, however, much greater in the Feldman-Sereda model than in that of Ishai, and this is reflected in the explanation of volume changes in the paste (see Chapter 5).

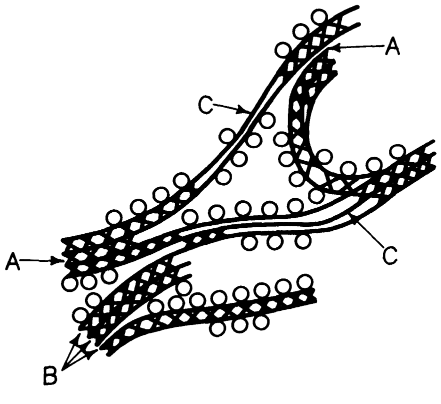

Figure 3.11 *Microstructure of the cement gel (after Feldman and Sereda*$^{20-21}$*).* (A *interparticle bond;* X, *interlayer hydrate water;* C CSH *sheets;* O, *physically adsorbed water*)

A schematic diagram showing the cement gel in accordance with the Feldman-Sereda model is presented in Figure 3.11. The gel particles are described as crumpled sheets made up of 2-4 layers of molecules. The water held in the gel is either interlayer water (marked x in Figure 3.11) or physically adsorbed water (marked o). Depending on temperature and vapour pressure of the surroundings, the space between the gel particles may contain water or be empty.

The work which formed the basis for this model was carried out at the Division of Building Research, National Research Council of Canada, Ottawa. Some of the relevant data and considerations associated with the development of the model are presented and discussed below. Further details can be found elsewhere.[20,21]

3.5.1 General considerations

Often, adsorption isotherms are not completely reversible and are characterised by some form of hysteresis. That is, the isotherm which is determined on adsorption (i.e. wetting) is different from that which is determined on desorption (i.e. drying). Generally speaking, three forms of hysteresis have been observed (Figure 3.12). In type 1 hysteresis, a loop is formed over a limited range in the high pressure region; such hysteresis is known as primary hysteresis. For this range a scanning loop may be obtained by, say, desorbing after reaching point X on the ascending curve. Point Y is reached on the descending curve and return to point X may be obtained by readsorption. In hysteresis of types 2 and 3, the loop extends over the whole pressure range. Hysteresis type 3 combines the characteristics of types 1 and 2, and is typical of cement paste. The broken part of the type 3 curve describes the pattern followed if adsorption recommences at point X.

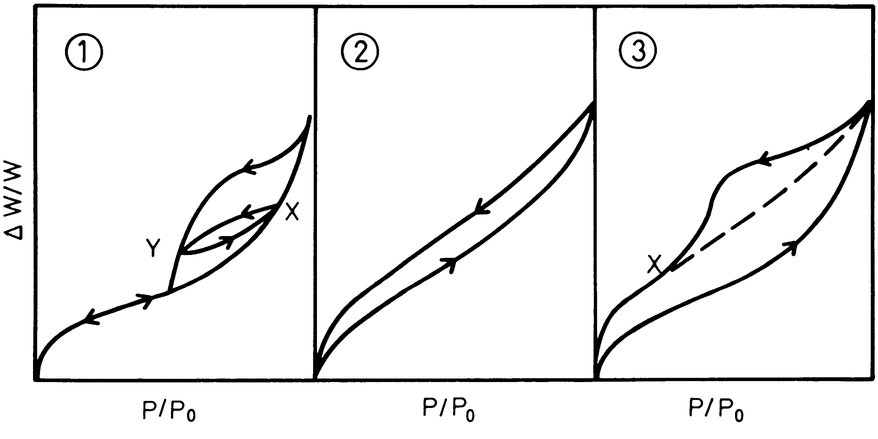

Figure 3.12 *Different types of sorption hysteresis*

The BET method is applicable in the vapour pressure range of $P/P_0 = 0.05$ to 0.35 provided that the adsorption isotherm is reversible within this range (i.e.

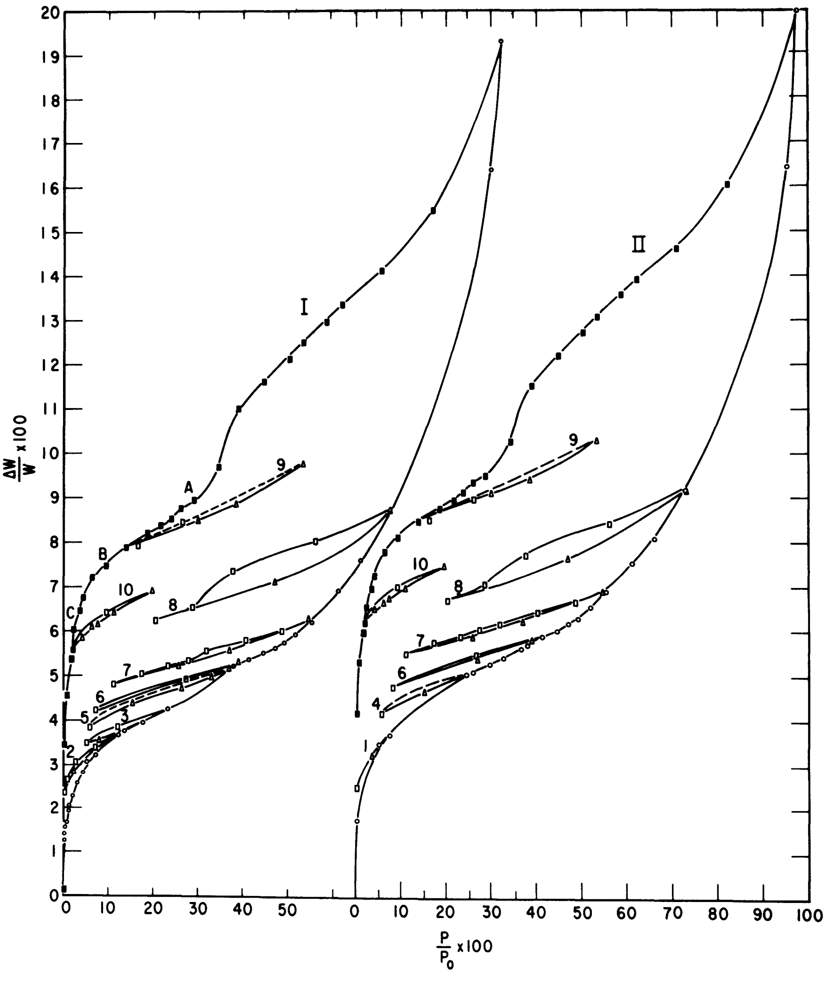

Figure 3.13 *Sorption isotherms with scanning loops for bottle-hydrated Portland cement compacts (after Feldman*[22]*)*

isotherm 1 in Figure 3.12). Cement paste, however, is characterised by the type 3 isotherm which is irreversible over any pressure range. This is clearly indicated by the scanning loops in Figure 3.13, which were obtained for the boundary isotherm over the whole pressure range.[22] In the high pressure region hysteresis is attributed to capillary effects, and in the low region, particularly in materials of layered structure, to movement of interlayer water. The layered structure of the CSH particles, and hysteresis in the low pressure region, may suggest that hysteresis in cement paste results from the removal and re-entry of interlayer water. If such were the case, the BET method could not be applied to water vapour isotherms on cement pastes and, accordingly, all the conclusions based on this assumption are erroneous and have to be modified.

The irreversibility of the water vapour isotherm alone for cement pastes does not constitute proof that the suggested movement of interlayer water actually does take place. There exist, however, some additional data and information which support this suggestion.

3.5.2 Separation of different types of water held in the paste

Separation of the physically adsorbed water and interlayer water can be achieved using scanning loops on the assumption that, due to small changes in vapour pressure, the physical adsorption of water is a reversible process whereas that of the interlayer water is irreversible. The method of separation is described schematically in Figure 3.14. Consider, for example, the loop at the point O on the ascending isotherm which was obtained by decreasing the vapour pressure from P_2 to P_1. The amount of adsorbed water decreases by the amount A but

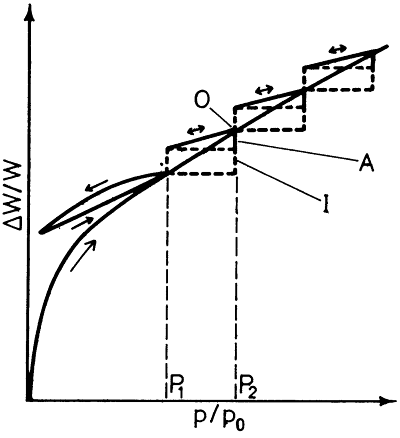

Figure 3.14 *Method of separation of adsorbed and interlayer water (after Feldman and Sereda*[21]*)*

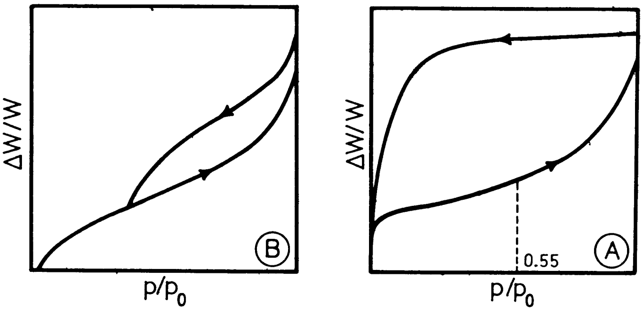

Figure 3.15 *Sorption isotherms for* (A) *interlayer water and* (B) *adsorbed water (after Feldman and Sereda*[21]*)* remains greater than the corresponding amount at P_1 on the ascending isotherm by an amount I. If, as mentioned, only physical adsorption is assumed to be reversible, A represents the amount of physically adsorbed water and I the amount of interlayer water. Summing the partial values of A and I determined from scanning loops systematically covering the whole pressure range, the amounts of physically adsorbed and interlayer water can be determined. The resulting two isotherms for physically adsorbed and interlayer water are shown schematically in Figure 3.15.

It can be seen that the isotherm for adsorbed water is a type 1 isotherm (Figure 3.12). It is reversible in the low pressure region and the BET method is therefore applicable. The interlayer water isotherm is irreversible over the whole pressure range. Hence, it may be concluded that hysteresis in the isotherm for cement paste is attributable in the low pressure region to the movement of interlayer water only. It may be further concluded (Figure 3.15A) that re-entry of interlayer water takes place over the whole pressure range, being very apparent at the initial stage where the isotherm is almost vertical. The desorption isotherm is rather different and indicates that removal of interlayer water takes place only at the low vapour pressure end of the isotherm.

3.5.3 Specific surface area from nitrogen adsorption

The use of nitrogen for specific surface area determination results in much lower values than those obtained when water vapour is used (Figure 3.16). Also nitrogen-determined surface area increases with *W/C* ratio whereas water vapour-determined surface area is independent of this factor. It can be seen from Figure 3.16 that the use of other gases, such as methanol, also gives lower surface area values. Similar results have been obtained elsewhere.[24–27]

The lower surface area obtained when nitrogen is used in the adsorption tests, is attributable to the greater diameter of the nitrogen molecule (4.05 Å) in comparison with that of water (3.25 Å). The greater diameter restricts the penetration of nitrogen into the smaller pores, and it cannot reach some of the surface which is accessible to the smaller water molecules. Hence, the nitrogen-determined surface area is smaller because it constitutes only part of the area. However, the ratio of water vapour to nitrogen surface areas may be as high as five. Considering the sizes of the molecules, it may be questioned whether such a small difference in diameter could produce such great differences in surface area results. It has therefore been argued by Kalousek[19] that water vapour adsorption includes interlayer water to an extent required to account for the difference between water vapour and nitrogen surface areas. In other words, the 'true' surface area of the gel is the one determined by nitrogen adsorption. Water vapour-determined surface area is considerably greater because it includes some of the internal surfaces of the CSH sheets.

This suggestion about the effect of interlayer water on surface area determination has been supported by the work of Feldman and Sereda. As pointed out previously, the isotherm for physically adsorbed water is reversible in the lower

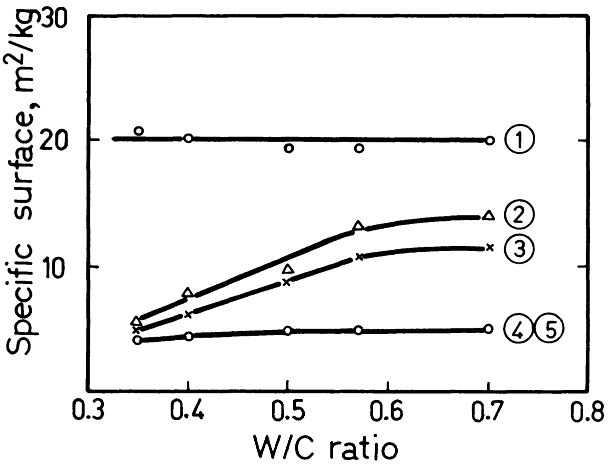

Figure 3.16 *Effect of W/C ratio on specific surface area of cement paste determined by different adsorbants (after Mikhail and Selim*[23]*).* (1) Water vapour, (2) nitrogen, (3) methanol, (4) isopropanol, (5) cyclohexane

pressure region (Figure 3.15), and can be used in surface area determination by the BET method. That is, if the isotherm in question represents the physically adsorbed water only, the calculations based on this isotherm would give the cement paste's 'true' surface area which, in turn, should be the same as that determined by nitrogen adsorption. Also, if water vapour adsorption includes interlayer water, the volume of this type of water should equal the difference between the total volume of adsorbed water and the volume of adsorbed nitrogen, i.e.

$$V_{\text{water}} - V_{\text{nitrogen}} = V_{\text{interlayer water}}$$

In many of Feldman and Sereda's tests this equation was found to hold, and the surface areas calculated from the physically adsorbed water data were similar to those calculated from nitrogen adsorption data.

3.5.4 Summary of Feldman and Sereda's model

Some of the work relevant to the model has been presented in the preceding sections. At this stage, discussion has been limited to adsorption studies from which the following conclusions have been drawn.

1. Water vapour isotherms for cement pastes are irreversible over all pressure regions and therefore cannot be used for BET calculations.
2. The evaporatable water includes some interlayer water which enters the CSH layered structure over all regions of the isotherm.

3. The evaporatable water content, including some interlayer water, the 'true' surface area of the paste, as well as its density, are lower than the values calculated from water vapour adsorption data.
4. Nitrogen surface area determination gives a better estimate of the cement paste's true surface area than that obtained from water vapour adsorption. Nitrogen measures 'external' surface area, whereas water also measures the 'internal' surface area of the layers.
5. Interlayer water can be separated from the physically adsorbed water (Figure 3.14). It will be seen later that the two isotherms (Figure 3.15) can be used to evaluate and describe the properties of the cement paste.

Specific surface areas and densities of different cement pastes, determined in accordance with the above, are presented in Table 3.5.[28] In this respect it may be noted that water vapour specific surface area averages 200 m^2/g, and is independent of the *W/C* ratio (Table 3.3 and Figure 3.16). The density of the hydration products, as reported by others, averages about 2.5 g/cm^3.

Table 3.5 Specific surface area and density of cement pastes (after Feldman[28])

W/C ratio	*Specific surface area,** m^2/g	*Density,†* g/cm^3
0.4	30	2.19
0.5	55	–
0.6	51	2.28
0.8	57	2.30
1.0	57	2.29

*Nitrogen adsorption; †determined by helium pycnometer.

3.6 Summary and concluding remarks

The hardened cement paste is a heterogenous solid consisting of an apparently amorphous mass containing crystals of calcium hydroxide (and occasionally also small amounts of aluminates and sulphoaluminates), unhydrated cement grains, and voids containing either water or air. The amorphous mass is a rigid gel of colloid-size particles, and is characterised by a porous structure and large specific surface area. Most of the gel particles are poorly crystallised hydrates of calcium silicate. The cement gel is therefore referred to as 'calcium silicate hydrate' gel (CSH gel).

A few models have been suggested to describe the microstructure of the cement paste. Essentially, the models differ in their classification of the water held in the paste and in the importance assigned to the different types of water in determining the paste's properties and behaviour. In particular, this difference is reflected in the discussion of interlayer (zeolitic) water. The difference in classification of the water is not limited to differences in definition and terminology only, but is also reflected quantitatively in values assigned to some of the paste properties such as specific surface area and density. The difference is much greater when the properties and behaviour of the paste are considered.

3.7 References

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4 Strength of the hardened paste

4.1 Bond between gel particles

In discussing the hydration process it was stated that setting and hardening of the cement paste is brought about by the formation of a CSH gel. The gel fills the space between the cement grains, bridges between them, and thereby causes stiffening of the paste and its subsequent hardening. The continued formation of the gel gradually fills the capillary pores, the porosity of the paste decreases, and its strength is increased. However, the mechanical strength of the paste and its stability in water require further discussion with respect to the nature of the bond between gel particles. Generally speaking, the strength of the paste may be attributed to cohesion forces (van der Waals forces) acting between the gel particles (secondary bonds), or to the intergrowing of the crystallites and the formation of chemical bonds (primary bonds) at their points of contact. In this context it is generally meant that a chemical bond is a solid to solid contact similar to that existing at the grain boundary of a polycrystalline material, where some of the atoms approach the spacing of the atoms in the crystals, and a close fit exists between the lattices of the neighbouring crystals. Such bonds could be formed during a crystallisation process accompanying a chemical reaction when the mobility of the atoms allows for a regular arrangement. The strength of a material characterised by such bonds (e.g. gypsum) is determined by the number of bonds per unit volume, the bond strength, and the strength of the crystals themselves. The number of bonds, in turn, is dependent on the shape and size of the crystals involved. In any case such bonds are strong and when broken would not be remade under normal circumstances. The secondary bonds are much weaker. It is generally assumed that the cohesion forces in the cement system act across the adsorbed water, and that the adsorbed water is a constituent part of the bond between gel particles (see, for example, Figure 3.10). Accordingly, the strength of such bonds depends on the amount of adsorbed water and this dependence is sometimes used to explain the decrease in the strength of the paste with an increase in its moisture content (Figure 4.24).

The magnitude of the cohesion forces is also dependent on the size of the particles involved, i.e. on their specific surface area; larger forces (stronger bonds) are to be expected for higher specific surface areas. The CSH gel is characterised by very high specific surface area (Table 3.3), and the strength of the cement paste may be attributed, therefore, to cohesion forces. On the other hand, the CSH gel is rigid, i.e. it exhibits limited swelling on water absorption, and this behaviour suggests the presence of chemical bonds as well as secondary bonds. It is difficult to estimate the relative importance of these two types of bond. It has been suggested, however, that the contribution of both types to the strength of the paste is more or less the same.[1]

A different type of bond between gel particles is postulated in the model of Feldman and Sereda,[2] which assumes solid to solid contact without an intervening layer of adsorbed water (Figure 3.11). The atoms at the contact boundaries have no regular atomic arrangement or spacing, and bond strength is determined therefore by the degree of disorder and the average spacing. This type of bond differs from the stronger chemical bonds found in more regular atomic arrangements, and in which the spacing of the atoms may approach that of the lattice spacing in the crystal. Also, unlike chemical bonds, this type of bond can be broken and subsequently remade under certain conditions.

This description of the bond between particles in the gel (after Feldman and Sereda) is based mainly on a study in which the hardness and modulus of elasticity of different gypsum systems were compared with those of similar cement systems. The following test specimens were used:[3,4]

1. specimens hydrated under normal conditions;
2. normally hydrated specimens later compacted in a closely fitting mould;
3. compacted samples of bottle-hydrated cement and gypsum;
4. in situ hydrated compacted samples of unhydrated cement and gypsum.

It can be seen that in the gypsum systems (Figure 4.1), which are distinctly crystalline, and where intergrowing of crystals is a distinct possibility, the modulus of elasticity is maximum for specimens in which the original structure was not destroyed, i.e. in systems (1) and (4). On the other hand, lower values were obtained for specimens in which the original structure was destroyed by compaction (system 2) or in those in which the formation of such structure was prevented (system 3). The same results, which are to be expected when chemical bonds are involved, were also obtained in hardness tests.

Testing of the cement specimens produced a different picture altogether (Figure 4.2). It can be seen that essentially the same results were obtained in all of the three systems involved. Assuming that chemical bonds form, lower values are to be expected in systems in which the structure has been destroyed (system 2), or formed by compaction of bottle-hydrated cement (system 3). Since chemical bonds are not remade, these essentially similar results imply that the structure of the hardened cement paste is not characterised by such bonds.

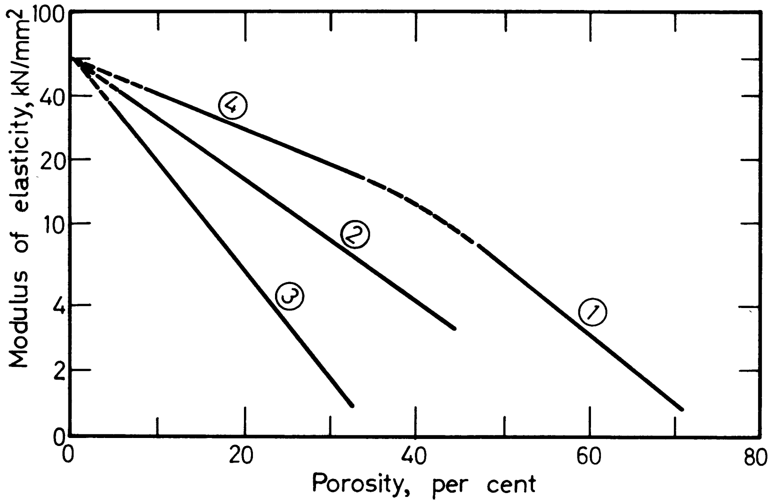

Figure 4.1 *Modulus of elasticity plotted against porosity for various gypsum systems (after Soroka and Sereda*[3]*).* (See text for the different methods of preparation)

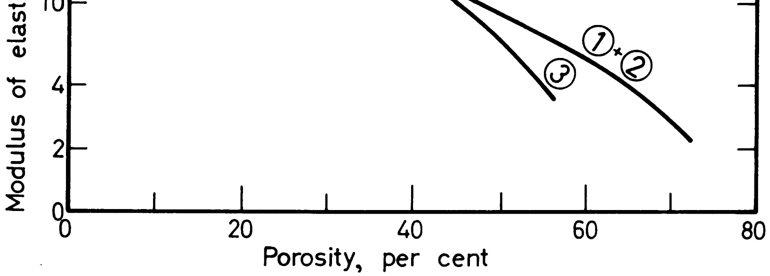

Figure 4.2 *Modulus of elasticity plotted against porosity for various cement systems (after Soroka and Sereda*[4]*).* (See text for the different methods of preparation)

The area of contact between the gel particles is approximately 5% of the cross section of a paste having a porosity of 50%. Hence, the resulting pressure at the contact area can reach 700 N/mm^2 when a compacting pressure of 35 N/mm^2 is employed. Under such pressure no water is expected to remain between the gel particles and, in view of the similar behaviour of the various cement systems, it is reasonable to assume that such water is also not present between the gel particles in a normally hydrated paste. This, in turn, suggests a solid to solid contact between the gel particles without an intervening layer of adsorbed water. In addition, the similarity in the results implies that these solid-to-solid bonds can be remade after being broken.

4.2 Failure mechanism

The theoretical strength of an elastic material depends on the intermolecular cohesion forces which, in turn, depend on the intermolecular spacing. The cohesive forces increase with increase in intermolecular spacing reaching a maximum when the spacing, brought about by tensile stress, is about twice the normal intermolecular distance. With further increase in spacing cohesion forces rapidly decrease and fracture occurs. The tensile strength of materials, calculated from atomic theory, has been found to be up to 1000 times larger than their observed strength. This difference between theoretical and observed strengths of brittle materials was attributed by Griffith in 1920[5] to the presence of cracks and other flaws within the material. Such cracks may be present in the material before any load is applied or may be formed as a result of its application. According to Griffith's theory, the presence of such cracks initiates fracture as a result of high stress concentrations induced at, or near to, the crack when the material is loaded.

Griffith considered an elliptic crack of length $2c$. The decrease in the elastic strain-energy, U, when such a crack is formed in a plate of unit thickness, was shown to be:

$$U = \pi c^2 \sigma^2 / E$$

where σ is the applied tensile stress normal to the plane of the crack and E is the modulus of elasticity of the material.

Griffith suggested that a crack would grow rapidly and cause fracture when the rate of strain energy release was at least equal to the rate of the increase in the energy required to allow for the formation of the new surface area. The total surface energy, W, of the newly formed surface area is given by

$$W = 4cT$$

where T is the specific surface energy. Accordingly, at onset of fracture the following may be written:

$$\frac{d}{dc}\left(\frac{\pi c^2 \sigma^2}{E}\right) = \frac{d}{dc}(4Tc),$$

which gives

$$\pi \sigma^2 c/E = 2T,$$

and the well known Griffith equation

$$\sigma = \sqrt{2ET/\pi c}$$

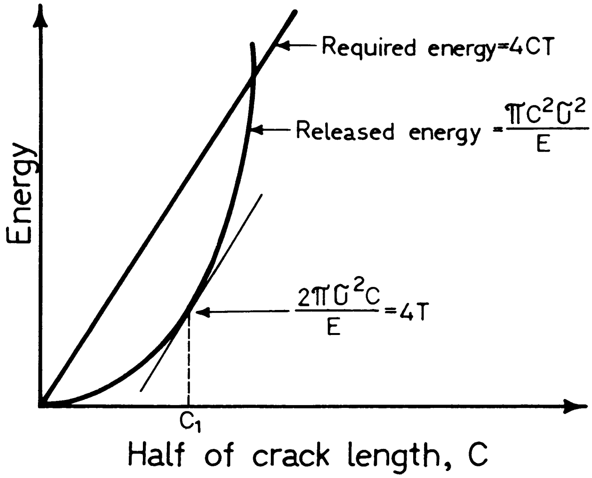

Figure 4.3 *Energy balance in tension for an ideal elastic and homogeneous material (after Glucklich*[9]*)*

Griffith's equation suggests that for a crack length of $2c$ the critical stress causing failure would be $\sqrt{2ET/\pi c}$ or, alternatively, for a given stress, σ, the critical crack length, c, is $2ET/\pi\sigma^2$. Hence, earlier failure (i.e. lower strength) is to be expected when longer cracks or other discontinuities are present in the material. As the presence of the adsorbed water reduces specific surface energy, lower strength is also to be expected when a material is wet.

The energy balance in tension for an elastic and homogeneous material is shown in Figure 4.3. The relation between energy requirement and crack length, c, is linear, being given by $W = 4Tc$. The rate of increase in the energy requirement equals $4T$ and is independent of crack length. The strain energy release curve is given by the second power parabola $U = \pi\sigma^2 c^2/E$ and the strain energy release rate by $dU/dc = 2\pi\sigma^2 c/E$. Onset of instability occurs at crack length c_1 when the slope of the two curves becomes equal.

Cement paste and concrete are brittle materials containing cracks and flaws which, on loading, would grow and subsequently cause failure. In the cement paste the capillary pores constitute such flaws, and in concrete (see Chapter 8) the existing cracks at the paste-aggregate interface do. Hence, Griffith's theory may be applicable to cement paste and concrete. The first person to examine the possibility of applying this theory to concrete was probably Kaplan[6,7] while later it was successfully applied by Glucklich to explain the failure mechanism of concrete.[8,9] Although both Kaplan and Glucklich dealt with concrete, the same considerations are essentially valid for cement paste. Here, both concrete and paste may be regarded as a two-phase materials, the concrete consisting of paste and aggregate, and the paste of CSH gel and unhydrated cement grains. Moreover, in both materials the continuous phase is the weaker one, i.e. the CSH gel in the cement paste, and the cement paste in the concrete. The following discussion is of a general nature and is applicable to both cement paste and concrete. The specific effect of the aggregate on failure mechanism is discussed in Chapter 8 along with a general treatment of concrete strength.

According to Griffith's theory, the energy requirement is determined by the length, c, of the growing crack and the specific surface energy of the material in question. It has been found, however, that in concrete the actual energy requirement exceeds that calculated from the surface area of the critical crack, i.e., the growing crack which caused failure. According to Glucklich,[9] fracture in concrete is not limited to one crack but is characterised by a great number of microcracks which develop in all the highly stressed zones. In other words, the newly formed surface area is much larger than the effective fracture area, and more than just the surface area of the critical crack should be considered in calculating energy requirement. Moreover, as the crack grows, the area of the highly stressed zone grows and the number of microcracks also increases. Consequently, the rate of energy absorption increases with crack length, c, and the energy requirement curve for

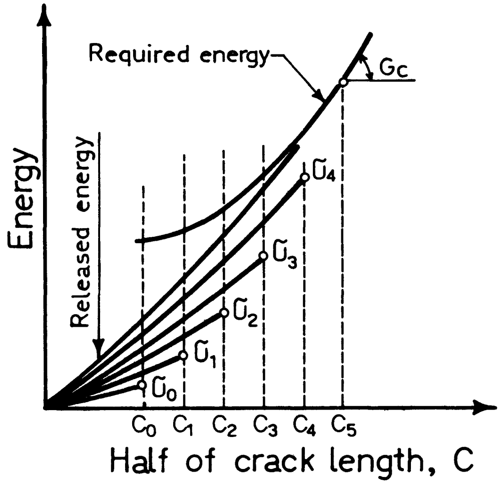

Figure 4.4 *Forced growth of a crack in tension*[9] concrete is not therefore a straight line but a curve with an increasing slope (Figure 4.4). At a certain stage (crack-length c_5), however, the slope ceases to increase because the highly stressed zone reaches its maximum size which is determined, among other things, by the geometry of the specimen.

Figure 4.4 shows schematically crack growth and the associated failure. An initial crack of the length c_0 begins to grow under a stress σ_0. This growth will be checked at length c_1 because of the increase in the energy requirement brought about by the increase in the area of the highly stressed zone, and the resulting increase in the number of microcracks. The crack will continue to grow to the length c_2 when the stress is increased to σ_1 and this process will continue up to the crack length c_5. At this stage the energy requirement ceases to increase, and no further increase of the stress beyond σ_5 is required for the crack to grow further. Consequently, onset of instability occurs and failure is brought about due to the spontaneous growth of the crack. At this stage the strain energy release rate equals the rate of energy requirement, and is known as the 'critical strain energy release rate', and is designated G_c. G_c is therefore the maximum slope of the energy requirement curve in Figure 4.4.

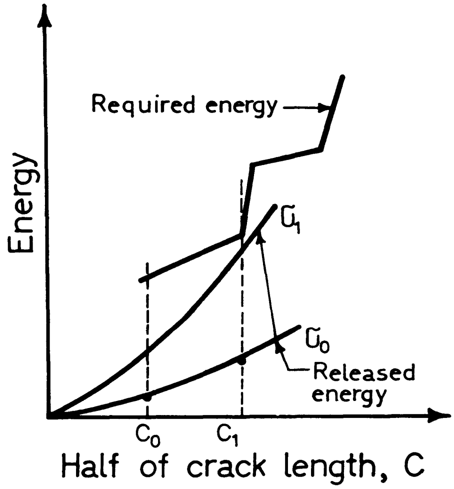

Figure 4.5 *The growth of a crack in a two-phase material*[9]

The heterogeneity of a material affects the energy requirement. This effect is demonstrated in Figure 4.5 which describes crack growth in a two-phase material. An initial crack of the length c_0 will start to grow under a stress σ_0, and will continue to grow up to length c_1 in accordance with the mechanism described in Figure 4.4. At crack length c_1, the crack reaches the second phase which is the harder of the two. At this point, due to the sudden increase in the energy demand, the stress must be significantly increased in order to allow the crack to penetrate the harder phase. Alternatively, the crack may continue to grow around the harder phase. In the latter case the energy demand would also increase because of the increased area of the highly stressed zone. In other words, such heterogeneity acts as a crack arrester and restricts crack growth, thereby delaying fracture and increasing strength.

The preceding discussion considers mainly fracture under tension, and essentially follows the mechanism described in Figure 4.4. Under homogeneous tension the crack initiating fracture would be the crack normal to the stress for which the value $EG_c/c\sigma$ is minimum, i.e. the crack that starts to grow under the lowest stress. At first both crack and stress grow gradually. At a later stage, however, the stress, σ, increases faster than the external load due to the decrease in the uncracked section, and the release of the strain energy, $\pi c^2 \sigma^2/E$, and its rate, $2\pi c\sigma^2/E$, increase even more quickly. Soon the rate of strain energy release becomes equal to the maximum rate of energy requirement. This, in turn, results in rapid growth of the crack and leads to failure.

The fracture mechanism under compression is much more difficult to explain. It can be shown that, under compressive load, localised tension zones are formed around the tips of already existing cracks, in which stress intensity depends on the direction of the crack with respect to the direction of the load and its length to width ratio. As a result of tensile stresses the crack grows in a plan parallel to the direction of the compression, and not in the plane containing the initial crack (Figure 4.6), and subsequently causes failure. In fact, all compression cracking is parallel to the direction of the load because this is the only direction that has no compression component normal to it.

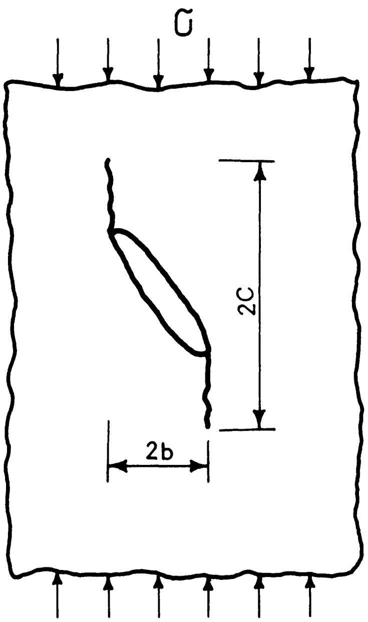

Figure 4.6 *Crack growth in a compression field*[9]

There are two basic differences between failure under tension and failure under compression. In tension the rate of energy release increases with crack length, c, whereas in compression, because crack growth only slightly affects the stress field, the rate of energy release is constant, and independent of crack length. Consequently, in tension, the first crack to grow is the critical crack which leads to failure. In compression, cracks that start to grow are often stabilised when they reach a harder phase. In this case, as pointed out earlier (Figure 4.5), a substantial increase in stress is required to enable the crack to grow into the harder phase. However, before such an increase takes place, other cracks, next in order of weakness, begin to grow until they too are stabilised. This progressive cracking serves as a mechanism of energy dissipation, and constitutes an alternative to fracture. Consequently, fracture is delayed and strength increased. This mechanism explains why cement paste and concrete are much stronger in compression than in tension. It will be shown in Chapter 8 that the tensile strength of concrete is only 10 to 20% of its compressive strength.

4.3 Factors affecting strength

In view of the preceding discussion on the nature of the bond between gel particles and on the fracture mechanism, it is clearly evident that the strength of the hardened cement paste will be determined by many factors. Attributing the forces between gel particles to chemical bonds, the strength of the paste would be related to the number of such bonds per unit volume, to the strength of these bonds, and to the strength of the gel particles themselves. The number of bonds per unit volume depends on the concentration of the hydration products and size and shape of the gel particles. The concentration of the hydration products depends, in turn, on the degree of hydration and the porosity of the paste. The presence of pores also introduces stress concentrations, the intensity of which depends on the size and shape of the pores. A similar picture is obtained when cohesion forces are considered to act between the gel particles, where the specific surface area of the gel particles and the presence of adsorbed water also play an important role. That is, the strength of the paste depends on many factors some of which are interdependent. These factors are discussed below, except that cement composition is dealt with separately in Chapter 7.

4.3.1 Porosity

As far as strength is concerned, the porosity of the paste is the dominant factor. As in other porous solids, the relation between the strength, S, of the paste and its porosity, p, may be generally expressed by

$$S = S_0 \exp(-bp)$$

where S_0 is the strength of the paste at zero porosity and b is a constant which depends on the type of the cement, age of the paste, etc. This expression is not derived from theoretical considerations but results from statistical curve fitting of experimental data. It may be noted that logarithmic transformation of this expression, i.e.

$$\log S = \log S_0 - Kp$$

($K = b \times \log e$), is analogous to the so-called Abrams' 'law' which relates concrete strength to the water/cement ratio, ω. This law plays an important part in concrete technology, and is discussed in some detail in Chapter 8. Generally it is expressed as

$$S = A/B^{\omega}$$

or, logarithmically, by

$$\log S = C - D\omega$$

where $C = \log A$ and $D = \log B$. That is, by a similar expression to the earlier one except that W/C is substituted for porosity. It will be shown later that, for the same degree of hydration, the W/C ratio determines porosity, and therefore such a similarity is to be expected.

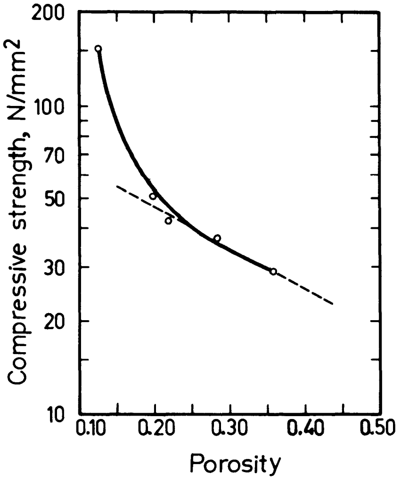

Figure 4.7 Relation between paste compressive strength and its porosity (after Feldman and Beaudoin[10])

The linear relation $\log S = \log S_0 - Kp$ does not necessarily satisfy all available data. This is demonstrated in Figure 4.7 where a deviation from linearity is quite marked in the lower porosity range. In some other tests[11] the expression $p = p_0 \exp(-kS)$ was found to give a good fit with the experimental data (Figure 4.8) (p_0 is the porosity at zero strength). In fact, a few more expressions may be suggested relating the strength of the paste to its porosity.* Powers, for

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*See references in reference 3.

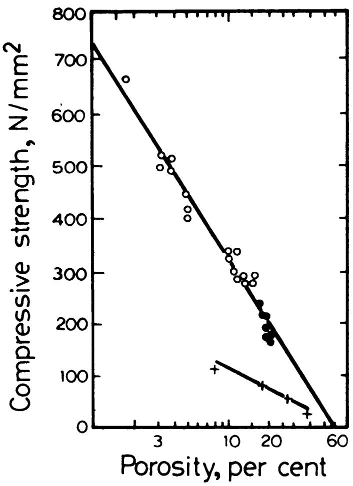

Figure 4.8 *Relation between paste compressive strength and its porosity (after Roy and Gouda*[11]*)*

example,[12] suggested that strength may be related to the concentration of the solid hydration products in the space available for these products, i.e. the sum of the volumes of the hydrated cement (gel volume) and the capillary pores. Accordingly, this concentration was termed 'gel/space ratio', X, and was defined by

$$X = \frac{\text{gel volume}}{\text{gel volume} + \text{capillary pore volume}}$$

It has been shown (Figure 4.9) that the strength of cement paste, f, may be expressed by $f = f_0 X^n$ where f_0 is the strength of the paste at zero capillary porosity (i.e. $X = 1$), and n is a constant which depends on the type of cement and the specific test conditions.

At a later date the definition of gel/space ratio was modified to include the air voids in the paste in the volume available for the hydration products.[30] It was termed 'gel/(space + air) ratio', X, and was defined by

$$X = \frac{\text{gel volume}}{\text{gel volume} + \text{capillary pore volume} + \text{air void volume}}$$

Powers' data, concerning the gel/(space + air) ratio, is presented in Figure 4.10 and gives a very similar picture to that in Figure 4.9. It may be noted, however, that, in both cases, and for all practical purposes, the relation between strength and gel concentration is linear. The suggested exponential expression, however, satisfies the boundary condition $f = 0$ for $X = 0$, and in this respect is preferable.

The data of Figure 4.9, when plotted against capillary porosity, give a linear relation (Figure 4.11) in contrast to the semilogarithmic one indicated in Figure

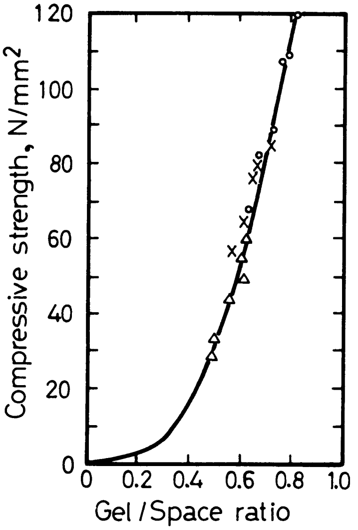

Figure 4.9 *The compressive strength of cement mortar (2 inch cubes) plotted against gel/space ratio (after Powers*[12]*)*

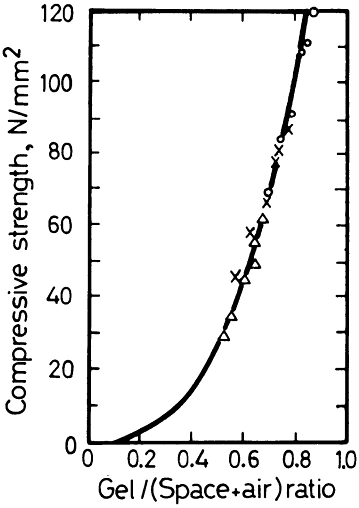

Figure 4.10 *Compressive strength of cement mortar (2 inch cubes) plotted against gel/(space + air) ratio (after Powers*[12]*)*

4.8. This difference may be attributed, partly at least, to the different presentation of the data, i.e. the strength being related to total porosity in Figure 4.8 and to capillary porosity in Figure 4.11. Nevertheless, it is evident from the preceding discussion that strength may be related to porosity by more than one expression. This may be due to the fact that all expressions discussed result from

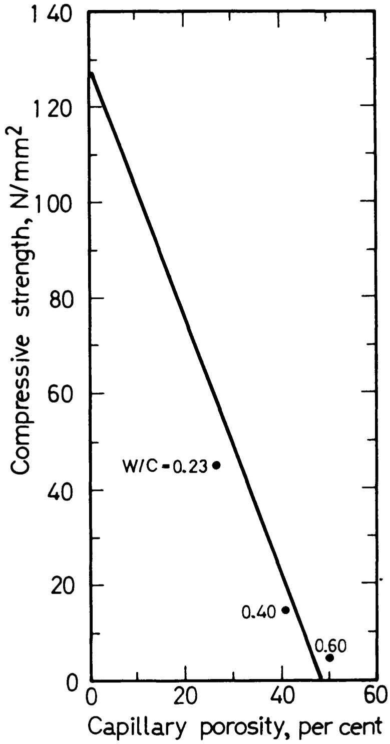

Figure 4.11 *Compressive strength of cement mortar (2 inch cubes) plotted against capillary porosity*[13]

curve-fitting of experimental data which, in turn, were obtained under different test conditions and which did not consider such parameters as pore size, shape, and distribution. In any case, it is generally agreed that porosity constitutes the most important single factor in determining strength. It follows that any factors which affect porosity of the paste would also affect its strength. In this context, the most important ones are *W/C* ratio and degree of hydration, which directly affect porosity. Some other factors, however, affect porosity indirectly mostly through their effect on the degree of hydration. A detailed discussion of these factors is presented below.

4.3.2 Water/cement ratio

The water/cement ratio determines the initial porosity of the paste, i.e. the relative water content in the paste. The volume of the cement paste is equal to the sum of the volumes of the anhydrous cement and the mixing water. Accordingly, the volume, V, of the paste is given by

$$V = C v_c + \omega C$$

and its initial porosity, p_i, by

$$p_i = \omega/(v_c + \omega)$$

where C is the weight of the cement, v_c is its specific volume, and ω is the water/cement ratio.

This relation between the initial porosity and the W/C ratio is plotted in Figure 4.12 for $v_c = 0.32\ \mathrm{cm^3/g}$. It can be seen that the initial porosity increases with increase in the W/C ratio.

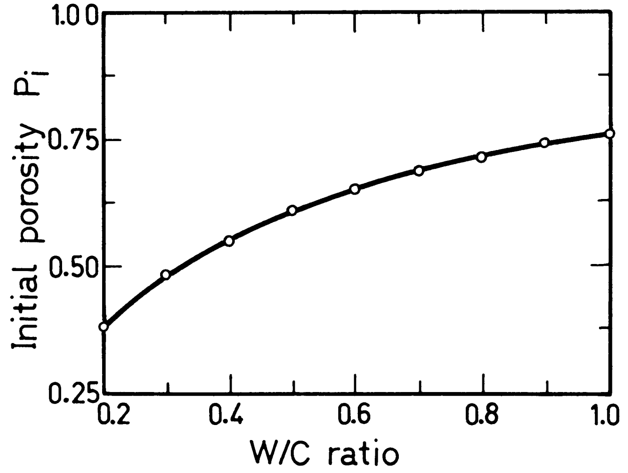

Figure 4.12 *The relation between initial porosity and W/C ratio in a cement paste*

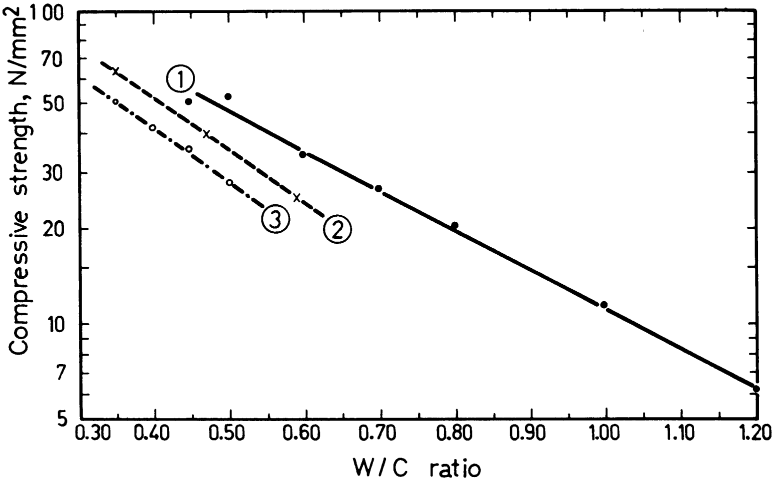

Figure 4.13 *Relation between the compressive strength of cement pastes and their W/C ratios (after* (1) *Soroka and Sereda,*[15] (2) *Spooner,*[14] and (3) *Feldman and Beaudoin*[10])

The porosity of the paste also depends on the degree of hydration; this dependence is treated quantitatively later in this chapter. At the same degree of hydration, the porosity of the paste is determined by its initial porosity, i.e. by its W/C ratio. In other words, in pastes of the same degree of hydration the W/C ratio is a measure of the porosity. Consequently, the relation between the strength of the paste and the W/C ratio should be similar to that between strength and porosity. Such a similarity is apparent from Figure 4.13, in which the logarithm of the strength, S, of cement pastes is plotted against the respective W/C ratios, ω. It can be seen that the relation is linear and may be expressed generally as $\log S = A - B\omega$. It may be noted that this expression is, in fact, identical to Abrams' 'law'.

4.3.3 Degree of hydration

As the volume of the hydration products is greater than that of the reacting cement, the porosity of paste decreases as hydration proceeds. This can be demonstrated quantitatively by assuming, after Powers, that the volume of the gel is 2.2 times the volume of the anhydrous cement and that it has a characteristic porosity of 28% (see Chapter 3). Also, it is assumed that no bulk volume changes occur during hydration. Accordingly the volume of the paste is constant, and equal to the volume of the original water-cement system, i.e. $V = Cv_c + \omega C$.

For a given degree of hydration, α, the volume fraction of the unhydrated cement, R_c, in the paste is given by ($v_c = 0.32\ \mathrm{cm^3/g}$)

$$R_c = \frac{Cv_c(1-\alpha)}{Cv_c + \omega C} = \frac{v_c(1-\alpha)}{v_c + \omega} = \frac{0.32}{0.32+\omega}(1-\alpha) \tag{4.1}$$

The volume of the solids in the paste is the sum of the volumes of the unhydrated cement and the hydration products. The volume of the gel being 2.2 times the volume of the reacting cement and the volume of the hydration products being 72% of the volume of the gel, the volume fraction of the solids, R_s, in the paste is given by

$$R_s = \frac{0.32}{0.32+\omega}(1-\alpha) + \frac{0.72 \times 2.2 \times 0.32\alpha}{0.32+\omega} = \frac{0.32 + 0.187\alpha}{0.32+\omega} \tag{4.2}$$

Similarly, the volume fraction of the gel and the cement, $R_c + R_g$ is given by

$$R_{c+g} = \frac{0.32}{0.32+\omega}(1-\alpha) + \frac{2.2 \times 0.32\alpha}{0.32+\omega} = \frac{0.32 + 0.384\alpha}{0.32+\omega} \tag{4.3}$$

Hence, the gel volume-fraction is given by

$$R_g = R_{c+g} - R_c \tag{4.4}$$

the volume-fraction of the hydration products, R_h, by

$$R_h = R_s - R_c \tag{4.5}$$

the volume-fraction of the gel pores, p_g, by

$$p_g = R_{c+g} - R_s \tag{4.6}$$

and the volume fraction of the capillary pores, p_c, by

$$p_c = 1 - R_{c+g} \tag{4.7}$$

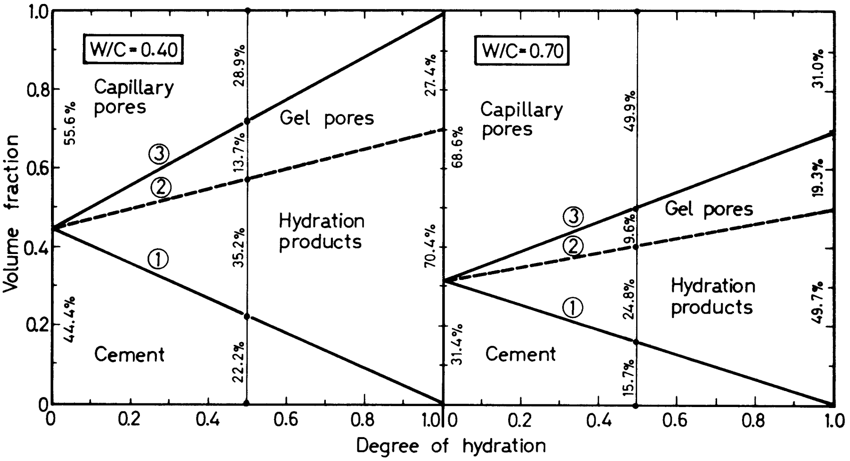

Figure 4.14 *Relation between porosity and degree of hydration for pastes having W/C ratios of 0.4 and 0.7. Volume fraction of* (1) *unhydrated cement,* (2) *solids, and* (3) *unhydrated cement + gel*

Table 4.1 Effect of W/C ratio and degree of hydration on the structure of the cement paste

Component	*Equation*	*Relative volume, %*					
		W/C = 0.40			*W/C* = 0.70		
		α, Degree of hydration, %					
		0	50	100	0	50	100
Cement	(4.1)	44.4	22.2	0	31.4	15.7	0
Gel	(4.4)	0	48.9	97.8	0	34.4	69.0
Capillary pores	(4.7)	55.6	28.9	2.2	68.6	49.9	31.0
Total		100.0	100.0	100.0	100.0	100.0	100.0
Hydration products	(4.5)	0	35.2	70.4	0	24.8	49.7
Gel pores	(4.6)	0	13.7	27.4	0	9.6	19.3
Total porosity		55.6	42.6	29.6	68.6	59.8	50.3

Equations (4.1), (4.2), and (4.3) are plotted in Figure 4.14 for W/C ratios of 0.4 and 0.7. The solutions of these equations for $\alpha = 50\%$ and 100% are given in Table 4.1.

It is evident from Figure 4.14 and Table 4.1 that for the same degree of hydration, the porosity of the paste is determined by the W/C ratio, and that a higher W/C ratio is associated with a higher porosity. Also, it can be seen that total and capillary porosities decrease with increase in the degree of hydration. The strength being related to porosity, a similar relation is to be expected between the strength and degree of hydration. This is confirmed by the data of Figure 4.15, in which the strength of the paste is plotted against the parameter V_m/W_0. V_m is the amount of water required to cover the surface of the gel with a monomolecular layer and W_0 is the original amount of mixing water. Accordingly, V_m measures gel surface area and thereby also the gel content of the paste. In a given paste W_0 is constant and V_m/W_0 is therefore a measure of the degree of hydration.

Since the strength of a paste is related to the degree of hydration, all factors affecting the latter will also affect the strength. These factors, which include age, type of cement (composition and fineness), admixtures, etc. were discussed in Chapter 2. In this respect, the effect of temperature is more complicated, and it is not always possible to attribute its effect solely to its effect on the rate of hydration. Consequently, the effect of temperature on strength is treated separately.

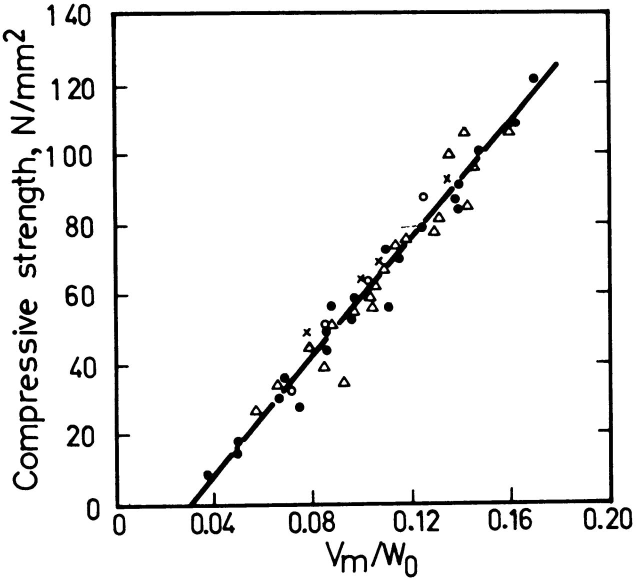

Figure 4.15 *Compressive strength of cement paste plotted against* V_m/W_0[16]

4.3.4 Temperature

In discussing the effect of temperature on strength, a distinction should be made between temperatures in the range of 0 to 100°C (i.e. above the freezing point and below the boiling point of water) and those exceeding 100°C. The following discussion is limited to the lower range in which exposure of the paste to water vapour can be effected under atmospheric pressure. The discussion also assumes that the paste is exposed to warm water vapour or is immersed in hot water. That is, conditions where drying-out of the paste is avoided and the degree of hydration is governed by temperature alone.

In Chapter 2, it was shown that increase in temperature up to, say, 90°C, increases the rate of cement hydration. This increased rate is evident mainly during the early stages of the hydration. The final degree of hydration was only slightly affected by curing temperature. The same behaviour is indicated in Figure 4.16, which shows the degree of hydration (combined water) at various ages for curing temperatures of 20°C and 80°C.[17] Here, although the difference in the degree of hydration decreased with time, a somewhat higher amount was obtained with the paste cured at 80°C. In other cases, however, a higher degree of hydration has sometimes been found for the hydration at a lower temperature.

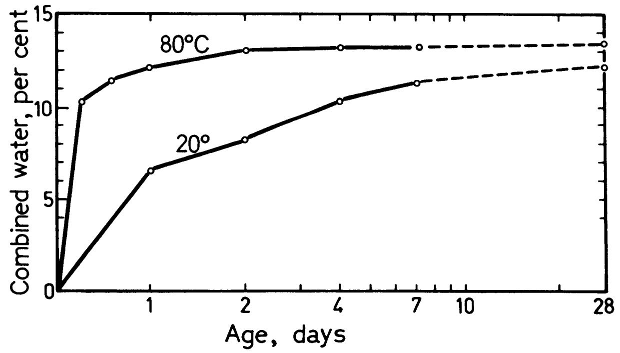

Figure 4.16 *Effect of temperature on degree of hydration (after Odler and Gebauer*[17]*)*

Such results have been obtained for cement pastes (Figure 4.17) as well as for dicalcium and tricalcium silicate pastes (Figure 4.18). The lower degree of hydration at higher temperatures was attributed to possible changes in the composition of the hydrates (the C/S ratio) and to the greater density of the gel layer which is formed around the cement grains.[20] However, the temperature effect on the ultimate degree of hydration is small.

Since temperature has only a limited effect on the ultimate degree of hydration, essentially the same ultimate strength is to be expected in pastes of the same *W/C* ratio irrespective of curing temperature. Generally speaking, this is not the case

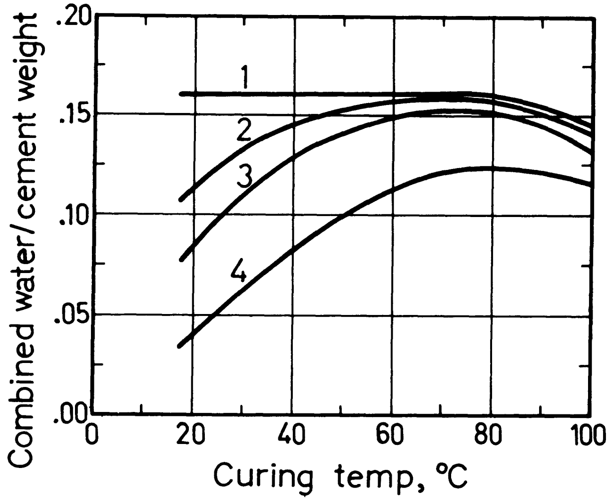

Figure 4.17 *Effect of temperature on degree of hydration* (*after Idorn*[18]). (1) *at* 28 *days after* 48 *hours of steam-curing followed by immersion in water at* 20°C *and* (2) *steam-curing for* 48 *hours,* (3) 24 *hours, and* (4) 6 *hours*

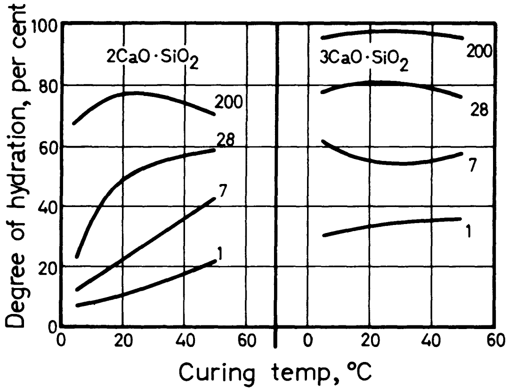

Figure 4.18 *Effect of temperature on degree of hydration of dicalcium and tricalcium silicate pastes* (*after Verbeck*[19]) *at various ages (days)*

and a lower curing temperature is usually associated with a higher strength. This effect is illustrated in Figure 4.19 which is based on the data of Figure 4.16. It can be seen that the increased degree of hydration results in higher strength only at early ages whereas at later ages, regardless of the increased degree of hydration, the paste hydrated at the higher temperature exhibits lower strength, particularly flexural strength. This behaviour suggests that the temperature effect involves

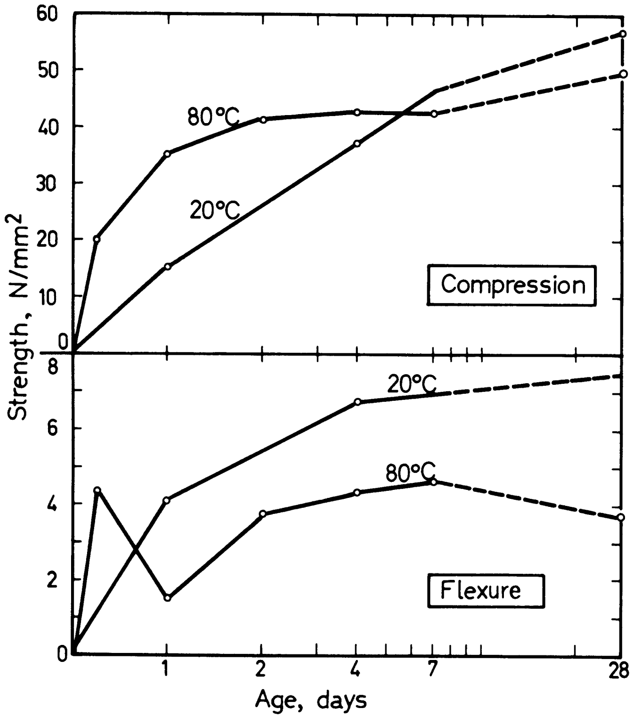

Figure 4.19 *Effect of curing temperature on strength of cement paste (after Odler and Gebauer*[17]*)*

two opposing factors and the final strength is dependent on which one is dominant at the time. Apparently, at early ages, the increased amount of hydration is the predominant factor and, consequently, the strength of the paste is greater when hydration takes place at a higher temperature. The difference in the amount of hydration at the different temperatures gradually decreases with time and hence the effect of this factor on strength also gradually decreases. At a certain stage the beneficial effect of the increased hydration equals, and later becomes lower than, the detrimental effect of the higher curing temperature; the strength of the paste is consequently reduced.

There is some disagreement about the exact nature of this detrimental effect on strength. It is generally agreed, however, that within the temperature range in question essentially the same hydration products are involved, and the detrimental effect may not be explained from physical or chemical changes in these products. This conclusion is, to some extent, evident from Figure 4.20(1), in which the ratio of the combined water to heat of hydration is plotted against curing temperature.[20] As both combined water and heat of hydration give a measure of the degree of hydration, the fact that the ratio remains constant implies that

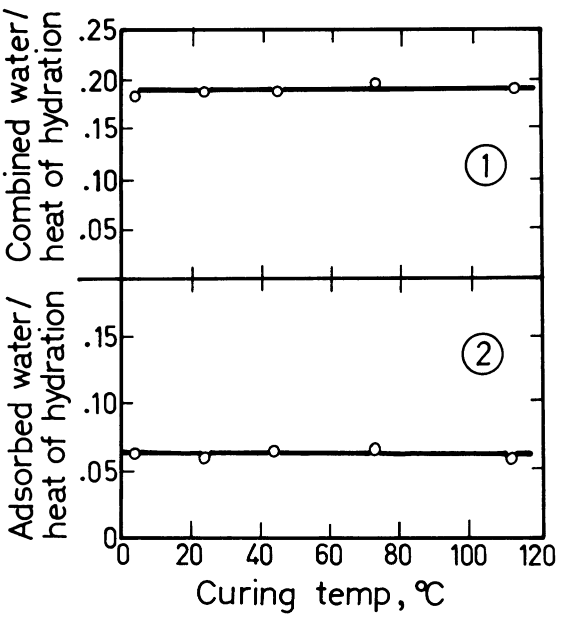

Figure 4.20 *Effect of curing temperature on ratio of* (1) *combined water to heat of hydration and* (2) *adsorbed water to heat of hydration* (*after Verbeck and Helmuth*[20])

no chemical change in the hydration products is brought about by the difference in curing temperatures. Similarly, it can be seen from Figure 4.20(2) that no physical changes are produced by change in curing temperature. The ratio of adsorbed water to heat of hydration is a measure of the ratio of the gel surface area to its content, i.e. the gel specific surface area. That the gel specific surface area remains constant implies, therefore, that no changes in the structure of the gel are involved.

As curing temperature has been considered to have no significant effect on the chemical and physical nature of the hydration products, there has been a tendency to attribute the detrimental effect of higher temperatures on strength to various physical factors. As mentioned earlier there is, however, some disagreement about the exact nature of these factors. Verbeck and Helmuth[20] attribute the detrimental effect of temperature to the heterogeneity of the gel which is produced when the cement hydrates at a high temperature. They suggest that at low temperature the hydration is slow and there is ample time for the hydration products to diffuse and precipitate relatively uniformly throughout the interstitial space between the cement grains. On the other hand, when the cement hydrates at high temperature, the high rate of reaction does not allow time for such diffusion and there is a tendency for the hydration products to precipitate in the immediate vicinity of the hydrating cement grains. This results in the formation of a highly concentrated and dense gel around the hydrating cement grains, and the formation of a less concentrated gel, and therefore a weaker one, in the space between the grains. This weaker part of the gel must limit the strength of the paste, and its formation therefore has a detrimental effect on the strength of the paste. Moreover, the formation of the dense layer encapsulating the cement grains would retard subsequent hydration (Figure 4.18). In other words, both the retarded subsequent hydration and, primarily, the non-uniform distribution of the hydration products are considered to be the cause of the detrimental temperature effect on the strength. In this respect, however, it should be noted that the suggested retarding effect on the cement hydration has not been observed in all cases (Figure 4.16) while the hypothesis of a non-uniform gel is not supported, as yet, by experimental data.

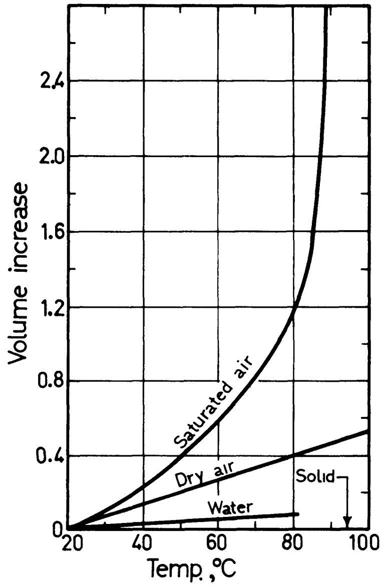

Figure 4.21 *Relative thermal expansion of water and air relative to that of solids (after Alexanderson*[25]*)*

Others have considered the difference in the coefficients of thermal expansion of the various constituents of the paste, to be the major cause of the detrimental temperature effect.[21-25] The greater thermal expansion of water and of air, and particularly of wet air (Figure 4.21), may produce internal stresses which, in turn, increase the porosity of the paste and may cause cracking. Such cracking has been observed in concrete specimens cured at high temperatures[25] and its presence is indirectly supported by the data of Figure 4.19. It can be seen that the reduction in flexural strength, which is more sensitive to cracking, is greater than the corresponding reduction in compressive strength. Also, it is to be expected that these effects would be more pronounced in weaker than in stronger pastes. As the strength of the paste increases with age, the delay in its exposure to high temperatures should decrease the detrimental effect of temperature on strength. This, indeed, is generally the case, and the beneficial effect of a delay period is sometimes used in the concrete industry when steam-curing is involved. This aspect is further discussed in Chapter 11.

4.3.5 Temperature combined with pressure (autoclave treatment)

Steam curing under pressure, i.e. treatment in an autoclave, is sometimes employed in the production of cement products. Such treatment allows the use of temperatures exceeding 100°C without causing drying out. Autoclave treatment has a detrimental effect on strength, which is even greater than the previously discussed effect for temperatures below 100°C. In addition, autoclave treatment causes structural and chemical changes in the paste and these may explain the detrimental effect on strength.

It was shown in Chapter 3 that temperatures above 100°C impart to the gel a coarser structure, which is reflected in the absence of small pores (i.e. gel pores according to Powers) (Figure 3.7) and in a lower specific surface area. It can be seen from Table 3.4 that the specific surface area decreases with increase in curing temperature, and that this decrease is associated with a corresponding reduction in strength. In part, this reduction in strength may be attributed to the reduced degree of hydration. It is clear, however, that the difference in the degree of hydration is rather small, and the reduction in strength can not be attributed to this factor alone. For example, the strength of the paste cured at 160°C is approximately 35% of that of the paste cured at 27°C whereas the degree of hydration of both pastes is essentially the same. It seems, therefore, that the decrease in strength may be attributable to the coarser gel structure obtained when high curing temperatures were employed. This effect is to be expected because the strength of the cement gel is determined, to an appreciable extent, by cohesion forces acting between the gel particles. Because the cohesion forces are a surface effect, a coarser structure will result in lower strength.

Autoclave treatment also affects the composition of the hydration products. The exact nature of this effect depends on curing temperature and on the CaO/SiO_2 molar ratio, as indicated by the phase diagram presented in Figure 4.22.[26] The C/S ratio in Portland cement varies from 2 to 3, and within this range the same hydration products, i.e. CSH gel, are obtained for temperatures up to 100°C (area 1 in Figure 4.22). Higher temperatures are characterised by the formation of $C_2SH(A)$ which is always present when the cement is exposed to the more commonly used temperature range 160 to 193°C (area 2). The detrimental effect of autoclave treatment may be attributed, in part at least, to this formation of $C_2SH(A)$. If such were the case, the effect may be eliminated if the formation of $C_2SH(A)$ is avoided altogether, i.e. when the C/S ratio is reduced to about one. This ratio may be obtained by mixing the cement with

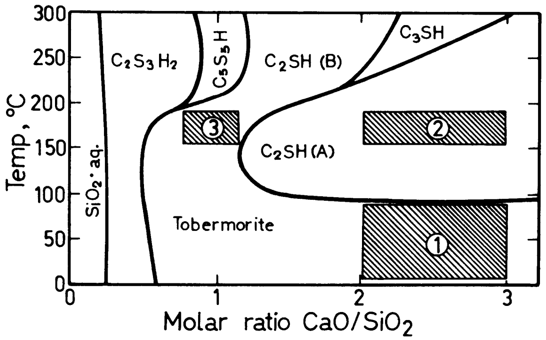

Figure 4.22 *Phase diagram of the* $CaO\text{-}SiO_2\text{-}H_2O$ *system (after Verbeck and Copeland*[26]*)*

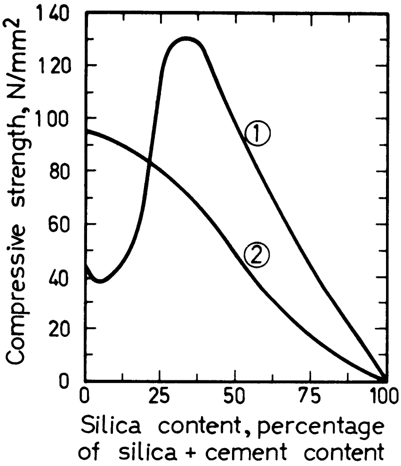

Figure 4.23 *Effect of silica content on strength of cement paste,* (1) *heated in an autoclave for* 24 *hours at* 160°C *and* (2) *normally cured at* 21°C *for* 28 *days*[27–28]

30 to 40% (by weight) of finely ground siliceous sand. This addition eliminates the detrimental effect of autoclave treatment on strength, as is clearly evident from Figure 4.23.[27] It can be seen that the strength of the autoclave treated paste (plot 1) is about half that of the normally cured paste (plot 2). The addition of silica improves the strength of the autoclave treated paste which reaches a maximum at the optimum content of, say, 30% silica. Moreover, this maximum is substantially higher than the strength of normally cured paste.

The detrimental effect of autoclave treatment on strength can also be explained by its effect on the porosity of the paste. For a given *W/C* ratio and degree of hydration, the porosity of the paste is determined by the density of the hydration products, with the porosity increasing with the increase in density of the products. It was observed by Feldman and Beaudoin[10] that the density of hydration products in autoclave treated pastes was greater than that of the products in normally cured pastes. In fact, such an observation is to be expected in view of the density of the individual hydration products. The density of CSH(I), which is characteristic of normally cured pastes, is 2.0 to 2.2 g/cm^3, and the density of CSH(II) is probably the same. On the other hand, the density of the hydration products which are present in autoclave treated pastes is higher being 2.80 g/cm^3 for $C_2SH(A)$, 2.71 g/cm^3 for xonotlite (C_5S_5H), 2.56 g/cm^3 for C_3SH and 2.42-2.46 g/cm^3 for tobermorite.[29] Hence, autoclave treatment involves increased porosity and this may explain, in part at least, the detrimental effect on strength.

It may be concluded that the detrimental effect of autoclave treatment on strength is attributable to the formation of $C_2SH(A)$ and the associated increased porosity, and to the resulting coarser structure of the gel. The addition of silica, in an amount required to give a C/S ratio of approximately one, results in the formation of tobermorite instead of $C_2SH(A)$. This, in turn, improves the strength to such an extent that the detrimental effect is completely eliminated. It seems, therefore, that the mineralogical composition of the paste, rather than its physical properties, is the major strength-affecting factor.

4.3.6 Moisture content

According to Griffith's theory, strength is expected to decrease with increase in the moisture content of a material because the presence of adsorbed water reduces specific surface energy. This applies to cement pastes in which the effect is more pronounced at the lower range of moisture content (Figure 4.24). It can be seen that moisture content at 15% relative humidity reduced the strength of the paste by approximately 30% whereas further increase in moisture content reduced strength by only a little more, the total reduction in the strength of the

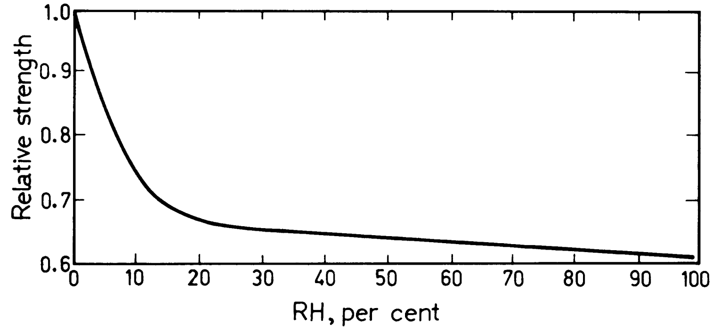

Figure 4.24 Effect of moisture content on compressive strength of cement paste (after Sereda and Feldman[32])

saturated paste being approximately 40%.[32] Similar results were obtained by others for compressive[1] as well as for flexural strength.[31]

According to Feldman and Sereda[32] the decrease in strength is due to the change in environment and not to the change in the state of the solid. It is suggested that stress concentrations at the apex of the pointed cracks are straining the Si-O-Si bonds and this strain energy contributes to a greater ease of formation of hydroxyl groups, Si-OH HO-Si, in the presence of water vapour. Thus, in the presence of water, the breaking of these bonds will occur more readily. When the concentration of the water molecules is sufficient to maintain a rate of diffusion that will deliver the minimum required amount of water into an extending crack, then no further decrease in strength will occur on further water addition.

Another explanation is to attribute the decrease in strength to the decrease in cohesion forces which results from the presence of adsorbed water. A decrease in the cohesion forces involves weaker bonds between gel particles and therefore results in weaker paste.

4.4 Summary and concluding remarks

The bonds between gel particles are a mixture of both chemical (primary) and weaker (secondary) bonds, the latter resulting from cohesion forces (van der Waals forces) acting between particles. Others have postulated a solid to solid contact with the forces acting between adjacent particles being dependent on the degree of disorder and the average spacing of the atoms at the particle boundary.

Griffith's theory of fracture mechanism is applicable to hardened cement paste and concrete. Failure is brought about by the spontaneous growth of a critical crack when the energy release rate equals the maximum rate of energy requirement for crack elongation. The former rate is known as the 'critical strain energy release rate', and is designated G_c. In cement paste and concrete most of the strain energy is converted into surface energy. The cracking of the two materials is not limited, however, to a single crack but involves a multitude of microcracks which develop in the highly stressed zones at the tips of the growing crack, i.e. the actual area of the newly formed surface is larger than the effective area of the main crack. The area of the cracked zone increases with increase in the crack length. Consequently, G_c increases and the strength of the paste increases correspondingly. Under tension the energy release rate increases with crack length whereas in compression it remains constant. Therefore, in tension the critical crack is the first crack to start growing whereas in compression cracking is progressive. This difference explains why paste and concrete are much stronger under compression than under tension.

Porosity is the major factor determining the strength of the paste. Porosity, in turn, is determined by the W/C ratio and the degree of hydration. Consequently, all the factors that affect the degree of hydration, will also affect the strength of the paste. Under otherwise similar conditions, and provided that there is sufficient moisture to ensure continued hydration, the degree of hydration depends on the type of cement, the age of the paste, etc. (see Chapter 2). High temperature curing (but below 100°C) improves early-age strength of the paste but may have a detrimental effect on its later strength. This detrimental effect is mainly due to differential thermal expansion of the constituents of the paste which causes increased porosity and possibly internal cracking. Temperatures exceeding 100°C combined with pressure have an even greater detrimental effect on strength which may be attributed to mineralogical and physical changes in the hydration products. This detrimental effect may be avoided by the addition of silica to give a cement + silica mixture with C/S ratio of approximately one.

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5 Volume changes in the hardened paste

5.1 Introduction

It was stated earlier that the volume of the hydration products is smaller than the combined volumes of the reacting cement and water by approximately 25% of the water volume. Under normal conditions this reduction in the volume of the cement-water system increases the porosity of the paste and is not reflected in the bulk dimensions. A change in bulk dimensions may be caused by the presence of excessive free lime or magnesia in the cement or, as will be seen later (Chapter 6), due to chemical attack of aggressive solutions, etc. These types of volume change take place only under special conditions and involve chemical changes in the cement paste. The following discussion, however, is limited mostly to volume changes caused by physical factors such as external loading and changes in moisture content and temperature, and involve no chemical changes. An exception is carbonation shrinkage which is included in this discussion.

5.2 Elastic volume changes

5.2.1 Modulus of elasticity

The modulus of elasticity of the cement paste is related to its compressive strength, increasing with increase in the latter (Figure 5.1). Consequently, all factors which affect strength also affect the modulus of elasticity of the paste. An exception to this is the moisture content of the paste which affects the two properties differently.

Like strength, the modulus of elasticity can be related to the porosity of the paste and a similar expression

$$E = E_0 \exp(-bp)$$

can be written where E_0 is the modulus of elasticity of a paste of zero porosity ($p = 0$) and b is a constant which depends on the specific test conditions. This

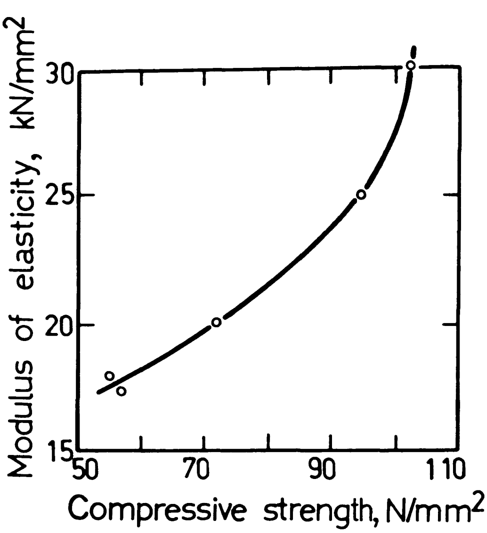

Figure 5.1 *Relation between modulus of elasticity and compressive strength for cement paste (after Feldman and Beaudoin*[1]*)*

expression, which is based on statistical curve fitting, is generally valid for porous solids.[2-4] A few other expressions have been suggested, some of which were developed analytically from physical and geometrical considerations.[5,6] Powers, for example, suggested the expression

$$E = E_g (1 - \epsilon_c)^3$$

where ϵ_c is the capillary porosity, E is the modulus of elasticity of the paste, and E_g is the modulus when $\epsilon_c = 0$, i.e. E_g represents the modulus of elasticity of the gel.[7] It was shown[8] that in this expression capillary porosity, ϵ_c may be replaced by total porosity, ϵ (Figure 5.2).

Generally speaking, the strength of the cement paste decreases with decreasing moisture content (Figure 4.24), whereas its modulus of elasticity increases. It can be seen from Figure 5.3 that the modulus of elasticity attains its maximum on saturation, and decreases considerably on drying at 47% relative humidity. On rewetting the modulus increases, and on redrying at 7% relative humidity it decreases again. The effect of moisture content, however, is not completely reversible due to irreversible changes in the structure of the paste. These changes are discussed later in relation to irreversible drying shrinkage of cement paste.

The effect of moisture content on the modulus of elasticity of the cement paste is also demonstrated in Figure 5.4.[10] It can be seen that drying of the saturated paste at 0% relative humidity decreases considerably the modulus of elasticity. Rewetting, however, starts to affect the modulus only at a moisture

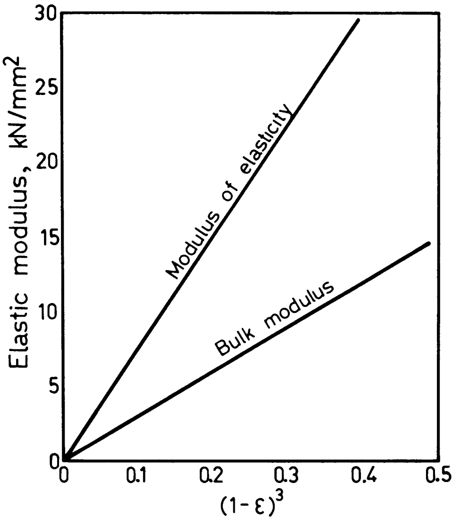

Figure 5.2 Effect of total porosity ϵ on modulus of elasticity of cement paste (after Helmuth and Turk[8])

content corresponding to a state of equilibrium at approximately 55% relative humidity, and on redrying the modulus is affected only at the very low end of relative humidity scale. It may be noted that this relation between modulus of elasticity and moisture content resembles the interlayer-water isotherm of Feldman and Sereda's model (Figure 3.15A). Indeed, this model attributes the

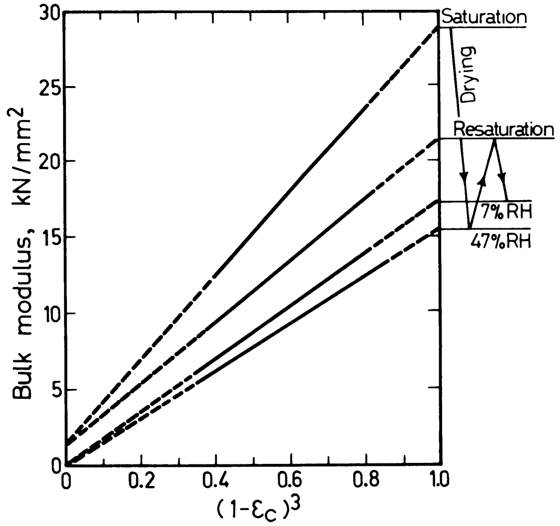

Figure 5.3 Effect of moisture content and capillary porosity on bulk modulus of elasticity of cement paste (after Verbeck and Helmuth[9])

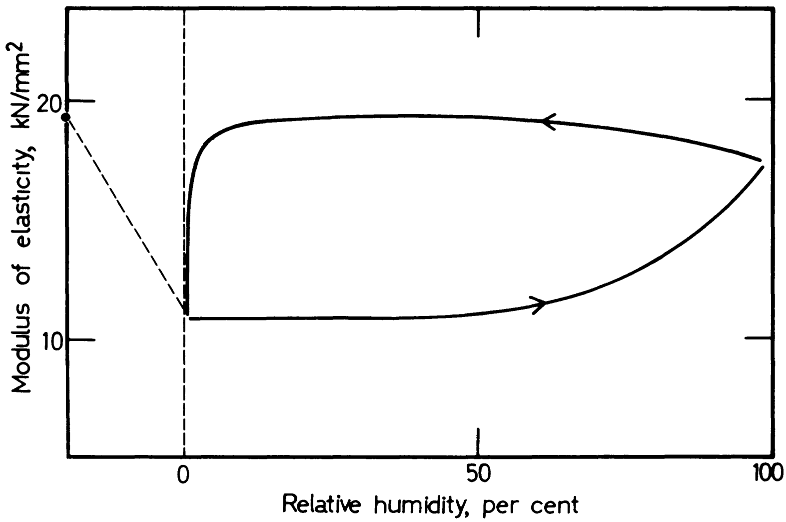

Figure 5.4 *Effect of moisture content on modulus of elasticity of cement paste (after Sereda et al.*[10]*)*

variation in the modulus of the cement paste with change in moisture content to movement of interlayer water.

The layered structure of the gel particles is described simply in Figure 5.5 by two parallel short lines. The water between the two lines, marked x in the figure, is interlayer water. The right hand part of the figure describes the variation in the modulus of elasticity of the paste with the change in its moisture content (i.e. Figure 5.4), and the left hand part is the isotherm for the interlayer water (i.e. Figure 3.15A). The letters A to G represent the very same stages in all parts of Figure 5.5.

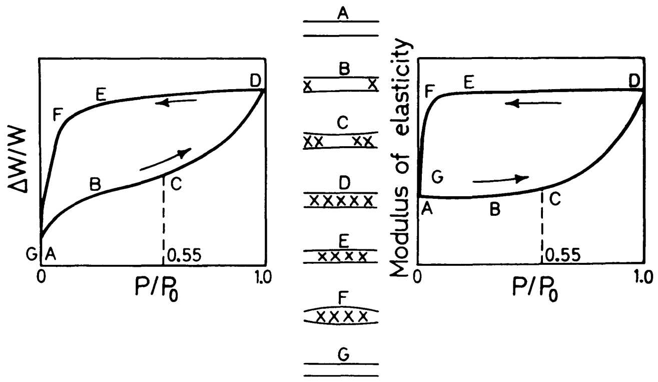

Figure 5.5 *Effect of exit and re-entry of interlayer water on modulus of elasticity of cement paste (after Feldman and Sereda*[11]*)*

On increasing the relative humidity, water starts to enter the structure from the edges causing expansion by opening up the layers (stages A to C). It will be shown later (Figure 5.8), as is also implied by Figure 5.5, that the greater part of the swelling of the cement paste takes place at this stage. On the other hand, there will be no significant increase in the modulus of elasticity until the middle starts to fill, and the water molecules begin to act as webs or cross-links in a sandwich-type construction. This stiffening effect, and the associated increase in the modulus, takes place from C to D and reaches a maximum when the layers are saturated (stage D). On drying from D to E, virtually no interlayer water is lost, and therefore the modulus is hardly affected. From E to F a small amount of interlayer water is lost from the edges, and the modulus, again, is hardly affected. Only when the interlayer water is removed from the middle (i.e. F to G) is the modulus of elasticity considerably decreased.

5.2.2 Poisson's ratio

Poisson's ratio is, by definition, the ratio of the lateral to the longitudinal (axial) strain in a loaded specimen. In a study by Helmuth and Turk[8] the ratio in a saturated paste was found to vary from 0.26 to 0.31. In a paste dried at 7% and 47% relative humidity the ratio was 0.18.

The *W/C* ratio apparently does not affect Poisson's ratio. In one study the ratio averaged 0.25 independent of the *W/C* ratio,[13] and in another 0.21.[14]

5.3 Shrinkage and swelling

5.3.1 Introduction and definitions

The volume of a cement paste varies with its water content. Drying causes volume decrease (i.e. 'drying shrinkage' or simply shrinkage), and wetting causes volume increase (i.e. swelling). Maximum shrinkage occurs on first drying of the paste, and a considerable part of this shrinkage is irreversible. That is, part of the volume decrease is not recovered on subsequent rewetting. Further cycles of drying and wetting result in additional, usually smaller, irreversible shrinkage. After some time, however, the process becomes more or less completely reversible. Hence, the distinction between 'reversible' and 'irreversible' shrinkage. A schematic description of the preceding volume changes, in which irreversible shrinkage is assumed to take place on first drying only, is presented in Figure 5.6. It may also be noted from the figure that continuous immersion in water causes swelling of the paste.

The shrinkage of a cement paste, which was subjected to drying at the relative humidities indicated,[9] is plotted in Figure 5.7 against the corresponding water losses. The resulting plot is linear with a distinct increase in the slope of the line at a water loss corresponding to drying at about 10% relative humidity. Accordingly, whereas a water loss of approximately 17% in the high humidity region results in a shrinkage of about 0.6%, an additional loss of only 6% in the lower region doubles the srhinkage to 1.2%. It seems, therefore, that the water lost during the last drying stages affects shrinkage to a much greater extent than the water lost during the early stages. The same conclusion is also apparent from Figure 5.8 which presents length change isotherms for cement pastes.[15] On desorption in the relative humidity range from 100 to 10%, the slope of the curve is fairly gentle, whereas from 10 to 0% it becomes almost vertical. It can be seen, both in this case and from the data of Figure 5.7, that most of the shrinkage is associated with water loss in the low-humidity range. It is also evident from the scanning loops that length change isotherms, like the adsorption isotherms, are irreversible over the whole region.

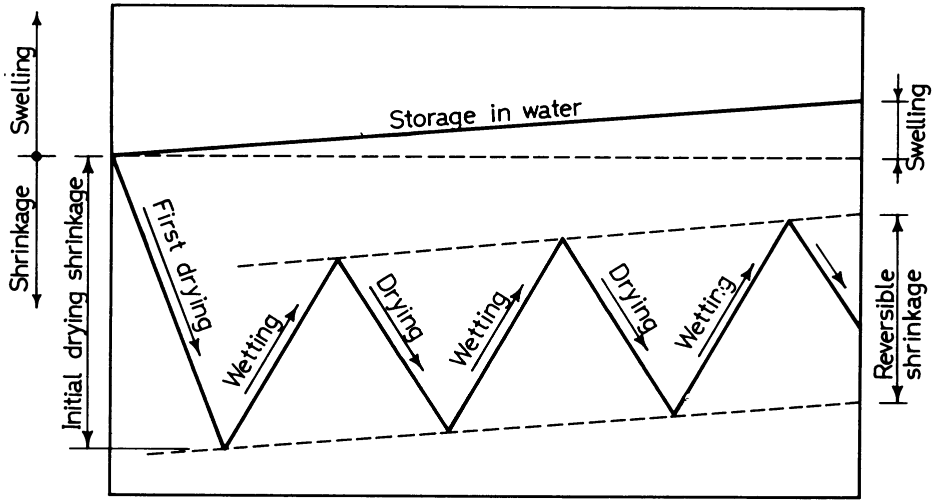

Figure 5.6 *Schematic description of volume changes in cement paste due to alternate cycles of drying and wetting*

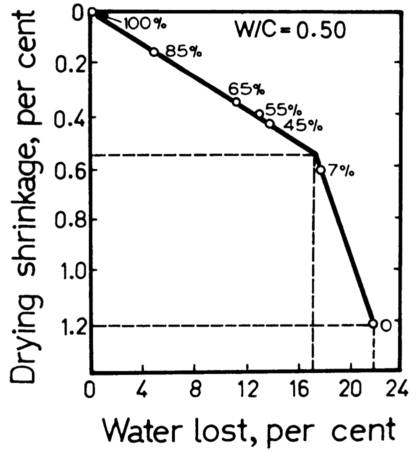

Figure 5.7 *Effect of water-loss on shrinkage of cement paste (after Verbeck and Helmuth*[9]*)*

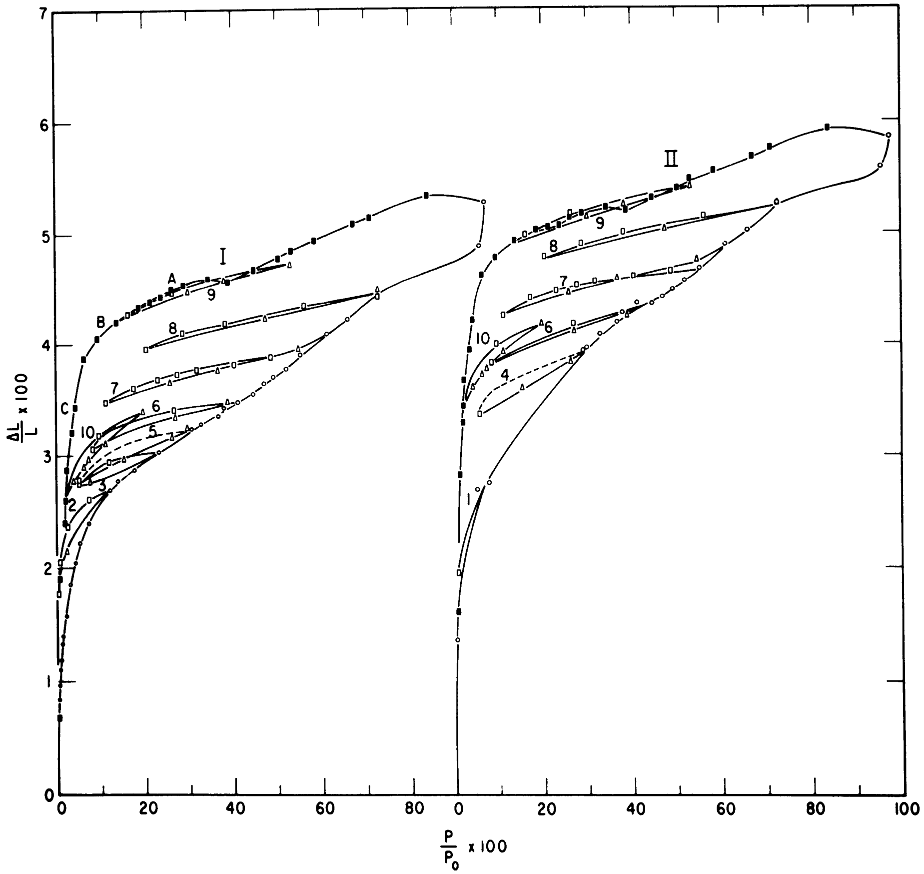

Figure 5.8 *Length change isotherms and scanning loops for Portland cement paste (after Feldman*[15]*)*

The change in slope in Figure 5.7 implies that shrinkage may be attributed to more than one mechanism. Moreover, in some tests of the same series[9] the slope changed twice while in tests by others the slope changed three times.[16] Again, this pattern implies that more than one mechanism is involved. It should be noted, however, that the relation between shrinkage and water loss has not been found to be linear in all tests and that the breaks in the relevant curves have not always been observed. Nevertheless, in all tests shrinkage was found to be related to water loss, and this relation was more pronounced at the later stages of drying.

5.3.2 Factors affecting shrinkage

Since the shrinkage of the cement paste is related to water loss, all the factors which affect drying (i.e. temperature, humidity, pressure, and air movement) will also affect shrinkage. Shrinkage is also affected by cement composition, though this subject is dealt with separately in Chapter 7, and the following discussion is limited to factors associated with structure of the paste such as *W/C* ratio, porosity, etc.

5.3.2.1 W/C ratio

The effect of *W/C* ratio on shrinkage is demonstrated in Figure 5.9.[17] At earlier stages, when shrinkage rate is high, the *W/C* ratio has no significant effect on shrinkage. At later stages, however, shrinkage decreases with the decrease in the

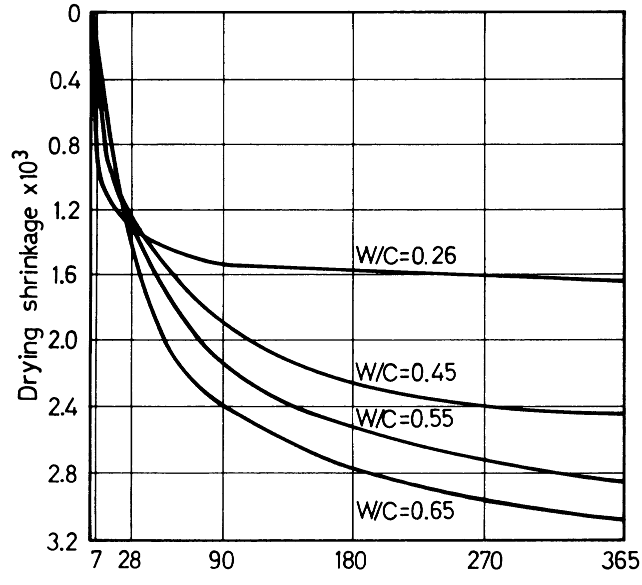

Figure 5.9 Effect of W/C ratio on shrinkage of cement pastes (after Haller[17])

W/*C* ratio, and stops at an earlier age for cements with a low *W*/*C* ratio. For example, in the paste of low *W*/*C* ratio, 0.26, shrinkage has virtually finished at, say, 90 days while in the other pastes it continues up to 365 days.

The shrinkage data of Figure 5.9 are related in Figure 5.10 to the corresponding water loss of the pastes. As could have been expected, shrinkage up to an age of 28 days is essentially the same for all pastes regardless of differences in the amounts of water lost, which are smaller the lower are the *W*/*C* ratios of the pastes. At a later age, however, the picture is changed. The amount of water lost from 28 to 365 days is nearly the same for all pastes (approximately 4%) while the shrinkage varied considerably and increased with the *W*/*C* ratio.

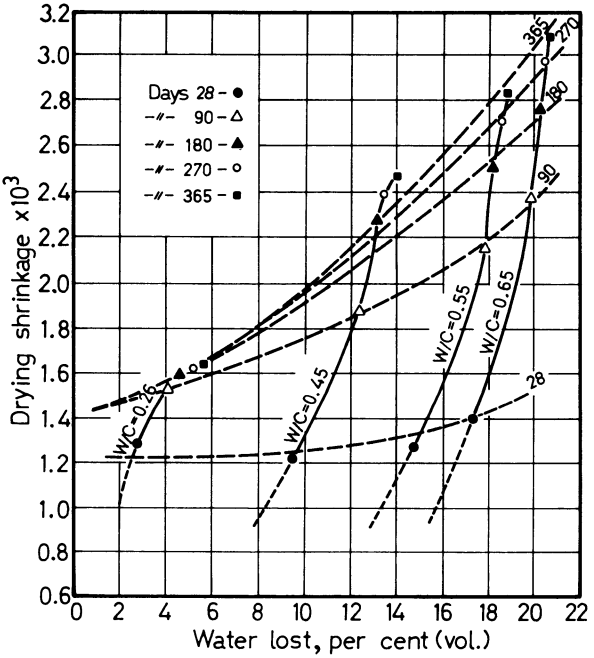

Figure 5.10 *Effect of water-loss on shrinkage of cement pastes of different W*/*C ratios* (*after Haller*[17])

The variation in shrinkage with *W*/*C* ratio may be explained by the difference in types of water lost at the various stages of drying. It was mentioned previously that at early stages of drying, water is lost from the bigger pores (i.e. capillary pores according to Powers), and only on more intensive drying do the smaller pores (i.e. gel pores) begin to empty. It is implied, therefore, that shrinkage is affected to a greater extent by the removal of gel water than by the removal of capillary water. In other words, the same amount of water loss may cause different amounts of shrinkage when the ratio of gel to capillary water is not the same. This difference of the different types of water lost may explain the similar shrinkages at 28 days, as is indicated in Figure 5.10. Apparently, at this age all the pastes have lost nearly the same amounts of gel water and the difference in the total water loss results from the different amounts of capillary water lost. The amount of capillary water increases with *W/C* ratio, hence the greater water loss in such pastes. As the removal of the capillary water only slightly affects shrinkage, the latter is nearly the same for all pastes regardless of the total amount of water lost. Apparently, further drying of the pastes beyond 28 days results mainly in removal of gel water. Assuming the same degree of hydration, the pastes must have the same gel content. Hence, roughly the same amount of water is lost up to the age of 365 days. The greater shrinkage of the pastes with the higher *W/C* ratio is attributable to their lower strength. Lower strength implies a lower modulus of elasticity (Figure 5.1), and a lower modulus brings about higher shrinkage. This effect of the modulus of elasticity is discussed later in some detail.

Strictly speaking, the preceding discussion is not complete because it assumes

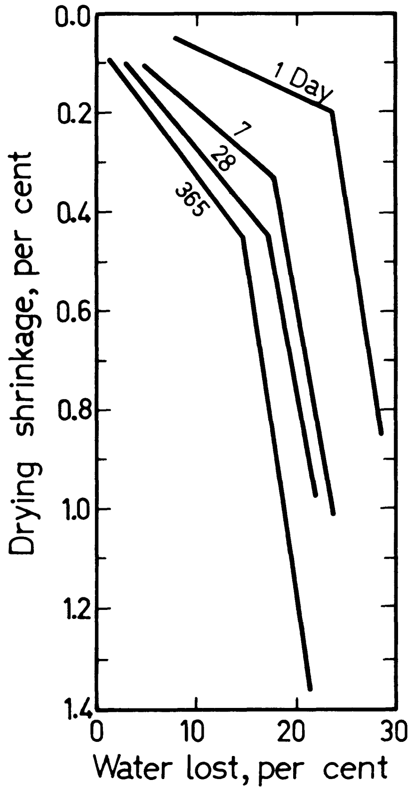

Figure 5.11 *Effect of water-loss on shrinkage of cement pastes cured for different periods (after Verbeck and Helmuth*[9]*)* that the pastes have the same degree of hydration, which is probably not the case. Nevertheless, in principle, it offers a basic explanation of the effect of the *W/C* ratio on shrinkage. It is yet to be explained why gel and capillary water affect shrinkage differently and why drying causes shrinkage at all. These aspects are dealt with in the discussion of shrinkage mechanisms.

5.3.2.2 Degree of hydration

The higher the degree of hydration, the higher the gel content of the paste. The increase in gel content increases the volume of gel pores at the expanse of capillary pores (Figure 4.14). Assuming that drying from gel pores causes greater shrinkage than that from capillary pores, greater shrinkage is to be expected, other things being equal, in pastes with a higher gel content, i.e. in longer matured pastes. This conclusion is supported by the data in Figure 5.11[9] which compares the shrinkage of cement pastes which were dried after being cured in water for different periods of time. It is evident that the shrinkage is higher the longer curing time, i.e. the higher the degree of hydration. Similar results are summarised in Figure 5.12[18] where the reciprocal of shrinkage is plotted against the degree of hydration expressed as the chemically bound water. Here, again, shrinkage increases with the degree of hydration. The data also indicate that the type of the cement used affects shrinkage. This subject is discussed later.

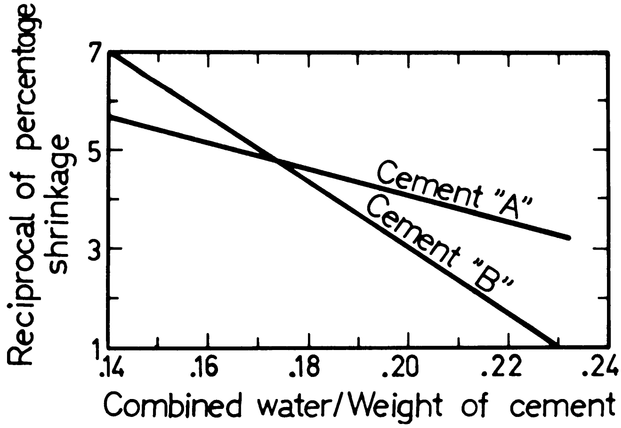

Figure 5.12 *Effect of degree of hydration on shrinkage of pastes made of different cements (after Roper[18])*

5.3.2.3 Porosity of the paste

The porosity of the paste is determined by the *W/C* ratio and the degree of hydration. Porosity increases with increase in the *W/C* ratio and the decrease in the degree of hydration. That is, the effect of porosity on shrinkage combines the effects of *W/C* ratio and degree of hydration. Figure 5.13 demonstrates the effect of porosity on shrinkage of well matured cement pastes. The pastes in question were prepared with *W/C* ratios which varied from 0.4 to 0.6, were subjected to wet-curing for 6-7 months, and then dried to equilibrium at 46% relative humidity. The data clearly indicate that shrinkage increases linearly with porosity. However, this conclusion applies only to the irreversible part of the shrinkage; the reversible part remains independent of porosity. Relevant information is rather limited and it is uncertain to what extent the preceding conclusions are generally applicable.

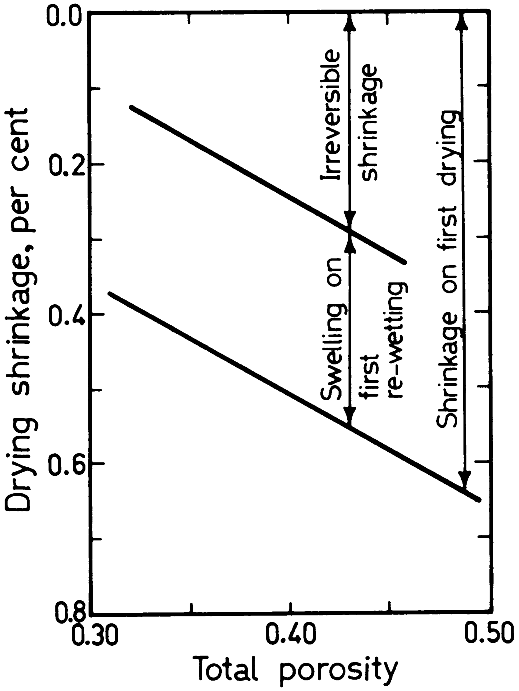

Figure 5.13 *Effect of total porosity on shrinkage of cement paste (after Helmuth and Turk*[19]*)*

5.3.2.4 Autoclave treatment

In discussing hydration it was shown that autoclave treatment affects the structure of the paste and its composition. As expected, this effect is reflected in the properties of the paste, including shrinkage. Generally, autoclave treatment considerably reduces shrinkage as is indicated in Figure 5.14.[20] It can be seen that shrinkage of normally cured paste containing no silica is approximately six times greater than the shrinkage of otherwise similar autoclave treated paste. Addition of silica increases the shrinkage of the autoclave treated pastes. Nevertheless, in all cases, shrinkage is considerably lower than that of the corresponding normally cured pastes. It was also found that the shrinkage of pastes containing no silica increases with autoclave temperature.[21] However, shrinkage of silica containing pastes is hardly affected by temperature.

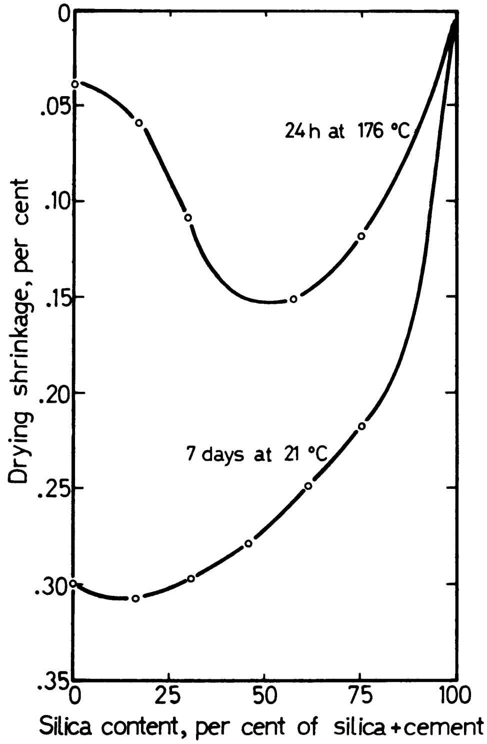

Figure 5.14 *Effect of autoclave treatment on shrinkage of cement pastes of different silica contents (after Menzel*[20-21]*)*

5.3.2.5 Admixtures

Information about the effect of admixtures on shrinkage is rather limited. In concrete the effect of some water-reducing agents based on hydroxylated carboxylic acid or lignosulphonic acid was found to be uncertain, i.e. in some cases the use of these additives resulted in reduced shrinkage and in others in increased shrinkage.[22] The same tendency was observed in lightweight aggregate concrete.[23] In other work it was found that both lignosulphonate, with or without calcium chloride, and triethanolamine increase shrinkage of cement pastes and concrete.[25] It seems that the effect of admixtures on shrinkage varies and depends on the specific admixture and conditions in use.

5.3.3 Shrinkage and swelling mechanisms

It was shown previously that the relation between shrinkage and water loss is different at different stages of drying. It was stated that this variation implies that more than one mechanism is involved in the shrinkage process. Indeed, shrinkage may be due to several mechanisms which are discussed below.

5.3.3.1 Capillary tension

Saturation vapour pressure or, in brief, simply vapour pressure of a liquid is the pressure at which liquid and vapour coexist at equilibrium, i.e. when the number of molecules leaving the liquid into the space above it (evaporation) is equal to the number returning to the liquid at any given time. When the vapour pressure over the liquid is lower than the saturated pressure, the number of molecules leaving the liquid is greater than the number returning, and the amount of liquid is gradually reduced, i.e. evaporation takes place. While discussing sorption isotherms it was stated that the relative vapour pressure P/P_0 is usually considered where P is the vapour pressure over the liquid, and P_0 is the saturated vapour pressure at the same temperature. In considering the vapour pressure of water reference is sometimes made to relative humidity (RH) which is the relative vapour pressure expressed as percentage of the saturation pressure i.e. $P/P_0 \times 100$.

Free water starts to evaporate off when the vapour pressure over the surface is lower than the saturation pressure, i.e. when the relative humidity drops below 100%. In capillary pores, the vapour pressure over the meniscus is different from that over a plane surface. This difference is readily explained with the aid of Figure 5.15. In this figure the circle represents the sphere of attraction of one molecule on the surface of the liquid (black dot). The molecules hindering evaporation of the molecule in question are enclosed in the shaded part of the circle. It can be seen that this area is greater for the concave surface than for the plane surface. In other words, the forces of attraction acting upon a molecule on a concave surface are greater. Consequently, the vapour pressure over the latter surface must be lower than the pressure over a plane surface in order to allow evaporation. Similarly, it can be shown that the vapour pressure over a convex surface is greater than the pressure over a plane surface. Water wets the hardened paste, so only the concave case is considered here.

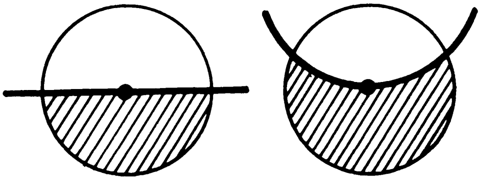

Figure 5.15 *Effect of surface curvature on vapour pressure (see text)*

The relationship between the radius of curvature, r, of the meniscus and the corresponding vapour pressure, p, is given by Kelvin's equation

$$\ln (p/p_0) = 2T/R\theta\rho r$$

where p_0 is the saturation vapour pressure over a plane surface, T is the surface tension of the liquid, R is the gas constant, θ is the temperature in kelvin, and ρ is the density of the liquid.

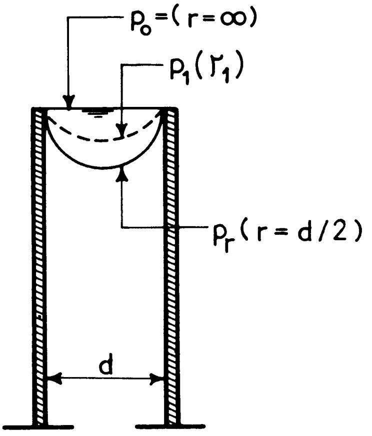

Figure 5.16 *Relation between radius of curvature and vapour pressure*

The implication of this vapour pressure variation with meniscus radius is demonstrated in Figure 5.16. At $p/p_0 = 1$ the surface of the water in the capillary is plane ($r = \infty$) and no evaporation takes place. With a decrease in vapour pressure to p_1, the water starts to evaporate until a meniscus of radius r_1, corresponding to the pressure p_1 in Kelvin's equation, is formed. Further decrease in pressure causes further evaporation with a corresponding decrease in the radius of the meniscus. However, the radius cannot be smaller than $d/2$ (d is the diameter of the capillary). Hence, when the pressure drops below the pressure corresponding to the minimum possible radius, evaporation continues until the capillary is empty. Therefore, on exposing the cement paste to a gradually decreasing pressure, the pores gradually become empty in order according to their size, i.e. the water is first lost from the bigger pores (i.e. capillary pores in Powers' model), and only later from the smaller gel pores. As may be remembered, such a drying process was considered in the discussion of sorption isotherms and in the explanation of the effect of W/C ratio on shrinkage of the paste.

The water in the capillary may be regarded as hanging from the surface film of the meniscus. Hence, the capillary water is subjected to a tensile stress, u, which is equal to γh (γ is the density of the water) (Figure 5.17). Maximum tension occurs immediately below the meniscus with the stress, u_1, being equal to γh_1. It can be shown that the maximum stress is also given by $u_1 = T(1/r_1 + 1/r_2)$ or $u_1 = 2T/r$ when $r = r_1 = r_2$. Hence, the tension in the water increases with the decrease in radius of curvature of the meniscus. As the radius of the meniscus decreases with the decrease in vapour pressure, the tensile stress in the capillary water increases.

Tensile stresses in the capillary water must be balanced by compressive stresses in the surrounding solid. Hence, the evaporation of capillary water and the formation of a meniscus will subject the paste to compressive stresses which,

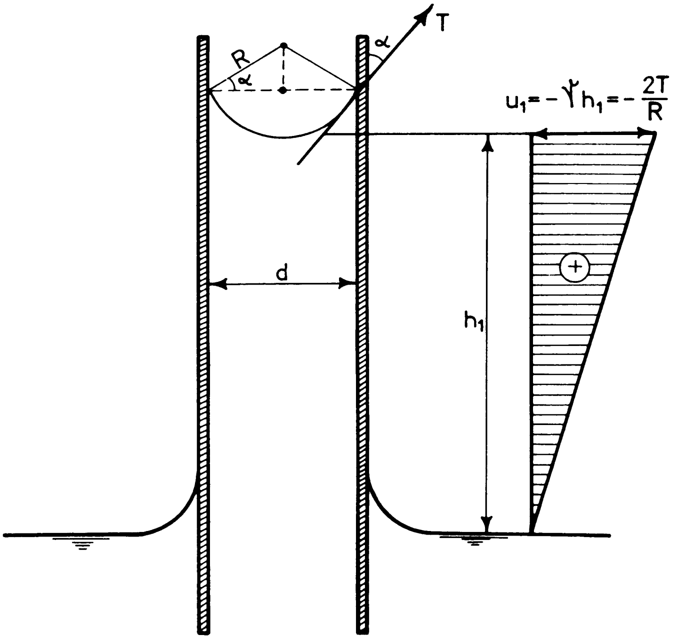

Figure 5.17 *Tensile stresses in capillary water*

in turn, will cause elastic volume decrease, i.e. shrinkage. Elastic deformation is dependent on the rigidity of the solid therefore, other things being equal, the shrinkage of the paste will decrease with the increase in its modulus of elasticity. It may be noted that this latter conclusion has been used to explain the effect of *W/C* ratio on shrinkage.

Such a mechanism can also explain why, at the early stages of drying, the amount of the water lost is large compared to the resulting shrinkage (Figures 5.8 and 5.7). At the early stages, water evaporates from the bigger pores accounting for a comparatively large amount of water loss. The resulting shrinkage, however, is small because of the relatively large diameter of the pores. At later stages, water evaporates from the smaller pores. Hence, the small amount of water loss with relatively high shrinkage.

At any given stage, there exists an equilibrium between the tensile forces in the capillary water and the compressive forces in the solid phase of the paste. The forces involved are equal to the product of the tensile stresses in the water and the cross sectional area of the water-filled capillaries. On drying, a stage will be reached at which the decrease in cross sectional area of the water-filled capillaries is greater than the associated increase in the tensile stresses in the capillary water. Hence, the forces acting on the solid, and the resulting shrinkage, will both decrease. In other words, at a certain stage the product of the cross sectional area and tensile stresses, and the resulting shrinkage, will reach a maximum, and on further drying the volume decrease due to shrinkage will be gradually recovered. On complete drying, when no water remains in the paste, complete recovery is to be expected with the paste returning to its original dimensions. In practice, however, this is not the case, and shrinkage takes place continuously throughout the drying of the paste. The absence of a maximum and the continued shrinkage is attributed to other mechanisms which become operative. Apparently, the shrinkage which is caused by these additional mechanisms is more than is required to compensate for the expected recovery due to the reduction in the tensile forces. Hence, the continued shrinkage on drying.

It is usually assumed that the mechanism of capillary tension is operative when drying takes place in the relative humidity region exceeding 40% and, according to Ishai[26] most of the shrinkage occurring is attributable to this mechanism. Powers regards capillary tension as of limited importance even when the relative humidity exceeds 50%, and considers swelling pressure to be the main mechanism at any relative humidity.[27] Feldman and Sereda consider the capillary mechanism to be of some importance when shrinkage takes place due to drying at relative humidities higher than 35%.[11] In their opinion, however, as far as the swelling of the paste is concerned, capillary tension mechanism is not of any great importance over the whole region, because some 80% of the volume increase is attributable to re-entry of water into the layered structure of the CSH particles. In other words, swelling pressure and movement of interlayer water constitute additional mechanisms by which shrinkage can be explained. Both are discussed later.

5.3.3.2 Surface tension (surface energy)

Molecule A (Figure 5.18), well inside a material, is equally attracted and repelled from all directions by the neighbouring molecules. This is not the case for molecule B at the surface for which, because of lack of symmetry, a resultant force acts downwards at right angles to the surface. As a result, the surface tends to

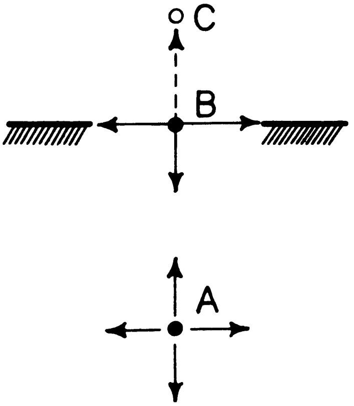

Figure 5.18 *Schematic representation of surface tension (see text)* contract and behaves like a stretched elastic skin. The resulting tension in the surface is known as 'surface tension', and is defined as the force which acts in a direction tangential to the surface, at right angles to any given line of unit length on the surface. Hence, surface tension is measured in N/m.

According to the preceding description some mechanical work has to be done to increase surface area, because such an increase involves acting against the downward pull acting on the surface molecules. The amount of work required to increase the surface area by one unit is known as 'surface energy' and is measured in erg/cm^2.

The force acting at right angles to the surface induces compressive stresses inside the material. It can be shown that for spherical particles the resulting stress, p, equals $2T/r$ when T is the surface tension and r is the radius of the sphere, i.e. the intensity of the stress is directly proportional to surface tension and inversely to the radius of the sphere. In particles of colloidal size, such as the cement gel particles, surface tension induces compressive stresses of the order of 250 N/mm^2,[28] and a change in the magnitude of such stresses will cause detectable volume changes. Changes in surface tension, which are brought about by variations in the amount of adsorbed water on the surfaces of the gel particles produce variations in the magnitude of the stresses. It can be seen that an adsorbed water molecule, C (Figure 5.18), opposes the resultant force acting on B. The force, therefore, decreases causing a corresponding decrease in surface tension. As a result, the compressive stress in the material is reduced and its volume increases due to elastic recovery. Similarly, drying increases surface tension and the increased compressive stress causes volume decrease, i.e. shrinkage. In other words, the proposed mechanism attributes volume changes to variations in surface tension of the gel particles which are brought about by variations in the amount of the adsorbed water. In this respect it should be noted that only physically adsorbed water affects surface tension. Hence, the suggested mechanism is valid only at low humidities where variations in the water content of the paste are mainly due to variations in the amount of adsorbed water. At higher humidities, some of the water in the paste (i.e. capillary water) is outside the range of surface forces and a change in the amount of this type of water cannot affect surface tension. Accordingly, it has been suggested that the surface tension mechanism is only operative up to 40% relative humidity.

It can be shown that length changes, $\Delta\ell/\ell$, are directly related to the corresponding changes, ΔT, in the surface tension or, alternatively, in surface energy, i.e.

$$\Delta\ell/\ell = k(T - T_0) = k\Delta T.$$

That is, provided that the suggested mechanism is valid, a plot of $\Delta\ell/\ell$ against ΔT will be a straight line passing through the origin. Tests conducted by Wittmann[28] produced the expected straight line. Moreover, assuming the strength of the cement paste is expressed by Griffith's formula $\sigma = \sqrt{2ET/\pi C}$, a change in surface energy from T to T_0 will cause the strength of the paste to change from

σ to σ_0, and the following may be written:

$$(\sigma/\sigma_0)^2 = T/T_0$$

and substituting $\Delta\ell/\ell = k(T - T_0)$ gives

$$\left(\frac{\sigma}{\sigma_0}\right)^2 = 1 - \frac{1}{kT_0}\,\frac{\Delta\ell}{\ell}$$

Accordingly, for pastes of different moisture contents, a plot of the strength ratios $(\sigma/\sigma_0)^2$ against length changes will again result in a straight line, and indeed such a line was obtained in Wittmann's tests (Figure 5.19). Hence, it was concluded that up to 40% relative humidity, shrinkage and swelling are mainly caused by changes in surface energy of the gel particles which are brought about by variations in the amount of adsorbed water. Later it was suggested that this mechanism is operative from 5 to 50% relative humidity and, in fact, the behaviour of the cement paste within this range has been attributed to changes in surface energy.[12,29] Substantial work on this has been carried out at the Technical University in Munich. The results of such work have been used to explain the behaviour of the cement paste; this explanation is sometimes referred to as the Munich model.[29,55]

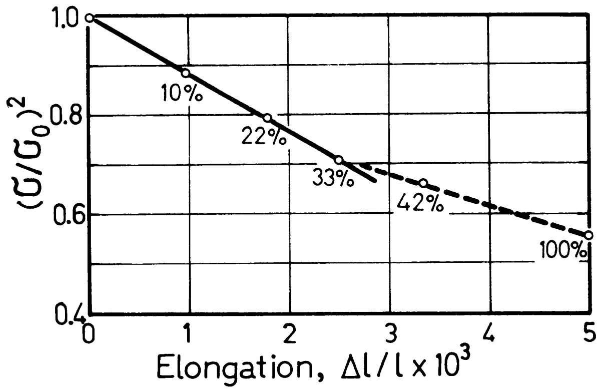

Figure 5.19 *Relation between relative strength and length-changes on swelling of cement paste (after Wittmann*[28]*). Percentage figures give the relative humidity at which the paste was brought to hygral equilibrium*

Different results were obtained by Feldman[15] who found the expected linear relation between length changes, $\Delta\ell/\ell$ and surface energy, ΔT, when only physically adsorbed water was considered (Figure 5.20). He also found that, over the whole region from 0 to 100% relative humidity only 20% of the swelling was attributable to changes in surface energy. Hence, it was concluded that as far as shrinkage and swelling are concerned, surface energy effects are of secondary

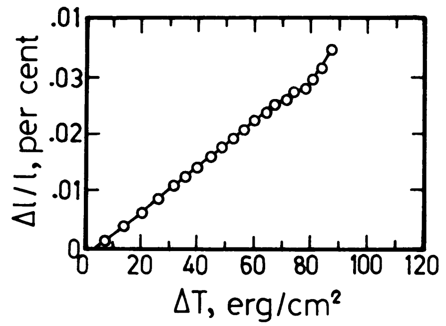

Figure 5.20 *Length changes plotted against surface energy changes in cement paste (after Feldman*[15]*)*

importance. Powers considered surface energy changes to be even less important, and suggested that such changes affect only slightly, if at all, volume changes of the cement paste.[27] It can therefore be seen that opinions differ widely about the role of surface energy changes in causing shrinkage.

5.3.3.3 *Swelling pressure*

Adsorption of a gas onto the surface of a solid is a result of mutual attraction between the molecules on the surface of the solid and the molecules of the gas. At a given pressure and temperature, a dynamic equilibrium is set up in which the number of molecules being adsorbed at any given time equals the number of molecules escaping the surface. The adsorbed layer is considered to be compressed perpendicular to the surface with a tangential pressure (spreading pressure) along the surface.

At a given temperature, the thickness of the adsorbed water layer is determined by the ambient relative humidity. The thickness increases with relative humidity reaching, apparently, a maximum equivalent to a layer 5 molecules deep (i.e. approximately 13 Å). According to the model presented in Figure 5.21,

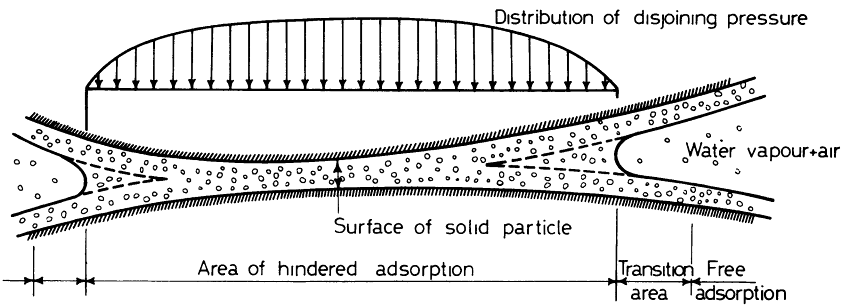

Figure 5.21 *Areas of hindered adsorption (after Powers' model)* it may be that two adjacent gel particles are sufficiently close to each other for the thickness of the adsorbed layer to be determined by the distance between the two and not by the existing ambient humidity. In fact such a situation may exist whenever the distance between two adjacent particles is less than 26 Å which is the maximum thickness of two adsorbed layers. On surfaces subjected to such geometrical constraint, the thickness of the adsorbed layer cannot always be fully developed, and accordingly, such surfaces have been called 'areas of hindered adsorption'. As a result, in these areas, a 'swelling' or 'disjointing' pressure is developed which tends to separate the adjacent particles, thereby causing swelling. As a result of the mutual attraction between the gel particles, swelling is limited and the water in the areas of hindered adsortion remains under pressure. Hence, reference is made to 'load-bearing water'.

The thickness of the adsorbed layer increases with relative humidity, and the swelling pressure increases correspondingly. Hence, the swelling of the cement paste increases with increase in moisture content. A decrease in relative humidity causes drying, hence the thickness of the adsorbed layer and the associated swelling pressure are decreased. When the swelling pressure is decreased, the distance between the mutually attracted gel particles is reduced, i.e. shrinkage takes place. In other words, according to this mechanism, volume changes are brought about by changes in interparticle separation which, in turn, are caused by variations in swelling pressure. Accordingly, in this mechanism it is assumed that the cement gel consists essentially of discrete particles. It may be noted that such an assumption is in agreement with Powers' model and, indeed, Powers was first to suggest that shrinkage and swelling may be mainly attributable to this mechanism over the whole vapour pressure range.[27]

According to the Munich model, the swelling pressure is important in the relative humidity range beyond 50%.[28,29] Feldman and Sereda completely reject this mechanism, and in their model it is assumed that the interparticle bond is a solid to solid contact which will not be broken due to adsorption of water.

5.3.3.4 Movement of interlayer water

Reversible movement of water into and out of the layered CSH particles could cause volume changes because such movement would affect the spacing of the layers. In the model of Feldman and Sereda it is assumed that such movement of water occurs whereas in other models it is assumed that interlayer water may be removed but will not re-enter the structure. Hence in these latter mentioned models movement of interlayer water may account only for the irreversible part of shrinkage,[26] whereas in that of Feldman and Sereda it is considered to be the main mechanism of shrinkage and swelling. Feldman and Sereda suggest that on drying at between 100 and 35% relative humidity, shrinkage results from capillary and surface energy effects. Below 35% relative humidity, however, and down to the d-dried state, the exit of interlayer water is the major cause of contraction, and re-entry of water is the main cause of expansion. In fact, as already mentioned, on rewetting to 100% relative humidity over 80% of the expansion was found to be attributable to re-entry of interlayer water.[11]

5.3.4 Mechanism of irreversible shrinkage

Some of the shrinkage which occurs in the first cycles of drying and wetting is irreversible. So far the discussion has been limited to the reversible part of shrinkage, while we now consider the mechanisms of the irreversible part.

According to Ishai's model (Figure 3.10) irreversible shrinkage is a result of more than one mechanism.[26] At relative humidities exceeding 40% the shrinkage of paste is due to capillary tension, which produces isotropic compressive stresses in the solid phase, and the sustained compression causes normal compression in the intercrystalline water (type 3 in accordance with the model). This compression, with time, squeezes out the water laterally, thereby reducing the particle spacing in the gel and the volume of the paste decreases. The reduced spacing involves a decrease in the total energy of the system and the associated volume decrease (shrinkage) is, therefore, not recoverable. It will be seen later that the same mechanism may be used to explain creep suggesting an interdependence between creep and shrinkage.

At relative humidities below 40% the intercrystalline water begins to evaporate causing, again, a reduction in the particle spacing, and a decrease in the total energy of the system. This contraction is not recoverable. At even lower relative humidity (i.e. less than 10%) the gradual exit of intracrystalline water commences,

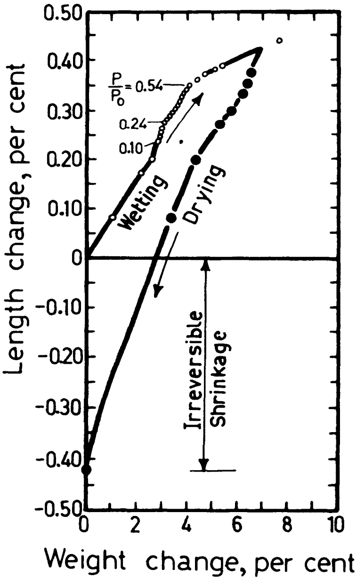

Figure 5.22 Effect of interlayer water loss on length-changes of a cement paste (after Feldman[15])

the interlayer spacing decreases and an additional contraction of the paste takes place. In this respect, it may be noted that, contrary to Feldman and Sereda's model, Ishai's does not consider possible re-entry of the intracrystalline water.

Feldman and Sereda[11] suggested that on first drying some surfaces of the gel particles approach each other to form new bonds (A in Figure 3.11). Many of these bonds remain on rewetting, hence the irreversible nature of the resulting volume decrease. It was found, however, that, as a result of intensive drying below 1% relative humidity, the final exit of the interlayer water also caused irreversible shrinkage. This is indicated in Figure 5.22[15] in which length changes are plotted against loss of interlayer water. In the tests considered, the irreversible shrinkage on complete drying, which was roughly the same in magnitude as the reversible part, was attributed to reorientation of the CHS layers. Nevertheless, according to Feldman and Sereda's model, the movement of interlayer water is essentially reversible, and explains to a considerable extent the behaviour of the cement paste.

5.3.5 Summary and concluding remarks about shrinkage and swelling

Variations in moisture content of the cement paste are accompanied by volume changes. The decrease in the volume of the paste on drying is referred to as 'drying shrinkage' or simply 'shrinkage', and its increase on rewetting as 'swelling'. In first cycles of drying and wetting some of the shrinkage is irreversible. In subsequent cycles, however, shrinkage becomes essentially a reversible process.

Shrinkage is related to water loss. This relation is not necessarily linear and may change at different stages of drying. Accordingly, all factors which affect drying, such as humidity, temperature, etc., will also affect the shrinkage of the cement paste. A greater shrinkage is to be expected with an increase in W/C ratio and the degree of hydration. Autoclave treatment reduces shrinkage.

Generally, shrinkage and swelling are attributable to the following mechanisms.

(1) *Capillary tension*

The formation of a meniscus on drying results in tensile stresses in the capillary water. The tension in the water is balanced by compression in the solids causing, in turn, elastic decrease in the volume of the paste, i.e. shrinkage. This mechanism is reversible and is considered to be operative when the relative humidity exceeds 40%.

(2) *Surface tension*

Surface tension produces compressive stress inside solid particles, and in particles of colloidal size, such as the CSH particles, the stress level may be rather high. For a given material and particle size, the stress level is determined by surface tension. In turn, surface tension depends on the amount of physically adsorbed water, and decreased adsorption involves higher surface tension, and vice versa. Hence, on drying the compression in the gel particles increases causing a corresponding elastic volume decrease, i.e. shrinkage. On rewetting, surface tension decreases, some of the compression in the solids is relieved, and the volume of the paste increases, i.e. swelling takes place.

(3) *Swelling pressure*

At a given temperature, the thickness of an adsorbed water layer is determined by the ambient vapour pressure. In some areas of the paste, due to the comparatively small interparticle spacing, the thickness of the layer is determined by this spacing and not by the ambient humidity. In such areas of 'hindered adsorption', due to the geometrical constraint, a 'swelling' or a 'disjointing' pressure is developed which tends to separate the gel particles. Hence, swelling takes place. Drying relieves some of the pressure because the thickness of the adsorbed layer is decreased. The cohesion forces acting between the gel particles reduce interparticle spacing, and the volume of the paste decreases, i.e. the paste shrinks.

(4) *Interlayer water*

Exit and re-entry of water into the layered structure of the gel particles cause volume changes due to resulting changes in the spacing of the layers, i.e. exit of water on drying causes volume decrease (shrinkage) and re-entry of water on wetting causes volume increase (swelling).

Generally, shrinkage and swelling are described by more than one mechanism. Opinions differ, however, with respect to the relative importance of each mechanism. This difference of opinion is clearly indicated in Table 5.1.

Table 5.1 Shrinkage mechanisms (after various authors)

Authority	*Relative humidity, %* 0 10 20 30 40 50 60 70 80 90 100	
Powers[27]	← Variations in swelling pressure →	
		← Augmentation by capillary effects →
Ishai[26]	← Variations in surface energy →	← Capillary tension →
Feldman and Sereda[11]	← Movement of interlayer water →	← Capillary tension and variations in surface energy →
Wittmann[28,55]	← Variations in surface energy →	← Variations in swelling pressure →

Irreversible shrinkage is attributed to (*a*) rearrangement of the gel particles on drying, and the formation of some new bonds at points of contact, (*b*) the removal of intercrystalline water and the resulting reduction in the interparticle spacing, and (*c*) the exit of interlayer (intracrystalline, zeolitic) water and the resulting reorientation of the CSH layers.

5.4 Creep

5.4.1 Introduction and definitions

Loading of the cement paste results in instantaneous deformation which is generally regarded as elastic, i.e. a deformation which appears and disappears completely immediately on application and removal of the load. Strictly speaking, in the cement paste, part of the instantaneous deformation in the first few loading cycles is not recoverable. This deformation, caused by irreversible changes in the structure of the paste such as cracking, is known as 'permanent set'. Also, the elastic deformation decreases with time due to the increase in the modulus of elasticity of the paste. The two effects are not relevant in the following discussion and are not therefore considered further.

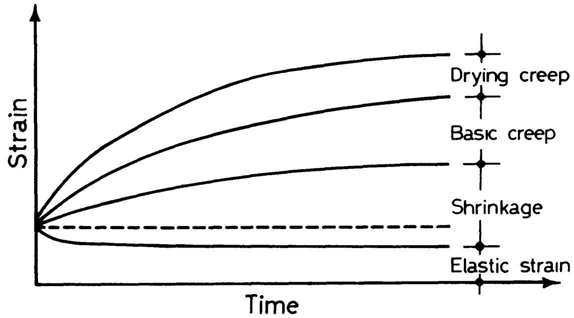

Figure 5.23 *Deformation with time of cement paste under sustained loading*

Under sustained loading the deformation of the paste increases at a gradually decreasing rate (Figure 5.23), approaching a value several times larger than the elastic deformation. If the paste is allowed to dry when under load, shrinkage occurs simultaneously. Creep is, therefore, the increase in deformation under a sustained stress excluding drying shrinkage. This is demonstrated in Figure 5.23 for a paste loaded under compression.

The preceding definition assumes creep and shrinkage to be independent of each other and therefore additive. Indeed, in many tests creep was taken as the difference between the total time-dependent deformation of loaded specimens and the shrinkage of unloaded companion specimens which were kept in the same environment. Strictly speaking, such a procedure is not correct because creep and shrinkage are mutually dependent, and the simultaneous shrinkage of the paste is associated with increased creep. Accordingly, a distinction is made between 'basic creep' and 'drying creep'. Basic creep is the creep observed in specimens which reached equilibrium with the surrounding medium with respect to water content, i.e. it is creep which takes place when no simultaneous drying of the paste is involved. Drying creep is the additional creep induced by simultaneous drying. Hence, the difference between the total time-dependent deformation and shrinkage is the sum of basic and drying creep (Figure 5.23). In engineering applications the distinction between basic and drying creep is not important. Accordingly, in such applications the term 'creep' usually refers to the total creep, i.e. to the sum of basic and drying creep.

As with shrinkage, creep is in part irrecoverable. On unloading, deformation decreases immediately due to elastic recovery. The instantaneous recovery is followed by a gradual decrease in deformation due to 'creep recovery'. Creep recovery is not complete, approaching with time a limiting value which is smaller than the previous creep. The remaining residual deformation is either

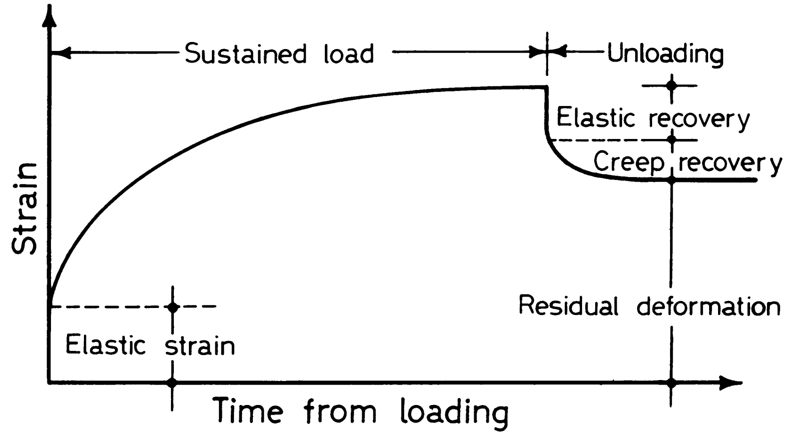

Figure 5.24 Creep and creep recovery of cement paste in hygral equilibrium with the surrounding medium

irreversible creep (Figure 5.24) or the algebraic sum of latter and shrinkage (or swelling), depending on whether or not loading has been accompanied by moisture exchange.

5.4.2 Factors affecting creep

5.4.2.1 Drying conditions

The simultaneous drying of the paste increases the amount of creep and this increase is referred to as drying creep. Hence, drying conditions would affect total creep through their effect on drying creep. Generally speaking, drying creep, and the resulting total creep, increases with the intensity of drying conditions, i.e. with the increase in temperature, decrease in relative humidity, etc.

Figure 5.25 describes the effect of simultaneous drying and loading on creep, and demonstrates the difference between basic and drying creep. The data relate to cement pastes of different *W/C* ratios, which were subjected to compressive stress of 9.8 N/mm^2 at an age of 28 days. Some of the specimens were simultaneously allowed to dry at 40% relative humidity and others were tested under saturated conditions. Curve 1 represents the total time-dependent strains in

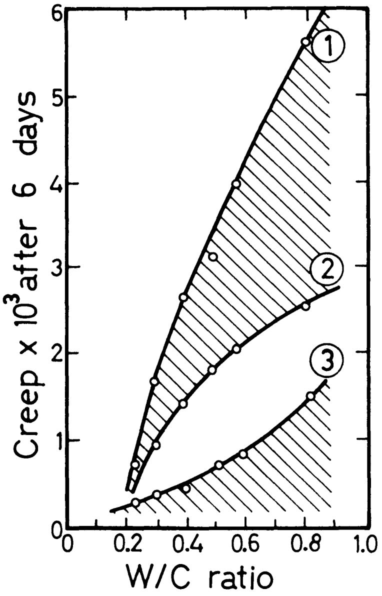

Figure 5.25 *Effect of simultaneous drying on creep of cement paste (after Ruetz*[30]*).* 1, *creep with simultaneous shrinkage;* 2, *shrinkage only;* 3, *basic creep* specimens which were allowed to dry and curve 2 the shrinkage of companion unloaded specimens. Hence, the total creep is given by the difference between the two curves. Curve 3 represents basic creep measured on specimens which were not allowed to dry. It can be seen that, under the chosen conditions, the creep of the specimens which were allowed to dry is about twice the basic creep. It may be expected that, under otherwise similar conditions, the ratio of total to basic creep will increase with the intensity of the drying conditions. Indeed, this effect of drying conditions has been confirmed in many tests.[31-33]

5.4.2.2 Strength of paste

It is evident from Figure 5.25 that creep increases with *W/C* ratio. Under otherwise similar conditions, the strength of the paste is related to the *W/C* ratio. Hence, it may be concluded that creep decreases with the increase in strength. The modulus of elasticity of the paste being related to its strength, a similar conclusion may be reached with respect to the effect of this modulus on creep.

The effect of strength on creep implies that all factors which affect the former will also affect creep. In Figure 5.26, for example, the effect of age is shown. Strength increases with age, so lower creep is to be expected with increase in the age of the paste at the time of loading, and such a trend is clearly evident from Figure 5.26. The effect of strength on creep is of practical importance in engineering applications. In the manufacture of prestressed concrete, for example, the loss of prestress due to creep can be reduced by delaying the prestressing operation and by using high strength concrete.

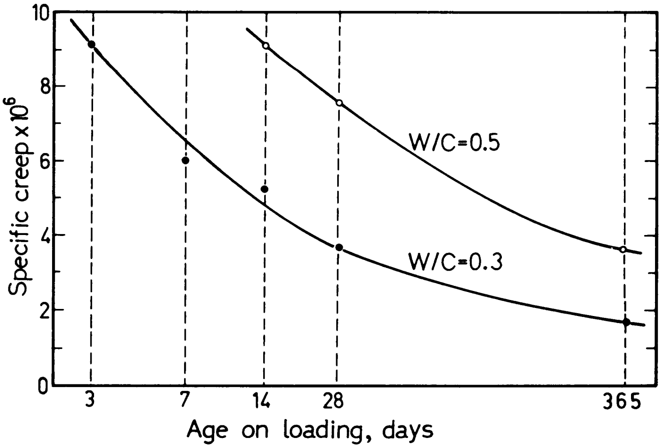

Figure 5.26 *Effect of age at loading on basic specific creep of cement paste (after Ruetz*[30]*)*

5.4.2.3 *Temperature*

It will be explained later that creep is associated with movement of water within the paste. Accordingly, creep depends on the viscosity of the water, which decreases with rise in temperature. The decreased viscosity, in turn, accelerates creep and creep is therefore expected to increase with rise in temperature. This conclusion is confirmed in Figure 5.27 for a temperature range up to about 60°C. However, any further rise in temperature resulted in lower creep. Such a reversed trend can be attributed to the accelerating effect of temperature on the hydration process. A higher rate of hydration implies a higher rate of strength development, and a higher strength results in lower creep. Apparently, in this particular case, the effect of the increased hydration on creep over the lower temperature range was less than the effect of the decreased viscosity. Hence, the net increase in creep. In the higher temperature range the relative magnitude of the two opposing effects was reversed resulting in a decrease in creep with rise in temperature. Of course, this explanation is not valid for well matured pastes or for those which contain insufficient water to allow hydration to continue. In such pastes creep steadily increases with the rise in temperature up to 80°C.[30] In this respect, note that in this temperature range the composition of the paste is not affected, and so composition changes have not been considered as contributing to the temperature effect on creep.

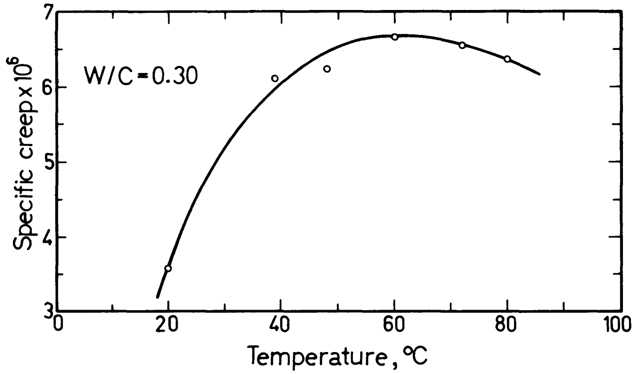

Figure 5.27 *Effect of ambient temperature on basic creep of cement paste (after Ruetz*[30]*)*

5.4.2.4 *Stress level and stress/strength ratio*

Creep of the paste increases with the increase in the stress level (Figure 5.28). On the other hand, creep decreases with the increase in the strength of the paste. It is to be expected therefore that creep will increase with the stress/strength ratio. This conclusion was confirmed in the tests summarised in Figure 5.29. The tests in question also indicated that a linear relation between creep and the stress/

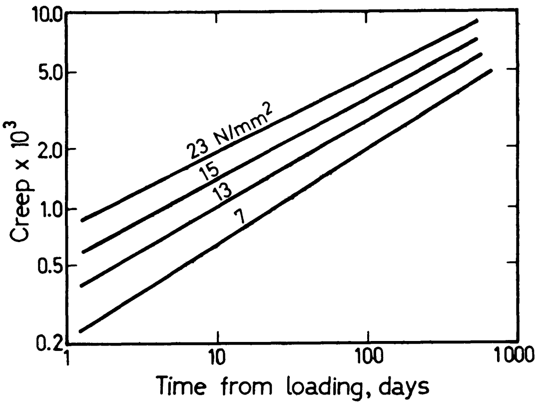

Figure 5.28 *Effect of stress level on creep of cement paste (after Wittmann[29])*

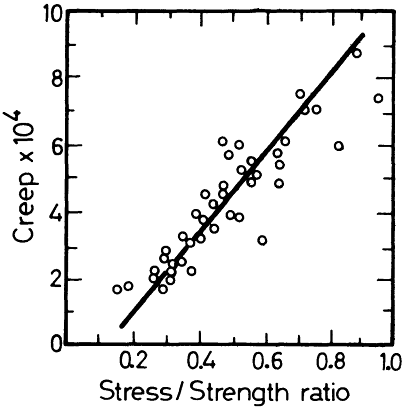

Figure 5.29 *Effect of stress/strength ratio on basic creep of cement mortars (after Neville[35])*

strength ratio holds up to a ratio of 0.85. The maximum value of this ratio varies from 0.3 to 0.75 according to one source[36] and from 0.25 to 0.40 according to another.[34]

In considering the effect of stress level on creep, reference is sometimes made to 'specific creep' (see Figures 5.26 and 5.27). Specific creep is defined as creep strain per unit stress. Accordingly, and bearing in mind the linear relation between creep and stress/strength ratio, the same specific creep is to be expected for different stress levels in pastes of the same strength.

5.4.2.5 Moisture content

The effect of moisture content on basic creep of cement paste is demonstrated in Figure 5.30. The data relate to cement pastes ($W/C = 0.4$) loaded to a stress/strength ratio of 0.2 after reaching equilibrium at the relative humidities indicat-

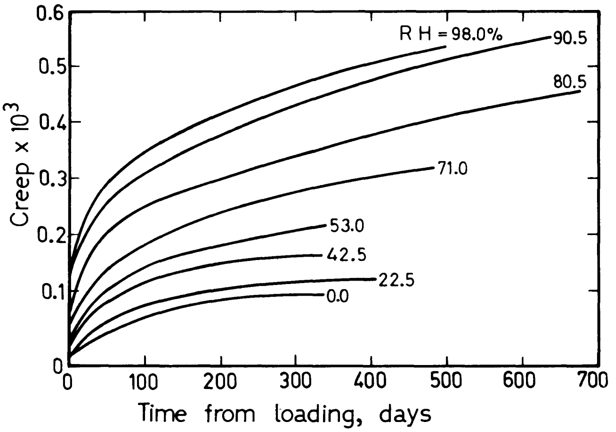

Figure 5.30 *Effect of ambient humidity on basic creep of cement paste (after Wittmann*[37]*)*

ed in the figure. It is clearly evident that creep increases with increase in the ambient relative humidity, i.e. with the increase in the moisture content of the paste. The very low creep of the paste dried at 0% relative humidity may be noted. A similar result was obtained in another study,[34] and in one case it was found that dried cement mortar did not creep at all.[40] These results imply that creep may be conditional on the presence of moisture in the paste. It will be seen later that all mechanisms which have been suggested to explain creep, are based on movement of water within the paste as a result of external loading.

5.4.2.6 Admixtures

Information about the effect of admixtures on creep of cement pastes is similar to that concerning their effect on shrinkage, i.e. it is rather limited and not conclusive.[22,23,25] It can only be concluded that admixtures affect creep of cement pastes with the exact nature of this effect varying with the specific admixture and test conditions.

5.4.3 Creep mechanism

Various mechanisms have been suggested to explain creep in the cement paste. A comprehensive survey can be found elsewhere,[38,39] and is not attempted here. Hence, the following discussion is limited to those mechanisms which are based on the previously presented models of the hardened cement paste (Chapter 3).

5.4.3.1 Powers' model[27]

The volume changes in the cement paste which accompany the variations in its moisture content, were attributed by Powers to corresponding variations in swelling pressure. Essentially, the same mechanism, induced by external loading and not by ambient humidity, was suggested by Powers to explain the reversible part of creep. According to his model, the swelling pressure is exerted by the load bearing water in areas of hindered adsorption. Due to external loading, some of this water is squeezed out into areas of unhindered adsorption by a time-dependent diffusion process. Swelling pressure gradually decreases bringing about a decrease in the volume of the paste (i.e. creep) as the spacing of the particles in the gel is reduced. Unloading causes a drop in the pressure in the load bearing water. Consequently, the reverse process takes place and water gradually diffuses from adjacent unhindered areas bringing the swelling pressure to its proper value in relation to the ambient humidity. The resulting gradual increase in swelling pressure causes volume increase, i.e. creep recovery.

The suggested mechanism can be used to explain most of the factors affecting creep which were discussed previously. Ambient temperature affects creep through its effect on the viscosity of the water. A rise in temperature decreases viscosity, hence the diffusion rate and the resulting creep are correspondingly increased. Also, the higher the stress level, the greater the diffusion rate and an increased rate of creep is therefore to be expected.

The load-bearing water is part of the gel water. The gel content, and associated gel water, increase with the degree of hydration, i.e. with the strength of the paste. At the same ambient humidity, the gel water content will therefore be greater in the stronger than in the weaker paste. Consequently, for the same load, the stress in the load-bearing water will be lower in the stronger paste and the resulting creep will therefore be smaller.

The irreversible creep is attributed by Powers, partly at least, to the formation of new bonds between surfaces when they are pressed together for the first time.

5.4.3.2 Glucklich and Ishai's model[26,40]

On application, the external load is distributed between the liquid and the solid phases of the cement paste. Under sustained loading the compressed liquid begins to diffuse from higher to lower pressure areas. This mechanism is accompanied by a gradual transfer of load from the liquid to the surrounding solid phase. The stress in the solid thus gradually increases causing a gradual volume increase, i.e. creep. Accordingly, creep may be regarded as a delayed elastic deformation, and a lower creep is to be expected in stronger pastes because such pastes have a higher modulus of elasticity. Also, greater creep is to be expected in pastes of higher moisture content. The higher the moisture content, the greater the part of the load which is taken initially by the liquid phase. Hence, the greater the load which is subsequently transferred to the solid phase. The greater the load transferred, the higher the resulting creep. It is self-evident that creep will also increase with the intensity of the stress level. Again, creep will increase with temperature due to its effect on the viscosity of water.

When the load is removed, the stresses in the solid phase are relieved and creep recovery takes place. Owing to the viscous resistance of the confined water, the process is not completed immediately but continues over a period of time.

Hence, the time-dependent nature of creep recovery (Figure 5.24).

The irreversible creep is attributed to the migration of inter- and intra-crystalline water (i.e. types 3 and 4 in Figure 3.10) induced by the imposed load. As a result of this migration the inter- and intra-crystalline spacing is reduced and the volume of the paste decreases. This volume decrease is not recoverable because it involves a reduction in the energy level of the system.

5.4.3.3 Feldman and Sereda's model[11]

In this model creep is attributed to exit of interlayer water resulting from the imposed external loading. On unloading, some of the water re-enters the structure; this accounts for the reversible part of the creep. The irreversible part is associated with the displacement of one CSH layer in relation to another or involves a process of breaking and remaking of interparticle bonds.[11]

In a later study,[41] however, a modified mechanism was suggested. It was concluded that

> creep is a manifestation of the gradual crystallisation or aging process of the layered material, resulting in further layering. Water movement, although occurring, is not the major mechanism. Other processes, such as slippage and micro-cracking, are also present.

5.4.3.4 Munich model[29]

The preceding mechanisms differ considerably, but all three attribute creep, one way or another, to movement of water within the paste. According to Wittmann, on whose studies the Munich model is mostly based, it is difficult to imagine that squeezing out of the load-bearing water (Powers' model) can play such an important role in the creep mechanism. Moreover, considering the mobility of adsorbed water, diffusion processes cannot account for the creep of the cement paste after periods as long as a few years. Accordingly, Wittmann suggested that the water affects creep only indirectly through its effect on swelling pressure which, in turn, weakens interparticle bonds. The weakening effect facilitates sliding of the gel particles with respect to each other and creep is, therefore, increased.[12]

The role of swelling pressure in the creep mechanism may be indicated in Figure 5.31.[37] In this figure, the creep rate is plotted against the ambient humidity under which the paste was brought into equilibrium. It can be seen that the rate of creep increases when the ambient relative humidity exceeds, say, 50%. On the other hand, it was found[12] that in about the same humidity region, swelling pressure may overcome van der Waals attraction and the gel particles are separated. As such separation weakens the structure, increased creep is to be expected. It can be seen that, particularly for short-time loading, the rate of

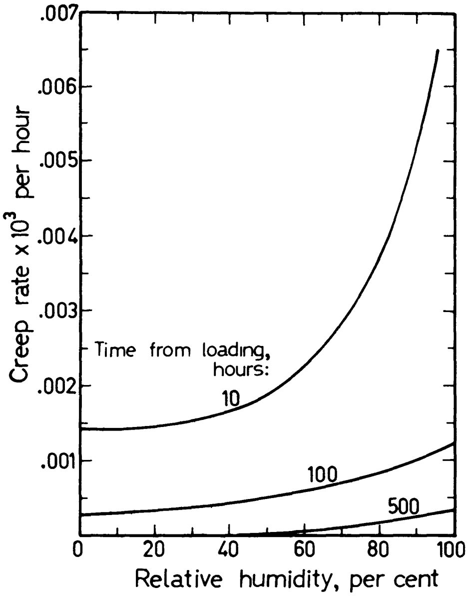

Figure 5.31 *Effect of ambient humidity on creep of cement paste after different periods of loading (after Wittmann*[37]*)*

creep increases when the ambient relative humidity excees about 50% (Figure 5.31).

5.4.4 Summary and concluding remarks about creep

Time-dependent deformation due to sustained loading is known as 'creep'. In the cement paste distinction is made between 'basic' and 'drying creep'. The former is the creep occurring in a paste which has attained equilibrium at ambient humidity. Creep which is taking place while the paste is being allowed to dry (i.e. at the same time as shrinkage) is higher than basic creep. The difference between the two is known as 'drying creep'. Creep is partly irrecoverable, hence the distinction between 'reversible' and 'irreversible creep'.

Creep increases with the increase in stress-level, moisture content, and intensity of drying (i.e. with the decrease in ambient relative humidity). Creep decreases with increase in strength of the paste and, accordingly, all factors which determine strength (i.e. *W/C* ratio, age, etc.) also affect creep. Generally, creep increases with temperature. The effect of admixtures is uncertain and varies according to the specific conditions.

A few mechanisms have been suggested to explain creep, and some of them are summarised in Table 5.2. It can be seen that opinions differ considerably with respect to the exact mechanism involved. In any case, it seems that creep in cement paste is attributable to more than one mechanism.

Table 5.2 Creep mechanism after various authors

Author	*Reversible creep*	*Irreversible creep*
Powers[27]	Diffusion of water from areas of hindered to unhindered adsorption reduces swelling pressure, and thereby causes reduction in the interparticle spacing.	Formation of new bonds between gel particles brought into close contact the first time.
Glucklich and Ishai[26,40]	Diffusion of water from high to low pressure areas causes gradual load transfer from liquid to solid phase, causing a delayed elastic volume decrease.	Removal of inter- and intra-crystalline water reduces inter- and intracrystalline spacing.
Feldman and Sereda[11,41]	Exit and re-entry of interlayer water.	Displacement of CSH layers in relation to each other and formation of new interparticle bonds.
Wittmann[29,55]	Weakening of the paste structure due to separation of gel particles by the swelling pressure at relative humidities exceeding 50%.	

5.5 Carbonation shrinkage

The cement paste contains free calcium hydroxide which is produced in the hydration of the alite and the belite. In the presence of water the calcium hydroxide reacts with atmospheric carbon dioxide to give calcium carbonate and water, i.e.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Carbon dioxide also attacks and breaks down the hydrated calcium silicates and aluminates giving silica and alumina gels as the end products.[42] The reaction between carbon dioxide and the hydration products (i.e. carbonation) is accompanied by a decrease in the volume of the paste; this is termed 'carbonation shrinkage'.

Carbonation affects the properties of the cement paste. For example, it increases the strength of the paste and decreases its permeability. Carbonation particularly affects drying shrinkage of the paste, an effect which reaches a maximum at approximately 50% relative humidity. This is reflected in Figure 5.32 which presents the shrinkage of cement mortars dried to equilibrium at various humidities and exposed to different sequences of carbonation. Curve A

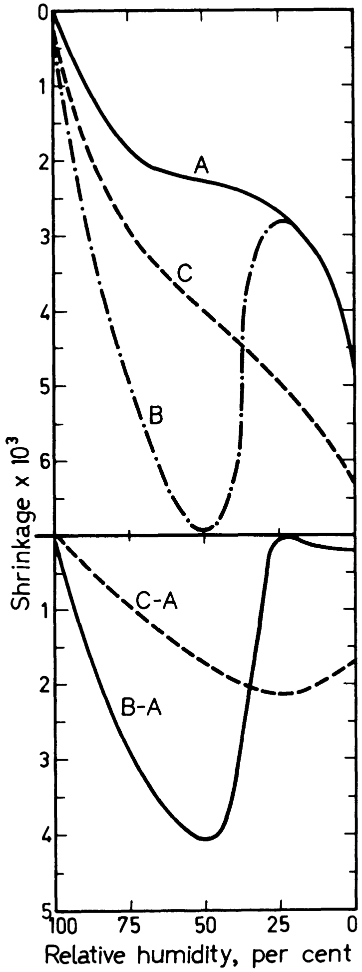

Figure 5.32 *Effect of carbonation on shrinkage of cement mortars (after Kamimura et al.*[43]*).* A, *drying in* CO_2 *free air;* B, *drying with subsequent carbonation;* C, *drying with simultaneous carbonation* describes the shrinkage of mortars as a result of drying in CO_2-free air, curve B as a result of drying with subsequent carbonation, and curve C as a result of drying with simultaneous carbonation.[43] Similar results,[44] but not necessarily identical results,[45] have been obtained by others. Accordingly, it may be concluded that carbonation involves a considerable shrinkage which depends on moisture content of the paste and stage at which carbonation occurs.

Carbonation shrinkage is affected by such factors as CO_2 concentration, porosity of the paste, and, particularly, its moisture content. Curve A in Figure 5.32 describes drying shrinkage only. Hence, curves BA and CA represent additional shrinkage due to subsequent or simultaneous carbonation, respectively. It can be seen that for subsequent carbonation maximum shrinkage occurs at about 50% relative humidity and for simultaneous shrinkage at about 25% . This difference in results was attributed to the difference in the carbonation sequence in the two series.[43] A major part of the carbonation reactions are accompanied by release of water. As drying is a time-dependent process, the internal relative humidity of the sample simultaneously undergoing carbonation, will be higher at any given time than the ambient relative humidity. Hence, the maximum occurs at an ambient relative humidity of about 25% rather than at 50%, as in the subsequent carbonation case.

The decrease in carbonation shrinkage with decrease in relative humidity in the low region is attributed to the decreased moisture content in the paste. The decreased moisture content limits the amount of the CO_2 which can be dissolved, and the intensity of the carbonation reactions is, therefore, reduced. On the other hand, increased moisture content reduces the rate of diffusion of CO_2 into the paste, and carbonation shrinkage is, again, reduced. Hence, maximum shrinkage is to be expected to occur as indicated in Figure 5.32.

On complete drying, where there is no water, carbonation shrinkage is not to be expected. This is confirmed in Figure 5.32 for subsequent carbonation whereas for simultaneous carbonation some shrinkage does occur at 0% relative humidity. Again, as a result of the release of water during carbonation and of the time required for drying, some moisture will still remain in the paste at 0% relative humidity when it is subjected to simultaneous carbonation and drying. Hence, the observed shrinkage occurs. As expected, no carbonation shrinkage was observed in saturated specimens, i.e. at 100% relative humidity.

The mechanism of carbonation shrinkage is not clear, especially when one considers that the formation of $CaCO_3$ involves volume increase. Powers[46] attributed the shrinkage to dissolution of the calcium hydroxide crystals while the crystals are under pressure. Such dissolution temporarily increases stress in the remaining solids of the paste bringing about a corresponding volume decrease. Deposition of the resulting calcium carbonate does not involve volume changes because it occurs in places where the sample is not under pressure. According to Powers carbonation of other hydration products takes place by topochemical reactions and not through solution. Hence, no volume changes are involved. According to Lea,[42] however, Powers' mechanism does not explain all the available data, and cannot offer a general explanation of the process of carbonation shrinkage.

Carbonation of calcium hydroxide is accompanied by release of one molecule of water per one combined molecule of carbon dioxide. This ratio is found at early stages of carbonation. At later stages, however, and in pastes containing added silica treated in an autoclave, and therefore containing no calcium hydroxide, this ratio drops below unity. Also, it was found that the amount of chemically combined water decreases as carbonation proceeds.[45,47] This implies, therefore, that in addition to calcium hydroxide, other phases are involved in the carbonation process and some changes in the composition of the gel are taking place. It was suggested, for example, that carbonation shrinkage is associated with dehydration and polymerisation of the hydrous silica carbonation products.[48]

The depth of carbonation depends on the porosity of the paste but usually does not exceed a few millimetres.[49] In other words, carbonation is essentially a surface effect, and it can cause crazing. In the practical application of Portland cement (concrete), the importance of carbonation is not great. In porous and cracked concrete, however, carbonation may reach as far as the reinforcing steel, and the resulting reduced alkalinity will make the steel susceptible to corrosion.

5.6 Thermal volume changes

The coefficient of thermal expansion of the cement paste varies between 10 and 20 x 10^{-6} per °C[50-52] depending, mainly, on the moisture content of the paste (Figure 5.33). It can be seen that this coefficient increases with the increase in

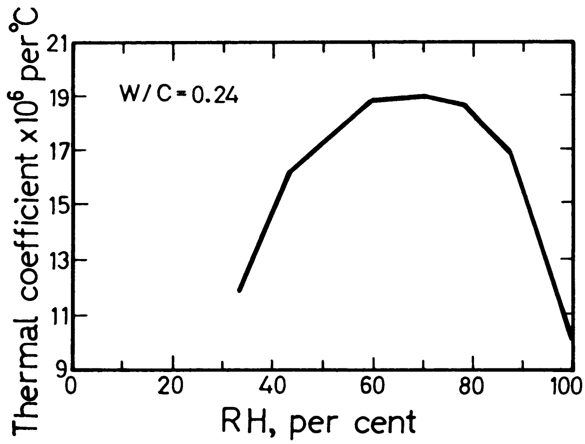

Figure 5.33 *Effect of ambient relative humidity on coefficient of thermal expansion of cement paste (after Meyers[50])* the relative humidity under which the paste was brought to equilibrium, passing through a maximum at about 70% relative humidity.

The nature of the coefficient against relative humidity curve was attributed by Meyers[50] to the effect of temperature on the surface tension of water. Under otherwise similar conditions, the tension in the capillary water depends on the surface tension which decreases with rise in temperature. That is, the tension in the water, and the resulting compression in the solid, will decrease with increasing temperature and the volume of the paste will correspondingly increase. It can also be shown that swelling pressure increases with temperature and, accordingly, the volume of the paste should increase. In other words, considering both mechanisms, a rise in temperature will cause a volume increase in addition to that caused by thermal effects. Accordingly, the true coefficient of thermal expansion is the one determined on dry or saturated pastes in which neither capillary tension nor swelling pressure are operative.

The maximum in the curve was attributed to the variations in the capillary forces with the change in moisture content of the paste. The capillary forces are equal to the product of the tensile stress in the water and the cross sectional area of the water-filled pores and, as earlier explained, are expected to pass through a maximum at a certain relative humidity. The thermal coefficient of expansion, being related to the capillary forces, will therefore pass through a similar maximum.

Another mechanism was suggested at the time by Mitchell,[51] and later further developed by Helmuth[52] and Bazant.[54] They attribute the variation in the thermal coefficient to flow of water between gel and capillary pores. From considerations of the entropy of the two types of water, Helmuth concluded that cooling will cause water to flow from the capillary into the gel pores and warming from the gel pores to the capillary pores. As drying of the gel pores causes shrinkage and re-entry of water swelling, cooling will cause swelling and warming shrinkage. In other words, according to this mechanism, the internal flow of water causes volume changes in an opposite direction to that simultaneously occurring due to thermal changes. Nevertheless, on cooling, the net result is contraction because the temperature-induced contraction is greater than the swelling of the paste due to the flow of water into the gel pores. Similarly, the net result of warming is expansion because the thermal expansion is greater than the shrinkage caused by the drying of the gel pores.

The flow of water within the cement paste is a time-dependent diffusion process and accordingly, the resulting volume changes must also be time-dependent. Since the diffusion induced volume changes are in the opposite direction to their thermally-induced counterparts, a partial recovery in the apparent thermal volume changes is to be expected with time. This is confirmed by the test results summarised in Figure 5.34,[53] in which length-changes are plotted against temperature. In the tests in question heating was stopped at 10°C intervals, and the temperature then kept constant for a few hours. It can be seen

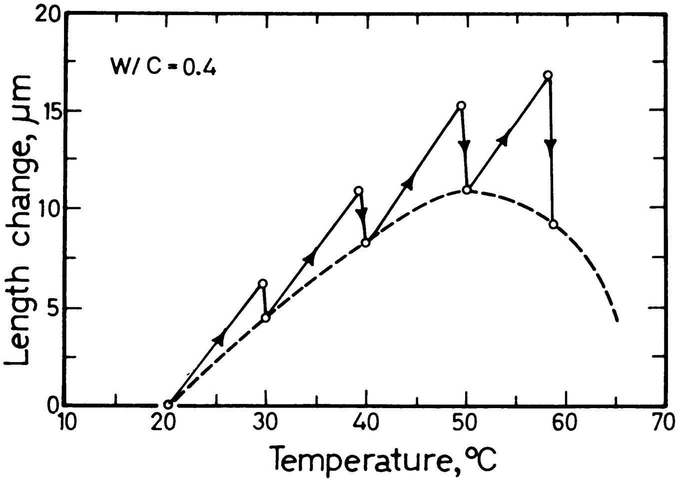

Figure 5.34 *Time-dependent recovery of thermal expansion (after Wittmann*[53]*). The 'saw-tooth' curve was obtained by stopping heating at* 10°C *intervals until complete recovery was attained*

that, at each stage, some time-dependent recovery takes place, giving the saw-tooth curve of Figure 5.34, and the resulting 'true' thermal expansion represented by the broken curve.

It was also found that the thermal expansion of pastes treated in an autoclave is unaffected by moisture content, their thermal coefficient of expansion remaining constant and equal to 11×10^{-6} per °C. As already explained, such pastes are characterised by the absence of gel-size pores. Hence, according to Meyers, as well as to Helmuth, no effect of moisture content is to be expected because both mechanisms connect this effect with the presence of gel water.

Finally, in the temperature range from –20 to +20°C, the coefficient of thermal expansion was found to increase with rise in temperature.[53] It was also reported that the coefficient increased with the fineness of the cement and perhaps also with the increase in its C_3A content.

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6 Chemical and frost resistance of hardened cement paste

6.1 Introduction

Hardened cement paste may be attacked either by a process of dissolution or by chemical transformation or by both at the same time. The intensity of the attack depends on the specific properties of the aggressive agent, its concentration, the presence of other ions in the solution, etc. Ambient conditions such as temperature and pressure, as well as the length of time and the nature of the contact (i.e. continuous or periodic) between the paste and the aggressive agent, also affect the intensity of the attack. Also, regardless of the specific nature of the agent, the intensity of the attack is determined to a considerable extent by the porosity of the paste. In a dense paste the attack is essentially limited to the surface proceeding with time to the inside. A porous paste, on the other hand, allows the aggressive solutions to penetrate it, and the attack takes place throughout the mass. Such an attack is, therefore, more intensive.

Porosity similarly affects frost-resistance of the paste. The freezable water content in the paste increases with porosity and the paste's strength decreases. Hence, frost damage is likely to be more severe in porous than in dense paste. In other words, porosity affects both chemical and frost resistance of the paste. Consequently, as will be shown later (Chapter 10), the use of dense concrete is always recommended when it is to be exposed to freezing conditions or to an aggressive environment.

'Permeability' and 'absorption' are both porosity related properties which are sometimes discussed in relation to chemical and frost resistance of the cement paste. The two properties are not necessarily related. Absorption is measured by the water content of the saturated paste expressed as a percentage of its weight, usually its dry weight. As such, absorption measures the porosity of the paste or, strictly speaking, the volume of the open pores accessible to water. Permeability, on the other hand, measures the rate of flow of water through the paste at a given pressure and temperature. Permeability, therefore, depends on the continuity of the pore system, pore-size distribution, etc., and not only on porosity as such.

The chemical resistance of the paste is related to its permeability. Under static conditions, the concentration of the aggressive agent in solution decreases as the chemical reactions proceed, and the intensity of the attack is gradually reduced. Flow of aggressive solution through the paste maintains the concentration of the agent and, consequently, also maintains the intensity of the chemical attack. The same applies when the attack involves a dissolution process. The flow removes the resulting saturated, or nearly saturated solution, and the process can proceed uninterrupted. In this respect, it should be pointed out that generally the most intensive chemical attack is to be expected when the paste is subjected to alternate cycles of drying and wetting. Such variations in moisture content repeatedly expose the paste to fresh solutions, and the intensity of the attack is continuously maintained.

6.2 Permeability and absorption

Figure 6.1 shows schematically the penetration of water into a porous solid. At first, the rate of penetration into the solid is determined by the external pressure and the capillary forces. On saturation, the capillary forces cease to exist and a steady flow, which depends on the external pressure and the properties of the material, is attained. At this stage the rate of flow is given by Darcy's equation, i.e.

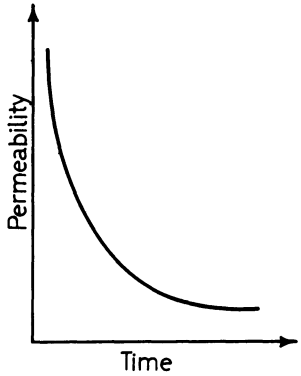

Figure 6.1 *Water penetration into a porous solid*

$$\frac{\mathrm{d}q}{\mathrm{d}t}\frac{1}{A} = K\frac{\Delta h}{L}$$

where $\mathrm{d}q/\mathrm{d}t$ is the rate of flow in m^3/s, A is the cross sectional area of the sample in m^2, Δh is the drop in hydraulic head across the sample in m, and L is the thickness of the sample in m. Hence, K, the coefficient of permeability, has units of m/s.

It was previously stated that permeability depends not only on the porosity of the paste, but also on other properties of the pore system, such as continuity and pore-size distribution. According to Powers[1] the coefficient of permeability of the cement gel equals 7×10^{-16} m/s, and it is a few degrees of magnitude lower than the coefficient of the paste. In other words, the effect of gel porosity on permeability is negligible, and the permeability of the paste is determined, therefore, by the capillary porosity. Since the capillary porosity is determined, at a particular degree of hydration, by the W/C ratio, the latter will also determine permeability. The data of Figures 6.2 and 6.3 clearly confirm this.

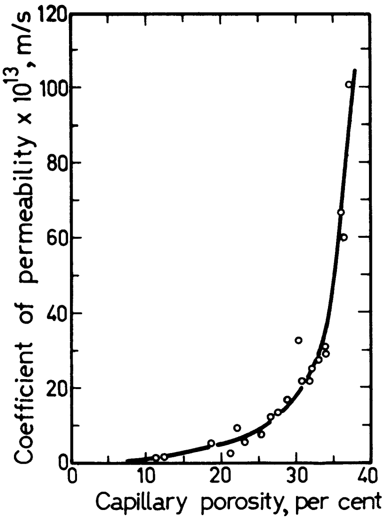

Figure 6.2 *Effect of capillary porosity on permeability of cement paste (after Powers*[1]*)*

It may be noted from Figure 6.3 that at W/C ratios of below, say, 0.5, the coefficient of permeability is rather low and is hardly affected by the W/C ratio. At higher ratios, however, the coefficient of permeability becomes highly dependent on W/C ratio, and a comparatively small increase in the latter results in a considerable increase in permeability. The change in the relationship is attributable to a change in the nature of the pore system. Apparently, in the low W/C ratio region the capillary pores are discontinuous, and are separated from each other by the gel. Hence, the permeability of the paste is determined by that of the gel which is rather low. In the high W/C ratio region the pore system becomes continuous, and increasing pore volume in such a continuous system will increase permeability. As the porosity is determined by the W/C ratio, permeability will increase with the increase in this ratio.

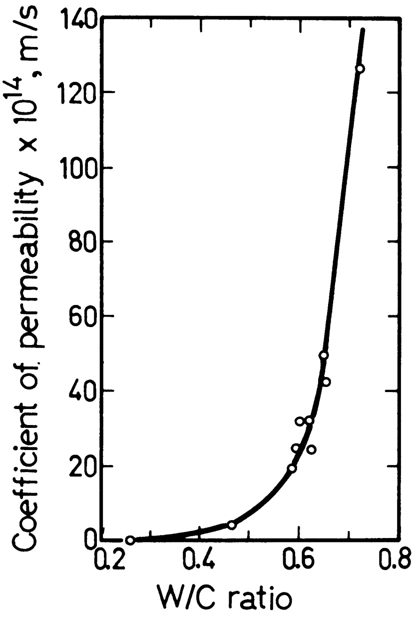

Figure 6.3 *Effect of W/C ratio on permeability of cement paste (after Powers et al.*[2]*)*

The continuity concept of the pore system has been used to explain the much higher permeability of pastes which were allowed to dry before being tested.[2] Apparently, drying causes internal cracking in the paste, and this cracking contributes substantially to the continuity of the pore system.

It may be concluded from Figure 6.3 that the use of pastes with a *W/C* ratio of 0.5 or less will produce virtually impermeable system. This conclusion, however, is valid only for well matured pastes because porosity is also determined by the degree of hydration, and even pastes of low *W/C* ratio will have a continuous pore system if they are not sufficiently hydrated (Figure 6.3 was obtained at 93% hydration). The conclusion that mature pastes having a *W/C* ratio below 0.5 are virtually impermeable is of practical importance, and is widely made use of in the production of dense impermeable concrete.

Permeability of the paste is not affected by curing temperatures up to 70°C. At higher temperatures, however, permeability increases up to 160°C.[3] Further rise in temperature does not increase permeability. This is attributable to the effect of temperature on the structure of the paste. It was explained earlier that autoclave treatment results in pastes of coarser structure which are characterised by the presence of larger capillary pores and the absence of small gel pores (Figure 3.7). The greater permeability is attributable, therefore, to the greater capillary porosity.

Absorption rather than permeability is usually considered as important in frost-resistance of cement pastes and concrete. Absorption, which is a measure of the porosity of the paste, is determined by the *W/C* ratio and the degree of hydration. Hence, the use of pastes with low *W/C* ratio will reduce both absorption and permeability.

6.3 Chemical resistance

*6.3.1 Dissolution and leaching in soft water**

Portland cement is a hydraulic cement and is not attacked by water, at least not to an extent which is of any practical importance. Nevertheless, water can damage the cement paste by a dissolution process.

Cement paste consists of about 65% lime part of which is present as free calcium hydroxide. The solubility of calcium hydroxide in water is about 1.7 g/litre, and it can be leached out by water. The action of water is not limited to the dissolution of the free calcium hydroxide. The hydrates of the calcium silicates, aluminates, and ferrites, are stable in aqueous solutions of a certain minimum concentration of lime. Water dilutes the solution causing hydrolysis of the hydration products, allowing further lime to go into solution in order to maintain equilibrium. In theory, under a continuous flow of water, this process will continue until all the lime is leached out, and the hydration products are completely decomposed leaving behind colloidal hydrates of silica, alumina, and ferrite oxide, rich in water and which have no strength.

It should be stressed, however, that the above possible effect is limited to pure water because the dissolution of calcium hydroxide in hard water, which already contains some lime in solution, is rather limited. Moreover, in order to cause appreciable damage, the attack must continue over a long period of time. Consequently, in practice such attack is limited, and may occur only when soft water, such as water resulting from condensation, melting of snow or ice, etc., is involved.

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*Hard water, as opposed to soft water, is water containing magnesium and calcium salts in solution. Temporary hardness is a form of hardness caused by the presence of the bicarbonates of calcium, $Ca(HCO_3)_2$, and magnesium, $Mg(HCO_3)_2$, and can be therefore removed by boiling (hence, the reference to temporary hardness). Permanent hardness, on the other hand, remains even after prolonged boiling and is due to the presence of calcium and magnesium chlorides or sulphates. The degree of hardness is measured by the equivalent $CaCO_3$ concentration (UK, France) or CaO concentration (Germany). In the UK, unit hardness is defined as that produced by one part $CaCO_3$ by weight in 80 000 parts of water, and in France by one part $CaCO_3$ in 100 000 parts of water. In Germany it is the hardness produced by one part CaO by weight in 100 000 parts of water.

6.3.2 Acids and acidic solutions

Most acids attack the cement paste by converting its constituents into readily soluble salts. For example, attack by hydrochloric acid ($HC\ell$) leads to the formation of chlorides of calcium ($CaC\ell_2$), aluminium ($A\ell C\ell_3$), and iron ($FeC\ell_3$) all of which are soluble in water and are therefore easily removed. A similar effect is produced by most strong acids, such as sulphuric and nitric acids. Exceptional in this respect are oxalic, $(COOH)_2 \cdot 2H_2O$, tartaric, $(CHOH \cdot COOH)_2$, and hydrofluoric, HF, acids which produce almost insoluble salts. Of some special interest are aqueous solutions of fluates* which are sometimes used to protect concrete against mild attack by certain aggressive agents. Fluates convert the lime into highly insoluble calcium fluoride, CaF_2, and lead to the precipitation of colloidal silica in the pores of the hardened cement paste. Thus, a protective coating is formed which prevents further penetration of the aggressive solution into the mass. In any case, as previously mentioned, such acids are exceptional, and a damaging effect to cement products is to be expected if the pH of an aggressive solution is lower than 6.† Sometimes solutions with a pH value as high as 6.5 may also damage Portland cement products.

In most cases, the acidity of naturally occurring water is due to dissolved carbon dioxide. In discussing carbonation it was stated that, when dissolved in water, carbon dioxide reacts with the calcium hydroxide of the cement to form calcium carbonate. The latter is practically insoluble in water and its formation, and its presence in the paste are not expected to affect adversely the integrity of the paste. Moreover, in some cases carbonation has been found to increase the strength of cement mortars.[6] The calcium carbonate, however, reacts with aqueous solutions of carbon dioxide to form a soluble bicarbonate of calcium, i.e.

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2$$

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*Fluates or silicofluorides, are salts of fluorosilicic acid, H_2SiF_6. In the building industry this term is used to describe waterproofing compounds consisting of solutions of sodium silicate or silicofluoride, and other silicofluorides such as those of zinc, $ZnSiF_6$, magnesium, $MgSiF_6$, and aluminium, $A\ell_2(SiF_6)_3$.[5]

†In solution, as a result of dissociation, acids produce hydrogen ions and alkaline substances hydroxide ions. The degree of dissociation is, therefore, a measure of the acidity or alkalinity of the solution. For certain reasons, beyond the scope of this discussion, the negative value of the logarithm (to the base ten) of the hydrogen ion concentration (mole per litre) is used to measure the acidity and alkalinity of solutions. This measure is referred to as the pH value of the solution. In absolutely pure water the concentration of hydrogen ions, H^+, is equal to that of hydroxyl ions, OH^-, each being equal to 10^{-7} mole per litre. The pH value of pure water equals, therefore, 7. The pH value varies from 0 to 14. The pH value of acid solutions is lower than 7 and that of alkaline solutions is greater than 7. The pH value decreases with increasing acidity of the solution and increases with alkalinity. Hence, the pH value of a molar aqueous solution of hydrochloric acid, which is a strong acid, equals 0. Similarly, the pH value of a molar solution of sodium hydroxide, which is a strong alkali equals 14.

It may be noted from this equilibrium that while some of the carbon dioxide is combined in the calcium bicarbonate, some 'free' carbon dioxide is required otherwise the bicarbonate reverts to carbon dioxide and the carbonate. The free carbon dixoide which is required to maintain equilibrium cannot combine with more calcium carbonate and is therefore not aggressive. Accordingly, the aggressive carbon dioxide, capable of dissolving more calcium carbonate is the free carbon dioxide which is present in excess of that combined in the calcium bicarbonate and that required to stabilise it. Moreover, only part of that excess carbon dioxide will react with more calcium carbonate because the remaining part will be required to stabilise the newly formed calcium bicarbonate. It is evident therefore, that in pure water even a small amount of carbon dioxide will be aggressive. In hard water, however, even a high amount may not be aggressive if the lime content in the water is high enough to ensure that all the carbon dioxide that is not combined will be required to stabilise the calcium bicarbonate.

The amount of free carbon dioxide required to stabilise a given amount of calcium bicarbonate increases in the presence of other calcium salts such as calcium sulphate. On the other hand, the amount decreases in the presence of salts of other bases such as sodium chloride.[7] It is implied therefore that, for the same free CO_2 content, the amount of aggressive carbon dioxide will be higher in sea water than in fresh water. Further details concerning corrosion of the cement paste due to carbon dioxide can be found elsewhere.[8,9]

6.3.3 Sulphate solutions

Most sulphates attack the hardened paste very severely. An exception is barium sulphate (barytes) which is almost insoluble in water and is, therefore, not aggressive. Hence, barytes may be used as an aggregate in the production of heavy concrete. Such concrete is sometimes used in the construction of atomic reactors and similar structures because of its improved shielding properties against radiation.

The sulphates react with free calcium hydroxide and with hydrated calcium aluminate. The reactions involve increase in volume of the solids and cause expansion. The expansion, in turn, causes cracking which, under continuous and severe exposure, may result in complete deterioration of the hardened paste. Sulphate attack may be considerable even for SO_3 concentrations as low as 500 mg/litre.

Gypsum reacts with hydrated calcium aluminate to form the less soluble calcium sulphoaluminate known as ettringite,

$$\begin{aligned}&4CaO\cdot A\ell_2O_3\cdot 19H_2O + 3(CaSO_4\cdot 2H_2O) + 7H_2O \rightarrow\\&\quad 3CaO\cdot A\ell_2O_3\cdot 3CaSO_4\cdot 31H_2O + Ca(OH)_2\end{aligned} \tag{6.1}$$

The alkali-metal sulphates Na_2SO_4 and K_2SO_4 react with free calcium hydroxide to form gypsum

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4\cdot 2H_2O + 2NaOH \tag{6.2}$$

and the resulting gypsum further reacts with hydrated calcium aluminate as in equation (6.1).

The alkali-metal sulphates hardly attack the hydrated calcium silicates because they are less soluble than the calcium sulphate and the alkali-metal silicates which would result. On the other hand, magnesium sulphate does attack and decompose the calcium silicates. As with the alkali-metal sulphates, magnesium sulphate reacts with calcium hydroxide,

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + Mg(OH)_2 \qquad (6.3)$$

The resulting magnesium hydroxide is of low solubility, and its saturated solution has a pH of about 10.5 compared with 14.0 and 12.4 for saturated solutions of sodium and calcium hydroxide respectively.[10] The value of 10.5 is lower than required to stabilise the hydrated calcium silicates and consequently the silicates liberate lime to the solution to maintain the pH equilibrium. The magnesium sulphate, however, reacts with the liberated calcium hydroxide according to equation (6.3), and the resulting magnesium hydroxide immediately separates from the solution reducing the pH value again to 10.5. More lime is dissolved causing further decomposition of the calcium silicates. In the presence of sufficient magnesium sulphate this process can cause complete decomposition of the calcium silicates:

$$3CaO \cdot 2SiO_2 \cdot aq + 3MgSO_4 \cdot 7H_2O \rightarrow CaSO_4 \cdot 2H_2O + 3Mg(OH)_2 + 2SiO_2 \cdot aq \qquad (6.4)$$

Moreover, the resulting silica gel reacts very slowly with the magnesium hydroxide to form a hydrated magnesium silicate of composition approximating $4MgO \cdot SiO_2 \cdot 8.5H_2O$. The strength of the paste is thereby further reduced apparently because the magnesium silicate possesses no binding properties. Hence, magnesium sulphate is particularly aggressive to Portland cement products.

It was mentioned earlier that sulphate attack involves expansion and disruption of the hardened paste. The molar volumes of $Ca(OH)_2$ and gypsum are 33.2 and 74.2 cm^3 respectively. Hence, the conversion of calcium hydroxide to gypsum as in equation (6.2) increases the volume of the solids by the factor $74.2/33.2 \sim 2.2$. The same applies when reaction (6.1) is considered. The molar volumes of C_4AH_{19} and ettringite are 369 and 715 cm^3 respectively. Hence, the volume increase equals $715/369 \sim 2$.

Because of the porosity of the cement paste, the increase in volume of the solids can take place without causing expansion. That is, the available pore volume in the paste can allow precipitation and crystallisation of the reaction products without the generation of swelling pressure. This would happen if the reaction occurred through solution, thereby facilitating the distribution of the products throughout the mass. As this is not the case, it was suggested that reaction (6.1) occurs directly on the surface of the calcium aluminate hydrate as a liquid-solid reaction, i.e. as a topochemical reaction.[11] The space available locally at the surface is not great enough to accommodate the newly formed solids. Hence, the volume constraint results in a pressure buildup which, in turn, causes expansion.

Chatterji and Jeffery[12,13] also considered that sulphate expansion results from a topochemical reaction. However, they suggested that the reaction involves the conversion of C_4AH_{13} to calcium monosulphoaluminate (molar volumes 277 and 313 cm^3, respectively) rather than the conversion of C_4AH_{19} to ettringite, i.e.

$$C_4AH_{13} + SO_4^{2-} + aq \rightarrow C_4A\bar{S}H_{12} + 2OH^- + aq \qquad (6.5)$$

It may be noted that reaction (6.5) is conditional on the presence of C_4AH_{13}, and it assumes that the formation of the monosulphoaluminate precedes that of the ettringite. Considering the available information on the nature of the hydrated aluminates and their reaction products with gypsum, the correctness of this mechanism is somewhat debatable, and it has been rejected by various authorities.[14–17]

At present, as already mentioned, the expansion and disruption of the cement paste due to sulphate attack is generally attributed to the expansion involved in the formation of ettringite by a topochemical reaction. Nevertheless, it has been suggested that some other mechanisms may be involved. Thorvaldson,[19] for example, suggested that expansion is produced by osmotic forces* which control volume changes in gels. The chemical reactions are involved only indirectly, weakening the structure of the cement gel. The formation of the new products is incidental and not the prime cause of the expansion. Hansen[16] further developed this suggestion to explain the expansion of cement products by magnesium sulphate. The liquid phase in the gel pores is saturated with respect to $Ca(OH)_2$. The magnesium sulphate, which diffuses into this phase, will react with the calcium hydroxide as in equation (6.3). Because of its low solubility, the $Mg(OH)_2$ precipitates out as extremely fine or colloidal particles. The precipitation of the $Mg(OH)_2$ introduces a new surface that upsets the equilibrium between the gel and its surrounding liquid. In order to reestablish the disturbed equilibrium water is drawn from the outside into the gel pores, causing them to expand. In other words, the expansion is not caused by the increase in the volume of the solids but rather by the increase in their surface energy. Consequently, additional water is drawn into the gel pores causing their enlargement by 'osmotic pressure'.

The presence of other ions affects the aggressiveness of sulphate solutions. Sodium hydroxide, for example, reduces considerably sulphate expansion although, apparently, the amount of ettringite formed is not affected by its

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*'Osmotic pressure' is the pressure exerted by a dissolved substance by virtue of the motion of its molecules. It may be measured by the excess pressure which, when applied to the solution, will just prevent osmosis. Osmosis is the passage of solvent through a membrane, which is permeable to the solvent but not to the solute, from a lesser to a more concentrated solution.

presence.[18] According to Hansen,[16] in alkaline solutions stronger than the liquid phase of the cement, ettringite is formed through solution and not by a topochemical reaction. Hence, no expansion is involved. The effect of chlorides is variable, i.e. in some cases it was found to increase sulphate expansion and in others to reduce it. Chlorides are present in sea water, and the specific effect of sea water on hardened cement is discussed separately.

If indeed sulphate expansion is a result of the formation of ettringite from hydrated calcium aluminate, the susceptibility of Portland cements to sulphate attack will decrease with decrease in C_3A content. This conclusion has been widely confirmed by laboratory tests and by practical experience, and forms a basis for the production of sulphate resisting cements (Chapter 7).

The ferrite phase of the cement also reacts with sulphates to form calcium sulphoaluminate and sulphoferrite. Accordingly, the content of the ferrite phase should also determine the susceptibility of the cement to sulphate attack. However, it has been found that, for reasons which as yet have not been fully explained, the effect of the ferrite phase on sulphate resistant properties of cements is considerably less than that of the C_3A. Hansen[16] and others[20] suggested that the ferrite phase reacts through solution and therefore no expansion is involved. Some other explanations have been suggested[21] but, as already mentioned, the exact reason is not known as yet.

6.3.4 Sea water

The salt content and composition of sea water vary slightly from place to place. Generally, however, sea water contains 3.6 to 4.0% salt, of which about 75-78% is sodium chloride ($NaC\ell_2$), about 10-11% is magnesium chloride ($MgC\ell_2$), and 10-11% is sulphates of which about half is magnesium sulphate ($MgSO_4$) and the remainder is gypsum and potassium sulphate (K_2SO_4). Sea water also contains small amounts of bromine and iodine compounds. The pH of sea water varies from 7.5 to 8.4.

Note that chlorides make up about 90% of the total, and sulphates the remaining 10%. Sodium chloride does not react either with the calcium hydroxide or with the other hydration products. Magnesium chloride, however, slowly reacts with calcium hydroxide as in equation 6.6).

$$MgC\ell_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaC\ell_2 \qquad (6.6)$$

$CaC\ell_2$ is highly soluble and is easily removed by leaching. Hence, there may be a possibility of damage to the hydrated cement by attack of magnesium chloride. In dense products the deposition of $Mg(OH)_2$ tends to slow up this process. Virtually no such slowing effect takes place in porous and more permeable products.

The sulphate concentration of sea water is about 3.5 g/litre which is equivalent to a SO_3 concentration greater than 2000 mg/litre. As mentioned earlier, a sulphate concentration as low as 500 mg/litre may cause appreciable damage to the hardened paste. Hence, extensive damage is to be expected in pastes exposed to sea water. Nevertheless, experience has shown that corrosion of cement products in sea water is much smaller than would be expected from the SO_3 concentration in the water. The exact reason for the reduced aggressiveness of the sulphates in sea water is still not very clear. It has been suggested that the greater solubility of gypsum and calcium sulphoaluminate in chloride solutions reduces the effect of the volume increase associated with sulphate attack.[22] It has also been suggested that the presence of sodium chloride slows down the formation of the ettringite which is completely inhibited in the presence of magnesium chloride.[23] Locher,[24] on the other hand, argues that the presence of chlorides hardly affects the formation of ettringite, attributing the reduced rate of its formation to the presence of carbon dioxide.

6.3.5 Summary and concluding remarks about chemical resistance

Portland cement paste can be attacked chemically either by a process of dissolution and leaching or by chemical transformation or by both. The intensity of the attack depends on the specific properties of the aggressive agent, its concentration, etc.

The intensity is reduced by a decrease in the porosity of the paste, i.e. with decrease in the *W/C* ratio. A water/cement ratio of 0.5 or less will result in a virtually impermeable paste.

Soft water Soft water may cause some damage to the hardened paste due to leaching out of calcium hydroxide. Continuous leaching will cause hydrolysis of the calcium silicates. In practice, however, the damage involved is rather limited, and occurs only in specific cases involving porous concrete and long periods of exposure to soft water.

Acids and acidic solutions Most acids attack the hardened cement by a process of dissolution and leaching. The damage due to acid attack may be considerable. Damage to the paste is to be expected if the pH of the acidic solution is lower than six. Sometimes solutions with a pH as high as 6.5 may also cause damage.

Dissolved CO_2 may attack the cement paste, but not all of the dissolved carbon dioxide is aggressive. Some of it is combined as calcium bicarbonate, $Ca(HCO_3)_2$ and some is required to stabilise the bicarbonate. Only the amount present in excess of that combined as bicarbonate and that required for stabilisation is therefore aggressive. For a given CO_2 content the amount of aggressive carbon dioxide will be higher in soft than in hard water.

Sulphate solutions All soluble sulphates attack hardened cement pastes and may cause considerable damage even when the SO_3 concentration is as low as 500 mg/litre. The sulphates attack the hydrated calcium aluminate (C_4AH_{19}) to form ettringite ($C_4A\bar{S}_3H_{31}$). The reaction is assumed to be topochemical and involves increase in the volume of the solids. Hence, a swelling pressure is generated and expansion results. Some sulphates, such as those of sodium (Na_2SO_4) and magnesium ($MgSO_4$) react with the calcium hydroxide to form gypsum which, in turn, reacts with the hydrated calcium aluminate. Magnesium sulphate also attacks the calcium silicates. The attack of this sulphate is, therefore, more intensive and damaging than that of the other sulphates.

Sea water The salt content in sea water is about 4%, of which about 90% is chlorides ($NaC\ell_2$, $MgC\ell_2$) and the remaining 10% is sulphates ($MgSO_4$, $CaSO_4$, K_2SO_4). $NaC\ell$ is inert with respect to the hardened paste but $MgC\ell_2$ reacts with calcium hydroxide to form soluble $CaC\ell_2$. Hence, damage may occur due to dissolution and leaching.

The SO_3 concentration in sea water is greater than 2000 mg/litre. Such a concentration may cause considerable damage, but experience has shown that the corrosion of cement products in sea water is much less than would be expected from this SO_3 concentration. The reason for the reduced aggressiveness of sulphates in sea water is not fully understood. Generally, it is attributed to the presence of the other salts in the water.

6.4 Frost resistance

6.4.1 Introduction

Pure water freezes at 0°C and its conversion into ice involves a 9% increase in volume. If water is present in confined spaces, such as the pores of cement paste, freezing will generate pressure, and the surrounding solid will be put under

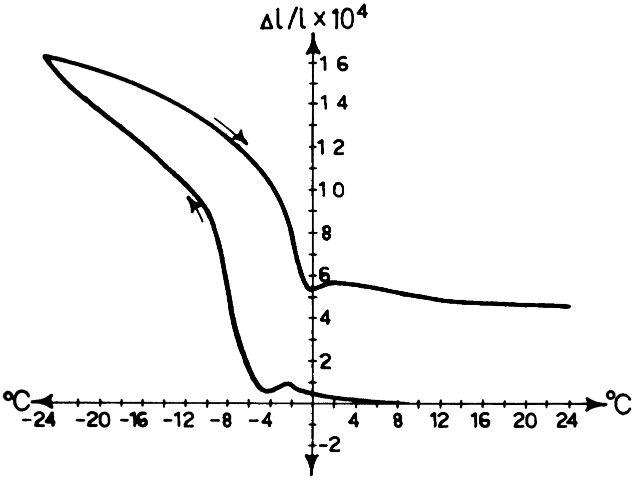

Figure 6.4 *Length changes in cement paste (W/C =* 0.65*) subjected to a single cycle of freezing and thawing (after Powers*[25]*)* stress. If the induced stress is lower than the strength of the solid, an elastic volume increase will take place. Hence, excluding creep effects, this increase in volume will be completely removed when the stress is relieved by melting of the ice. If the induced stress is higher than the strength of the paste, irreversible changes in structure, such as cracking, will occur and part of the volume increase will therefore be irrecoverable. Such irrecoverable increase is demonstrated in Figure 6.4 which describes length changes in a saturated cement paste ($W/C =$ 0.65) subjected to a single cycle of freezing and thawing.[25] It can be seen that in this case the irrecoverable length change (expansion) is approximately 30% of the total.

The damage to the paste increases with the number of freezing and thawing cycles. Further freezing also produces ice in the cracks which formed earlier, and the amount of damage to the paste, accordingly, increases.

6.4.2 Mechanism of frost action

The preceding discussion on frost damage treated the subject in a general and simple way, and is applicable to saturated porous solids only when all the water throughout the mass freezes at the same time. Actually the mechanism of frost damage is much more complicated, and opinions differ with respect to its exact nature. In fact, several mechanisms have been suggested, some of which are briefly described here.

6.4.2.1 Hydraulic pressure

Adsorbed water freezes at a temperature lower than 0°C because such water is subject to surface forces which limit the mobility of its molecules, and this hinders the crystallisation of ice. The water in the gel pores of the cement paste is such water and it freezes at –78°C.[28] In other words, in practice, frost action in cement products is limited to the formation of ice in the capillary pores.

On exposing saturated cement paste to temperatures below the freezing temperature of water, ice begins to form in the capillary pores near the exposed surfaces. With time, the temperature gradually falls within the mass, ice is formed in pores located further inside the paste, and the 'ice front' advances inward (Figure 6.5). When ice is formed in a pore, the combined volume of the remaining water and the ice is greater than the original volume of the pore. The excess water in the pore is, therefore, expelled giving rise to hydraulic pressure which, in turn, causes dilatation of the paste. The magnitude of the resulting pressure depends on the permeability of the paste, the elastic response of the solids, the rate at which freezing occurs, and the distance which the water is forced to travel from the pore to a point where the pressure can be relieved. The presence of an air void (i.e. 'escape boundary') can provide such a point of pressure relief (Figure 6.5). It will be seen later that the improved frost-resistance of concrete containing entrained air can be attributed to the role of air voids in relieving hydraulic pressure.

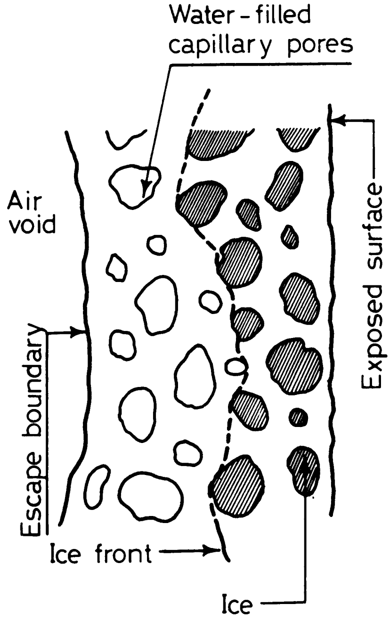

Figure 6.5 *Schematic description of ice formation in cement pastes*

This hydraulic pressure mechanism was first suggested by Powers[26,38] and was later further developed by Powers and Helmuth.[27] According to Powers[29] the generation of hydraulic pressure begins immediately the ice begins to form, and the generation of this pressure is the main cause of dilatation in relatively porous pastes in which the rate of ice formation is rapid.[29]

6.4.2.2 *Growth of capillary ice*

It has been stated that the mechanism of hydraulic pressure does not account for all the phenomena associated with freezing. Accordingly, it was suggested that a part of the effects is due to the tendency of the ice bodies in the capillaries to grow by drawing water from the gel pores.[27]

The ice bodies in the capillaries are surrounded by unfrozen water in the gel pores. It was found that the entropy* of the water that could be extracted from the gel at a given temperature is greater than the entropy of ice at the same temperature. Bearing in mind this difference in entropy between the ice and water, and the thermodynamic relation

$$(\partial F/\partial T)_p = -S$$

***A thermodynamic concept that, if a substance undergoing a reversible change takes in a quantity of heat dQ at temperature T, its 'entropy' is increased by dQ/T.**

it may be concluded that lowering the temperature will cause the water to gain free energy more rapidly than the ice.* Consequently, the gel water acquires an energy potential and diffuses into the capillaries causing the growth of the ice crystals. The growing of the ice exerts pressure on the surrounding solid and this therefore results in volume increase. It has been suggested that this mechanism is the main cause of dilatation in dense pastes.[29] In such pastes ice begins to form at relatively few points and the resulting hydraulic pressure is too low to cause significant dilatation.

According to the proposed mechanism, the growth of ice crystals is brought about by diffusion of gel water into the capillaries. Diffusion being a time-dependent process, dilation will not cease at the moment cooling is stopped.

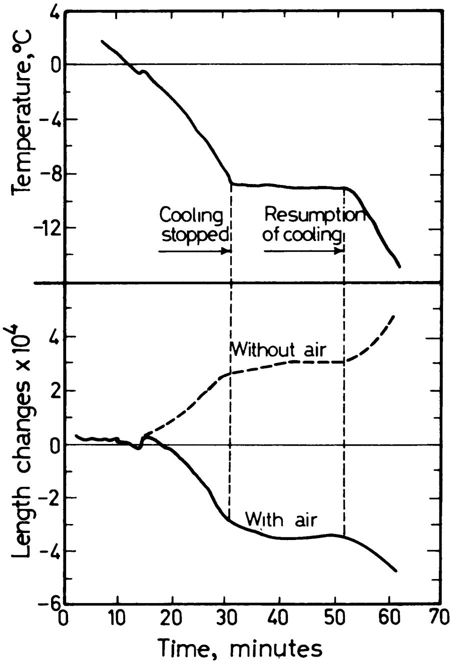

Figure 6.6 *Effect of interrupted cooling on dilatation of cement paste due to freezing (after Powers and Helmuth*[27]*)*

It can be seen (Figure 6.6) that when cooling is stopped at about –8°C, the paste without air entrainment continued to expand slightly (dotted line) for some time before dilatation ceased. The different behaviour of the air-entrained paste is quite obvious. The effect of air entrainment on frost-resistance, however, will be discussed in some detail later.

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*S denotes entropy, F free energy, and T temperature.

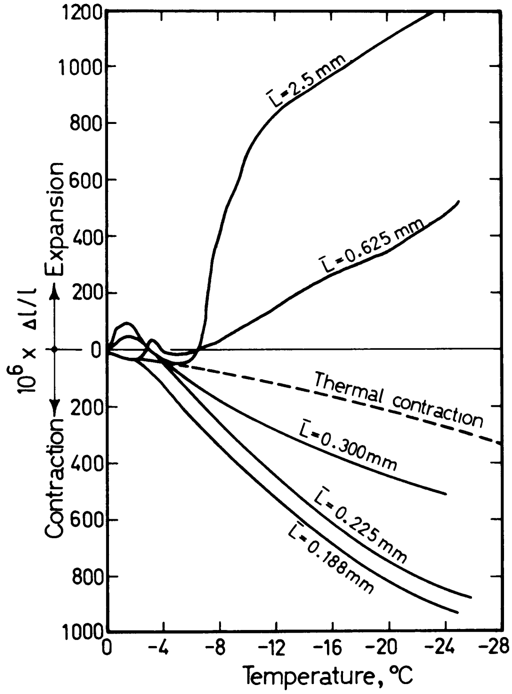

Figure 6.7 *Length changes due to freezing of cement pastes of different air contents (after Powers and Helmuth*[27]*). $\bar{L}$ is the 'spacing factor' which is a measure of concentration of air voids in the paste.*

The diffusion of water out of the gel pores causes self desiccation of the paste which, in turn, must cause shrinkage. In ordinary pastes the shrinkage is not apparent because the dilatation caused by freezing is greater than the shrinkage caused by self desiccation. On the other hand, in air-entrained pastes, for reasons which will be discussed later, dilatation due to freezing is eliminated and shrinkage may become evident. This is apparent in Figure 6.7 in which length changes in pastes of different air contents are plotted against temperature.[27] The dotted line represents the expected thermal contraction. It can be seen that the contraction of the air-entrained pastes is greater than the expected thermal contraction. According to the foregoing discussion, this difference in contraction is attributable to shrinkage caused by self desiccation.

This mechanism of ice growth in the capillaries is similar to that suggested by Taber[30,31] to explain frost upheavals in soils, and which was later used by Collins[32] to explain deterioration of low quality concrete due to frost action. According to Taber (Figure 6.8) the upheaval that occurs in soils is due to macroscopic ice segregation. When free water freezes in the larger cavities and

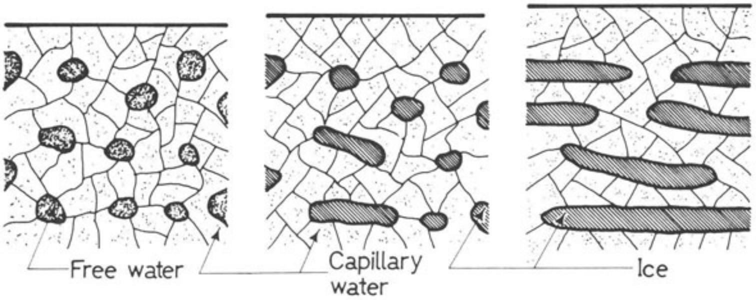

Figure 6.8 *Mechanism of soil upheaval due to macroscopic ice segregation (after Nerenst et al.*[33]*)*

voids, water is drawn from the surrounding unfrozen soil and ice lenses, parallel to ground surface, begin to develop and grow, and the growth of such ice lenses was suggested as the cause of soil upheaval. As mentioned, Collins applied this mechanism to concrete, and demonstrated the formation of ice lenses in low quality concrete frozen from the upper surface when its bottom face was in contact with water. Powers,[26] on the other hand, suggested that the mechanism of ice segregation could not be applied to ordinary concrete because the tensile strength of concrete is much higher than the cohesion forces in soils. Nevertheless, he did not reject the possibility that ice segregation may occur in concrete on a sub-microscopic scale. In fact, the previously described mechanism for ice growth in the capillary pores may be regarded as ice segregation on such a scale.

6.4.2.3 Osmotic pressure

The foregoing discussion did not take into account the presence of alkalis or other soluble substances in the capillary water. If pure water in a given capillary freezes at a certain temperature, an alkali solution will only partly freeze in the same capillary at the same temperature. Hence, crystallisation of ice will concentrate the solutions in the capillary pores without producing a similar change in the concentration of the solutions in the gel pores. The difference in the concentrations of the solutions will cause diffusion of gel water into the more concentrated solution in the capillary pores. The resulting diffusion, when opposed, results in the appearance of osmotic pressure which, in turn, causes dilatation of the paste.[29] In Powers' view, osmotic pressure is not the major mechanism in ordinary freezing-thawing tests because all freezing effects have been observed when the capillary water contained only a trace of alkalis. It may be, however, a mechanism involved in the scaling of concrete surfaces when the concentration of the solute is augmented, in regions near the surface, by the use of deicing salts. As the osmotic pressure depends on concentration difference, its magnitude and the resulting effects will be increased under such conditions.

On the other hand, Helmuth, who co-operated with Powers in developing the described mechanisms,[27] concluded later that[34]

> the expansion producing mechanism is not the development of pressure in all pores but the production of localised osmotic pressures at cites of ice formation.

The hydraulic pressure mechanism assumes the generation of pressures by ice formation, and the relief of this pressure by saturated hydraulic flow into air voids. Helmuth rejected the assumption of a saturated flow because of self desiccation of the paste which takes place on cooling. He therefore concluded that only unsaturated flow by suction and surface diffusion can be considered in the mechanism for frost damage of the cement paste. As already mentioned, such an unsaturated flow and the resulting accretion of ice in the capillaries was considered by Helmuth to cause dilatation in cement pastes.

6.4.2.4 Diffusion due to decreasing relative humidity

Litvan[35] attributed the diffusion of water out of the gel pores to the decrease in relative humidity over the adsorbed water on cooling. It was mentioned earlier that adsorbed water in the gel pores will not freeze when the temperature drops below 0°C. Such water will remain, therefore, as a supercooled liquid. The paste will continue to remain saturated on cooling provided that the ambient relative humidity is maintained at 100%. This provision can be satisfied only when the water vapour pressure over the system is equal to the pressure over the supercooled water. This condition, however, does not normally occur because the vapour pressure of the supercooled water exceeds the vapour pressure of bulk ice. The vapour pressure over the ice, on the other hand, can increase only temporarily because formation of new ice will restore its original value. Hence, the relative humidity over the supercooled water is less than 100% and continues to decrease with fall in temperature. As adsorption decreases with decrease in the relative humidity, the decrease in the latter over the supercooled water causes the excess amount of water to migrate towards the outer surface of the paste. If the water reaches the surface freezing takes place without causing dilatation. This may be the case when the rate of cooling is slow and the water has to travel only a short distance, otherwise the water will freeze in the larger pores and cause dilatation. In other words, the mechanism suggested by Litvan, also those of Powers and Helmuth, involves the migration of water from small to large pores, i.e. from gel to capillary pores. Nevertheless, according to Litvan, this migration is induced by the decreasing relative humidity over the supercooled water whereas, according to Powers and Helmuth, it is brought about by differences in the entropy of the gel water and the ice in the capillaries, and by differences in alkali concentration in the gel and in the remaining capillary water.

6.4.3 Factors affecting frost-resistance of cement pastes

6.4.3.1 Moisture content

It is obvious that frost action is conditional on the presence of moisture, and the preceding discussion applies, therefore, only to saturated or nearly saturated pastes. This fact is clearly demonstrated in Figure 6.9 which presents length changes in cement pastes which were brought to equilibrium with water vapour at 84% relative humidity before being subjected to a freezing cycle between +5°C and –60°C.[35] It can be seen that freezing causes hardly any permanent

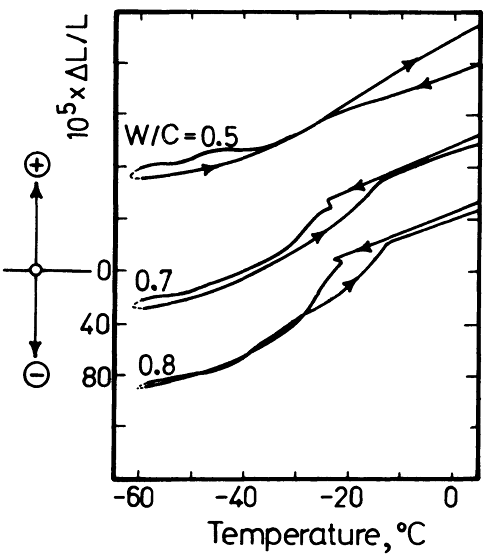

Figure 6.9 *Length changes in cement pastes subjected to a freezing cycle after reaching hygral equilibrium at* 84 *per cent relative humidity (after Litvan*[35]*). (For the sake of clarity the curves have been shifted along the length changes axis)*

dilatation in the unsaturated pastes. On the other hand, similar saturated pastes exhibit irrecoverable dilatation when subjected to the same freezing cycle (Figure 6.10).

In discussing moisture content, reference is sometimes made to 'degree of saturation' which is the ratio between moisture content and the volume of the open pores in a porous solid. Theoretically for an increase in volume on freezing of 9%, no dilatation should occur in porous solids in which the degree of saturation is lower than 1/1.09 = 0.917. This conclusion, however, is limited to conditions in which the water is homogeneously distributed throughout the mass.

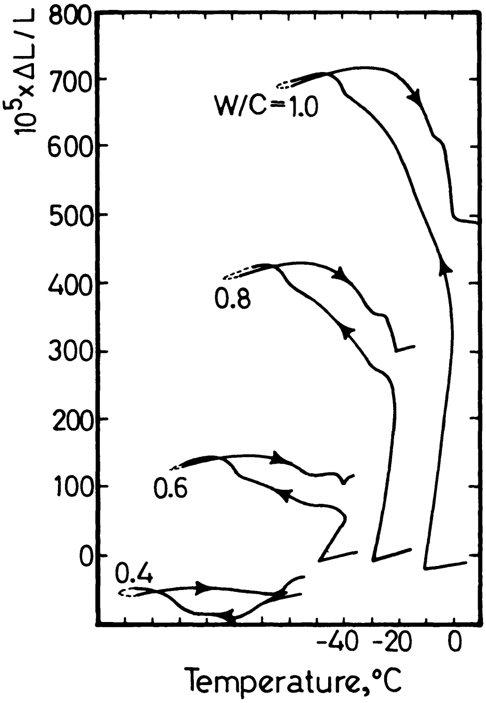

Figure 6.10 *Effect of W/C ratio on length changes of saturated cement pastes subjected to a freezing cycle (after Litvan*[35]*). For the sake of clarity the curves have been shifted along the temperature axis. In each case, however, starting temperature was* +5°C *as indicated for W/C* = 1.0

Moreover, in cement paste only water contained in the larger (capillary) pores can be frozen. Hence, for frost action in cement pastes, only this type of water must be considered.

Some degree of correlation has been found between frost resistance of concrete and its degree of saturation, S, when only the freezable water, V_f, was considered,[36] i.e. when the degree of saturation was defined as $V_f/(V_f + V_a)$ (V_a is the volume of air per unit volume of concrete). Rapid deterioration was found in concrete for which S exceeded 0.91, and high durability when S was lower than 0.88. In any case, without trying to establish a precise quantitative limit, we can say that the adverse effect of frost action disappears completely at some level of moisture content. It may be noted that such an effect is to be expected regardless of the mechanism adopted to explain frost action.

6.4.3.2 Water/cement ratio

Generally, frost resistance of cement pastes increases with the decrease in the *W/C* ratio. It can be seen from Figure 6.10 that total expansion, as well as its irrecoverable part, is greater the higher the *W*/*C* ratio. This effect is not necessarily self-evident. A lower *W*/*C* ratio implies a denser paste, i.e. a paste with increased resistance to flow of water. Hence, assuming the hydraulic pressure mechanism is applicable, the generated pressure, and the resulting potential dilatation will be greater in pastes of low *W*/*C* ratio than in those of high *W*/*C* ratio. On the other hand, the strength of the paste increases, and its capillary porosity (i.e. amount of freezable water) decreases with the decrease in the *W*/*C* ratio. Increased strength and lower amount of freezable water improve frost resistance, an apparently this effect is greater than the opposing effect of increased hydraulic pressure. Hence, the improvement in frost resistance for cement pastes with lower *W*/*C* ratio.

6.4.3.3 Air content

The presence of air voids reduces the dilatation of cement pastes. Dilatation may be eliminated altogether if the spacing of the voids is sufficiently close. This effect is to be expected whether frost damage is attributed to hydraulic pressure or to the growth of ice crystals in the capillaries. Hydraulic pressure is relieved due to the flow of the expelled water into the voids and ice growth can take place in such pores without causing overall expansion. This conclusion is reflected in Figure 6.11 which presents length changes in a cement paste containing 16% air which was subjected to a single freezing cycle.[25] It can be seen that the length changes were completely reversible, in contrast to the permanent dilatation which was observed when the paste contained no air (Figure 6.4). The same features are evident from Figure 6.7 in which dilatation is related to the spacing

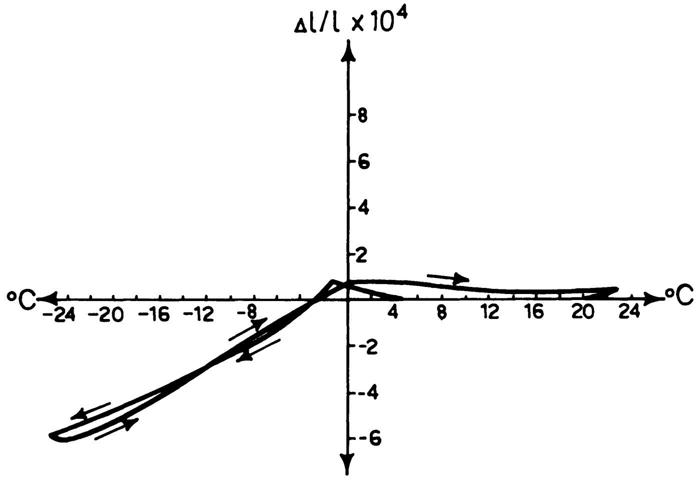

Figure 6.11 *Length changes in cement paste containing* 16 *per cent air due to a single freezing-thawing cycle* (*after Powers*[25]) of the air voids.* Note that dilatation decreases with decrease in spacing factor, and that, at some stage, it completely disappears and the paste begins to contract on freezing. This implies that a certain air content will result in a frost resistant paste. According to Powers,[38] such resistance is reached when the spacing factor is smaller than 0.25 mm.

This beneficial effect of air voids is widely made use of in concrete which is to be used in conditions where it is likely to be exposed to freezing temperatures. This is further discussed in Chapter 10.

6.4.4 Summary and concluding remarks about frost resistance

The formation of ice involves a volume increase of about 9%. In saturated, or nearly saturated pastes, such volume increase will produce internal pressure which, in turn, will cause dilatation and cracking of the paste. A few mechanisms have been suggested to explain frost action. The action may result from the generation of hydraulic pressure due to flow of water expelled from the capillaries,[26,27] or from growth of already existing ice bodies due to migration of water from the smaller to the larger pores (i.e. from gel to capillary pores). The water migration can be attributed either to the difference in free energy of the gel water and that of the ice in the capillaries,[27] to the difference in the alkali concentrations in the gel and the remaining capillary water,[29] or to the decrease in relative humidity over the supercooled water in the small pores.[35]

The adverse effect of frost requires the presence of moisture, and no such effect is to be expected in pastes in which the degree of saturation is less than about 85%. The susceptibility of the cement paste to frost damage decreases with decrease in the *W/C* ratio and with increase in its air content. A sufficient amount of air entrainment results in frost resistant pastes. A ‘spacing factor’ is used to measure air void concentration. Pastes with a spacing factor smaller than 0.25 mm are frost resistant.

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*Spacing factor, $\bar{L}$, is a convenient and practical index for measuring the concentration of air voids in the cement paste. It is related to the maximum distance of any point in the paste from the boundary of a void. The calculation of the factor is based on the assumption that all air voids in the paste are spheres of equal diameter arranged in a simple cubic system throughout the mass. Methods for determining the spacing factor are given in ASTM C457. According to this standard, the parameters of the air void system should be determined by optical microscopy (i.e. linear transverse or point-count methods). The obtained data are then used to calculate the spacing factor with the aid of the expressions given in the standard. The expressions are based on the previously mentioned assumptions, and were mostly developed by Powers.[37,38]

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7 Effect of cement composition and fineness on its properties

7.1 Introduction

As explained in Chapter 1, Portland cement is a heterogeneous material comprising mainly alite, belite, tricalcium aluminate, and celite, which make up about 90% of the whole. It is to be expected, therefore, that the properties of the cement will be determined by the properties of the individual constituents and their relative content in the cement. The properties of the individual constituents were summarised earlier in Table 1.4. In this chapter, the effect of these properties on the properties of the cement is considered, and the use of this effect to produce different types of Portland cement is discussed. The effects of minor constituents and of the cement fineness, are also included in the discussion.

7.2 The major constituents

7.2.1 Effect on heat of hydration

Hydration of the individual constituents of the cement is exothermic and liberates a considerable amount of heat (i.e. heat of hydration). The heats of hydration of the pure constituents of the cement are given in Table 7.1.

The data of Table 7.1 imply that cements rich in tricalcium silicate and tricalcium aluminate will be characterised by a high heat of hydration and vice versa. This expected effect is confirmed by the data in Figures 7.1 and 7.2, and is made use of in the production of low heat Portland cements, i.e. cements which are characterised by a low heats of hydration.

Experience has shown that, to a first approximation, the heat of hydration of a cement equals the weighted average of the heats of hydration of the individual components, and can be calculated from the equation

$$Q_H = a(C_3S) + b(C_2S) + c(C_3A) + d(C_4AF)$$

Table 7.1 Heats of hydration of the pure constituents of Portland cement (after Lerch and Bogue[1])

Constituent	*Heat of hydration* J/g
C_3S	503
C_2S	260
C_3A	867
C_4AF	419

where Q_H is the heat of hydration of the cement, a, b, etc., the heats of hydration of the individual constituents, and (C_3S), (C_2S), etc., their fractional contents in the cement. It should be noted that the data of Table 7.1 were determined for pure compounds whereas the compounds in cement contain some impurities in solid solution (Table 1.8). The presence of impurities affects the properties of the compounds, including their heats of hydration.

The heat evolution of the constituents, when they are hydrated as part of the cement, is presented in Tables 7.2 and 7.3. It can be seen that there is some agreement among the data concerning the heat evolved during hydration of the calcium silicates but that considerable differences exist concerning the heat evolved in the hydration of tricalcium aluminate and the ferrite phase, i.e. the evolution of heat from hydration of the calcium silicates in the cement approximates that of the pure compounds (Table 7.1) whereas similar data for tricalcium aluminate and the ferrite phase are contradictory and differ considerably from those of the pure compounds.

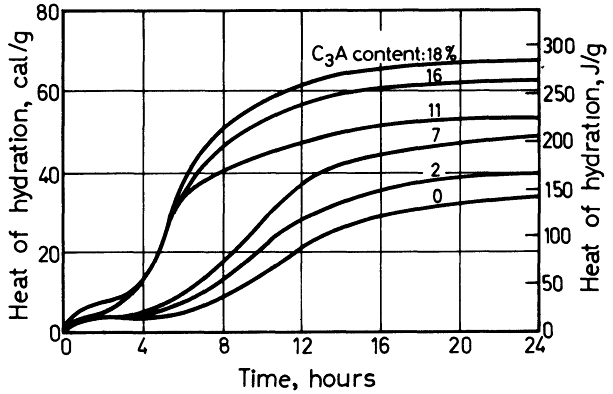

Figure 7.1 Effect of C_3A content on heat of hydration of Portland cements of approximately equal C_3S content (after Lerch and Bogue[1])

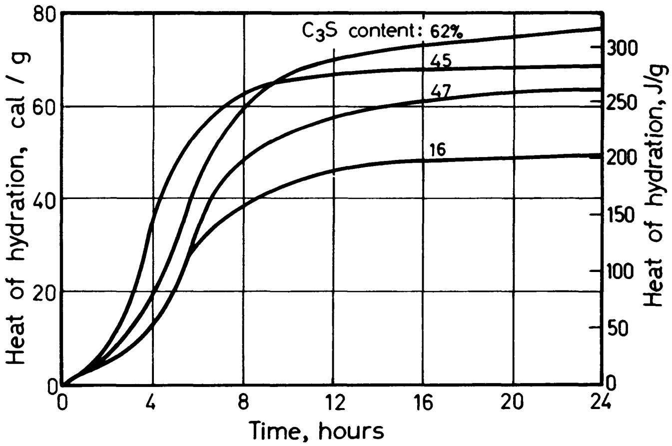

Figure 7.2 Effect of C_3S *content on heat of hydration of Portland cements of approximately equal* C_3A *content (after Lerch and Bogue*[1]*)*

Table 7.2 Heat evolution from the constituent compounds of Portland cement (after Verbeck and Foster[2]*)*

	Heat evolution, J/g *at the age of:*					
Constituent	3 days	7 days	28 days	90 days	1 year	$6\frac{1}{2}$ years
C_3S	243	222	377	436	490	490
C_2S	50	42	105-	17.6	226	222
C_3A	888	1559	1378	1303	1169	1374
C_4AF	289	494	494	410	377	465

Table 7.3 Heat evolution from the constituent compounds of Portland cement at an age of one year (after Woods et al.[3]*)*

Constituent	*Heat evolution,* J/g
C_3S	570
C_2S	260
C_3A	838
C_4AF	126

According to Table 7.3 the heat evolved in the hydration of tricalcium aluminate in the cement roughly equals that of the pure form, while the heat evolution of the ferrite phase is considerably lower than that of its pure counterpart. According to Table 7.2, on the other hand, the heat evolution from tricalcium aluminate in the cement is much higher than that of the pure form, whereas the heat evolution from the ferrite phase is roughly equal in both cases. The contradictory nature of the data is attributable, in part at least, to the difficulties involved in determining the true tricalcium aluminate and the ferrite phase contents in the cement.

To demonstrate the practical implications of the differences among the data of Tables 7.1, 7.2, and 7.3, the heat of hydration at an age of one year, Q, is calculated for ordinary Portland cement assuming the following composition: C_3S 45%, C_2S 25%, C_3A 10%, and C_4AF 10%. From the data of Table 7.1 we get:

$$\begin{aligned} Q_1 &= 0.45 \times 503 + 0.25 \times 260 + 0.10 \times 867 + 0.10 \times 419 \\ &= 420 \text{ J/g} \end{aligned}$$

from the data of Table 7.2:

$$\begin{aligned} Q_2 &= 0.45 \times 490 + 0.25 \times 226 + 0.10 \times 1169 + 0.10 \times 377 \\ &= 431 \text{ J/g} \end{aligned}$$

and from the data of Table 7.3:

$$\begin{aligned} Q_3 &= 0.45 \times 570 + 0.25 \times 260 + 0.10 \times 838 + 0.10 \times 126 \\ &= 418 \text{ J/g} \end{aligned}$$

i.e. the difference in the results is not significant.

The heat of hydration of ordinary Portland cement varies from 420 to 500 J/g. The calculated heat may differ by up to 40 J/g or more from the heat determined by direct measurement. Such a difference may be significant and the calculated value, as mentioned earlier, should be considered as an approximate rather than a true value.

7.2.2 *Effect on strength*

Bearing in mind the strengths of the individual constituents (Figure 1.5), it may be expected that the strength of the cement will be determined mainly by its calcium silicates content. Also, assuming that strength development is not affected by the presence of the other constituents, the strength of the cement at an age of 28 days will be determined mainly by its C_3S content. Here, it should be noted that the presence of C_3A and gypsum, as well as the fineness of the cement, will also affect the development of strength (Figure 7.10). Nevertheless, the foregoing conclusion is generally true and has been confirmed by many tests. For example, Figure 7.3 describes strength development in mortars made from cements which differed in their C_3S/C_2S ratios.[4] Curve 1 represents mortars

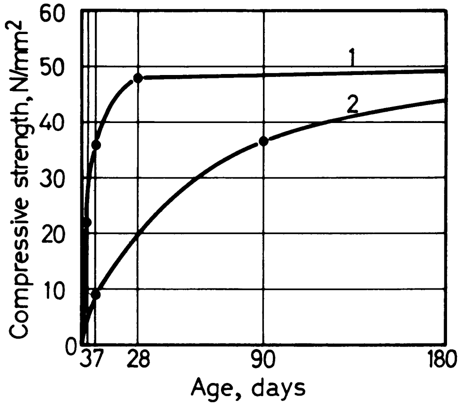

Figure 7.3 *Effect of* C_3S/C_2S *ratio on strength of Portland cement mortars (after Woods et al.*[4]*).* (1) *cements of high* C_3S *content*; (2) *cements of low* C_3S *content*

made from cements rich in C_3S (65.7-71.3%) and poor in C_2S (6.2-11.8%), and curve 2 mortars made from cements low in C_3S (26.0-31.0%) and rich in C_2S (47.1-59.7%). It is evident that the cements rich in C_3S attain most of their strength up to an age of 28 days while strength development in the others continues up to 180 days. In other words, strength development of the mortars was essentially what would have been expected from strength development of the individual constituents (Figures 1.5 and 1.6).

The effect of tricalcium silicate on the strength of cement is also demonstrated in Figure 7.4. It can be seen from the slopes of the regression lines that the effect is most significant up to an age of 28 days becoming less pronounced, but not disappearing completely, at later ages of 90 and 180 days.

Figure 7.5 illustrates the effect of dicalcium silicate on the strength of cement mortars between the ages of 28 and 180 days. It is evident that the increase in later-age strength depends on the C_2S content. These effects of the calcium silicates were observed by Gonnerman[5] who concluded that

> the principal strength-giving constituents of Portland cement are the tricalcium and dicalcium silicates. Tricalcium silicate not only contributed much of the strength at early ages but continued to be effective in increasing strength at the later ages also. Dicalcium silicate contributed little to strength up to about 28 days, but was largely responsible for the increase in strength beyond this period.

As already mentioned, this conclusion is generally accepted and is made use of in the production of rapid-hardening cement. However, in a more recent work[6] it was concluded that the foregoing conclusion is valid only for cements having

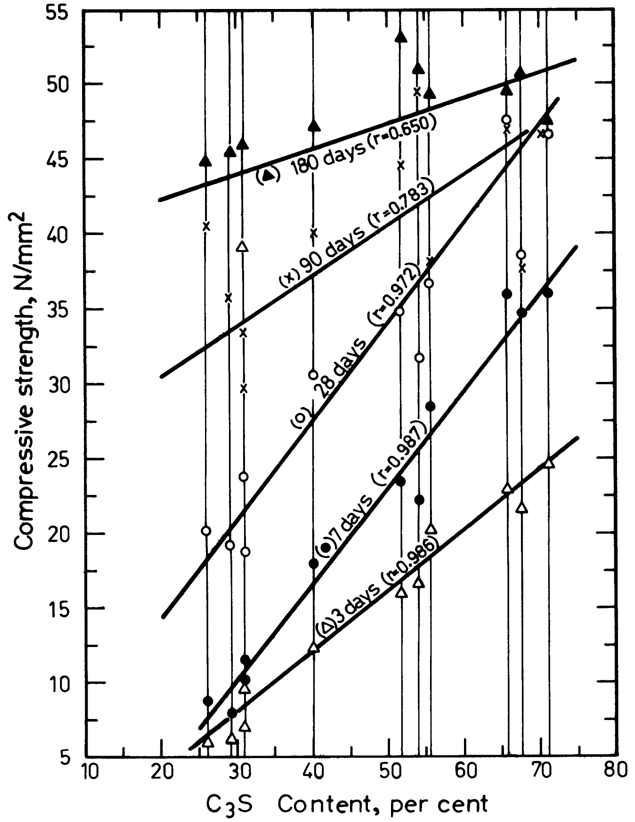

Figure 7.4 Effect of tricalcium silicate content on strength of cement mortars (after Woods et al.[4]*) (r is the coefficient of correlation)*

more or less the same C_3A content. If this is not the case, strength differences between cements may be attributed mainly to differences in C_3A content rather than in C_3S content.

The effect of tricalcium aluminate on the strength of the cement is less clear. Considering the strength development in the individual compounds (Figure 1.5), and the dominant effect of the calcium silicates, it may be expected that tricalcium aluminate will affect, at most strength at very early ages when its strength is relatively high compared to that of the other constituents. This conclusion is not, however, supported by experimental data. Gonnerman[5] concluded that tricalcium aluminate contributes to strength to an important degree up to 28 days. This effect, however, diminishes at later ages becoming zero or negative after one or two years. Moreover, as mentioned earlier, Alexander *et al.*[6] concluded that strength differences between cements were largely attributable to differences in their C_3A content. This effect of C_3A on strength was

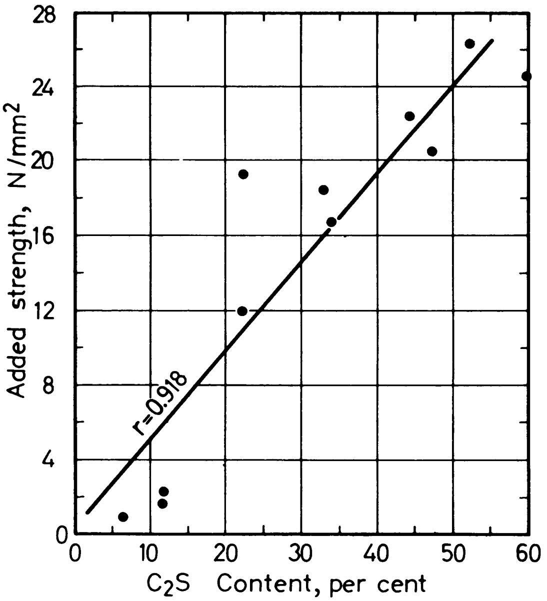

Figure 7.5 *Effect of dicalcium silicate content on the increase in strength of cement mortars between* 28 *and* 180 *days (after Woods et al.*[4]*)*
(r is the coefficient of correlation)

considered to result mainly from its accelerating effect on the hydration of the cement. This is further demonstrated in Figure 7.6 in which the strength of ISO standard cement mortars is plotted against the C_3A content of the cements.[7,*] Four cements are included having essentially the same C_3S and C_2S contents (48-50% and 20-28% respectively) and $C_3A/CaSO_4$ ratio (1.70-1.82). It can be seen that strength, and particularly early-age strength, increases with increase in the C_3A content passing through a maximum at an optimum C_3A content which decreases with age. It may also be noted that the increase in strength with the increase in C_3A content is much more evident at the early ages of one or three days than at the later age of 28 days; the adverse effect of increased C_3A content on strength is particularly evident at the later ages.

Unlike the heat of hydration, the strength of the cement and its other properties, such as shrinkage and creep, are not weighted averages of the corresponding properties of the individual components. Nevertheless, some attempts have been made[5-10] to establish the relationship between cement strength (or other property) and composition. Generally, the strengths of cements of different compositions have been determined experimentally and statistical means (i.e.

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*ISO (International Standards Organisation) specifies 1:3 mortars and 4 cm cubes.

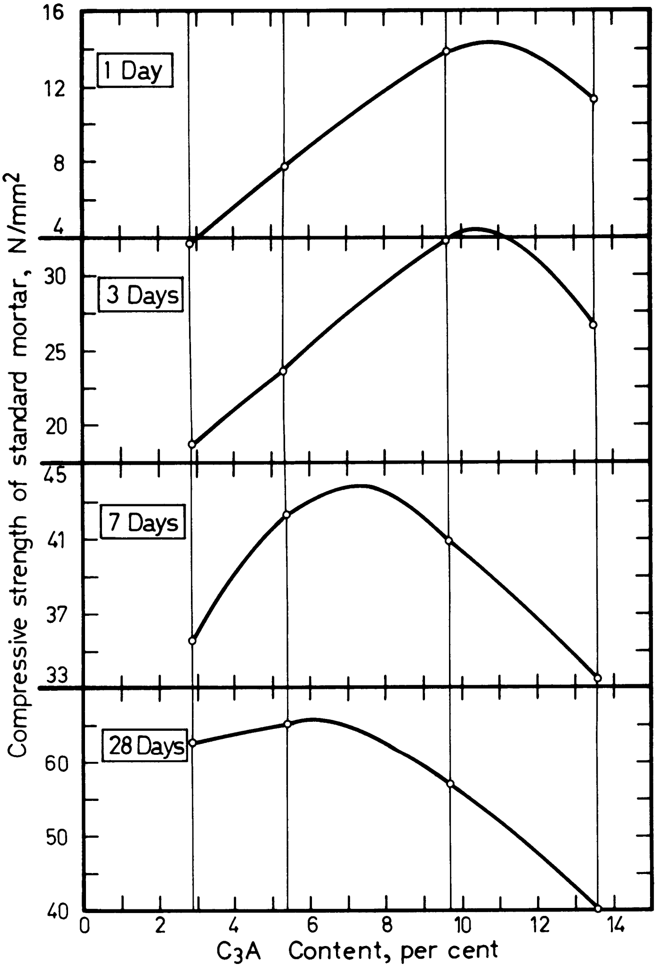

Figure 7.6 Effect of C_3A *content of Portland cement on compressive strength of standard ISO mortars (after Celani et al.*[7]*)*

multi-dimensional linear regression analysis) employed to establish the coefficients *a, b, c,* etc., in the following equation:

$$P = a(C_3S) + b(C_2S) + c(C_3A) + d(C_4AF) + \ldots$$

where P is the strength, or some other property of the cement and (C_3S), (C_2S), etc., are the fractional contents of these compounds in the cement. At first[5] only the major constituents were considered but in later work some additional factors, such as presence of minor constituents and fineness of the cement, have been included in the analysis.

Note that the coefficients *a, b, c,* etc., represent the contributions per unit weight of each constituent to the particular property in question under the specific test conditions. It is assumed that these contributions are additive and remain constant. These assumptions were question by Lea[11] because strength and related properties depend, not only on the specific properties of the individual constituents and their concentration in the cement, but also on the structure of the hardened paste and the way in which it was formed. On the other hand, a linear relationship was established between strength-affecting factors, such as the specific surface area of the gel[12] and the amount of chemically combined water,[13] and the composition of the cement. However, the results of the tests varied considerably and could not, therefore, be generally applied in any estimation of the strength of a cement from its composition.

7.2.3 Effect on shrinkage

The effect of the composition of the cement on shrinkage is uncertain. Gonnerman[5] found that tri- and di-calcium silicates contributed to the shrinkage of the cement approximately to the same degree. This contribution was somewhat greater than that of the ferrite phase but much smaller than that of the tricalcium aluminate. The dominant effect of C_3A content on shrinkage of the cement was also observed by Roper.[14] He found that shrinkage increased with increasing C_3A content, and that up to 80% of the difference between the amounts of shrinkage of different cements was attributable to variations in their C_3A contents. The effect of other constituents of the cement, as well as of fineness, proved to be insignificant. It should be noted that the effect of C_3A content on shrinkage is influenced by the gypsum content of the cement, i.e. shrinkage of cements of the same C_3A content differs for different gypsum contents. It will be seen later that, in this context, reference is often made to 'optimum' gypsum content which is that content which produces, in a given cement, the highest strength and lowest drying shrinkage.

7.2.4 Effect on sulphate resistance

In Chapter 6 it was shown that the susceptibility of Portland cement to sulphate attack is due mainly to the presence of hydrated calcium aluminate which reacts with sulphates to form ettringite. It is implied, therefore, that sulphate resistance of the cement will increase with the decrease in C_3A content. This conclusion has been confirmed both by tests and by experience, and this property forms the basis for the production of sulphate resisting cements. It is demonstrated, for example, in Figure 7.7,[15] in which the potential expansion of Portland cement mortars due to sulphate attack (ASTM C452) is plotted against the C_3A content of the cement.* There is some scatter in the results which, in part at least, is

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*According to ASTM C452, the expansion is determined on 1 × 1 × $11\frac{1}{4}$ inch mortar bars made from a mixture of Portland cement and gypsum in such proportions that the mixture has a SO_3 content of 7% by weight (see Chapter 10).

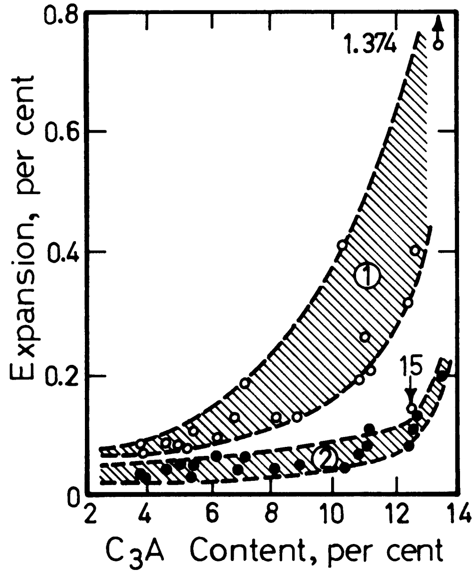

Figure 7.7 *Effect of* C_3A *content on potential sulphate expansion of Portland cement mortars* (ASTM C452) (*after Mather*[15]): (1) *after one year,* (2) *after one month*

attributable to the uncertainty in determining the C_3A content.[18] Nevertheless, with the exception of cement 15, it is evident that sulphate expansion of the cements decreases with decrease in their C_3A content. As mentioned earlier, this conclusion is widely supported by other data. In fact, it is generally accepted that the C_3A content is the greatest single factor affecting the resistance of Portland cements to sulphate attack.[16]

As ettringite is also formed as a result of the reaction between gypsum and the ferrite phase, the latter may also affect sulphate resistance of the cement. As explained earlier (Chapter 6), the susceptibility of the ferrite phase to sulphate attack is much lower than that of the tricalcium aluminate. Consequently, whereas in sulphate resisting cements the C_3A content must generally be limited to a maximum of 5% (Tables 7.6 and 7.7), the C_4AF content is limited, if at all, to a much higher value, which is related to the C_3A content of the cement (Table 7.7).

The effect of the calcium silicates on sulphate resistance of the cement is less clear. Sulphates, with the exception of gypsum, react with calcium hydroxide. The $Ca(OH)_2$ content in the hardened paste is higher for cements richer in C_3S. Hence, C_3S rich cements may be more susceptible to sulphate attack than their C_2S rich counterparts. On the other hand, the calcium silicates may affect sulphate resistance through their effect on the density and strength of the cement paste. As the rate of hydration is greater in cements rich in C_3S, both density and strength will be higher in pastes made of such cements than in those made of cements rich in C_2S. Hence, at early ages, when the foregoing effects are mostly apparent, the sulphate resistance of the high C_3S pastes will be greater. At later ages, however, as more and more C_2S is hydrated, a reverse trend will appear because, for the same *W/C* ratio, the density of a C_2S paste is greater than the density of a C_3S paste.[17] In other words, as far as sulphate resistance is concerned, a low C_3S content is preferable. Indeed, at one time C_3S content in sulphate resisting cements was limited to a maximum of 50%. At present, however, the calcium silicates content is not considered to affect sulphate resistance significantly, and the relevant standards (Tables 7.6 and 7.7) include no limitation on C_3S content.

7.3 The minor constituents

7.3.1 Effect of gypsum

Gypsum is added to cement to regulate its setting time. However, it also affects some other properties of the cement. It was established by Lerch,[20] Meissner *et al.*,[21] and others that, depending on C_3A and alkali contents and the fineness of the cement, there is an optimum gypsum content which produces in a particular cement the highest strength and the lowest drying shrinkage. In cements low in C_3A (i.e. below 6%) the optimum SO_3 content may be as low as 2% for low alkali contents (i.e. below 0.5%), increasing to 3-4% as the alkali content rises to 1%. For cements high in C_3A (i.e. 10% or more) the optimum SO_3 content is about 2.5-3% and 3.5-4% for cements of low and high alkali contents, respectively.[22] These optimum contents are for conditions where hydration takes place at normal temperatures. At higher temperatures, such as when steam curing is employed, the optimum SO_3 content is greater and, depending on the composition of the cement, may reach 7% or more.[23,24]

7.3.2 Effect of alkalis and trace elements

The effect of alkalis and trace elements on the properties of cement, such as heat of hydration, sulphate expansion, strength, drying shrinkage and frost resistance, has been studied under various curing conditions for 200 different cements.[25] It was found that the alkalis and some trace elements (i.e. Ba, Cu, Rb, and Zr) affect many properties but that their effects are rather small as compared to the effects of the major constituents. Nevertheless, differences in the properties of cements of apparently the same composition may be attributed to the presence of trace elements, and to differences in their alkali contents.

7.4 Specific surface area

7.4.1 Fineness

It was shown earlier that fineness affects the rate of hydration, and it will be shown later that it also affects other properties of the cement, such as strength development. Consequently, this property must be considered in the relevant cement standards. At one time, fineness was specified by the amount retained on British Standard sieve No. 170. The size of this sieve opening (aperture) is 90 μm. However, nowadays, most cement grains are smaller, having an average diameter of about 10 μm. Hence, the use of a No. 170 sieve provides very little information. The use of finer sieves is impractical because the meshes tend to become clogged with the cement. At present, therefore, fineness is generally defined by the specific surface area, i.e. the total surface area of all grains contained in a unit weight of cement.

7.4.2 Determination of specific surface area

7.4.2.1 Air-permeability method

This method is based on the fact that the resistance offered to gas flow by a bed of powder of a given volume and porosity depends on the specific surface area of the powder. The method was first developed by Lea and Nurse,[27] and later adopted in British Standards for cements. The permeability apparatus in BS 12 is illustrated schematically in Figure 7.8. A steady stream of air is passed for five

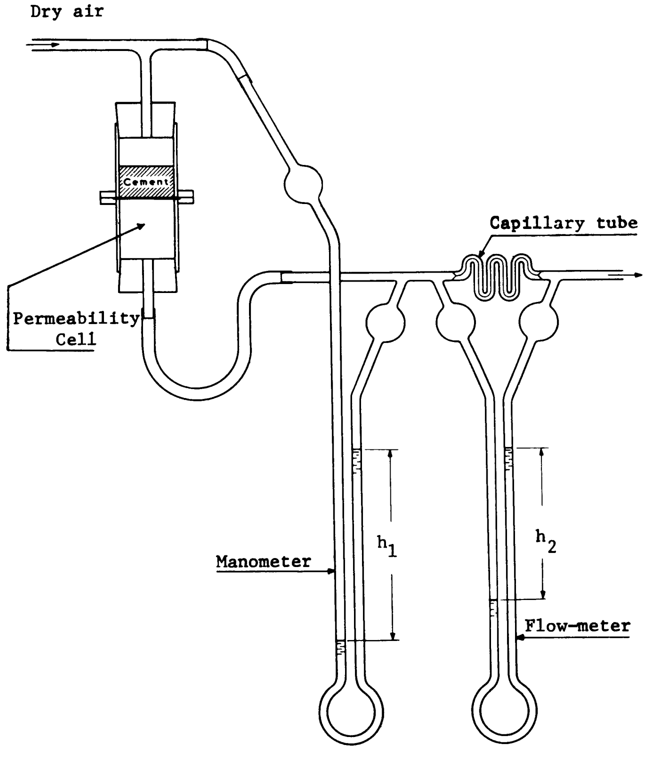

Figure 7.8 ***Air-permeability apparatus for determining specific surface area of cement*** (from BS 12)

minutes through a bed of cement, 1 cm thick with a porosity of 0.475. The rate of air flow is given by the difference h_2 between the levels of the two columns of the flowmeter, which consists of a capillary placed in the circuit with a manometer connected across its ends. The fall in pressure across the bed is given by the difference h_1 between the two columns of the manometer connected to top and bottom sides of the bed. It can be shown that for a given apparatus the specific surface area, S, is given by

$$S = \frac{K_1}{\rho} \sqrt{h_1/h_2}$$

where ρ is the density of the cement and K_1 is a constant. Further details of the method can be found in BS 12.

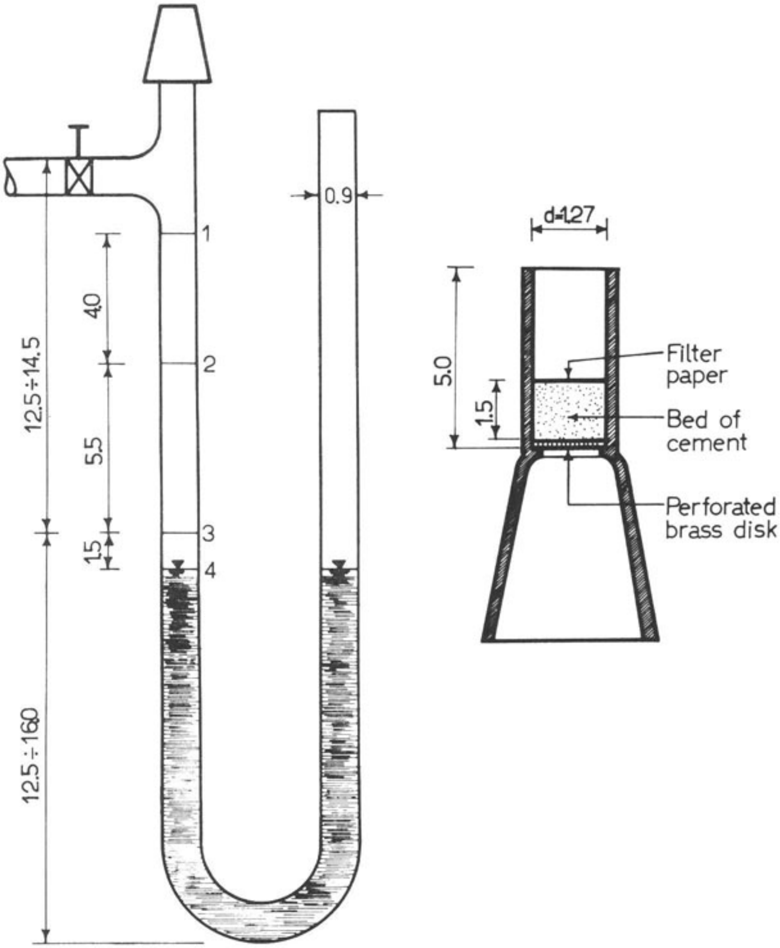

Figure 7.9 Blaine air permeability apparatus for determining the specific surface area of cements (from ASTM C204)

A similar method was developed independently in the USA by Blaine[28] and is described in ASTM Standard C204. In this method a definite quantity of air passes through a bed of cement at a steadily diminishing rate, and not at constant rate as in the BS method. The air-permeability apparatus of ASTM C204 is illustrated schematically in Figure 7.9. A cement bed, 1.5 cm thick and with porosity of 0.5, is prepared in a cell which is later attached to the top of a manometer tube. The manometer is filled with a non-hygroscopic liquid of low viscosity and density (e.g. a light grade of mineral oil) to the level marked 4 in Figure 7.9. Air is then evacuated from the manometer through the side tube until the oil reaches the top mark, i.e. level 1 in Figure 7.9. The air valve is closed and the oil level in the manometer begins to fall as air flows through the bed. The time, T, taken for the oil to fall from level 2 to 3 is measured by means of a stopwatch. The specific surface area of the cement is given by

$$S = k\sqrt{T}$$

where k is the apparatus constant. k is determined by calibration using a standard sample of cement obtainable from the US National Bureau of Standards.

7.4.2.2 Turbidimetric method

The intensity of light transmitted through a suspension depends, under otherwise similar conditions, on the concentration of the solid in the suspension, and on the diameter of its particles. The rate of fall under gravity of fine solid particles in a liquid medium depends on their diameter, and the terminal velocity of the particles is given by Stokes' law. The foregoing principles were used by Wagner[26] in the development of a turbidimeter for determining the specific surface area of cements. In this method the turbidity of a suspension of cement in kerosine, which is chemically inert with respect to cement, is measured. A parallel beam of light of constant intensity passes through the cell containing the suspension, and the intensity of the emergent beam is measured by use of a photocell. From the difference in the intensities of the light transmitted through the clear kerosine and through the suspension (i.e. turbidity) the surface area of all particles of diameter smaller than d in the sample can be calculated, where d is the diameter of the particles which have settled from the surface of the suspension to the centre of the light beam by the time the reading is taken. Readings are taken at known times and at known depths below the surface of the suspension. The results can be used to determine the specific surface area of the cement and its particle size distribution. Further details of this method can be found in ASTM Standard C115.

Generally, Lea and Nurse's method gives similar results to those of Blaine's method. These results, however, are much higher than those obtained by use of Wagner's turbidimeter. The difference is attributed mainly to the assumption made in the latter method that particle-size distribution below 7.5 μm is uniform, and that the mean diameter of these particles equals 3.75 μm. In fact, this value

Table 7.4 Effect of testing method on the value of specific surface area of cements (after Lea[29])

Cement	*Specific surface area*, m^2/kg Wagner's method	Lea and Nurse's method	Nitrogen adsorption
A	179	260	790
B	227	415	1000

is too high, explaining the lower results of this method. The ratio of the results obtained by air permeability methods to those obtained by Wagner's method depends on the fineness of the cement and on its gypsum content, and generally varies from 1.6 to 2.2. In most cases, a value of 1.8 may be adopted (Table 7.4). It should be noted, however, that neither method gives the 'true' specific surface area of the cement. On the other hand, both are reliable enough to indicate variations in the fineness of cements and, as such, provide useful and practical means of specifying and controlling this property.

7.4.2.3 Gas adsorption

In discussing the structure of the hardened paste (Chapter 3) it was shown that specific surface area can be determined from adsorption isotherms by use of the BET method. In measurements on cements the adsorbate is usually nitrogen, and the test is conducted at the temperature of liquid oxygen, i.e. at about −190°C. The specific surface area determined from gas adsorption is two to three times greater than that determined by air permeability methods (Table 7.4). The latter methods measure the external surface of the cement grains while in gas adsorption methods some internal surface is included, i.e. the surface of the walls of cavities and voids which are accessible to the gas molecules. Hence, the greater surface area of gas adsorption methods.

7.4.3 Effect on strength

The rate of strength development increases with the fineness of the cement (Figure 7.10). The increased fineness is associated with a greater surface area which comes in direct contact with the water. Hence, the rate of hydration, and the associated strength development, are increased. The effect of fineness on strength is greatest at early ages, decreasing with time as the hydration proceeds. At later ages, as earlier explained, the cement grains are surrounded by dense CSH gel which retards diffusion of water and thereby slows down the hydration process. The rate of hydration is then mainly determined by the rate of water diffusion; the size of the cement particles becomes of secondary importance.

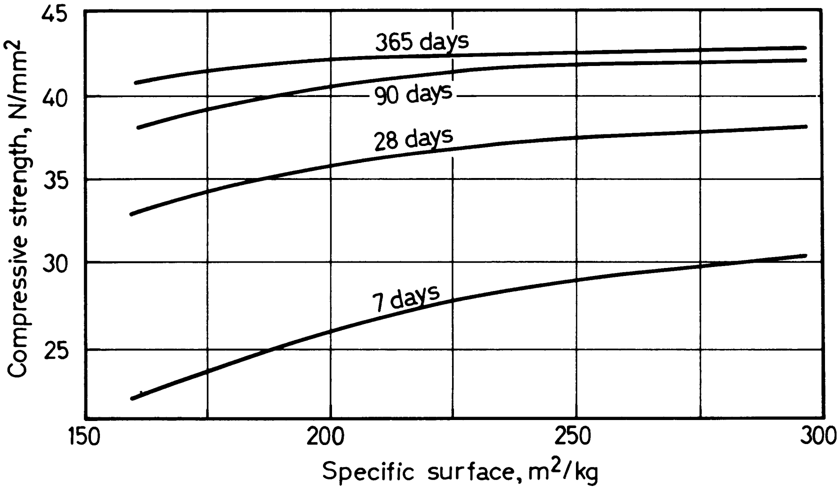

Figure 7.10 *Effect of specific surface area of Portland cement on strength development in concrete (after Price*[30]*)*

7.4.4 *Effect on drying shrinkage*

The effect of fineness on drying shrinkage probably results from its effect on the rate of hydration. Figure 7.11 seems to indicate that shrinkage increases with fineness. The difference between the shrinkage of the cements is, however, small, and in part at least may be attributed to differences in the *W/C* ratios of the pastes. The paste made of the coarsest cement also had the lowest *W/C* ratio and, as explained earlier (Figure 5.9), a lower ratio involves lower shrinkage. Hence, in this particular case, the effect of fineness is uncertain. In other work, however, it has been concluded that shrinkage is solely determined by the degree of hydration and the modulus of elasticity of the cement paste.[14] Accordingly,

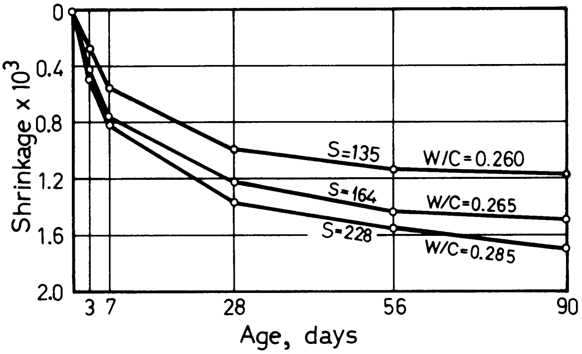

Figure 7.11 *Effect of fineness on shrinkage of cement pastes (after Haller*[31]*) (S is the specific surface area in* m²/kg *by Wagner's method)* it may be further concluded that fineness can affect shrinkage only indirectly through its accelerating effect on hydration. The increased rate results in a higher degree of hydration which, in turn, involves greater shrinkage. Hence, the shrinkage of the paste will increase with the increase in the fineness of the cement.

7.4.5 Other effects

Adsorption of water from the atmosphere will be greater in finer cements. Hence, such cements will deteriorate more rapidly in storage and on exposure to the atmosphere. Finer cements will also react more strongly with alkali-reactive aggregates.[32]

The amount of water required to produce a given consistence is greater the higher the fineness of the cement. On the other hand, the workability of the paste improves with fineness because of increased cohesion and reduced bleeding. These effects are attributable to the greater specific surface area of the finer cements. The finer the cement, the greater is the amount of water which is required to cover the surfaces of its particles. Hence, the greater water requirement for a given consistence. On the other hand, the greater the specific surface area the greater the amount of water which can be held by surface forces. Hence, the reduced bleeding. Also, the cohesiveness of the paste is improved because cohesion forces increase with decrease in the size of the solid particles.

The finer the cement, the greater the amount of gypsum which must be added to the clinker. The increase in gypsum requirement can be explained by the increased availability of C_3A at early stages of hydration. The C_3A availability increases with the specific surface area of the cement. As already explained, an increased C_3A content requires a corresponding increase in the amount of the added gypsum.

7.5 Summary–different types of Portland cement

It was explained earlier that C_3A and C_4AF contribute only slightly to the strength of the cement which is mainly determined by the calcium silicates. On the other hand, the presence of C_3A increases the susceptibility of the cement to sulphate attack, its heat of hydration, and probably its shrinkage as well. Accordingly, it may be concluded that an increase in calcium silicates content of the cement is desirable at the expense of the C_3A and the C_4AF contents–particularly the C_3A content. The application of this, however, is impracticable because the alumina and iron oxide act as a flux and lower the clinkering temperature of the cement. Hence, their presence is necessary for economic and technical reasons. Usually therefore the combined content of the calcium silicates is about 70 to 75% and that of the C_3A and the C_4AF about 15 to 20%. Variations in cement composition generally fall within the above ranges, i.e. a variation in the C_3S content involves a corresponding variation in the opposite direction in the

C_2S content and, similarly, a variation in the C_3A content involves an opposite variation in the C_4AF content.

As pointed out earlier, variations in the composition of the cement affect its properties, and this effect is made use of in the production of different types of cement. In addition to 'ordinary' (or sometimes 'normal') Portland cement, the following types are manufactured.

Table 7.5 Typical composition of different types of Portland Cement produced in the USA (after US Bureau of Reclamation[34])

Type of cement	*Designation* ASTM C150	*Potential composition*, wt %			
		C_3S	C_2S	C_3A	C_4AF
Ordinary	I	49	25	12	8
Moderate	II	46	29	6	12
Rapid hardening	III	56	15	12	8
Low-heat	IV	30	46	5	13
Sulphate resisting	V	43	36	4	12

Table 7.6 Properties of Portland cements (after British Standards)

	Type of cement (standard)			
Component/Property	*Ordinary*	*Rapid hardening*	*Low-heat*	*Sulphate resisting*
	BS 12, Part 2, 1971		BS 1370, Part 2, 1974	BS 4027, Part 2, 1972
Chemical composition				
1. Lime saturation factor (LSF)	0.66-1.02	0.66-1.02	*	0.66-1.02
2. Insoluble residue, % max.	1.5	1.5	1.5	1.5
3. Magnesia (MgO), % max.	4.0	4.0	4.0	4.0
4. Sulphuric anhydrite (SO_3), % max.				
C_3A content $\leqslant 7\%$	2.5	2.5	2.5	2.5
C_3A content $> 7\%$	3.0	3.0	3.0	–
5. Loss on ignition, % max.				
temperate climates	3.0	3.0	3.0	3.0
tropical climates	4.0	4.0	4.0	4.0

Table 7.6 cont.

	Type of cement (standard)			
Component/Property	*Ordinary*	*Rapid hardening*	*Low-heat*	*Sulphate resisting*
	BS 12, Part 2, 1971		BS 1370, Part 2, 1974	BS 4027, Part 2, 1972
Mineralogical composition				
C_3A content, % max.	–	–	–	3.5†
Physical properties				
1. Compressive strength, MN/m^2, minimum				
7 cm mortar cubes,				
at 3 days	15	21	8	15
at 7 days	23	28	14	23
at 28 days	–	–	28	–
10 cm concrete cubes,				
at 3 days	8	12	3	8
at 7 days	14	17	7	14
at 28 days	–	–	14	–
2. Fineness, m^2/kg, minimum	225	325	320	250
3. Setting time, Vicat apparatus				
initial, min, not less than	45	45	60	45
final, h, not more than	10	10	10	10
4. Soundness, mm, max.	10	10	10	10
5. Heat of hydration, J/g, max.				
7 days	–	–	250	–
28 days	–	–	290	–

*$2.4\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3 \geq CaO \geq 1.9\ SiO_2 + 1.2\ Al_2O_3 + 0.65\ Fe_2O_3$ after correction for the lime combined with SO_3.

†Calculated from the formula $2.65\ Al_2O_3 - 1.69\ Fe_2O_3$.

7.5.1 Rapid-hardening cement

In this cement the alite content is increased at the expense of that of the belite (Table 7.5) by clinkering a mixture of raw materials comparatively rich in lime. Also, rapid-hardening cement is ground to a greater fineness than other types of cement. This is reflected, for example, in BS 12 which prescribes a minimum specific surface area of 325 m^2/kg as compared with 225 m^2/kg for ordinary

Table 7.7 *Properties of Portland cements according to ASTM C150-74*

Property/Constituent	I *Ordinary*	II *Moderate*	III *Rapid hardening*	IV *Low-heat*	V *Sulphate resisting*
Chemical composition					
1. Magnesium oxide (MgO), % max.	5.0	5.0	5.0	5.0	5.0
2. Sulphur trioxide (SO_3), % max.					
C_3A content $\leqslant 8\%$	3.0	3.0	3.5	2.3	2.3
C_3A content $\geqslant 8\%$	3.5	–	4.5	–	–
3. Loss on ignition, % max.	3.0	3.0	3.0	2.5	3.0
4. Insoluble residue, % max.	0.75	0.75	0.75	0.75	0.75
Mineralogical composition					
1. Tricalcium silicate (C_3S), % max.	–	–	–	35	–
2. Dicalcium silicate (C_2S), % min.	–	–	–	40	–
3. Tricalcium aluminate (C_3A), % max.	–	8	15	7	5
4. $C_4AF + 2C_3A$, % max.	–	–	–	–	20
Physical properties					
1. Specific surface area (Blaine), minimum, m^2/kg	280	280	280	280	280
2. Autoclave expansion, % max.	0.80	0.80	0.80	0.80	0.80
3. Time of setting, Vicat appartus initial set, min, not less than	45	45	45	45	45
final set, h, not more than	8	8	8	8	8
4. Compressive strength, minimum, MN/m^2					
1 day	–	–	12.4	–	–
3 days	12.4	10.3	24.1	–	8.3
7 days	19.3	17.2	–	6.9	15.2
28 days	–	–	–	17.2	20.7
5. Heat of hydration, max., cal/g*					
7 days	–	70	–	60	–
28 days	–	80	–	70	–

*Multiply by 4.19 to convert to J/g.

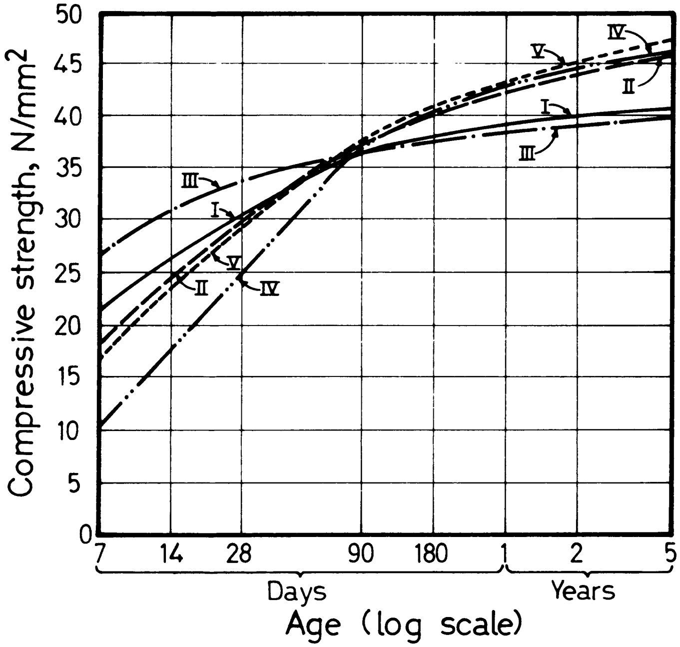

Figure 7.12 *Effect of type of cement on concrete strength development (after US Bureau of Reclamation*[33]*)*

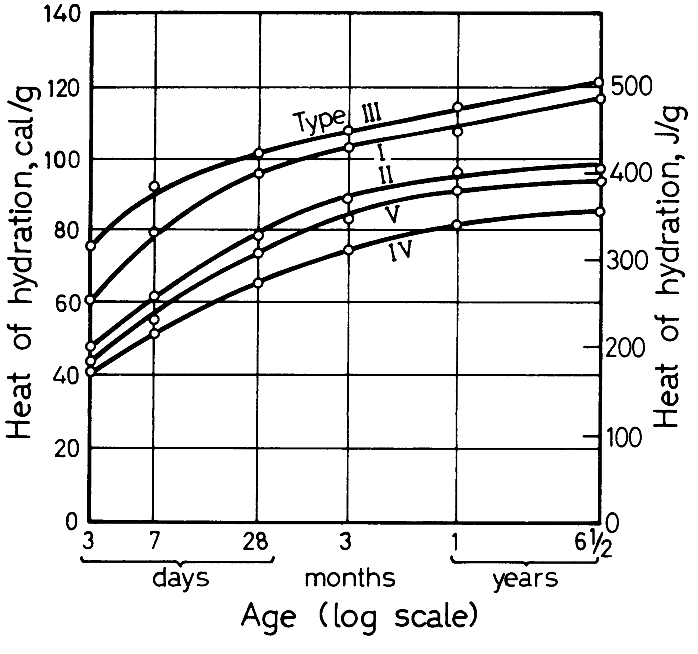

Figure 7.13 *Heat evolution in concrete made of different types of Portland cement (after Verbeck and Foster*[2]*)* cement (Table 7.6). In practice, however, the specific surface area of rapid-hardening cement may be much higher, 700 m^2/kg and more. The foregoing changes in composition and fineness of the cement increase the rate of its strength development, and consequently at early ages concrete made of rapid-hardening cement is stronger than that made of ordinary cement. Again, this is reflected in the relevant standards for cements (Tables 7.6 and 7.7) and also in Figure 7.12 in which (see ASTM Standard C150) I is ordinary Portland cement, II is moderate sulphate resisting or moderate low-heat Portland cement, III is rapid-hardening Portland cement, IV is low-heat Portland cement, and V is sulphate resisting Portland cement.

The heat of hydration of rapid-hardening cement is greater than that of ordinary cement because the former is richer in C_3S. Moreover, the greater fineness increases the rate of hydration causing a corresponding increase in the rate of heat evolution (Figure 7.13).

7.5.2 Low-heat cement

The heats of hydration of tricalcium aluminate and tricalcium silicate are higher than those of the other constituents of Portland cement (Table 7.3). Accordingly, the heat of hydration of the cement can be lowered by reducing the content of these two constituents (Table 7.5). This reduction is achieved by clinkering a mixture of raw materials low in lime and alumina. It can be seen from Figure 7.13 that, indeed, heat evolution in this type of cement (type IV) is lower than that in any of the others.

In view of the comparatively low C_3S and C_3A contents in low-heat cements, the rate of strength development in such cements will be slow. However, its ultimate strength may be higher than that of ordinary or rapid-hardening cements (Figure 7.12). In order to ensure a sufficient rate of strength development at early ages, low-heat cement is usually ground to a high fineness. Accordingly (see BS 1370), the minimum specific surface area of low-heat cement must be 320 m^2/kg as compared with the minimum of 225 m^2/kg which is specified in BS 12 for ordinary cement (Table 7.6). Finally, the reduced C_3A content improves the sulphate resistance of the cement. In fact, as will be seen in the next section, the properties of low-heat cement are similar to those of sulphate resisting cement.

7.5.3 Sulphate resisting cement

The susceptibility of Portland cements to sulphate attack is a result mainly of the presence of tricalcium aluminate. A cement low in C_3A can be produced by clinkering a mixture of raw materials with a low $A\ell_2O_3/Fe_2O_3$ ratio, i.e. a ratio of one or less. In most standards the C_3A content in sulphate resisting cement is limited to 5% or less (BS 4027). In some standards, such as ASTM Standard C150, a limitation is also placed on the C_4AF content (Table 7.7).

The reduction in C_3A content reduces the heat of hydration of the cement (Figure 7.13). As the presence of the C_3A accelerates the hydration of the calcium silicates, the reduction in its content also produces a cement having a slow rate of strength development. It can be seen (Figure 7.12) that the strength development of sulphate resisting cement is slower than that of ordinary cement. That is, sulphate resisting cement exhibits similar properties to those of low-heat cement. Hence, in certain applications, the two are interchangeable. This is reflected to some extent in ASTM C150 which recommends Type II cement both when moderate sulphate resistance is required and when moderate heat of hydration is desired.

7.5.4 White cement

The grey colour of Portland cements is due mainly to the ferrite phase. Hence, a white cement can be produced by using raw materials low in iron oxide. The iron oxide content is generally less than 0.5% and the resulting content of the ferrite phase in the cement is about 1%. Generally, the strength of white cement is lower than that of ordinary cement but, in many cases, it complies with strength requirements specified in the standards for ordinary cement.

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8 Strength of concrete

8.1 Failure mechanism[1-3]

The application of Griffith's theory to explain failure in hardened cement paste is discussed in Chapter 4. Failure due to external loading is brought about by the spontaneous growth of the critical crack when the strain energy release rate equals the maximum rate of energy requirement. At this point the rate of energy release is known as the 'critical strain energy release rate', G_c, and is, apparently, a characteristic property of the material.

The strength of a material depends on G_c, and a higher strength is to be expected with an increase in the value of this parameter. G_c, however, is not the only property which determines strength. In fracture mechanics strength is related to a parameter known as 'fracture toughness', K_c. K_c is given by $(G_c E/\pi)^{1/2}$ for plane stress or by $[G_c E/\pi(1 - \nu^2)]^{1/2}$ for plane strain (E is the modulus of elasticity and ν is Poisson's ratio). It can be seen that K_c depends on the elastic properties of the material, i.e. on the other properties which determine strength.

The presence of aggregate particles in the paste matrix affects its G_c value. In ordinary concrete (i.e. concrete made of aggregates stronger than the cement paste), the aggregate particles act as crack arresters and prevent crack propagation. The extension of the crack into the stronger aggregate particles demands an increase in the rate of energy requirement (Figure 4.5). However, before this takes place, other cracks, next in order of weakness, begin to grow until they too become stabilised. In other words, this mechanism delays fracture and thereby increases strength. This explains why the first crack that starts to grow may not be the critical crack. Delayed fracture is also brought about by the increase in the area of the microcracked zone at the crack tip with the increase in crack length. That is, the formation of a multitude of microcracks, rather than a single crack, and the stabilisation of crack growth due to the arresting effect of the aggregate increase concrete strength because both effects increase G_c and consequently also K_c.

The preceding mechanism is valid for ordinary concrete in which the strength of the aggregate is greater than that of the paste. It assumes that in such concrete cracking takes place in the paste, and only to a limited extent, if at all, in the aggregate.[4] Accordingly, in this type of concrete the strength of the aggregate would hardly affect concrete strength. On the other hand, concrete modulus of elasticity depends on that of the aggregate (see Chapter 9) and the modulus affects the value of K_C. It is to be expected, therefore, that the rigidity of the aggregate will affect concrete strength, and the use of harder aggregate will result in stronger concrete. It will be shown later that, to some extent, concrete strength is affected by the strength of the aggregate.

According to the proposed mechanism, when the aggregate is weaker than the paste, cracking will occur within the aggregate also and in this case concrete strength will be affected to a much greater extent by the strength of the aggregate.[5] It will be seen later that for a particular W/C ratio, the strength of concrete made of lightweight aggregate, which is weaker than the paste, is lower than that of similar concrete made of ordinary aggregate.

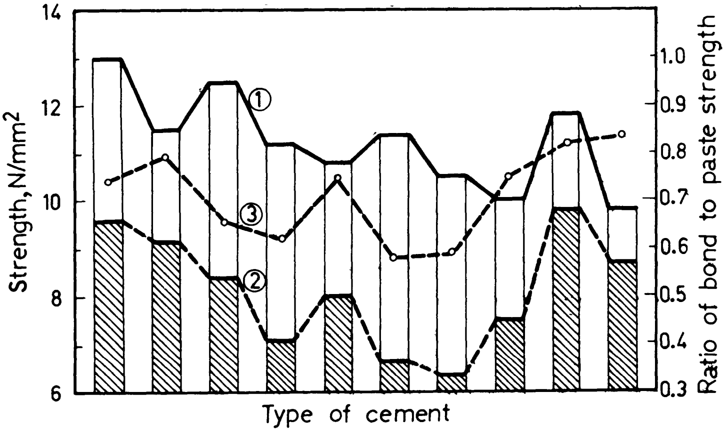

Figure 8.1 *Relation between flexural strength of cement paste and strength of the paste-aggregate bond for different cements (after Alexander et al.*[6]*).* (1) *Flexural strength of paste,* (2) *strength of paste-aggregate bond, and* (3) *ratio of bond to paste flexural strength*

The strength of ordinary concrete depends to a large extent on the strength of the aggregate to paste bond. It may be seen from Figure 8.1,[6] and other data,[7] that this bond strength is lower than paste strength. Under such conditions, at the initial stages at least, cracking will tend to develop at the aggregate-paste interface rather than in the paste itself. This tendency has been demonstrated in concrete specimens loaded under compression, where the existence of cracks at the aggregate-paste interface was observed even prior to loading.[8] It was found

Figure 8.2 *Cracking of concrete due to compressive load (after Hsu and Slate*[4]*)*

that for loading up to 70% of the ultimate strength, cracking was mainly a result of the growth of bond cracks, and only at higher loading did cracking take place in the paste. It seems that cracking in the paste tends to form a bridge between bond cracks over the shortest distance between them. This bridging occurs between the larger aggregate particles, so that the resulting cracks continue for a minimum distance through the paste (Figure 8.2). Such a cracking pattern would be expected if one considers that the strength of the paste is greater than that of the paste-aggregate bond and that the strength of the aggregate is greater than that of the paste. Moreover, this cracking pattern implies that the strength of ordinary concrete will be determined mainly by the strength of the paste, and that of the paste-aggregate bond rather than the strength of the aggregate. As mentioned, the strength of ordinary concrete is, indeed, only slightly affected by the strength of the aggregate.

The preceding discussion about cracking pattern also implies that aggregate concentration and particle size should affect concrete strength. A lower strength is to be expected with increase in aggregate concentration and size because such increases are associated with a corresponding decrease in the length of the bridging cracks within the paste. Relevant experimental data are discussed later. In any case, the paste-aggregate bond plays an important role in determining concrete strength, and a higher strength is to be expected with increase in bond strength. Accordingly, the nature of the paste-aggregate bond and the factors affecting its strength are discussed here.

8.2 Paste–aggregate bond

The bond between the paste and the aggregate is due to mechanical and physical effects, and in some cases, to chemical reaction between the aggregate and the paste. The strength of the paste–aggregate bond depends on both paste and aggregate properties. Many studies have been carried out to identify the many factors which affect bond strength and to determine to what extent these effects are reflected in concrete strength. These studies have included specimens made of different rock + paste combinations, and concretes made with different aggregates. The use of the former specimens made possible the study of the effect of such factors as paste strength and type of rock (chemical composition) and its surface characteristics on the strength of the bond between the paste and the rock. The use of the latter specimens made possible the determination of the extent to which variations in bond strength are reflected in concrete strength.

8.2.1 Water/cement ratio

The effect of the *W/C* ratio on bond strength is similar to its effect on compressive strength, i.e. decrease in *W/C* ratio increases the paste compressive strength as well as the strength of its bond to the aggregate.[6,7] This effect of the *W/C* ratio can only be demonstrated on paste + rock specimens because in concrete it affects both paste and bond strength. In any case, the fact that the strength of ordinary concrete is determined mainly by the strength of the paste and the strength of its bond to the aggregate explains why the *W/C* ratio is the most important factor in determining concrete strength.

8.2.2 Surface roughness of aggregate

It is to be expected that the surface characteristics of the aggregate will affect bond strength and that a rougher surface would result in higher strength. Tests have indicated that concrete made with crushed aggregate is stronger than otherwise similar concrete made with gravel.[8] This effect is particularly evident in stronger concrete ($W/C = 0.40$), in which the use of crushed aggregate was associated with a 38% increase in strength. This effect, however, decreases with decrease in concrete strength and disappears completely in concrete having a *W/C* ratio of 0.65. Apparently for concrete with a high *W/C* ratio strength is determined mainly by the paste strength with bond strength playing only a minor role. Similarly, in another study it was found[10] that both compressive and flexural strength of concrete increase with surface roughness. Moreover, the effect of roughness on strength, particularly in strong concrete, was found to be more important than the effect of some other aggregate properties, such as modulus of elasticity and particle shape.

Note that the use of concrete specimens to study the effect of aggregate roughness on concrete strength may lead to inconclusive and perhaps even contradictory results. The use of aggregates of different surface roughness involves the use of aggregates which also differ in some of their other properties such as chemical and mineralogical composition. The latter properties may affect bond strength and hence concrete strength. In the paste + rock specimens, the same type of rock is used throughout and the different degrees of roughness are achieved by use of different surface treatments, such as polishing, sawing, or grinding. Consequently, in this type of specimen the effect of surface roughness on bond strength is separable from the possible effects of the other properties of the rock. The use of such specimens is therefore more reliable. From tests involving such specimens it is clear that aggregate surface roughness has a considerable affect on bond strength, and that the greater the roughness the higher is the bond strength. This improvement in bond strength may be attributed to increased surface area and improved mechanical interlocking.

8.2.3 Chemical composition

Generally speaking, with the exception of aggregates that react with alkalis, common concrete aggregates are considered to be inert in the water + cement system. However, to some extent the chemical composition of the aggregate does affect bond strength and, in some cases, the properties of the layer at the paste-aggregate interface are different from those of both the aggregate and the paste. This, in turn, suggests that a chemical reaction has taken place at the interface, and such a reaction may explain the dependence of bond strength and the associated concrete strength on the chemical composition of the aggregate.

In the study by Alexander *et al.*[6] it was found that bond strength with extrusive rocks* increases with increase in their silica content within the range 45 to 70%. The improved bond was attributed to chemical reactions between the silica and the lime of the cement, reactions similar to those occurring in the cement + water system in the presence of pozzolana. With silica-containing aggregates, these reactions are limited to the paste-aggregate interface and apparently determine bond characteristics and strength. In support of this explanation the authors cite the development of appreciable bond strength between basalt prisms lightly held together in pairs, and stored in lime water. Moreover, it was found that in such aggregates a wide contact zone is formed at the interface, the properties of which differ from those of either the aggregate or the paste. This contact zone, when viewed under the microscope with transmitted light, appears as a dark rim at the aggregate surface. A similar rim was also observed at the surface of granite,[11] and this rim was found to differ in hardness from both the granite and the paste.

In a study by Farran[12] it was found that calcareous aggregates produce

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*Extrusive rocks, commonly referred to as lava flows, are formed by consolidation of magma on the surface of the ground (e.g. basalt) as distinct from intrusive rocks which consolidate below ground (e.g. granite). Both types are collectively known as igneous rocks.

stronger concrete. This was attributed to slight dissolution of the calcite, and the epitaxial growth of a layer of the solid solution $CaCO_3$-$Ca(OH)_2$ at the aggregate surface. A similar conclusion was reached in another study[13] where the improved bond between the calcareous aggregates and the cement paste was attributed to the formation of an oriented $Ca(OH)_2$ layer due to attack on the carbonate rock by the alkali solutions in the cement paste. Lyubimova and Pinus,[11] however, have suggested that this layer is monocalcium carboaluminate ($C_3A \cdot CaCO_3 \cdot 10$-$11\ H_2O$) formed by reaction of the calcium carbonate with C_3A. It has also been observed that the layer at the paste-aggregate interface consists of $Ca(OH)_2$ having a preferred orientation, and that the formation of this layer is not related to the type of the aggregate involved.[14]

It may be concluded that, as yet, the exact nature of the paste aggregate bond is not fully understood. Generally speaking, the bond is characterised by the presence of a thin layer which bridges between the aggregate and the paste. This layer is formed as a result of a chemical reaction between the cement and the aggregate, or of epitaxial growth, or of a combination of both. That is, the type of aggregate affects bond strength but the exact nature of this effect is not understood and may vary depending on the type of aggregate.

8.2.4 Effect of paste-aggregate bond on concrete strength

The strength of ordinary concrete is determined mainly by the strength of the paste and the strength of its bond to the aggregate. Bond strength, in turn, is governed by various factors which were considered in the preceding section. The expected effect of these factors is not always reflected in concrete strength because the use of different aggregates involves the simultaneous change of several of their properties. Consequently, it is virtually impossible to examine separately the effects of each factor on concrete strength though the latter can be related to the strength of the paste-aggregate bond. Alexander and Taplin,[15,16] for example, showed that concrete strength, S, in compression or in flexure, is given by the expression

$$S = S_0 + b_0 + b_1 m_1 + b_2 m_2$$

where m_1 is the flexural strength of the paste, m_2 its bond strength to the aggregate, and b_i are constants which depend on the particular test conditions. The ratio b_1/b_2 was found to be approximately two indicating that for a given change, the strength of the paste has an effect on concrete strength that is approximately twice that of the paste-aggregate bond. This result implies that, strengthwise, the paste is much more important than the paste-aggregate bond. Other studies, however, emphasised to a much greater extent the dependence of concrete strength on paste-aggregate bond strength. Nepper-Christensen *at al.*[51] found that the strength of concrete made with glass marble aggregate is approximately 2.5 times that of the same concrete made with lubricated, but otherwise the same, aggregate. Similarly Lezy *et al.*[52] found that improving the bond by coating the aggregate with a polymer increased concrete strength by a factor

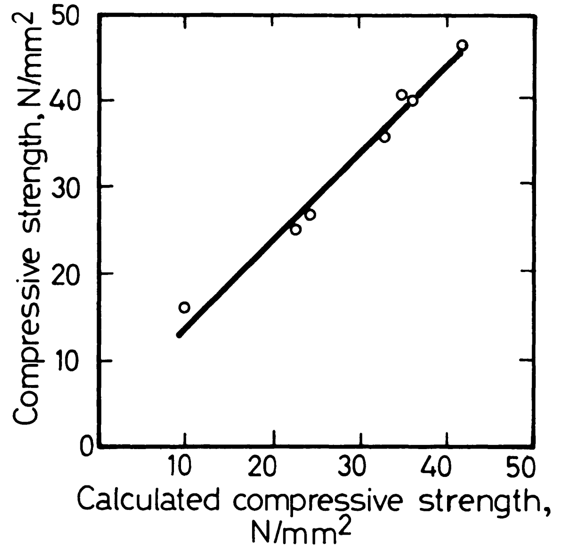

Figure 8.3 *Comparison between observed and calculated compressive strength of concrete (after Alexander et al.*[6]*)*

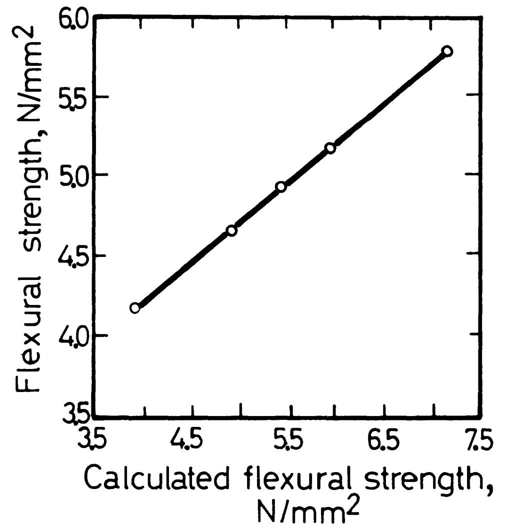

Figure 8.4 *Comparison between observed and calculated flexural strength of concrete (after Alexander et al.*[6]*)*

varying from 1.5 to 2.

Figures 8.3 and 8.4 compare observed and calculated concrete strength using the data of Alexander *et al.*[6] The good fit of the regression lines confirms, once again, that concrete strength is mainly governed by the strength of the paste and the strength of its bond to the aggregate. It should be noted, however, that the data relate to ordinary concrete in which the strength of the aggregate is greater than the strength of the paste. In concrete made of weaker aggregates, the strength of the aggregate is expected to affect concrete strength to a much greater extent, and the preceding conclusion must be modified accordingly.

8.3 Effect of aggregate properties on concrete strength

The preceding discussion was limited to aggregate properties which indirectly affect concrete strength through their effect on the strength of the paste-aggregate bond. However, it may be expected that other properties of the aggregate, such as strength, particle size, and concentration, will also affect concrete strength. For example, a decrease in concrete strength is to be expected with increase in aggregate concentration and particle size because the length of the critical crack length through the paste will be shorter. Also it may be expected that aggregate strength will be reflected in concretes made of weak aggregates. Such properties of the aggregate directly affect concrete strength, and the following discussion presents some relevant experimental data.

8.3.1 Strength

Generally speaking, for the same W/C ratio, concretes made of lightweight aggregates are weaker than those made of normal-weight aggregates. This difference in strength may be attributed to the lower strength of the lightweight aggregate and is reflected in Figure 8.5. The difference is also visible in the

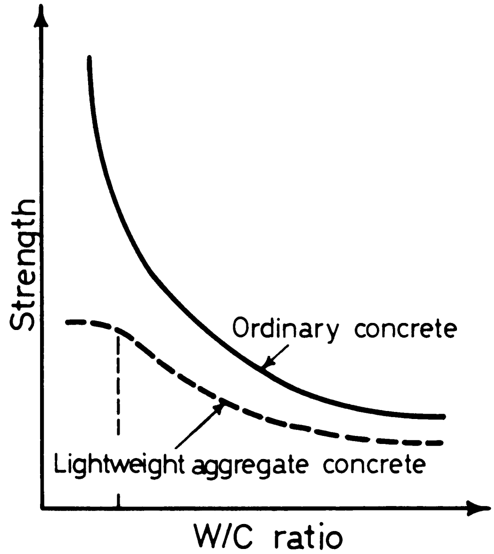

Figure 8.5 *Relation between strength and W/C ratio for lightweight and normal-weight aggregate concrete* cracking pattern of lightweight aggregate concrete, in which cracks propagate through the aggregate to a much greater extent than in normal concrete. This mode of failure explains the existence of a limiting strength in light-weight aggregate concrete, which any further reduction in W/C ratio cannot increase (Figure 8.5). Apparently, at this strength, the strength of the aggregate becomes the dominant factor and further increase in the strength of the paste does not significantly affect concrete strength. In normal-weight concrete, however, this is not the case[17] and for practical purposes it is generally assumed that aggregate strength hardly affects concrete strength.

8.3.2 Modulus of elasticity

From the expressions defining fracture toughness, it would be expected that the modulus of elasticity of the aggregate will affect concrete strength. Fracture toughness is related to the modulus of elasticity of the material considered. In concrete the modulus of elasticity is related to that of the aggregate, a relationship which is discussed in some detail in Chapter 9. Kaplan, for example, found that concrete flexural strength increased with increase in the modulus of elasticity of the aggregate.[10] To a lesser extent the modulus was also found to affect the compressive strength, and it was concluded that the modulus of elasticity of the aggregate constitutes one of the factors determining concrete strength. This effect of the modulus of elasticity of the aggregate on concrete strength has been observed, with some exceptions,[18] by others.[17]

The increase in concrete strength with the increase in the modulus of elasticity of the aggregate may be explained from the effect of aggregate rigidity on stress distribution in the concrete during external loading. Assuming equal strains, the fraction of the load which is taken by the aggregate increases with its rigidity and consequently the fraction taken by the paste decreases. The strength of ordinary concrete is determined mainly by the strength of the paste, so a decrease in loading on the paste delays fracture and thereby increases concrete strength. It should be noted that a higher modulus of elasticity involves a stronger aggregate. That is, strictly speaking, the strength differences indicated in Figure 8.5 are due to differences in both aggregate strength and modulus of elasticity.

8.3.3 Particle size

In considering the fracture mechanism it was concluded that, for the same aggregate concentration, a lower strength is to be expected in concrete made of coarser aggregate.[2] This conclusion is supported by considerable experimental data[19–22] and may be predicted from the effects of aggregate particle size on stress concentration. The presence of aggregate particles in the cement paste induces stress concentrations at, and close to, the paste–aggregate interface. The volume of this region of stress around an aggregate particle increases with increasing particle size. Consequently, assuming that the weakest-link concept is applicable, concrete strength will decrease with increasing particle size (Figure 8.6).[23]

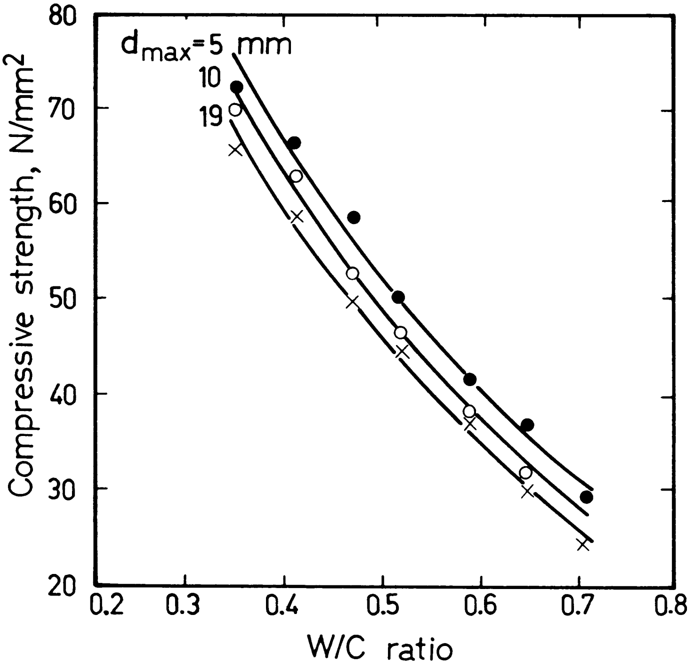

Figure 8.6 *Effect of aggregate particle size on concrete strength (after Hobbs*[22]*)*

8.3.4 Concentration

Increase in aggregate concentration reduces the interparticle separation and involves therefore a decrease in the length of the fracture which takes place through the paste. Accordingly, concrete strength should decrease with increase in aggregate concentration or, alternatively, for the same *W/C* ratio, cement-rich concrete would be stronger than lean concrete. If such were the case, the strength of a paste will be greater than the strength of a mortar of the same *W/C* ratio, and the strength of a mortar will be greater than that of a concrete. This conclusion is supported by the data of Gilkey which are presented in Figure 8.7. In other studies,[19,25–27] however, the opposite conclusion was drawn, namely, that concrete strength increases with increase in aggregate concentration (Figure 8.8). As already mentioned, the presence of the aggregate within the paste induces stress concentrations. These regions of stress concentration around neighbouring aggregate particles overlap more and more strongly as the aggregate volume is increased. Consequently, the average stress concentration induced by the aggregate particles decreases as the concentration of the aggregate increases, and concrete strength is increased. Apparently the increase in aggregate concentration also involves the development of a greater number of secondary cracks prior to failure. This, in turn, will increase the energy requirement for fracture and will result, therefore, in higher strength.

The data of Gilkey (Figure 8.7) are not supported by the findings of others,

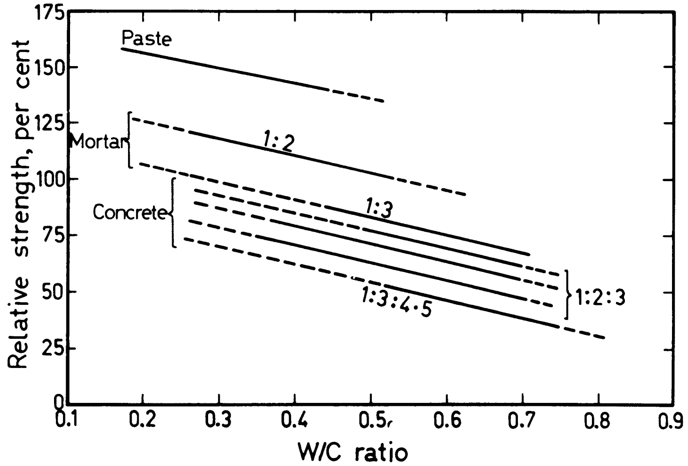

Figure 8.7 *Effect of aggregate concentration on strength of mortar and concrete (after Gilkey*[24]*)*

and it is generally accepted that concrete strength increases with increase in aggregate concentration. In this respect it should be noted that the foregoing conclusion is valid provided that the reduced paste content remains high enough to allow complete consolidation of the concrete. At a certain level of aggregate concentration, the content of the paste does not allow such consolidation, and the resulting void-containing concrete will be weaker. That is, there is an opti-

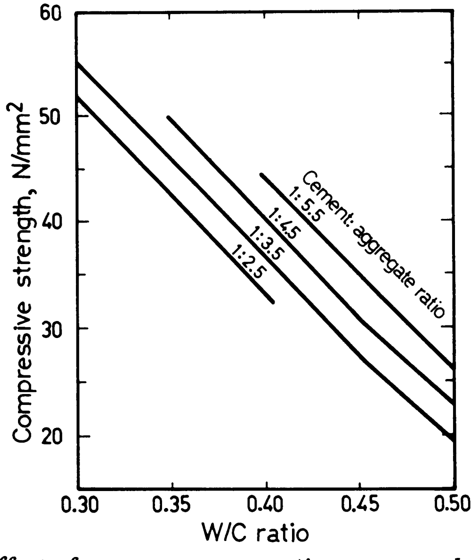

Figure 8.8 *Effect of aggregate concentration on strength of concrete (after Emtroy and Shacklock*[25]*)* mum aggregate concentration as far as strength is concerned. In cement mortars this optimum was found to be 30% for compressive strength,[54] and 36% for flexural strength.[55]

8.3.5 Summary of aggregate properties

Aggregate properties affect concrete strength. The exact nature of this effect is not always clear but, generally speaking, concrete strength increases with increase in aggregate modulus of elasticity and concentration and with decrease in its particle size. The strength of ordinary concrete is only slightly affected by the strength of the aggregate.

Surface characteristics of the aggregate affect the strength of the paste-aggregate bond and hence concrete strength. The use of smooth aggregate (gravel) involves lower strength, particularly flexural strength. The chemical composition of the aggregate may affect concrete strength through its affect on the paste-aggregate bond. It seems that the use of calcareous aggregates produces concrete of greater strength.

8.4 Effect of *W/C* ratio on concrete strength—Abrams' law

In Chapter 4 it was shown that porosity determines the strength of the cement paste and that porosity, in turn, is determined by the *W/C* ratio and the degree of hydration. That is, for the same degree of hydration, differences in strength of pastes are determined solely by the *W/C* ratio.

Concrete strength is determined by the strength of the paste, the strength of the paste-aggregate bond, and by some properties of the aggregate. In this respect, particularly when compressive strength is considered, the paste strength is the main factor. The strength of the paste is determined by the *W/C* ratio; this is also one of the main factors determining the strength of the paste-aggregate bond. In other words, ignoring the effect of the aggregate, and for the same degree of hydration, concrete strength differences are determined by the *W/C* ratio alone. The first person to recognise this dependence was Abrams[28] who showed in 1918 that concrete strength, S, is given by

$$S = A/B^{\omega} \tag{8.1}$$

where ω is the *W/C* ratio and A and B are constants which depend on age, curing regime, type of the cement, and testing method.

In view of the preceding discussion, the value of the constants A and B will also be affected by the properties of the aggregate. At the time, however, Abrams found that aggregate properties affect concrete strength only indirectly through their effect on the amount of mixing water required. Accordingly, the relation between concrete strength and the *W/C* ratio established by Abrams (Figure 8.9) was considered to be independent of aggregate concentration, particle size, etc., and applicable therefore not only to concrete but also to mortars and pastes.

Expression (8.1) is sometimes referred to as 'Abrams law' or the '*W/C* ratio law'. Actually the expression resulted from curve-fitting of experimental data and is not strictly speaking a law. It has, however, found extensive use in concrete technology, even though the possible effect of aggregate properties on concrete strength was not originally considered in its formulation. In practice this effect of aggregate is of limited significance because the variation in properties of ordinary aggregates is not great enough to have much effect on concrete strength. In practice, at present, even though the effect of aggregate properties is well recognised, allowance is usually only made for surface roughness effects. It is stressed again that this practice is valid for concrete made of ordinary aggregates (i.e. aggregates stronger than cement paste) having a particle size of, say, 10–30 mm. The use of lightweight aggregate (i.e. weaker than the paste), or aggregates having larger particle size, requires an appropriate modification to the constants *A* and *B*. In any case, Abrams' law should be quantitatively determined for any particular set of conditions, particularly bearing in mind the type of the cement in use and the method of testing concrete strength. Relevant data for British practice can be found in references 29 and 30.

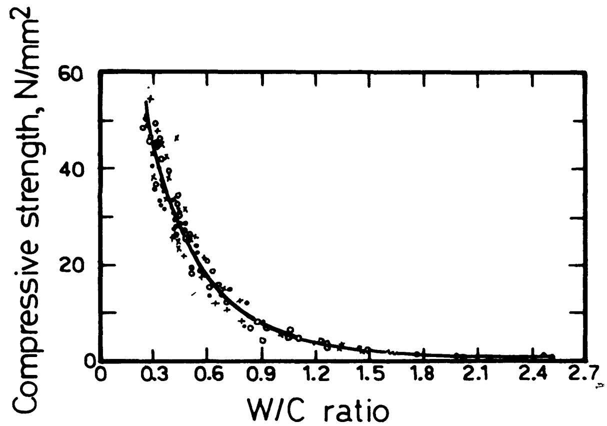

Figure 8.9 *Strength plotted against W/C ratio for concrete, mortars, and pastes (after Abrams*[28]*)*

Once established for a given set of conditions, Abrams' law can be used to estimate concrete strength from *W/C* ratio or, more importantly, it can be used to select the *W/C* ratio required to produce a concrete of desired strength. Consequently, this law plays an important role in concrete mix design and in this context it is widely used.

The *W/C* ratio law is valid provided the concrete is fully compacted. This is the reason why, below a certain minimum, further reduction in the *W/C* ratio

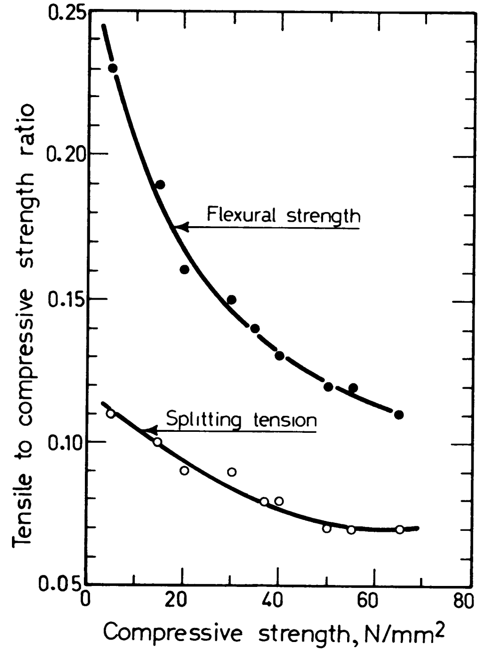

Figure 8.10 *Effect of concrete compressive strength on tensile to compressive strength ratio (after Price*^{31}*)*

does not result in the expected increase in strength. At such low W/C ratios the concrete is not workable enough to allow full compaction of the fresh mix. The incompletely compacted concrete contains voids and pores and its strength is therefore reduced (Figure 11.5).

Air-entrainment reduces concrete strength and this effect should be allowed for when using the W/C ratio law. Additional air content, ΔA,* may be considered to have the same effect on strength as an additional amount of water, and hence the water/cement ratio in air-entrained concrete is defined by

$$\omega = (W + \Delta A)/C \tag{8.2}$$

In this context it may be remembered that a similar approach was used by Powers in relating paste strength to gel/(space + air) ratio (Figure 4.10).

So far the effect of the W/C ratio has been discussed in relation to compressive strength only. In principle, the same considerations apply to tensile strength of concrete whether this is determined from flexure or splitting tests. However, tensile strength is less sensitive to the effect of W/C ratio, particularly at lower values of this ratio. In other words, a given reduction in W/C ratio would be

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*The air content in fully compacted concrete depends on aggregate size and generally varies from 10 to 30 litre/m^3. The optimum air content in concrete varies from 45 to 65 litre/m^3. Accordingly, usually ΔA = 35 litre/m^3.

associated with a greater increase in compressive than in tensile strength of the concrete. Consequently, the tensile to compressive strength ratio varies with the *W/C* ratio, decreasing with decrease in its value, i.e. with increase in concrete strength. It can be seen from Figure 8.10 that this ratio ranges from, say, 0.10 to 0.20 and from 0.07 to 0.10 for the flexural and splitting strengths, respectively.

Under normal hydration conditions, and using ordinary Portland cement, concrete having a compressive strength 70 N/mm^2 and flexural strength 7 N/mm^2 can be produced. For practical purposes it is generally assumed that the final (ultimate) strength of concrete is reached at an age of 28 days, and this strength is usually used for quality control purposes and in structural design. At this age the greater part of the concrete's potential strength is developed, particularly under site conditions where curing is discontinued after a few days. Moreover, the usefulness of later-age strength tests is limited because it is not really possible to use these late results for quality control.

The development of concrete strength with age depends on a few factors such as type of the cement, *W/C* ratio, and curing conditions. It is therefore virtually impossible to predict accurately concrete later-age strength from early-age tests. Nevertheless, when required, a rough estimate can be made from the data presented in Table 8.1.[56]

Table 8.1 Strength development in concrete with age[56]

Age, days	*Relative strength*, %		
	Compression		*Flexure*
	Ordinary	Rapid-hardening	Ordinary
3	0.40	0.55	0.40
7	0.65	0.75	0.70
28	1.00	1.00	1.00
90	1.20	1.15	1.05
360	1.35	1.20	1.10

8.5 Effect of temperature on strength

The effect of temperature on the strength of cement paste was discussed in some detail in Chapter 4. It was seen that the early-age strength of the paste is improved with rise in curing temperature but its later-age strength is adversely affected (Figure 4.19). The same effect is evident in concrete where, in this context, 'early-age' generally refers to ages less than seven days and 'later-age' to ages exceeding 28 days. The effect of temperature is reflected in Figure 8.11,[32] and other data show the same trend.[31–35] Figure 8.11 covers a temperature range up to 50°C, but similar results have been obtained for temperatures up to 100°C.

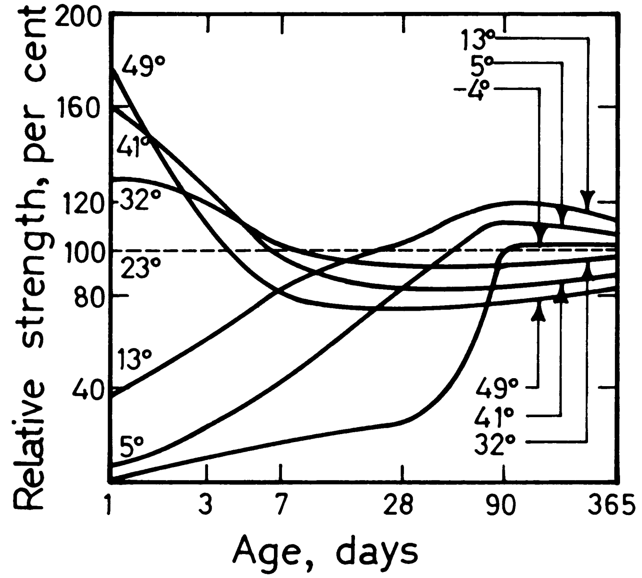

Figure 8.11 *Effect of curing temperature on concrete strength (after Klieger*[32]*). (Ordinary Portland cement, W/C ratio* = 0.41)

The effect of temperature is further discussed in Chapter 11 when steam-curing of concrete is considered. Here, the discussion is confined to the temperature range up to 50°C, i.e. up to the expected maximum under extreme climatic conditions. Generally speaking, in this temperature range the detrimental effect of elevated temperatures on later-age strength is observed even after curing of only two hours[31] and strength reductions up to 25% have been recorded.[32,35,37] The detrimental effect was found to increase with increase in cement content of the concrete.[35]

The exact nature of the temperature effect on concrete strength is not completely understood and the available data are sometimes contradictory. A gradual decrease in concrete strength with increase in curing temperature within the range 5 to 46°C, was found by the US Bureau of Reclamation (Figure 8.12A).[33] On the other hand, Klieger[32] found, for the same temperature range, an optimum temperature which produced in the concrete a maximum strength. This optimum was 13°C for concrete made with ordinary Portland cement (Figure 8.12B) and 5°C for concrete made with rapid-hardening cement. In another study[35] an optimum was found to exist between 20 and 40°C (Figure 8.12D) and in yet another,[36] a critical temperature producing minimum strength was observed in the 20 to 50°C range (Figure 8.12C).

The contradictory nature of the results indicates the complexity of the problem and suggest that the temperature effect on strength is a result of several factors. Considering that, under otherwise similar conditions, concrete strength is determined by the properties of the cement, it is reasonable to assume that the

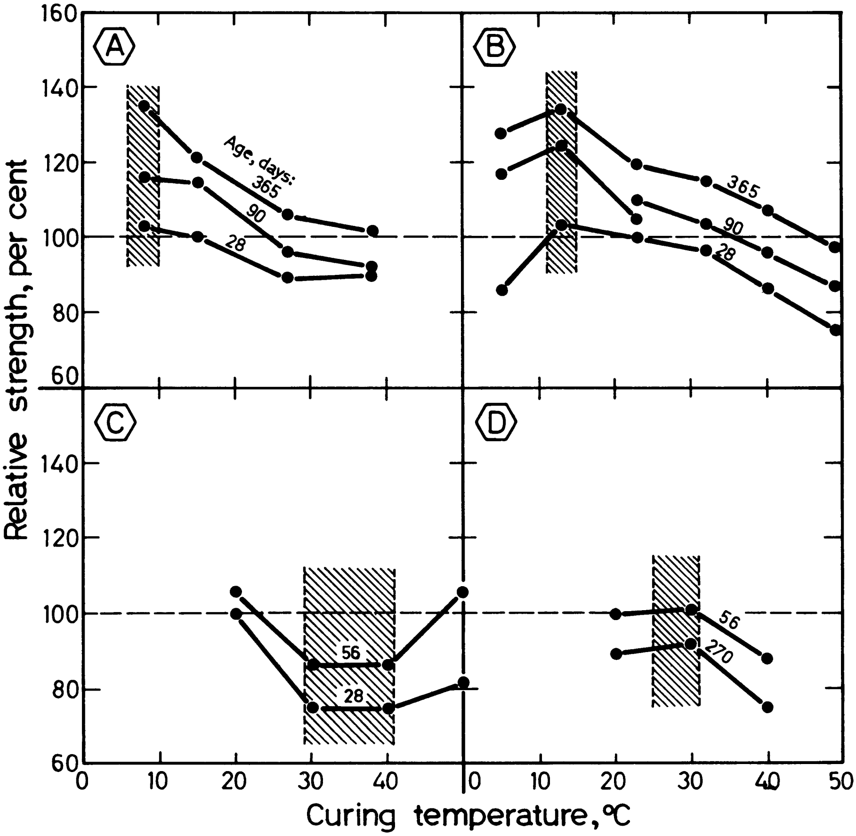

Figure 8.12 *Effect of initial curing temperature on concrete later-age strength*[35]

cement composition and probably also its specific surface area will influence the temperature effect on strength. Shalon and Ravina[37] found that the detrimental effect of temperature is smaller for concrete made of cement low in C_3A and high in C_2S. The same results have been obtained by others[38] and it may be concluded therefore that the detrimental effect of temperature on concrete strength may be minimised by the use of a cement low in C_3A and high in C_2S, i.e. by use of a sulphate-resisting cement. In a later study,[35] however, this conclusion was not confirmed and it seems that the question of cement composition and temperature effect on strength is still far from receiving a satisfactory answer.

Finally, it may be expected that the detrimental effect of increased curing temperature would depend on the length of the curing period and in this context the concept of concrete 'maturity' is sometimes mentioned. The maturity is defined as the product of the curing period and temperature, and it represents therefore their combined effect. An increase in concrete strength is to be expected with the increase in its maturity. This aspect, however, is discussed in some detail in Chapter 11 when steam-curing of concrete is considered.

8.6 Factors affecting the results of strength tests

8.6.1 Compressive strength

Concrete strength is determined on cubes or cylinders. Strength is defined as the maximum stress sustained by the test specimen, i.e. the maximum load registered on the testing machine, P_{max}, divided by the cross sectional area, A, of the specimen (Figure 8.13). However, test results depend to a considerable extent on the specific test conditions, such as sample shape and dimensions, rate of loading, etc. That is, different results may be obtained with the same concrete because of differences in the testing methods employed. To avoid such a difference, standard tests are adopted, i.e. tests carried out in accordance with a carefully detailed

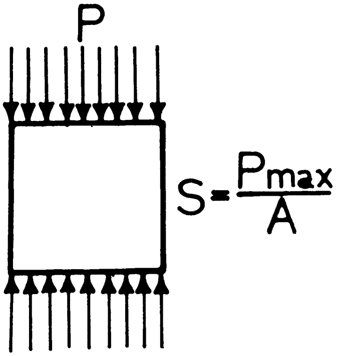

Figure 8.13 *Testing of concrete in compression*

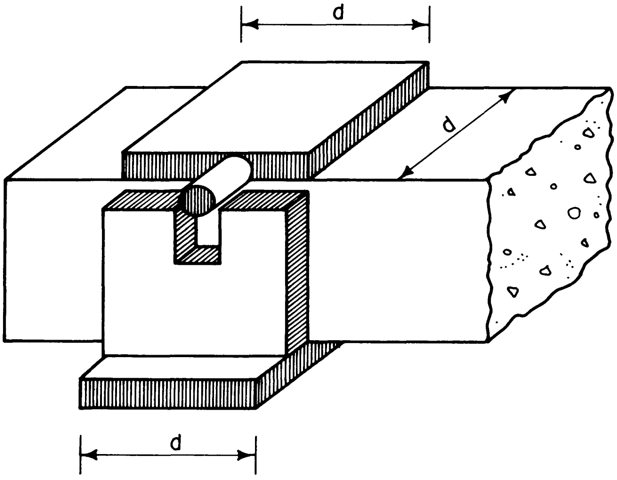

Figure 8.14 *Compressive testing of concrete using portions of beams broken in flexure* and defined procedure. Strength which is determined in such a way is referred to as 'standard strength'. In the UK standard concrete tests, including compressive strength tests, are dealt with in BS 1881, *Methods of Testing Concrete.*

The compressive strength of concrete can also be determined on the remaining portions of the beams used in determining flexural strength. To this end the beam portion is loaded after being placed between two bearing plates which are aligned by means of a suitable device (Figure 8.14). At one time, only beams of square cross section were used, and the test procedure was known as the 'modified cube method'. This terminology is no longer applicable because beams of rectangular cross section may now be tested (ASTM C116). In any case, it should be born in mind that strength results obtained using portions of beams are not interchangeable, and not necessarily comparable, with those obtained from tests on cubes or cylinders.

As already mentioned, the results of strength tests are affected by various factors. These are briefly discussed below.

8.6.1.1 End conditions and capping

In order to avoid stress concentration, both ends of test specimens should be truly plane. It can be appreciated that the lack of planarity will reduce the effective contact area between the specimen and the bearing plate of the testing machine, and the resulting formation of stress concentrations will lead to reduction in the apparent strength of the concrete.[39]

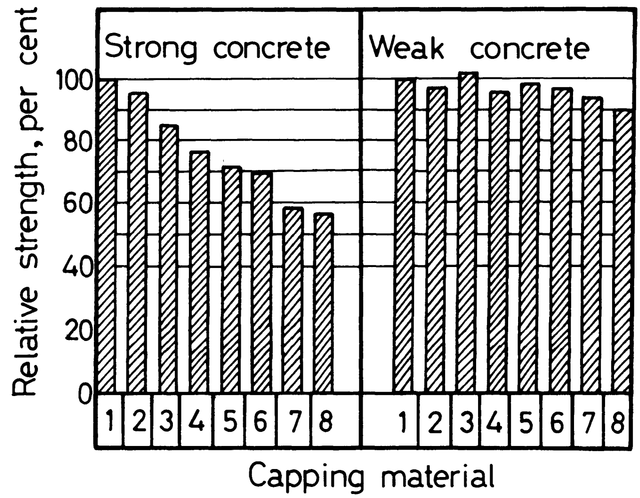

Figure 8.15 *Effect of capping material on results of strength tests (after Werner*[40]*). Capping material* (1) *aluminous cement*; (2) *and* (3) *gypsum plaster*; (4) *and* (5) *sulphur with mineral filler*; (6) *pure sulphur*; (7) *plaster of Paris*; (8) *plaster of Paris and Portland cement*

Concrete cubes are cast in steel moulds. The ends of cubes which are cast against the mould are sufficiently smooth and plane to require no further treatment of the ends before testing. On the other hand, the top end of a cylinder cannot be finished to the required planeness and capping is usually necessary. The cap may be made from pastes, or mixtures, based on Portland cement, aluminous cement, gypsum plaster or sulphur. It can be seen from Figure 8.15[40] that the type of cap affects the test results. This effect is minimum when the strength and the elastic properties of the capping material are similar to those of the concrete under test. A weaker material results in lower figures and the effect of such materials is more evident therefore in stronger than in weaker concretes (Figure 8.15).

The effect of capping material on test results may be attributed to the difference between its lateral expansion and that of the concrete. The lateral expansion depends on the elastic properties of the material, being greater for materials having a lower modulus of elasticity and a higher value of Poisson's ratio, i.e. a higher ν/E ratio. This ratio is high in weak, soft materials and consequently their lateral expansion is greater than that of concrete. The higher expansion increases lateral strain in the concrete, the cracks parallel to the direction of the load grow more rapidly, and the specimen fails under a lower load. In strong rigid materials, having a ν/E ratio lower than that of the concrete, the lateral strains of the capping are smaller than the corresponding concrete strains. This smaller lateral expansion of the capping restrains concrete expansion, the rate of crack growth is restricted and the specimen fails under a higher load. The same restraining effect is produced by the bearing plates of the loading machine. The plates are made of steel, and their lateral expansion is smaller than that of the concrete. That is, the plates restrain the expansion of the test specimen and thereby increase its apparent strength. The degree of restraint depends on the friction between the plates and the specimens. High friction increases the degree of restraint and results, therefore, in greater apparent strength. This effect is particularly evident when the friction is reduced to a minimum by using, say, wax as the capping material. In this case, as expected, great lateral strains are observed and the specimen fails under a lower load. Moreover, the mode of

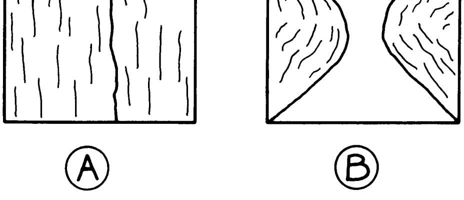

Figure 8.16 *Effect of degree of restrain on mode of failure of concrete.* A, *low restraint*; B, *high restraint* failure is changed being characterised by cracking parallel to the direction of loading (Figure 8.16A). However, in the more common case, when the bearing plates restrain the lateral strain, cracking takes the form of two pyramids (cones in cylinders), the bases of which coincide with the top and bottom ends of the cube and their apexes point inwards (Figure 8.16B).[57]

8.6.1.2 Shape and dimensions of the test specimen

In discussing the fracture mechanism it was pointed out that failure is brought about by the spontaneous growth of the critical crack when the strain energy release rate equals the maximum rate of energy demand. According to Griffiths' theory, long cracks should start to grow under a lower stress than short ones. Hence, the presence of long cracks will weaken the concrete. Some other flaws or discontinuities may further weaken the concrete if their geometry gives rise to high stress concentrations. The probability of a test specimen containing such weak elements will increase with the increase in its volume, i.e. with the increase

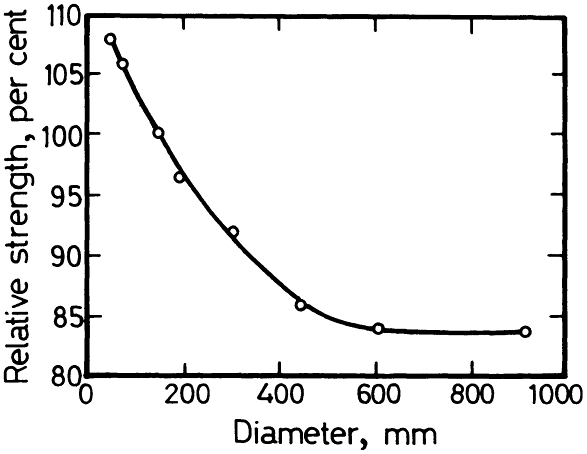

Figure 8.17 *Effect of cylinder diameter on strength test results (after Blanks and McNamara*[41]*)*

Table 8.2 Effect of cube dimensions on strength test results

Dimensions, mm	*Relative strength*
70	1.10
100-150	1.00
200	0.95
300	0.90

in its dimensions. Accordingly, it is to be expected that small specimens will give higher values than larger ones. This conclusion is confirmed by experimental data[41,42] some of which are presented in Figure 8.17. Similar results have been obtained for cubes and are summarised in Table 8.2.

In cylinders used for testing concrete, the ratio of the height, h, to the diameter, d, usually equals two. It was pointed out earlier that the bearing plates of the testing machine restrain the lateral expansion of the specimen and thereby increase its apparent strength. This restraining effect is operative, however, only to a distance of $\sqrt{3}/2$ times the diameter from the end surfaces. This is why the value two was adopted as the standard h/d ratio. It can be seen in Figure 8.18[43] that strength results are different for cylinders having an h/d ratio lower than 1.7. Similarly, no effect is to be expected for cylinders having an h/d ratio greater than 1.7 provided that this ratio is not high enough to produce buckling. It seems that buckling need be considered only for h/d ratios exceeding five.[44]

It is apparent from Figure 8.18 that the effect of the h/d ratio decreases with the increase in concrete strength. This is to be expected because the degree of restraint is smaller the smaller the difference between the rigidity of the loading plates and that of the concrete specimen. It follows, that for conditions where there is no friction between the plates and the concrete, the h/d ratio will not affect measured strength. This conclusion is confirmed by the data of Figure 8.19, in which the effect of h/d ratio on strength is presented for different degrees of friction between the loading plates and the concrete. The different degrees of friction were obtained by using different materials for packing: 8 mm soft wallboard (curve 2) and 2.4 mm plastic board (curve 3). Curve 1 describes test results when no packing was used, i.e. it represents test conditions for

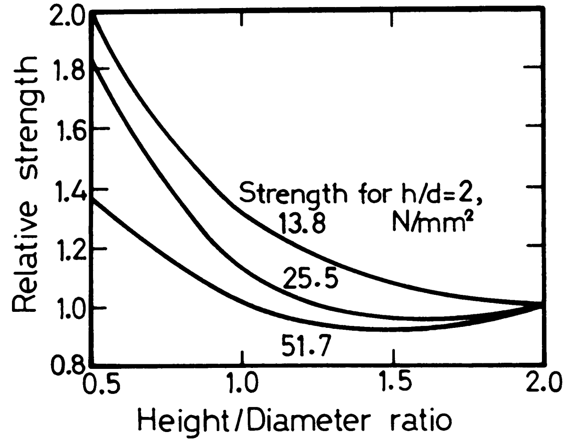

Figure 8.18 *Influence of h/d ratio on strength of concrete cylinders (after Murdock and Kesler*[43]*)*

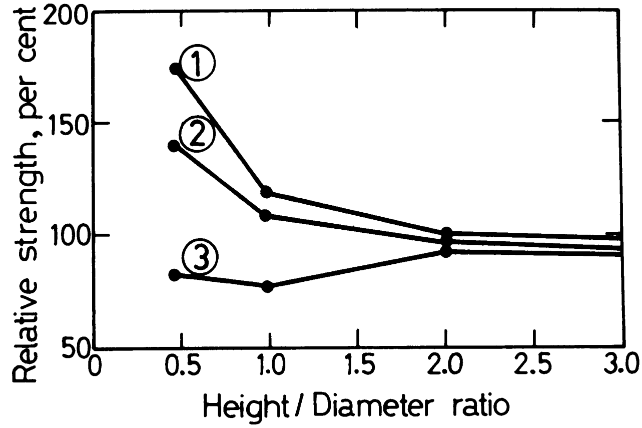

Figure 8.19 *Effect of h/d ratio on strength of concrete cylinders tested with different packing materials (after Hansen et al.*[45]*);* (1) *no packing*; (2) 8 mm *soft wallboard*; (3) 2.4 mm *plastic board*

maximum friction. It can be seen that under these conditions the effect of the *h/d* ratio on strength was maximum, whereas it disappeared completely when friction was minimised (curve 3). In any case, and in agreement with the previous discussion, the effect of the *h/d* ratio was evident only for values below about two.

The effect of *h/d* ratio on strength according to ASTM C42-68 and BS 1881, 1970 is summarised in Table 8.3. The effect is expressed as a 'correction factor' i.e. by a factor by which test results for non-standard cylinders ($h/d \neq 2$) must be multiplied to give the equivalent standard strength. In view of the many factors which affect test results, and the dependence of the effect of *h/d* ratio on concrete strength, some caution should be exercised in using the data of Table 8.3.

The measured strength of cylinders for which the *h/d* ratio equals two is not influenced by the restraining effect of the loading plates. The strength of such a

Table 8.3 Strength correction factors for cylinders of various h/d ratios

	Correction factor	
h/d ratio	ASTM C42-68	BS 1881, 1970
2.00	1.00	1.00
1.75	0.99	0.98
1.50	0.97	0.96
1.25	0.94	0.94
1.00	0.91	0.92

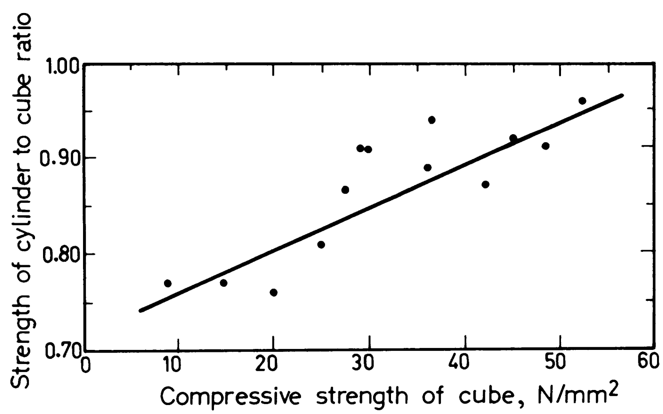

Figure 8.20 *Effect of concrete strength on ratio of cylinder to cube strength (after Evans*[46]*)*

cylinder will therefore be lower than that of a similar cube, i.e. a cube with edge length equal to the diameter of the cylinder. The degree of the restraint decreases with concrete strength, so the difference between cylinder and cube strength will decrease similarly. Evans' results[46] for six inch cubes and 6 x 12 inch cylinders are presented in Figure 8.20 and indicate that the ratio of cylinder to cube strength varies from 0.75 to 0.95. BS 1881, 1970 disregards the effect of concrete strength on this ratio, and recommends a single value of 0.80 for general use.

8.6.1.3 Loading rate

Generally speaking, an increase in the rate of loading yields higher strength results, and according to Figure 8.21[48] the effect of loading rate may produce strength differences of up to 100%. Figure 8.21 shows the effect on compressive

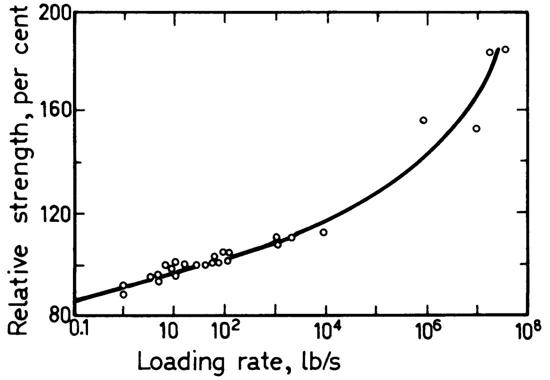

Figure 8.21 *Effect of loading rate on compression test results (after McHenry and Shideler*[48]*)* strength but the loading rate was found to affect flexural strength in a similar way.[49]

Assuming that the strength criterion for concrete is the ultimate strain and not the ultimate stress, then the effect of loading rate on strength can be attributed to creep. As a result of creep the ultimate strain is reached earlier when the load is applied slowly and consequently failure occurs at a lower stress.

8.6.2 Tensile strength

Direct determination of concrete tensile strength involves some difficulties, such as the avoidance of accidental eccentricity due to non-axial loading of the test specimen. Also, gripping of the specimen at both ends involves stress concentration which may lead to local deterioration of the concrete. Consequently, indirect methods are preferred, namely flexure and splitting tests.

8.6.2.1 Flexural strength

Concrete strength in flexure (modulus of rupture) is determined by loading concrete beams to failure. The loading may be by central-point loading (Figure 8.22A) or by symmetrical two-point loading (Figure 8.22B). In both cases the modulus of rupture, F, is calculated from

$$F = M/Z$$

where M is the bending moment at failure and Z is the section moment of resistance. This calculation assumes that the stress is proportional to the distance

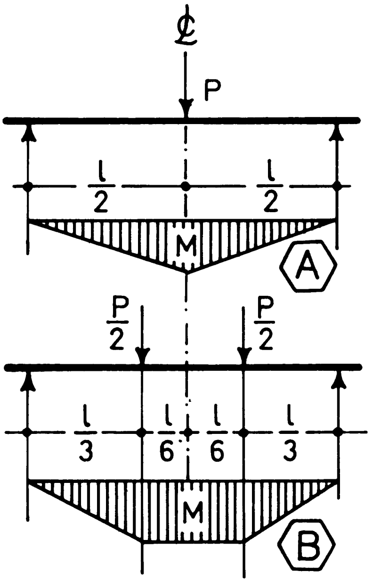

Figure 8.22 *Loading arrangements for testing concrete in flexure*

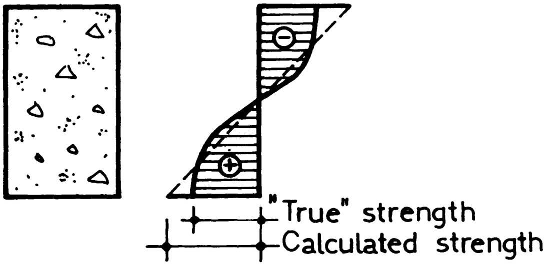

Figure 8.23 *Assumed and actual stress distribution in a concrete beam subjected to bending*

from the neutral axis of the beam (i.e. triangular stress distribution) whereas near failure the actual stress distribution departs from linearity as indicated schematically in Figure 8.23. The modulus of rupture overestimates therefore the tensile strength of concrete, and gives higher values than would be obtained by a direct tensile test or by the splitting test.

Theoretically the loading arrangement should not affect the modulus of rupture but actually, due to concrete heterogeneity, this is not the case. Central point loading produces a maximum moment at the beam centre (Figure 8.22A) and under such conditions failure will occur when the tensile strength of the concrete at, or in the immediate vicinity of, this section is reached. Two-point loading produces the same maximum moment between the loads (Figure 8.22B) and failure will occur at the weakest section within that part of the beam which is subjected to the maximum bending moment. It is highly probable that this part, which

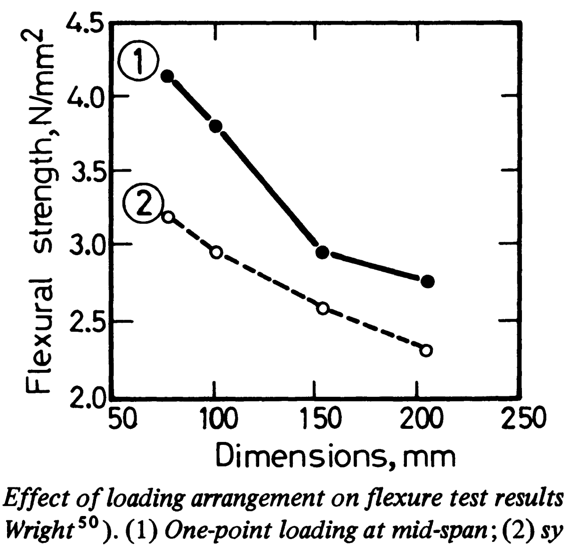

Figure 8.24 *Effect of loading arrangement on flexure test results (after Wright*[50]*).* (1) *One-point loading at mid-span*; (2) *symmetrical two point loading at a third point* is usually one third of the span, will contain sections which are weaker than those at, or adjacent to, the mid-span. It is to be expected, therefore, that two-point loading will give lower results than one-point loading. This is confirmed by the data of Wright which are summarised in Figure 8.24.[50]

8.6.2.2 Splitting test

Concrete tensile strength may be determined by the splitting test, sometimes referred to as the 'Brazilian' test. In this test a load is applied along the generatrix of a standard cylinder (Figure 8.25) by means of narrow strips of packing material, usually plywood, which are interposed between the cylinder and the

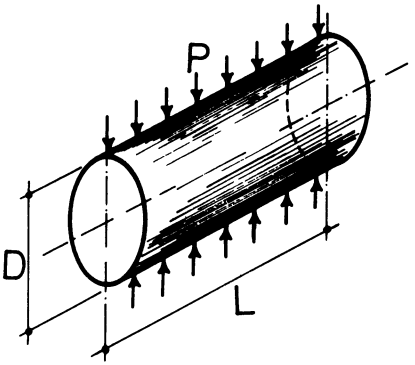

Figure 8.25 *Schematic description of splitting tests using a cylinder*

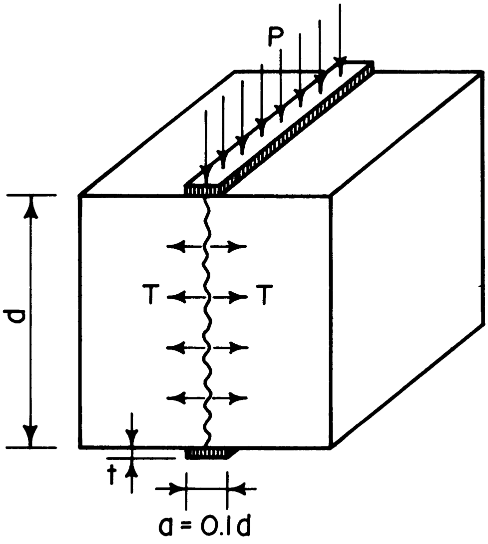

Figure 8.26 *Schematic description of splitting tests using a cube* loading plates (ASTM C496). It can be shown that under this loading arrangement the vertical mid-section of the cylinder is subject to a horizontal tensile stress, T, which is determined by

$$T = 2P/\pi DL$$

where P is the load at failure and D and L are the diameter and the length of the cylinder respectively.

Cubes can also be used in splitting tests (Figure 8.26) with the tensile strength being given by

$$T = 2P/\pi d^2$$

where d is the edge length of the cube.

8.7 Summary and concluding remarks

Concrete strength is determined by (1) the strength of the cement paste, (2) the strength of the paste–aggregate bond, and (3) some of the properties of the aggregate. The strength of the paste plays an important role and hence all the factors which affect its strength necessarily affect concrete strength. Amongst these factors, the W/C ratio is the most important one, and under otherwise similar conditions, concrete strength differences are determined solely by this ratio. Accordingly, concrete strength, S, may generally be expressed by $S = A/B^{\omega}$ where ω is the water/cement ratio and A and B are constants which depend on the type of the cement and the aggregate involved, age, curing conditions, and testing method. This expression, sometimes referred to as Abrams' law, plays a very important part in concrete mix design.

The strength of the paste–aggregate bond depends on the strength of the paste (i.e. again on the W/C ratio), and on some properties of the aggregate. Generally, an improved bond, and the associated improved strength, are to be expected with an increase in the roughness of the aggregate surface. The chemical composition of the aggregate may have some effect on strength, and the use of calcareous aggregate is sometimes associated with improved strength. Concrete strength decreases with the use of coarser aggregate. On the other hand, strength increases with increase in aggregate concentration and rigidity, i.e. its modulus of elasticity. In ordinary circumstances the strength of the aggregate hardly affects the strength of the concrete. The effects of all these factors are summarised in Figure 8.27.

Generally speaking, the preceding discussion is valid for compressive as well as for tensile strength of concrete. Quantitatively, however, some factors affect these two differently. For example, the tensile strength is less sensitive to variations in the W/C ratio. Consequently, the ratio of the tensile to compressive strength is not constant and decreases with increasing concrete strength. Generally speaking, this ratio varies from 0.10 to 0.20 for strong and weak concretes, respectively, when the tensile strength is determined in flexure. The correspond-

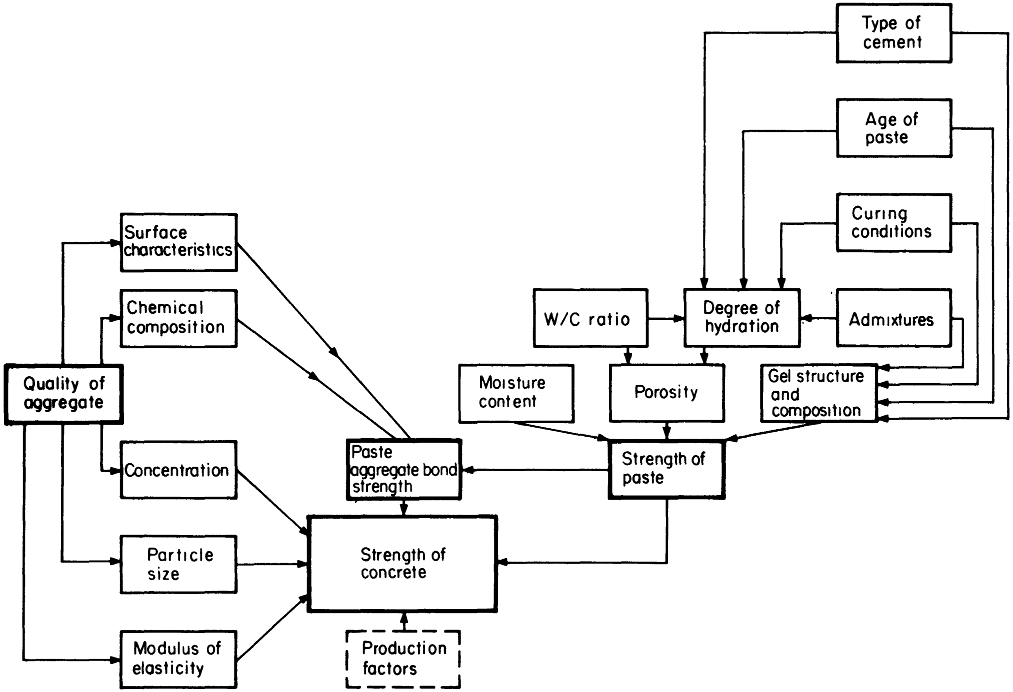

Figure 8.27 *Scheme showing the factors affecting concrete strength*

ing ratio when the tensile strength is determined by the splitting method varies from 0.07 to 0.11. Using ordinary Portland cement, concrete having a compressive strength of the order of 70 N/mm^2 at 28 days may be produced.

The type of test method affects test results, and variations in shape and size of test specimen, rate of loading, etc., may result in significant variations in the apparent strength of the concrete. To avoid such differences standard tests are employed. In the UK the details of such tests are given in BS 1881.

Finally, the strength of concrete and its quality are affected by the effectiveness of its compaction, curing conditions, etc. The effects of these technical aspects are discussed separately in Chapter 11.

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9 Volume changes in hardened concrete

9.1 Introduction

Concrete may be regarded as a composite two-phase material in which the discontinuous phase is the aggregate particle and the matrix phase is the hardened cement paste. Volume changes in the hardened paste were discussed in some detail in Chapter 5 and the following deals with the corresponding changes in concrete. These changes are discussed by considering the effect of the added aggregate and its properties on volume changes of the paste.

9.2 Stress–strain curve

Figure 9.1 illustrates schematically strain against stress curves for rock (curve 1), concrete (curve 2), and hardened cement paste (curve 3) loaded in uniaxial compression.[1] The strains are longitudinal strains, i.e. strains measured in the direction of load application, and the stress is the average applied stress over the cross-section perpendicular to this direction. In most cases, rocks which are used as concrete aggregates exhibit a linear stress-strain relationship up to failure. At low stress level, the stress-strain curves for cement paste and concrete depart only slightly from linearity. At higher levels, however, both paste and concrete exhibit non-linear behaviour, particularly on approaching failure. Moreover, in tension, and also in compression when the concrete is loaded at a constant rate of strain, the increase in strain near failure is accompanied by a decrease in stress (Figure 9.2). The departure of the stress–strain curve from linearity is generally attributed to the development of cracking. Accordingly, the stress at which the curve departs from a straight line indicates the onset of cracking.[2]

The approximate maximum strains in compression for aggregate, paste, and concrete containing an aggregate which is stiffer than the paste, are 0.4 to 1.0%, 0.6 to 0.8%, and 0.1 to 0.25%, respectively.[1] The maximum strain in concrete depends on the aggregate concentration and decreases as the latter increases.[2]

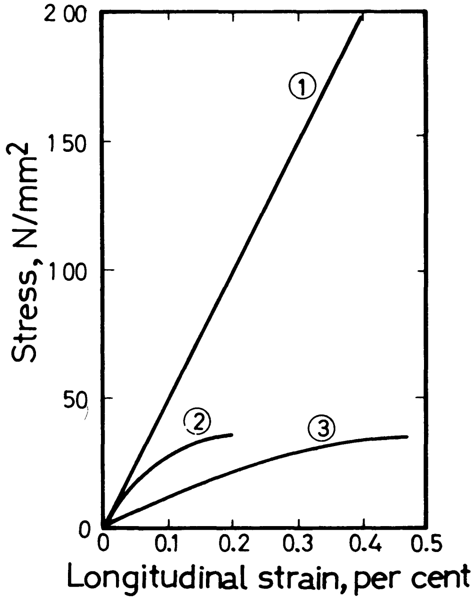

Figure 9.1 *Schematic stress against strain curves for* (1) *rock*, (2) *concrete, and* (3) *cement paste* (*after Hobbs*[1])

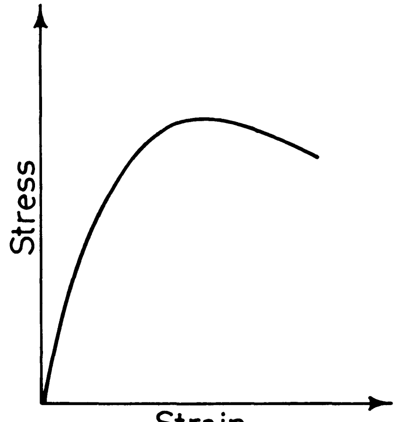

Figure* 9.2 *Schematic stress-strain curve for concrete loaded in tension or in compression at a constant rate of strain

The effect of aggregate concentration is demonstrated in Figure 9.3 in which longitudinal strains at 95% of the concrete failure stress in compression are plotted against aggregate volume concentration. The data in Figure 9.3 are for concretes and mortars made with different aggregates and with *W/C* ratios of 0.5 and 0.6. It seems that neither the type of aggregate nor the difference

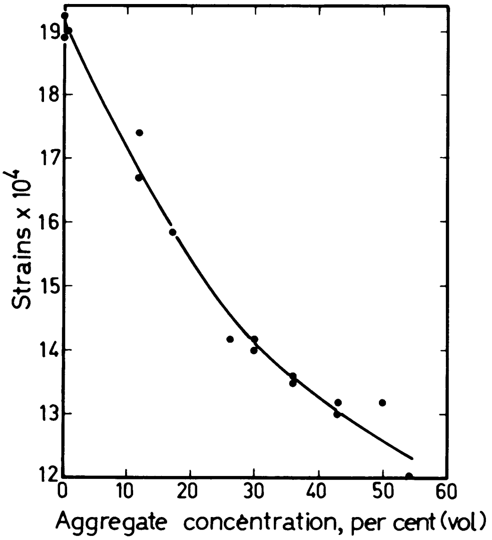

Figure 9.3 *Effect of aggregate volume concentration on compressive strain of concrete at* 95 *per cent of failure stress* (*after Kaplan*[2])

in W/C ratios in this range affect maximum strain.

The maximum strains in tension are much smaller than those in compression and vary from about 0.005 to 0.01%. Maximum strains in tension were also found to depend on the concentration of the aggregate in the concrete and to decrease with increase in the latter.[2] Also, the strains were found to be unrelated to the type of aggregate used and to the change in W/C ratio from 0.5 to 0.6. In another study, however, it was concluded that both tensile and compressive strains are affected by the modulus of elasticity of the aggregate and its particle size,[3] and that maximum strains decrease with increase in the modulus of elasticity and increase in particle size. These effects of aggregate concentration and modulus of elasticity on concrete strain are to be expected because both factors affect the modulus of elasticity of concrete.

9.3 Poisson's ratio

Longitudinal strain in the direction of the applied load is accompanied by strain at right angles to it, i.e. by lateral strain. Figure 9.4 presents the longitudinal and lateral strains in a concrete specimen, which was loaded to failure in compression, together with the associated volumetric strains.[4] Up to about 70% of the stress at failure, the rate of increase in the lateral strain equals that in the longitudinal strain. At higher stress levels, however, the lateral strain increases at a higher rate than the longitudinal strain. Also, near failure, the gradual contraction of the specimen is reversed and its volume begins to increase. This increase in volume is generally attributed to severe microcracking of the concrete and to

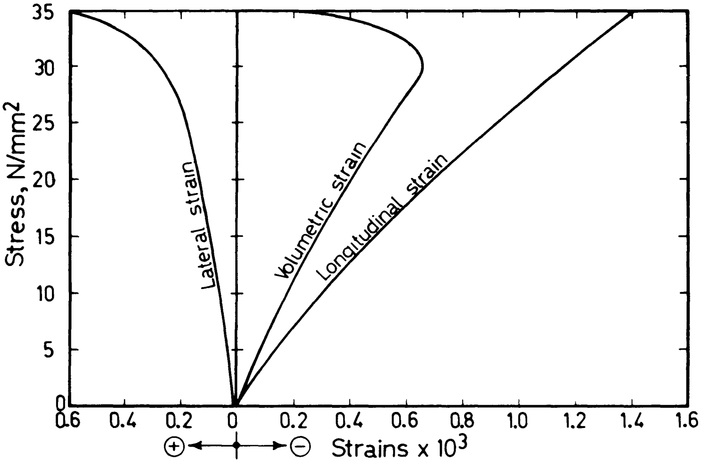

Figure 9.4 *Stress–strain curves for concrete prisms loaded to failure in compression (after Rüsch*[4]*)*

the extension of existing cracks at the aggregate–paste interface. The stress at the level when the concrete starts to expand is sometimes referred to as 'critical stress'.

Poisson's ratio is the ratio of lateral to longitudinal strains. It is evident, therefore, that the ratio will remain unchanged and independent of the stress level so long as the longitudinal and lateral strains increase at the same rate.

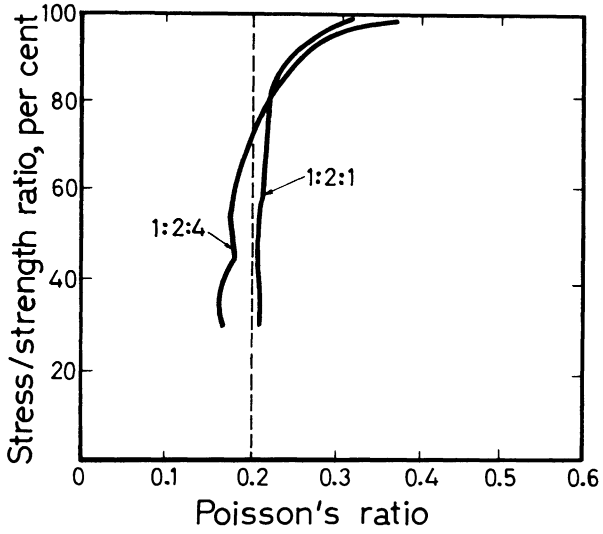

Figure 9.5 *Effect of stress-level on Poisson's ratio of concrete (after Shah and Chandra*[5]*)*

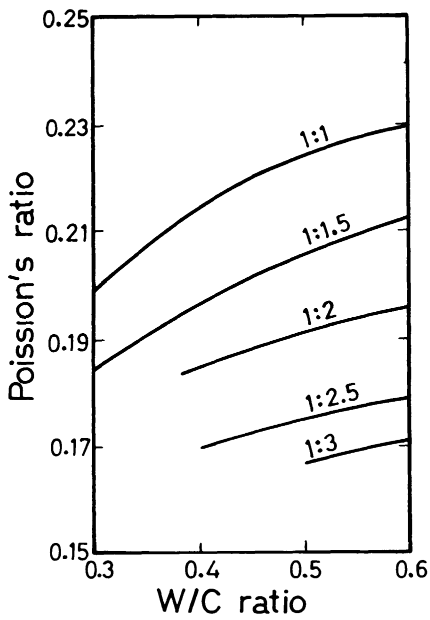

Figure 9.6 Effect of aggregate concentration and W/C ratio on Poisson's ratio of cement mortars (after Anson[7]). The figures against the curves are cement:sand ratios

However, when the lateral strain begins to increase at a greater rate than the longitudinal strain, Poisson's ratio will begin to increase with increase in the applied stress. This behaviour is shown in Figure 9.5, in which the increase in Poisson's ratio begins at about 80% of the stress at failure. Generally, this increase takes place at 70 to 90% of the stress at failure.

In discussing Poisson's ratio for the cement paste, it was stated that the ratio is not affected by *W/C* ratio, and that average values of 0.27 and 0.25 have been reported for dynamic[6] and static[7] determinations, respectively. The introduction of aggregate into the paste decreases these values due to its restraining effect on the lateral strain. The lower Poisson's ratio of the concrete can also be attributed, in part at least, to the presence of cracks and voids at the paste–aggregate interface. In any case the effect of the aggregate depends on its concentration, and Poisson's ratio decreases as the concentration of the aggregate increases. The effect of aggregate concentration was observed by Anson[7] and by Ishai[8] who tested cement mortars of different cement/sand and *W/C* ratios. Anson's data are presented in Figure 9.6, and seem to indicate that the *W/C* ratio also affects Poisson's ratio. Since the *W/C* ratio does not affect Poisson's ratio for cement pastes, it seems that in mortars the effect is through the influence of *W/C* ratio on the strength of the paste-aggregate bond. The decrease in *W/C* ratio increases bond strength, and thereby also increases the restraining effect of the aggregate on lateral strain. Hence, Poisson's ratio decreases with decrease in W/C ratio. On the other hand, the effect of the W/C ratio is rather small, particularly in the leaner mixes (Figure 9.6). Hence, the effect of the W/C ratio is generally neglected, and Poisson's ratio of concrete is assumed to be determined by Poisson's ratio of the paste and by concentration and elastic properties of the aggregate. Accordingly, Newman has suggested[9] that Poisson's ratio for concrete can be given by

$$\nu_c = \nu_p (1 - V_a)^n = \nu_p V_p^n$$

where ν_c and ν_p are Poisson's ratios for the concrete and the paste respectively, V_a and V_p are the fractional volumetric concentrations of aggregate and paste (i.e. $V_a + V_p = 1$), and n is a constant which depends on the specific test conditions. In Anson's tests, which are summarised in Figure 9.7, the calculated value of n was 0.42 for $\nu_p = 0.25$. It will be shown later that aggregate concentration has a similar effect on drying shrinkage of concrete.

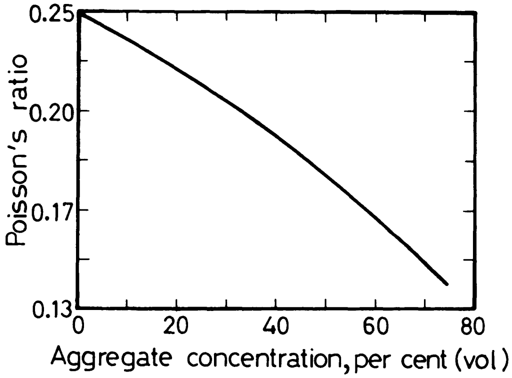

Figure 9.7 Effect of aggregate concentration on Poisson's ratio of mortars and concretes (after Newman[9] following Anson's tests[7])

9.4 Modulus of elasticity

Modulus of elasticity when determined from the stress-strain curve is known as the 'static' modulus of elasticity, and when determined by dynamic methods as the 'dynamic' modulus.

The modulus of elasticity, by definition, is the ratio of the stress to the corresponding elastic strain. As the stress-strain relationship for concrete is not linear, the modulus of elasticity of concrete is not constant and depends on the stress level at which it was determined. The modulus which is given by the stress/strain ratio, σ_x/ϵ_x, (i.e. the slope of OB in Figure 9.8) is known as the 'secant' modulus. Reference is sometimes made to the 'tangent' modulus of elasticity, which is the slope of the stress-strain curve at a given stress

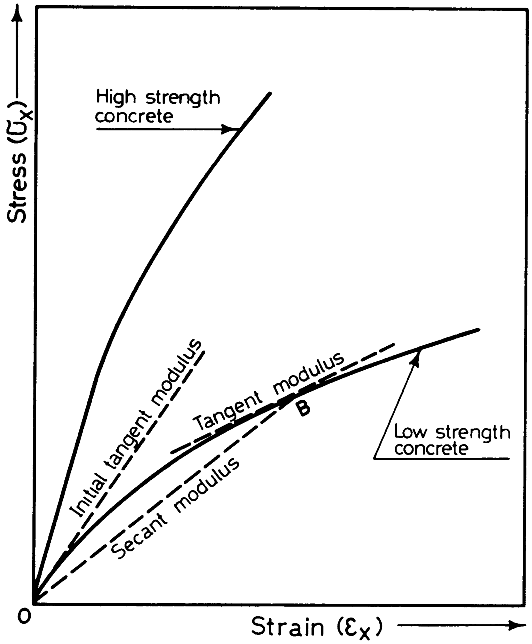

Figure 9.8 *Definitions of modulus of elasticity of concrete*

level, or to the 'initial tangent' modulus, which is the slope of the curve at the origin. Note that the initial tangent modulus gives the highest values, the tangent modulus the lowest ones, and the secant modulus intermediate values.

In determining the modulus of elasticity only elastic strains are considered, i.e. strains which appear and disappear completely immediately on loading and unloading respectively. In concrete under load, however, creep occurs and the departure of the stress against strain curve from linearity is partly attributable to this cause. Nevertheless, for short-time loading, and for stress levels not exceeding 30 to 40% of concrete ultimate strength, the stress-strain curve is approximately linear. Accordingly, it is generally assumed that for such stress levels the secant modulus remains unchanged, and that the strains measured immediately on loading are elastic strains only. Testing can be made under compression, tension, or flexure, and the resulting modulus varies accordingly. The modulus will also vary according to other test conditions.

9.4.1 *Effect of properties of the aggregate*

It was shown earlier that, with the exception of moisture content, all factors which affect the strength of the paste similarly affect its modulus of elasticity, which varies from 5 to 25 kN/mm^2.[9] The introduction of aggregate into the paste affects its modulus to an extent which depends on the concentration of the aggregate in the paste and the aggregate's stiffness. The modulus of elasticity of ordinary concrete, where the aggregate is stiffer than the paste, is greater than that of the paste and increases with increasing aggregate concentration and stiffness. When the paste is stiffer than the aggregate, the modulus of elasticity of the concrete is lower than that of the paste and decreases with increasing concentration of the aggregate.

A few models have been suggested for use in predicting concrete stiffness from the stiffness of the paste and of the aggregate, and from their volume concentrations. For this purpose, it is generally assumed that the concrete consists of two phases, aggregate particles and paste, or alternatively, coarse aggregate particles and mortar. It is further assumed that both the aggregate and the paste are elastic, an assumption which is generally true for the aggregate but not for the paste. The models also consider only aggregate stiffness and concentration, and disregard possible effects of other factors such as particle size, aggregate-paste bond, etc. Hence, the predicted modulus of elasticity cannot be the true modulus of the concrete. Nevertheless, the values predicted by some models are fairly close to actual test results.

Since the modulus of elasticity of the aggregate and of the paste are different, the stress and strain throughout the concrete will not be uniform, regardless of the exact mode of external loading.[3,9] The two simplest models, however, assume that either the stress or the strain is uniform. The Ruess model, for

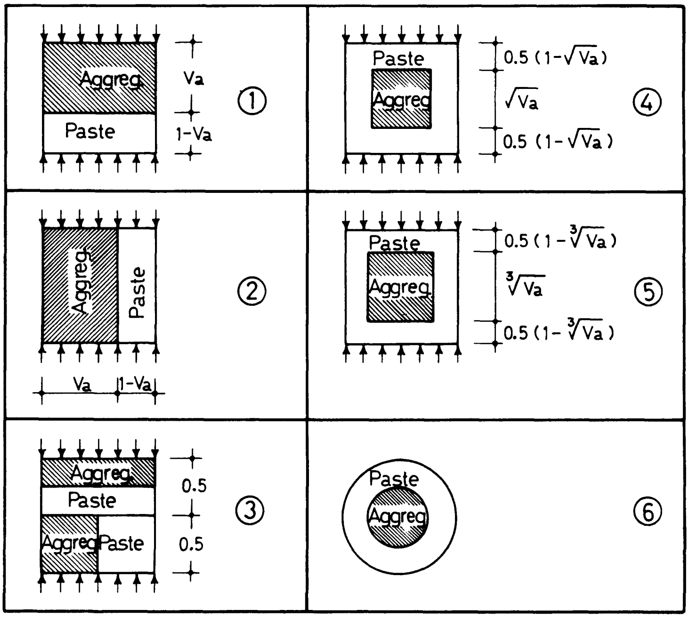

Figure 9.9 Models for predicting modulus of elasticity of concrete

example, assumes uniform stress distribution (model 1 in Figure 9.9). Equating the strain in a unit volume of concrete to the sum of the strains in the paste and the aggregate, the following equation is produced:

$$\frac{1}{E_c} = \frac{V_a}{E_a} + \frac{1 - V_a}{E_p} \tag{9.1}$$

where here, and throughout the following discussion, E_c, E_a, and E_p are the moduli of elasticity of concrete, aggregate, and paste, respectively, and V_a and V_p are the fractional volume concentrations (as well as the length and area concentrations) of the aggregate and the paste, respectively. Hence, by definition, $V_a + V_p = 1$.

The Voigt model (2 in Figure 9.9) assumes a uniform strain distribution in the concrete. Equating the load on a unit volume of concrete to the sum of the loads on the paste and aggregate, it can be shown that the modulus of elasticity of the concrete is given by

$$E_c = V_a E_a + (1 - V_a)E_p \tag{9.2}$$

The difference between Ruess' and Voigt's models is demonstrated in Figure 9.10,[15] from which it can be seen that the Voigt modulus (curve 2) is always

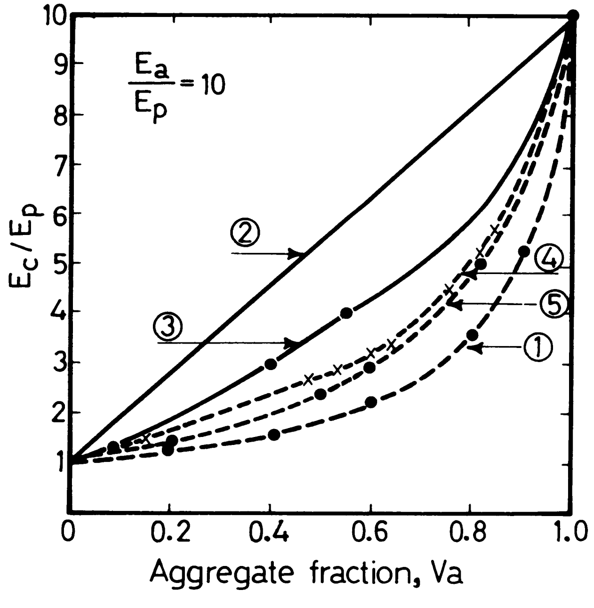

Figure 9.10 *Effect of aggregate concentration on modulus of elasticity of concrete (after various authors*[15]*).* (1) *Ruess' model (equation 9.1)*; (2) *Voigt's model (equation 9.2)*; (3) *Hirsch's model (equation 9.3)*; (4) *Counto's model (equation 9.4)*; (5) *Hobbs' model (equation 9.8)* greater than that of Ruess (curve 1). Hansen[13,14] found that Voigt's model better estimates the modulus of elasticity of lightweight-aggregate concrete and Ruess' model the modulus of ordinary concrete. The two models, however, represent boundary conditions, and the modulus of elasticity of concrete actually lies somewhere between the two estimates, i.e. between curves 1 and 2 of Figure 9.10. Moreover, in Ruess' model $E_c = 0$ when $E_a = 0$, i.e. it predicts that the modulus of elasticity of porous solids, regardless of pore content, will always be zero. This is obviously not correct.

To get a better estimate of the modulus, some other models have been suggested. Model 3 of Figure 9.9, for example, was suggested by Hirsch,[16] and is represented by the equation:

$$\frac{1}{E_c} = 0.5\left[\frac{V_a}{E_a} + \frac{1 - V_a}{E_p} + \frac{1}{V_a E_a + (1 - V_a)E_p}\right] \tag{9.3}$$

Hirsch's model is actually the geometric mean of Ruess' and Voigt's models. Again, this model predicts zero stiffness for porous solids, and apparently is not suitable for estimating the modulus of concretes made with soft aggregate.[17]

To overcome the deficiencies of the previous models, Counto[17] suggested a model in which the aggregate is represented by a cylinder (or prism) located at the centre of a concrete cylinder (or prism), with both cylinders having the same ratio of height to area of cross section (model 4, Figure 9.9). Assuming uniform loading, it can be shown that

$$\frac{1}{E_c} = \frac{1 - \sqrt{V_a}}{E_p} + \frac{1}{\dfrac{1 - \sqrt{V_a}}{\sqrt{V_a}}\,E_p + E_a} \tag{9.4}$$

Counto found that the estimates made with his model agree fairly well with experimental data. However, in many cases there is little difference between the estimates of Hirsch's model and those of Counto's.

A model proposed by Paul[18] represents the aggregate as a cube which is placed at the centre of a concrete cube (model 5, Figure 9.9). Assuming uniform boundary stress, the modulus of elasticity of concrete is given by

$$E_c = E_p\left[\frac{1 + (E_a/E_p - 1)V_a^{2/3}}{1 + (E_a/E_p - 1)(V_a^{2/3} - V_a)}\right] \tag{9.5}$$

Assuming a uniform boundary strain rather than stress in Paul's model, Ishai[19] showed that the modulus of elasticity of concrete is given by

$$E_c = E_p\left[1 + \frac{V_a}{(E_a/E_p)/(E_a/E_p - 1) - V_a^{1/3}}\right] \tag{9.6}$$

Ishai's model was found to give better agreement with experimental results than Counto's when epoxy resin composites containing a high concentration of quartz sand were compared. The better agreement was considered by Ishai to indicate that the physical basis of his model is more correct than that of Counto's model.

Another model was suggested by Hansen.[14] In this (model 6 in Figure 9.9) the aggregate is represented as a sphere at the centre of a sphere of concrete. The equation giving the bulk modulus for such a model was developed by Hashin.[20] Using Hashin's equation, and assuming that Poisson's ratios for the paste, aggregate, and concrete are the same and equal to 0.2, Hansen showed that

$$E_c = E_p \left[\frac{(1 - V_a)E_p + (1 + V_a)E_a}{(1 + V_a)E_p + (1 - V_a)E_a} \right] \tag{9.7}$$

Equation (9.7) applies only when there is a good bond between paste and aggregate, and it is recommended for use with lightweight-aggregate concrete, i.e. with concrete for which $E_p > E_a$. For ordinary concrete Hansen recommends the use of Ruess' equation [equation 9.1], and for mortars the one of Hirsch's [equation 9.3].

Finally, Hashin and Shtrikman[21] obtained upper and lower bounds for the bulk modulus of a two phase material. Assuming, again, that Poisson's ratios for the paste, aggregate, and concrete are the same and equal to 0.2, Hobbs[1] showed that the modulus of elasticity of concrete is given by

$$E_c = E_p \left[\frac{(E_a - E_p)V_a + (E_p + E_a)}{(E_p - E_a)V_a + (E_p + E_a)} \right] \tag{9.8}$$

It is a matter for debate which of the foregoing equations is basically more correct, and better represents therefore the actual behaviour of concrete. This question is outside the scope of the present discussion. It can be seen, however, that quantitatively (Figure 9.10), with the exception of Ruess' and Voigt's models, they all give fairly close estimates, though they are based on different assumptions. In any case, it may be concluded that the aggregate affects the modulus of elasticity of concrete, mainly through its stiffness and concentration. Generally, the modulus of elasticity of concrete increases with increase in modulus of the aggregate. In ordinary concrete, for which $E_a > E_p$, the modulus of the concrete also increases with increase in the concentration of aggregate. On the other hand, in lightweight-aggregate concrete, for which $E_a < E_p$, the modulus decreases with increasing concentration of the aggregate.

9.4.2 Effect of concrete strength

The use of the equations (9.1)-(9.8) to predict the modulus of elasticity of concrete is not very practical, since it requires a knowledge of the moduli of the paste and the aggregate. Consequently, in engineering practice, the modulus is estimated from the compressive strength of the concrete. The modulus of elasticity of the concrete depends on the modulus of the paste and the modulus of the paste is related to its strength (Figure 5.1). Hence, for essentially the same aggregates, it is to be expected that the modulus of elasticity of concrete, E_c will be related to its compressive strength, S. Indeed, such a relation exists, and has the general form

$$E_c = k\sqrt{S} \tag{9.9}$$

where k is a constant which depends on the specific conditions. In American practice (ACI Committee 318),[23] for example, where strength and modulus of elasticity are expressed in psi and S is the specified compressive strength of the concrete, k equals 57 000. In CEB recommendations,[24] where the strength and modulus are expressed in N/cm^2 and S is the average compressive strength of the concrete at the age considered, k = 66 000. CP 110, however, does not specify a value for k but recommends, in the absence of better information, the use of the values presented in Table 9.1.

Table 9.1 Moduli of elasticity of normal-weight concretes of various strengths (according to CP 110, Part 1, 1972)

Cube strength at the age considered, N/mm^2	*Static modulus of elasticity,* kN/mm^2	*Dynamic modulus of elasticity,* kN/mm^2
20	25	35
25	26	36
30	28	38
40	31	40
50	34	42
60	36	44

It was explained earlier that concrete strength is affected by the modulus of elasticity of the aggregate and its concentration. These factors, however, affect the modulus of the concrete to a greater extent than their corresponding effects on its strength. Hence, concrete made with soft aggregate will have a lower modulus of elasticity than concrete of the same strength made with harder aggregate. It can be seen from Figure 9.11[22] that, indeed, the modulus of elasticity of lightweight-aggregate concrete is only 35 to 65% of the modulus of normal-weight concrete. Hence, the above mentioned values of k, as well as the CP 110 values presented in Table 9.1, must be modified if lightweight aggregate concrete is used. In practice, this is usually done by incorporating into expression (9.9) the density of the concrete, ρ. Equation (9.9) then takes the form

$$E_c = k_1 \rho^{3/2} \sqrt{S} \tag{9.10}$$

Again, k_1 is a constant which depends on the specific test conditions. According to ACI Committee 318,[23] k = 33 when ρ is expressed in pounds per cubic foot, and S and E_c are in psi; and according to CEB recommendations,[24] where ρ is

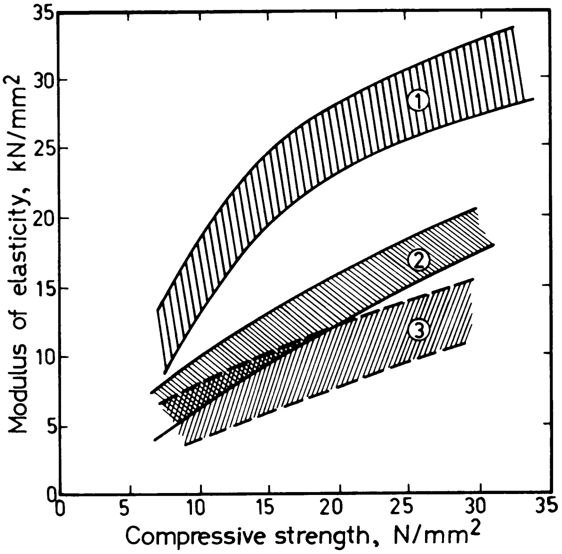

Figure 9.11 *Effect of stiffness of aggregate on modulus of elasticity of concrete (after Short and Kinniburgh*[22]*): (1) ordinary gravel concrete; (2) foamed slag concrete; (3) expanded clay concrete*

expressed in kg/m^3 and S and E_c are in N/cm^2, k = 18 000. According to CP 110 the values of Table 9.1 should be multiplied by $(D_c/2300)^2$ where D_c is the density of the lightweight-aggregate concrete in kg/m^3.

9.4.3 Determination of modulus of elasticity

9.4.3.1 Loading tests

As already mentioned, the modulus of elasticity which is determined from loading tests is known as the static modulus. Loading can be effected either in compression or flexure, and test results vary accordingly. Test procedures for determining the static modulus in compression are described in BS 1881 and ASTM C469. In both standards the secant modulus (the 'chord' modulus in the ASTM definition) is determined, i.e. the modulus which is given by the stress/strain ratio at a given stress level. In ASTM C469 the stress level is 40% of the ultimate strength of the concrete and in BS 1881 it is one third. The British Standard calls for repeated loading cycles until the difference in strain between consecutive readings at the specified stress level does not exceed 5%.

9.4.3.2 Electrodynamic determination

In this method the modulus of elasticity is determined by subjecting a concrete specimen to vibration at its natural (fundamental) frequency. Hence this method

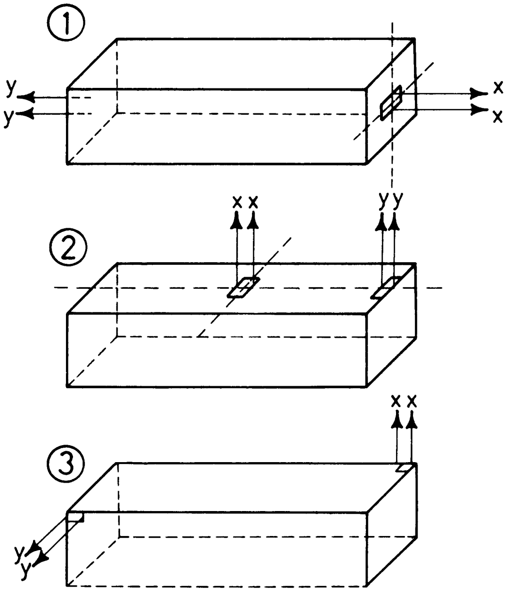

Figure 9.12 *Modes of vibration according to* ASTM C215. (1) *Longitudinal vibration*, (2) *transverse vibration, and* (3) *torsional vibration*

is known as the 'resonant frequency method' and the resulting modulus is commonly referred to as the 'resonance' or 'dynamic' modulus of elasticity. According to BS 1881, the test specimen should be a standard beam of 150 mm x 150 mm x 750 mm or 100 mm x 100 mm x 500 mm which is subjected to longitudinal vibration. The beam is clamped at its centre with an electromagnetic exciter placed against one end face of the specimen and a pick-up against the other (mode 1, Figure 9.12). The frequency of the excitation is varied until resonance is obtained at the fundamental frequency, n, of the specimen. The dynamic modulus of elasticity, E, expressed in MN/m^2, is then determined from the expression:

$$E = 4n^2 \ell^2 w \times 10^{-12}$$

where ℓ is the length of the specimen in mm and w is its density in kg/m^3.

In ASTM C215 three modes of vibration are described, longitudinal (mode 1 in Figure 9.12), transverse or flexural (mode 2), and torsional (mode 3). The natural longitudinal or transverse frequency, n, being known, the dynamic modulus of elasticity, E, can be calculated from the equation

$$E = CWn^2$$

where W is the weight of the test specimen and C is a constant which depends on the mode of vibration, the dimensions of the test specimen, and Poisson's ratio of the concrete.

Knowing the torsional fundamental frequency, n'', the dynamic modulus of rigidity (i.e. shear modulus of elasticity), G, can be obtained from

$$G = BW(n'')^2$$

where, again, W is the weight of the specimen and B is a constant which depends on essentially the same factors as the previous constant C. If G is known Poisson's ratio, ν, can be calculated from the equation

$$\nu = (2G/E) - 1.$$

Poisson's ratio determined by this method is known as the dynamic ratio.

In the dynamic determination of the modulus, the specimens are subjected to negligible stress. Hence, the dynamic modulus involves mostly elastic effects and the determination is virtually free of creep effects. Consequently, the dynamic modulus is greater than the secant (static) modulus (Table 9.1), with its value approaching that of the initial tangent modulus. The static/dynamic modulus ratio varies and increases with concrete strength as indicated in Figure 9.13.[26] It can be seen, however, that this effect of strength appears mainly in the low strength range and seems to disappear in concretes of strength greater than, say, 20 N/mm^2. In CP 110 the relation between the static, E_c, and the dynamic, E_d, moduli of elasticity, expressed in kN/mm^2, is given by the expression

$$E_c = 1.25\,E_d - 19$$

regardless of concrete compressive strength.

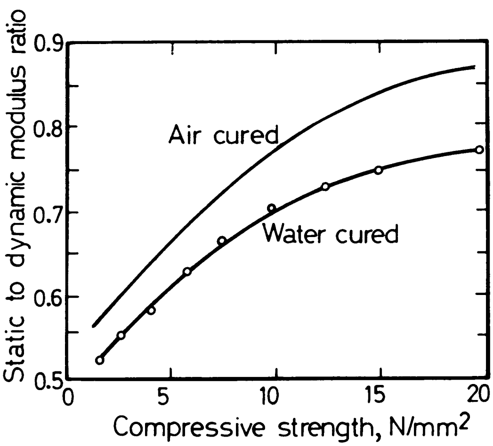

Figure 9.13 *Effect of compressive strength of concrete on static to dynamic moduli of elasticity ratio (after Takabyashi*[26]*)*

9.4.3.3 Ultrasonic pulse method

The modulus of elasticity of the concrete can also be determined from the velocity of propagation of a pulse of compressional waves, at ultrasonic frequency, through the concrete.[25] The modulus of elasticity determined by this method is known as the 'pulse' modulus. The pulse velocity can be determined, for example, by the method described in BS 4408: Part 5: 1974 or ASTM C597. The method consists essentially of measuring the time, T, taken by a pulse of waves to travel through the concrete and determining the pulse velocity, V, from the measured path-length, L, i.e. $V = T/L$. The modulus can be determined from the equation:

$$E = \rho V^2 \frac{(1+\nu)(1-2\nu)}{1-\nu}$$

where ρ is the density of the concrete and ν is its Poisson's ratio. This method of determination requires a knowledge of Poisson's ratio for the concrete. The ratio, however, is usually not known and an estimated value has to be used. Moreover, the test is sensitive to variations in moisture content of the concrete. Hence, the ultrasonic pulse method may give misleading results and at present, therefore, its practical use is limited.

In view of the general relationship between modulus of elasticity and strength, attempts have been made to relate the latter to pulse velocity. The relation between strength and pulse velocity, however, is much more complicated. Consequently, the value of this test for estimating concrete strength is rather limited. It can be put, however, to some use in detecting variations in concrete quality. Accordingly, it can be employed for quality control of concrete elements, particularly in the precast concrete industry.

9.5 Drying shrinkage

9.5.1 Effect of properties of the aggregate

Drying shrinkage of cement paste, which may involve length changes up to 5% is discussed in some detail in Chapter 5. The shrinkage of the aggregates normally used for concrete is much smaller than that of the paste. Accordingly, for a paste of given quality, the shrinkage of the concrete will decrease with increasing concentration of aggregate. As the aggregate restrains the shrinkage of the paste, the shrinkage of the concrete will also decrease with the stiffness of the aggregate.

The effect of aggregate concentration on shrinkage is shown in Figure 9.14.[27] In this figure the shrinkage of the concrete, which is related to that of the cement paste, is plotted against the concentration of aggregate which includes the unhydrated part of the cement. It can be seen that shrinkage of concrete may be only 20% of that of the cement paste.

The effect of aggregate stiffness on modulus of elasticity of concrete is indicated in an indirect way in Figure 9.15,[28] in which shrinkage is plotted against modulus of elasticity of the concrete. It is evident that the shrinkage depends on the modulus and decreases with increase in its value. The modulus of elasticity of concrete depends to a large extent on that of the aggregate. Hence,

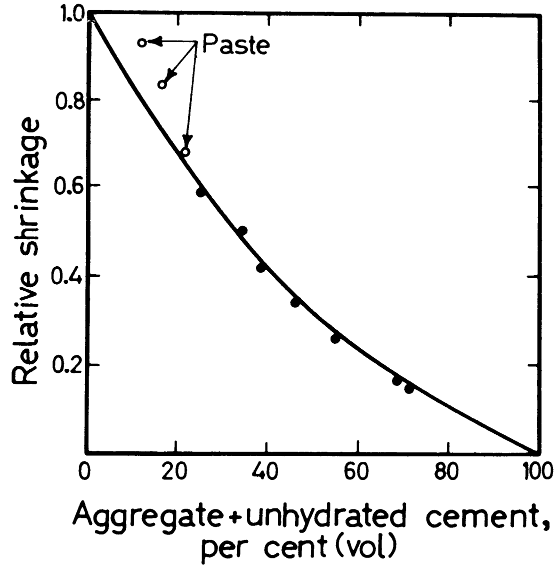

Figure 9.14 *Effect of aggregate concentration on shrinkage of concrete (after Powers*[27]*)*

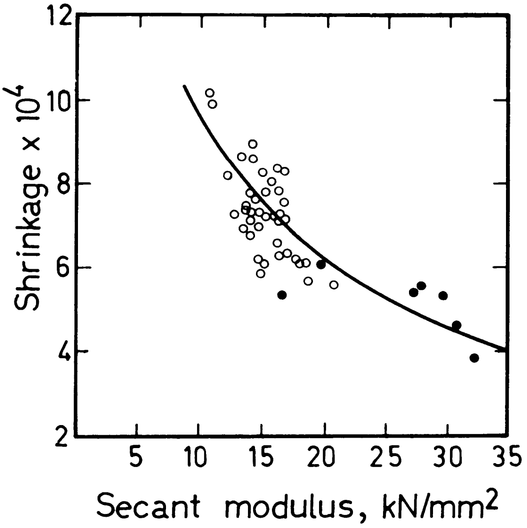

Figure 9.15 *Shrinkage of concrete plotted against its secant modulus of elasticity (after Reichard*[28]*)*: (●, normal-weight concrete; ○, lightweight-aggregate concrete) it can be expected that the shrinkage of concrete will also depend on the modulus of elasticity of the aggregate, and that the shrinkage of light weight-aggregate concrete will therefore be greater than that of otherwise similar normal-weight concrete. This conclusion is supported by the data of Figure 9.15 where the shrinkage of the lightweight-aggregate concrete is visibly greater than that of the normal-weight one.

This conclusion applies for concretes of equal *W/C* ratio and aggregate concentration. In practice, however, the comparison of concretes of equal strength is much more important. It was shown earlier (Figure 8.5) that the strength of lightweight-aggregate concrete is lower than that of normal-weight concrete with the same *W/C* ratio. Hence, to obtain the same strength, lightweight-aggregate concrete must be made with a lower *W/C* ratio than normal-weight concrete. The lower *W/C* ratio reduces the shrinkage of the cement paste and the resulting shrinkage of concrete made of such paste. On the other hand, the lower *W/C* ratio involves a higher cement content which, in turn, increases shrinkage of concrete. Apparently, the effect of the *W/C* ratio is greater than that of the increased cement content to such an extent that, in many cases, the shrinkage of lightweight-aggregate concrete roughly equals the shrinkage of normal-weight concrete of the same strength (Figure 9.16).

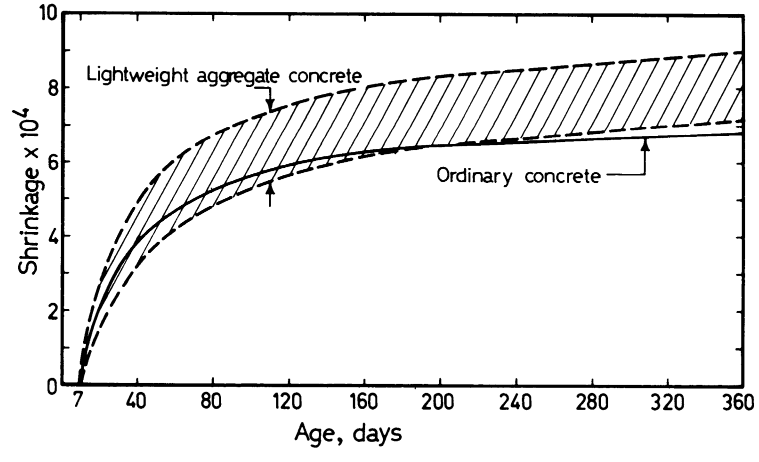

Figure 9.16 *Shrinkage of normal-weight and lightweight-aggregate concretes of equal strength (after Shideler*[29]*)*

The effect of aggregate stiffness and concentration on shrinkage of concrete was studied by Pickett, who considered the effect of a single, small, and non-shrinking aggregate particle on the shrinkage of concrete.[30] He assumed that the aggregate particle is a sphere which is located at the centre of the body of the concrete which is also a sphere, and that both the aggregate and the rest of the body are elastic. On the basis of these assumptions, a differential equation can be set up which describes the effect of the addition of any subsequent particle on the shrinkage of the concrete. Integration of the equation results in the following expression which relates shrinkage of concrete, S_c, to that of the paste, S_p, and to the concentration of the aggregate and its elastic properties:

$$S_c = S_p (1 - V_a)^n \tag{9.11}$$

where V_a is the fraction volume of the aggregate and n is given by the expression:

$$n = \frac{3(1 - \nu_c)}{1 + \nu_c + 2(1 - 2\nu_a)E_c/E_a} \tag{9.12}$$

where E_c and E_a are the moduli of elasticity of the concrete and the aggregate, respectively, and ν_c and ν_a are the respective Poisson's ratios. Hence, n represents the elastic properties of the aggregate relative to those of the concrete.

Logarithmic transformation of the equation (9.11) gives

$$\log (S_p/S_c) = n \log \left(\frac{1}{1 - V_a}\right)$$

in which n is the slope of the straight line describing a plot of $\log (S_p/S_c)$ against $\log 1/(1 - V_a)$. The data of Pickett are presented in Figure 9.17. The value of n in Pickett's tests was 1.7 while in others it varied from 1.2 to 1.7.[31] This difference n values is attributable to the difference in the elastic properties of the aggregates used, and probably also to creep effects.

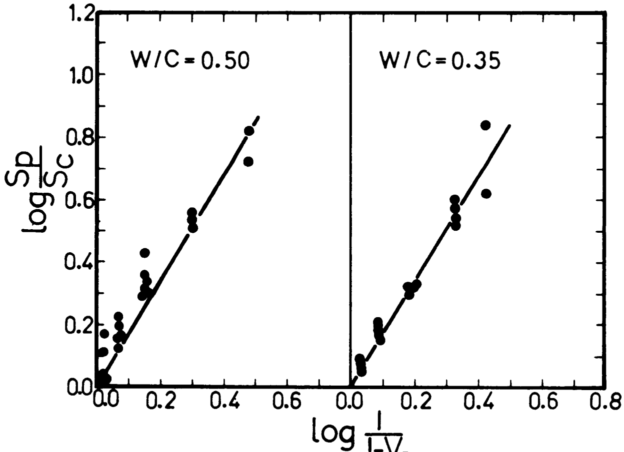

Figure 9.17 *Effect of aggregate concentration on the ratio of paste to concrete shrinkage (after Pickett*[30]*)*

9.5.2 Shrinkage-induced cracking

Shrinkage may cause cracking in concrete. In practice such cracking must be considered in most concrete applications because, under normal conditions, drying of the concrete is unavoidable, and when drying takes place shrinkage occurs. However, shrinkage-induced cracking can be reduced and even eliminated altogether.

In most engineering applications shrinkage is restrained. The restraining effect induces tensile stresses in the concrete, and if these stresses exceed concrete strength cracking takes place. Assuming elastic behaviour, the tensile stress, σ, which is induced when shrinkage is completely restrained is given by

$$\sigma = \epsilon_s E$$

where ϵ_s is shrinkage strain and E is the modulus elasticity of the concrete. For $E = 30\ \mathrm{kN/mm^2}$ and $\epsilon_s = 200 \times 10^{-6}$, the tensile stress in the concrete will be

$$\sigma = 30\,000 \times 2 \times 10^{-4}$$
$$= 6\ \mathrm{N/mm^2}$$

i.e. a stress level which is likely to be greater than concrete strength and which will therefore cause cracking. In practice the possibility of shrinkage-induced cracking is reduced due to creep effects which relieve some of the tensile stresses in the concrete. The effect of creep is schematically described in Figure 9.18. In this case, however, creep does not prevent cracking but merely delays its appearance from time t_1 to t_2. On the other hand, when the residual stress in the concrete remains lower than its tensile strength, cracking is eliminated altogether. In practice, both situations occur, and cracking may occur or not, according to the particular conditions.

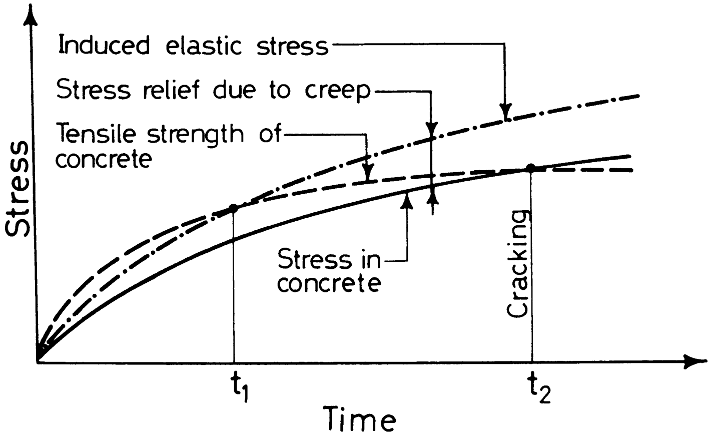

Figure 9.18 *Schematic description of shrinkage cracking*

Shrinkage-cracking may also be caused by differences in the rate of drying between the outer and inner parts of concrete members. Clearly, drying of the outer parts is more rapid than that of the inner parts. Consequently, the former tends to shrink more than the latter. The shrinkage of the outer parts is partly restrained, however, by the lower shrinkage of the inner parts. This restraining effect induces tensile stress in the outer parts which are balanced by compressive stress in the inner parts of the concrete member (Figure 9.19). The tensile stress is maximum at the surface, and may cause cracking if it exceeds concrete tensile strength.

The restraining effect of aggregate on shrinkage of concrete may result in internal cracking. As mentioned earlier, this cracking takes place mostly at the aggregate-paste interface, and plays an important role in the failure mechanism of concrete. It may be noted that in practice shrinkage is measured by the change in the bulk dimensions of concrete specimens. The occurrence of internal cracking implies that part of the shrinkage takes place inside the mass and is not reflected in the bulk dimensions of the specimen. The weaker the paste-aggregate bond, the greater the internal shrinkage at the expense of that reflected in the bulk dimensions. Hence, under otherwise similar conditions, shrinkage of concrete will increase with the increase in the strength of the paste-aggregate bond, and vice versa.

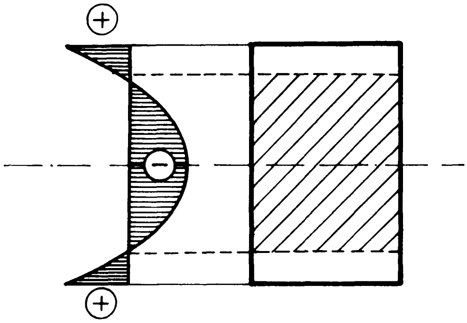

Figure 9.19 *Stress distribution in a concrete beam due to differential shrinkage*

Cracked concrete is, of course, an inferior concrete because it is weaker, more permeable, more susceptible to chemical attack and frost damage, and poorer at protecting the reinforcing steel against corrosion than uncracked concrete. In practice it is very important, therefore, to prevent cracking. As already mentioned, under normal conditions shrinkage cannot be avoided, and cracking therefore must be considered as a distinct possibility. Nevertheless, the likelihood of cracking can be reduced by taking the following measures.

1. Concrete mixes containing the lowest possible cement content should be used. Decrease in cement content means increase in that of the aggregate, thereby reducing shrinkage.
2. The concrete should be kept moist for as long as possible after casting. The shrinkage of the concrete is thereby delayed until a time when a higher strength has been reached. The higher the concrete strength, the lower the possibility of shrinkage-cracking.
3. Joints should be provided in concrete members to reduce the restraining effect of the structure on shrinkage. The lesser the restraint, the lower the induced tensile stresses in the concrete. Hence, the reduced possibility of shrinkage-cracking.

4. Shrinkage-compensating cement may be used. The setting of this cement is accompanied by expansion which, when restrained by friction, reinforcement, etc., induces compressive stresses in the hardened concrete. These compressive stresses compensate for the shrinkage induced tensile stresses, and thereby may prevent cracking. At present, the use of such cement is very limited.

9.5.3 Summary and quantitative estimate of shrinkage

The shrinkage of concrete is determined by shrinkage of the cement paste and by aggregate concentration and elastic properties. As shrinkage results from drying, all factors which affect the latter also affect shrinkage. Accordingly, higher shrinkage is to be expected with rise in ambient temperature, with decrease in relative humidity, with increase in the rate of air movement over the concrete, and with increase in the length of time for which concrete is subjected to drying. The effect of specimen geometry on shrinkage is sometimes represented by its 'theoretical thickness' which is defined as the area of the cross section of the concrete member divided by the semi-perimeter in contact with the atmosphere.[24] It follows that a higher ratio will be associated with a slower rate of drying. Hence, shrinkage will decrease with increase in the theoretical thickness (Figure 9.21C).

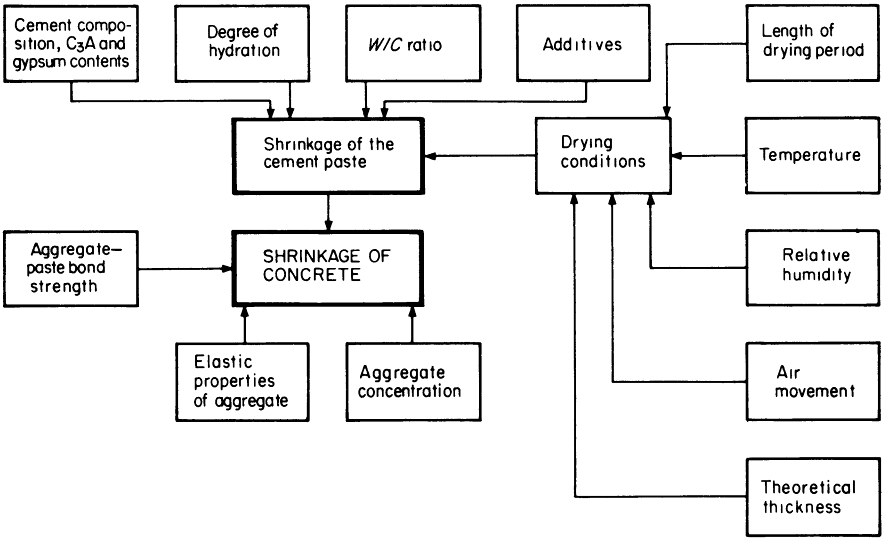

Figure 9.20 *Schematic representation of the factors affecting shrinkage*

In view of the many factors which affect shrinkage (Figure 9.20), it is difficult to calculate accurately an expected value for any given set of conditions. Nevertheless, in certain applications, such as in the design of prestressed concrete elements, shrinkage must be considered quantitatively, and to this end it can be estimated roughly from the curves recommended by the Comité Européen du

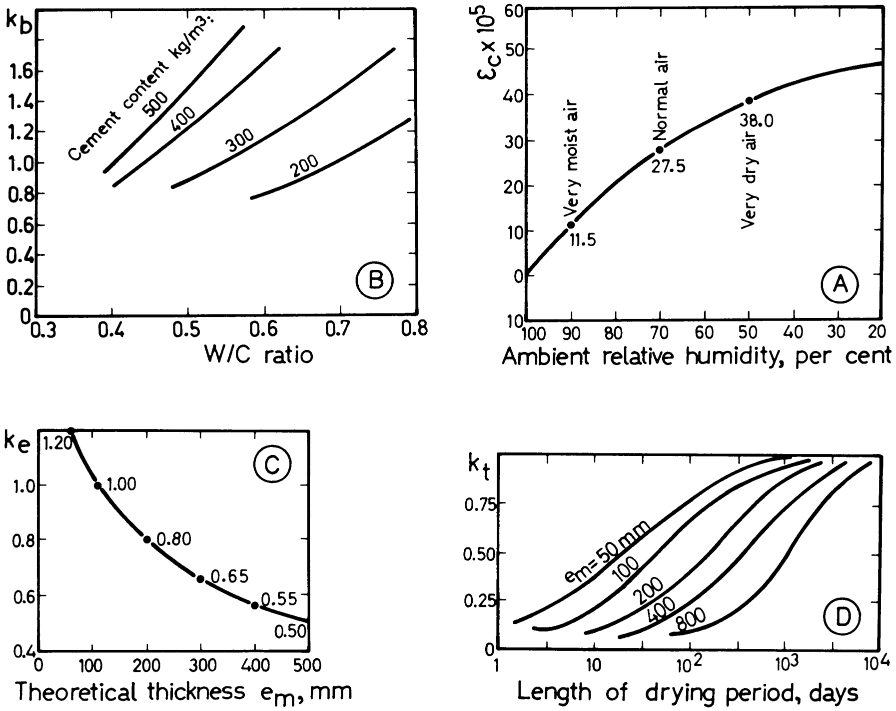

Figure 9.21 *Shrinkage coefficients* (*after CEB recommendations*[24])

Béton (CEB) (Figure 9.21). According to the CEB, shrinkage ϵ_r, at any given time t, is given by

$$\epsilon_r = \epsilon_c k_b k_e k_t k_p$$

in which ϵ_c is the estimated shrinkage with respect to the ambient relative humidity (section A of Figure 9.21) and k_b, k_e, k_t, and k_p are coefficients which allow for the composition of the concrete (section B), the geometry of the member (section C), the length of the drying period (section D), and the restraining effect of the reinforcing steel, respectively. The coefficient k_p is given by $k_p = 100/(100 + 20p)$ where p is the percentage of longitudinal reinforcement with respect to area A_c of the cross section of the concrete member i.e. $p = 100\,A_s/A_c$. Consider, for example, a 400 x 600 mm concrete column which is exposed to the atmosphere on its four sides. Assuming that the concrete is made with a W/C ratio of 0.65 and contains 300 kg cement per m^3, that the reinforcement constitutes 2%, and that the average ambient relative humidity is 65%, the CEB coefficients are (Figure 9.21).

$\epsilon_c = 31 \times 10^{-5}$ for 65% relative humidity (sectionA)
$k_b = 1.3$ for $W/C = 0.65$ and $C = 300$ kg/m^3 (section B)
$k_e = 0.75$ for $e_m = 400 \times 600/(400 + 600) = 240$ mm (section C)

$k_t = 1.0$ for $t = \infty$
$k_p = 100/(100 + 20 \times 2) = 0.7$,

and the estimated ultimate shrinkage will be

$$\begin{aligned}\epsilon_\infty &= 31 \times 10^{-5} \times 1.3 \times 0.75 \times 1.0 \times 0.7 \\ &\approx 20 \times 10^{-5}\end{aligned}$$

9.6 Creep

9.6.1 Effect of aggregate properties

The aggregates normally used in concrete mixes do not experience creep. Hence, the creep of concrete is determined by the creep of the cement paste and its concentration in the concrete. Accordingly, a higher creep is to be expected with an increase in paste content or, alternatively, with a decrease in aggregate concentration. This conclusion is confirmed by the data of Neville which are presented in Figure 9.22.[32]

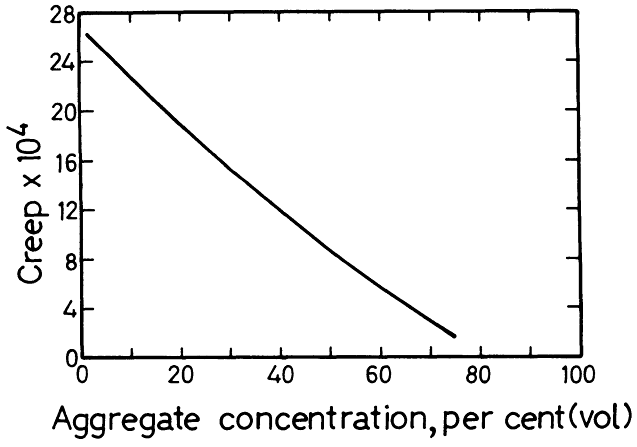

Figure 9.22 *Effect of aggregate concentration on creep of concrete (after Neville*[32]*). (Loading at the age of* 14 *days, creep after* 60 *days)*

As the aggregate does not experience creep, its presence restrains creep of the paste to an extent which depends on aggregate stiffness. Hence, for the same *W/C* ratio and aggregate concentration, concretes made with soft aggregate will exhibit higher creep than those made with hard aggregate. It can be seen from Figure 9.23 that creep of lightweight-aggregate concrete is higher than that of ordinary concrete of the same *W/C* ratio. The lower creep of the latter is attributable to the greater stiffness of ordinary aggregate as compared with that of lightweight-aggregate.

On the other hand, the creep of lightweight and normal-weight concretes are

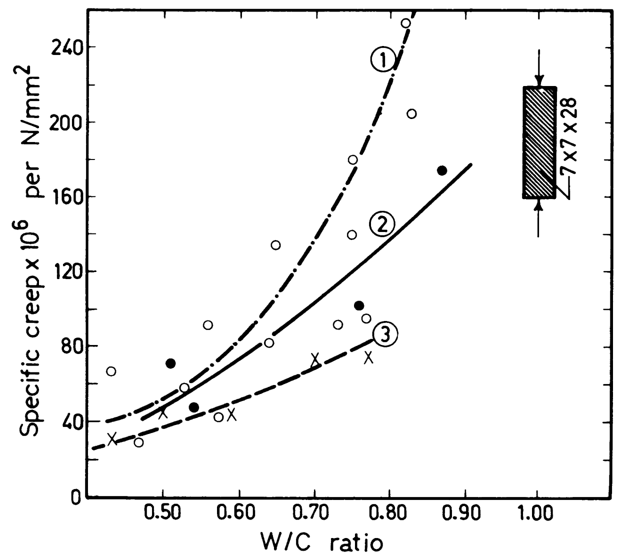

Figure 9.23 *Creep of concretes made with lightweight and normal-weight aggregates (after Soroka and Jaegermann*[33]*). (1) Air-entrained lightweight aggregate concrete made with crushed scoria; (2) as (1) but with no air entrainment; (3) normal-weight concrete*

essentially the same when concretes of equal strength are compared (Figure 9.24). The strength of lightweight-aggregate concrete is lower than that of normal-weight concrete of the same *W/C* ratio. Hence, to obtain the same strength, lightweight-aggregate concrete must be made with a paste of lower *W/C* ratio than normal-weight concrete. The lower *W/C* ratio reduces the creep of the paste and the resulting creep of the concrete as a whole. On the other hand, the lower *W/C* ratio involves a higher paste content at the expense of the aggregate, and the creep of the concrete will therefore be increased. Apparently, the reducing effect of the *W/C* ratio is greater than the opposite effect of the increased cement content. Hence, essentially the same creep is exhibited by lightweight and normal-weight concretes which are of the same strength. This conclusion is further confirmed in Figure 9.25 which compares the creep of lightweight-aggregate concretes with that of ordinary concrete of the same compressive strength, 21 N/mm^2.[29] The creep of the lightweight-aggregate concretes varied over a wide range. Nevertheless, similar variations were also observed in normal-weight concretes made with different aggregates.[34] Accordingly, it may again be concluded that both types of concrete exhibit approximately the same degree of creep provided that the two are compared on the basis of equal strength.

The similarity in the effects of aggregate on shrinkage and on creep is clearly evident. Consequently, Neville[32] suggested that creep of concrete can be expressed by an equation analogous to that suggested by Pickett for shrinkage of concrete,

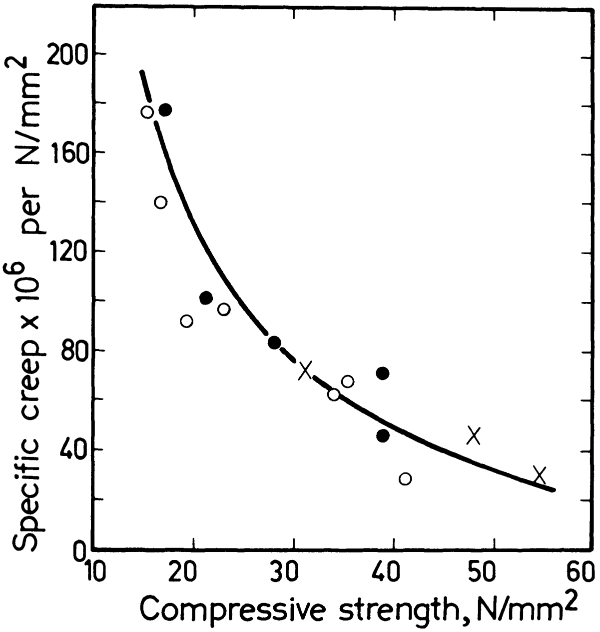

Figure 9.24 *Creep of concretes made with lightweight and normal-weight aggregates* (*after Soroka and Jaegermann*[33]). ●, *air-entrained lightweight aggregate concrete made with crushed scoria;* ○, *as* (1) *but with no air-entrainment;* ×, *normal-weight concrete*

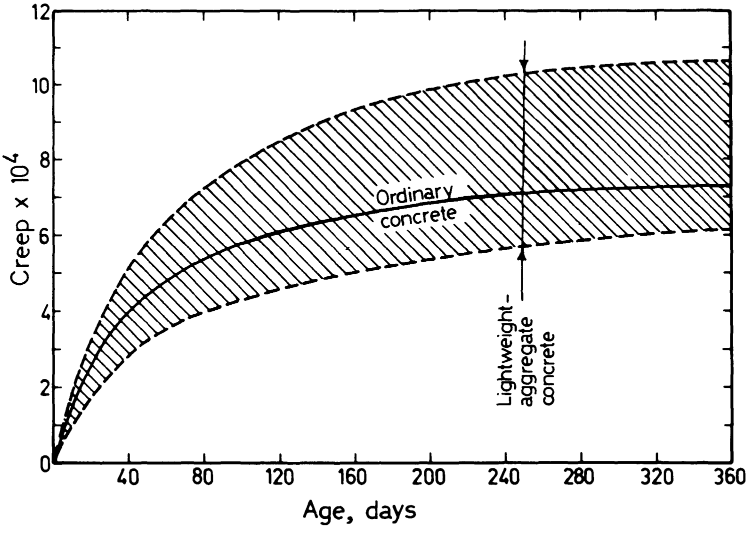

Figure 9.25 *Creep of lightweight and normal-weight aggregate concretes of equal strength* (21 N/mm²) (*after Shideler*[29])

$$c = c_p (1 - V_a)^n$$

where c and c_p are the creep of the concrete and the paste, respectively, and V_a is the volume fraction of the aggregate. n depends on the elastic properties of the aggregate, and is given by

$$n = \frac{3(1 - \nu_c)}{1 + \nu_c + 2(1 - 2\nu_a)E_c/E_a}$$

where E_c and E_a are the moduli of elasticity of the concrete and the aggregate, respectively, and ν_c and ν_a are the Poisson's ratios. In Neville's tests the value of n varied from 1.8 to 2.0.[32]

Apparently, the grading of the aggregate, its particle size and shape, do not affect creep. A considerable variation was observed in the creep of concretes made with different aggregates.[24] This difference may be attributed to differences in their stiffness and perhaps, also to creep effects in some of the aggregates used.

9.6.2 Quantitative estimates

A considerable number of expressions has been suggested to predict creep. In developing these expressions, it is generally assumed that creep is directly proportional to the stress/strength ratio at least up to, say, 35% of the ultimate strength of the concrete. It is also assumed that the superposition concept is applicable to creep strains, i.e. that creep strains at the time t, caused by subjecting the concrete to a certain stress at time t_0, are independent of the stress applied before or after t_0. Accordingly, the specific creep, c, can be related to the length of loading time, t, by various expressions some of which are listed below:

(1) Shank[35] $c = at^{1/b}$
(2) Ross[36] $c = t/(a + bt)$
(3) Lorman[37] $c = mt/(n + t)$
(4) McHenry[38] $c = [a + \beta \exp(pt_0)]\ [1 - \exp(nt)]$
(5) Wittmann and Setzer[39]
  (i) for basic creep strains, ϵ_0 (σ is the stress in concrete due to external load): $\epsilon_0 = at^n \sinh(b\sigma)$
  (ii) for total creep strains, ϵ_c (σ_s is the stress in concrete due to shrinkage): $\epsilon_c = at^n \sinh[b(\sigma + \sigma_s)]$

where a, b, β, m, n, and r are constants which depend on concrete properties and environmental factors.

Some of these expressions, as well as that of Jones *et al.*[40] and the CEB recommendations,[24] were compared by Neville and Meyers.[41] Such a comparison is shown in Figure 9.26. It can be seen that, except for Jones' expression, the equations agree reasonably well with experimental data. However, the practical value of the foregoing expressions is rather limited because their use

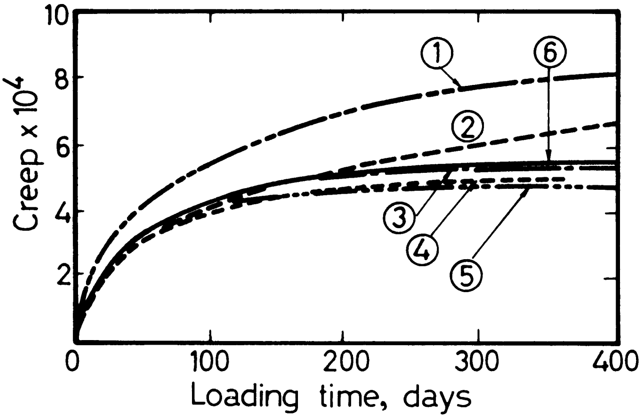

Figure 9.26 *Comparison of some expressions for predicting creep (after Neville and Meyers*[41]*): (1) after Jones; (2) after Shank; (3) after Ross; (4) after CEB; (5) after Lorman; (6) actual test data*

requires knowledge of the various constants for the particular conditions. The comparison in Figure 9.26 is based on measured creep for up to 100 days under loading. In practice such long preliminary testing is impractical, and the values of the relevant constants are therefore not available. Hence for engineering purposes, simpler methods are usually employed, such as the one recommended by CEB.[24] In this method creep strain ϵ_f, is related to the elastic strain on loading by the following expression (σ is the stress in the concrete and E_c its modulus of elasticity):

$$\epsilon_f = \frac{\sigma}{E_c} k_c k_d k_b k_e k_t$$

where k_c is a factor which depends on environmental conditions (section A, Figure 9.27), k_d on concrete age (i.e. strength) at the time of loading (section B), k_b on the composition of the concrete, k_e on the theoretical thickness, e_m, of the member (i.e. the cross-section area divided by the semi-perimeter in contact with the atmosphere) (section D), and k_t on the period of time for which the concrete is loaded. Consider, for example, a 400 x 400 concrete column exposed to the atmosphere on four sides, i.e. e_m = 400 x 400/2 x 400 = 200 mm. Assuming a W/C ratio of 0.65 and a cement content of 300 kg/m^3, the ultimate creep of the column, subjected to a stress of 6 N/mm^2 at the age of 28 days, will be:

$$\epsilon_f = \frac{6}{30 \times 10^3} 2.7 \times 1.0 \times 1.3 \times 0.85 \times 1.0$$
$$= 6 \times 10^{-4}$$

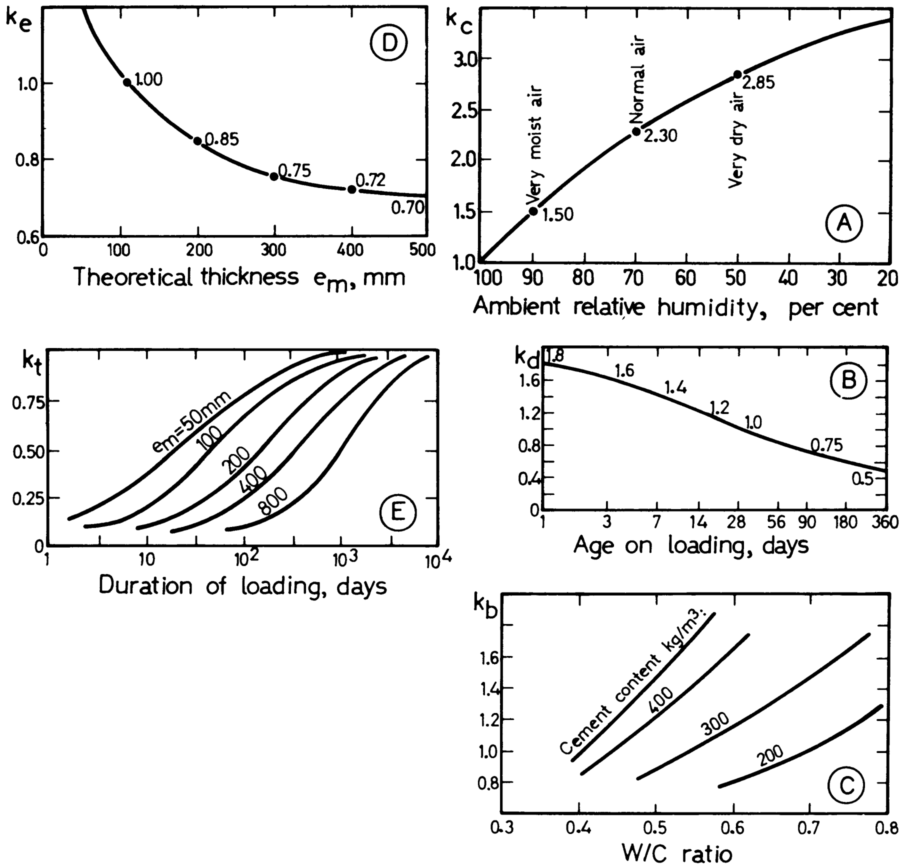

Figure 9.27 *Prediction of creep from CEB recommendations*[24]

if $E_c = 30\ \text{kN/mm}^2$ and the average ambient humidity is 65%. Again, in view of the many factors which affect creep, this result must be regarded as a rough estimate. In many cases, however, this estimate may be sufficiently accurate for use in the design of reinforced concrete structures.

9.6.3 Summary and concluding remarks

Creep of concrete is determined by the creep of the cement paste, the stiffness of the aggregate, and its concentration in the concrete. The creep of concrete increases with increase in the creep of the paste and its content, and decreases with increase in the stiffness of the aggregate. Accordingly, creep of concrete, c, can be expressed as

$$c = c_p (1 - V_a)^n$$

where c_p is the creep of the paste, V_a is the volumetric content of the aggregate per unit volume of concrete, and n is a constant which depends on the elastic properties of the aggregate. In ordinary concrete n varies from 1.8 to 2.0.

Various expressions have been suggested to predict creep with time. These expressions are of limited practical use because they include constants which depend on the specific conditions being considered. A rough estimate of creep, however, can be made by the method recommended by CEB. This is summarised in Figure 9.27.

9.7 Volume changes due to thermal expansion

The coefficient of thermal expansion of cement paste depends on its moisture content,[43] and varies from 11 to 20 x 10^{-6} per °C.[42] The coefficient of thermal expansion of aggregates is usually lower and varies, in most cases, from 5 to 13 x 10^{-6} per °C. Hence, the coefficient of concrete will decrease with increase in concentration of the aggregate. This is clearly confirmed by the data of Table 9.2.[44]

Table 9.2 Effect of aggregate concentration on the coefficient of thermal expansion of concrete (after Meyers[44])

Cement: Aggregate (wt)	*Coefficient of thermal expansion* x 10^{-6} *per* °C
Neat paste	18.5
1:1	13.5
1:3	11.2
1:6	10.1

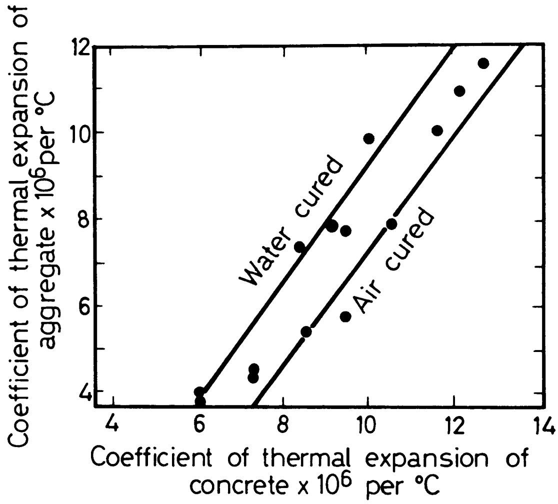

Figure 9.28 *Coefficient of thermal expansion of concrete plotted against the coefficient of the aggregate (after Bonnell and Harper[45])*

It is to be expected that the coefficient of thermal expansion of concrete will decrease with decrease in aggregate coefficient. This conclusion is clearly shown in Figure 9.28, which also indicates that curing conditions affect the coefficient of thermal expansion. For a particular aggregate, the coefficient is lower in concrete cured in water. This result agrees with the observation made elsewhere[43] that the coefficient of thermal expansion decreases with increasing concrete age, i.e. with degree of hydration. Curing in water produces a higher degree of hydration accounting, therefore, for the lower coefficient of the water-cured concrete.

From Figure 9.28 it may be noted that the coefficient of thermal expansion of air-cured concrete varies from 6 to 13 x 10^{-6} per °C. In engineering practice an average value of 10^{-5} per °C is usually adopted.

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10 Durability of concrete

10.1 Introduction

The ability of concrete to withstand the damaging effects of the environment and of its service conditions without deterioration for a long period of time is referred to as its 'durability'. Clearly the durability of concrete is of prime importance in engineering applications, and it is not surprising therefore that this subject has been widely discussed in a number of publications.[1–5]

Chemical corrosion of cement paste due to attack of soft and acidic waters, sulphate solutions, and sea water, was discussed in Chapter 6. Physical factors such as fire, frost, and abrasion, may also damage concrete and bring about its deterioration. The extent of such damage depends on the particular agent involved, on the one hand, and on the quality of the concrete, on the other. In this respect, the density of the concrete is of particular importance and sometimes also the properties of its constituents. As a rule the durability of concrete is improved with increase in its density. Nevertheless, high density alone is not always sufficient to give the concrete the required durability, and in some cases the use of special materials must be considered. For example, the use of sulphate resisting cement in concrete intended for use in sulphate-bearing soils, or the use of hard aggregate in concrete exposed to abrasion. Under very severe conditions, such as prevail when concrete is exposed to highly acidic solutions or to soils of a high sulphate concentration, even the use of special materials and dense concrete may be insufficient to provide the required durability. Consequently, under these conditions the concrete must be protected by suitable coatings to prevent direct contact between the concrete and the aggressive agent.

In the following discussion the more common agents which may damage concrete are considered together with suitable means which can be employed to reduce or prevent such damage. For convenience and for the sake of simplicity, these factors are dealt with separately. In practice, however, concrete may be subject to the effect of two or more factors, and the treatment of practical problems may therefore require consideration of the combined effect.

10.2 Concrete in ground-water or soils containing sulphate salts

In Chapter 6 it was stated that sulphates attack severely the hardened cement paste, and the chemical reactions and the expansion mechanisms involved were also presented.

The intensity of sulphate attack depends on many factors. Generally, however, damage caused by sulphate attack may be very severe, and under extreme conditions may involve complete deterioration of the concrete. In nature, considerable quantities of sulphates are often present in soils and in ground-water. Sulphates are also present in sea water. The comparatively wide occurrence of sulphates, on the one hand, and the severe damage which they may cause to the concrete, on the other, explain the practical importance of this type of attack. Accordingly, the performance of concrete subjected to sulphate attack has been widely studied and reported.[5-7] The main findings of these studies are presented in the following discussion.

10.2.1 Classification of aggressiveness

As mentioned earlier, many factors affect the intensity of sulphate attack and the concentration of sulphates in the soil or in the water which is in contact with the exposed concrete is of particular importance. Nevertheless, the intensity of the attack also depends on the type of sulphate involved; magnesium sulphate, for example, is more aggressive than, say, gypsum. The presence of other ions in the sulphate solution also affects the intensity of the attack. Also, the nature of the contact between the sulphates and the concrete is an important factor, and more intensive attack takes place on concrete which is exposed to alternate cycles of wetting and drying, i.e. in marine structures at water level or in underground structures at ground-water level. Accordingly, less corrosion takes place in concretes which are fully and continuously submerged in the aggressive water or when the sulphate-bearing soil is dry. In fact, no attack is to be expected in completely dry soils, though such conditions hardly exist. In practice, however, it is very difficult to consider all the factors involved. Consequently, in most cases, the expected intensity of sulphate attack is related solely to the sulphate concentration, and the means for combating such an attack are specified accordingly. CP 110 requirements for concrete exposed to sulphate attack are given in Table 10.1 and, in line with the previous discussion, these requirements are related only to sulphate concentration in the soil or in the ground-water. Similarly, in the USA the aggressiveness of soils and ground-water is classified only in terms of sulphate concentration (Table 10.2).[8] Again, in view of the many factors involved, these classifications should be regarded as guidelines which, in practice, must be examined in relation to the particular conditions.

Table 10.1 Requirements for concrete exposed to sulphate attack (after CP 110*)*

Class	*Concentration of sulphates expressed as* SO_3			*Type of cement*	*Requirements for dense, fully compacted concrete made with aggregates complying with the requirements of* BS 882 *or* BS 1047			
	In soil				*Nominal maximum size of aggregate* (mm)			*Maximum free water/cement ratio*
	Total SO_3, %	SO_3 in 2:1 water extract, g/litre	In ground water, parts per 100 000		40	20	10	
					Minimum cement content, kg/m^3			
1	less than 0.2	–	less than 30	Ordinary Portland or Portland-blastfurnace	240	280	330	0.55
2	0.2 to 0.5	–	30 to 120	Ordinary Portland or Portland-blastfurnace	290	330	380	0.50
				Sulphate resisting Portland	240	280	330	0.55
				Supersulphated	270	310	360	0.50
3	0.5 to 1.0	1.9 to 3.1	120 to 250	Sulphate resisting Portland or supersulphated	290	330	380	0.50

				High alumina	290	330	380	0.45
4	1.0 to 2.0	3.1 to 5.6	250 to 500	Sulphate resisting Portland or supersulphated	330	370	420	0.45
				High alumina	300	340	410	0.40
5	over 2	over 5.6	over 500	Sulphate resisting Portland or supersulphated plus adequate protective coating	330	370	420	0.45
				High alumina	330	370	420	0.35

This table applies only to concrete made with aggregates complying with the requirements of BS 882 or BS 1047 placed in near-neutral groundwaters of pH 6 to pH 9, containing naturally occurring sulphates but not contaminants such as ammonium salts. Concrete prepared from ordinary or sulphate resisting Portland cement would not be recommended in acidic conditions (pH 6 or less). High alumina cement can be used down to pH 4.0 and supersulphated cement has given an acceptable life, provided that the concrete is dense and prepared with a free water/cement ratio of 0.40 or less, in mineral acids down to pH 3.5.

The cement contents given in Class 2 are the minima recommended by the manufacturers. For SO_3 contents near the upper limit of Class 2 cement contents above these minima are advised.

Where the total SO_3 in column 2 exceeds 0.5% then a 2:1 water extract may result in a lower site classification if much of the sulphate is present as low solubility calcium sulphate. Reference should be made to BRS Digest 90, 1970.

For severe conditions, e.g. thin sections, sections under hydrostatic pressure on one side only and sections partly immersed, consideration should be given to a further reduction of water/cement ratio and, if necessary, an increase in cement content to ensure the degree of workability needed for full compaction and thus minimum permeability.

Table 10.2 Effect of sulphate concentration on aggressiveness of water and soils (after US Bureau of Reclamation[8])

Relative degree of sulphate attack	*Percentage of water-soluble sulphates (expressed as SO_3) in soil samples*	*Sulphates in water expressed as SO_3, parts per 100 000*
Negligible	Less than 0.08	Less than 12.5
Positive*	0.08-0.17	12.5-125
Severe†	0.17-1.67	125-830
Very severe‡	More than 1.67	More than 830

*Use moderate sulphate resisting cement (type II). †Use sulphate resisting cement (type V) or approved Portland-pozzolana cement providing comparable sulphate resistance when used in concrete. ‡Use sulphate resisting cement (type V) plus approved pozzolana which has been determined by tests to improve sulphate resistance when used in concrete with type V cement.

10.2.2 Factors affecting sulphate resistance

It has been mentioned previously that the susceptibility of Portland cement to sulphate attack is determined to a considerable extent by its C_3A content, and the use of sulphate resisting cement (i.e. cement low in C_3A) improves sulphate resisting properties of concrete (Figure 7.7). This conclusion is further confirmed in Figure 10.1, which presents data from exposure tests which were carried out on concrete beams made with different cements and mix proportions. The intensity of sulphate attack is expressed in Figure 10.1 as rate of deterioration (per cent per year), and it is evident that this rate decreases with decrease in the C_3A content of the cement.

It is also evident from Figure 10.1 that the cement content of concrete significantly affects its sulphate resisting properties and that, regardless of the C_3A content, the rate of deterioration decreases with increase in cement content. For example, the rate of deterioration of concretes containing 390 kg/m^3 of type IV or V cements was found to be approximately 2% per year, increasing to about 40% for a cement content of 225 kg/m^3. On the other hand, a high cement content of 390 kg/m^3 results in a low rate of deterioration even in concretes made from cements high in C_3A (i.e. types I and III). In other words, to produce sulphate resistant concrete, the use of sulphate resisting cement must be combined with a certain minimum cement content. This conclusion is reflected in CP 110 recommendations (Table 10.1), which also specify such a minimum. This minimum varies, according to exposure conditions and maximum size of aggregate particles, from 240 to 420 kg/m^3.

The cement content affects sulphate resisting properties of concrete mainly through its effect on the *W/C* ratio. Under otherwise similar conditions an increase in cement content reduces the *W/C* ratio. Consequently, the density of the concrete is increased and its sulphate resisting properties are improved. This effect of the *W/C* ratio is shown in Figure 10.2, which is based on data from

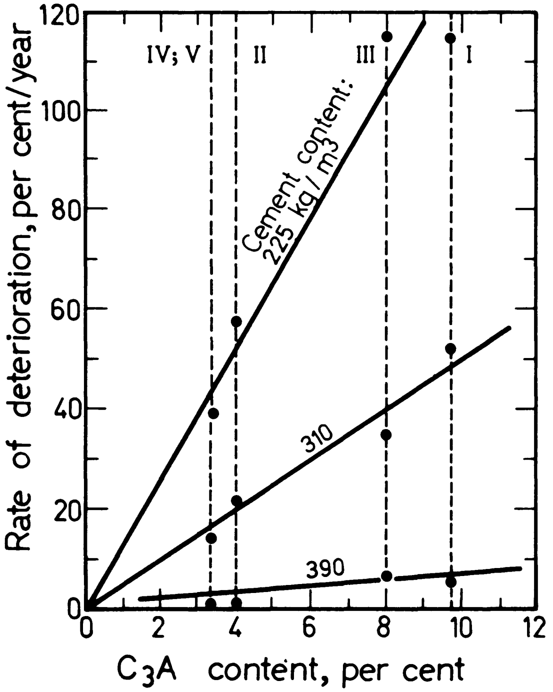

Figure 10.1 *Effect of* C_3A *content of different cements on rate of deterioration of concrete exposed to sulphate-bearing soils (after Verbeck*[9]*)*

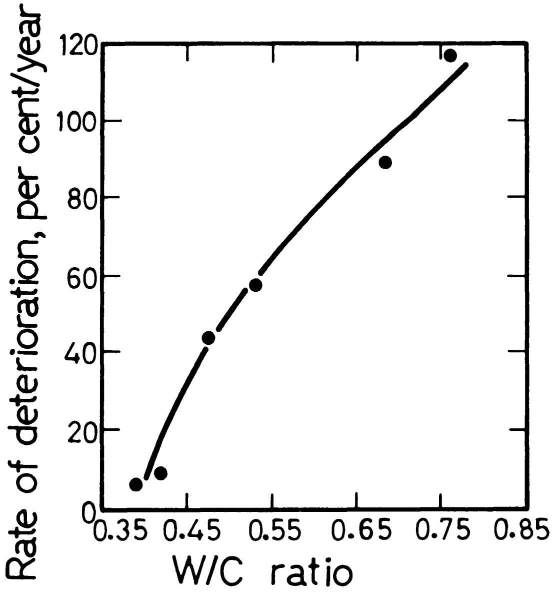

Figure 10.2 *Effect of W/C ratio on rate of deterioration of concrete exposed to sulphate-bearing soils (after Verbeck*[9]*)* exposure tests[9] for beams made from ordinary Portland cement. If the cement content does affect the sulphate resistance of concrete through its effect on the *W/C* ratio, then the required quality of the concrete can be specified in terms of a maximum *W/C* ratio rather than of a minimum cement content. Such an approach was adopted by ACI Committee 211[10] which specifies a maximum *W/C* ratio of 0.40–0.45 for concretes made of ordinary Portland cement and 0.45–0.50 for those made of sulphate resisting Portland cement. It may be noted that CP 110 specifies both minimum cement content and maximum *W/C* ratio, and that the specified values of the *W/C* ratio of CP 110 are somewhat higher than those specified by ACI Committee 211.

The use of air-entraining agents was found to improve sulphate resistance of concrete somewhat, apparently because of their reducing effect on the *W/C* ratio.[9,11] This beneficial effect was observed mostly in concretes having a low cement content and virtually disappears in cement-rich concretes.[9] In other words, the use of air-entraining agents is of limited practical value, i.e. in lean concretes the improvement is insufficient to produce sulphate resistant concrete, and in cement-rich concretes the improvement is insignificant.

As for other additives, it was found that use of calcium chloride adversely affects sulphate resisting properties of concrete, particularly when the ambient temperature exceeds 5°C.[11]

The substitution of suitable pozzolanas for part of ordinary Portland cement improves sulphate resisting properties of the concrete and, under moderate conditions of sulphate attack, such a substitution may be sufficient to produce sulphate resistant concrete.[12] This is not necessarily the case when the cement replaced by the pozzolana is sulphate resisting Portland cement. According to Lea[12] the effect of the pozzolanas is related to their SiO_2/R_2O_3 ratio (i.e. the ratio of silica content to the combined contents of alumina and ferric oxide), and sulphate resistance of sulphate resisting Portland cements are improved only when pozzolanas with a high ratio, like some of the Italian pozzolanas, are used. Fly ash usually has a high R_2O_3 content and a low silica content, i.e. a low SiO_2/R_2O_3 ratio. Indeed, in many tests, the addition of fly ash was not found to improve sulphate resistance of concretes made with sulphate resisting cement.

The pozzolanas combine with free calcium hydroxide which is formed during hydration of alite and belite. The resulting reduction in the calcium hydroxide content cannot be the only explanation for the improvement in sulphate resistance of the cement because sulphate expansion is mainly due to the formation of ettringite from the hydrate of calcium aluminate. A few theories have been advanced to explain the beneficial effect of pozzolanas on sulphate resistance of concrete. It has been attributed, for example, to the effect of the calcium hydroxide on the solubility of the hydrated calcium aluminates. The solubility of these hydrates is very low in saturated lime solution. Hence, the topochemical nature of the sulphate reaction and the resulting expansion. The decrease in the calcium hydroxide concentration due to reaction with pozzolana increases the solubility of the hydrated calcium aluminates. Consequently, the sulphate reaction occurs through solution and therefore without expansion.

In another theory it is suggested that the decreased calcium hydroxide concentration increases the sulphate concentration which is required to convert the solid solution $3CaO \cdot A\ell_2O_3 \cdot CaSO_4 \cdot 12H_2O$–$4CaO \cdot A\ell_2O_3 \cdot 12H_2O$ which eventually is formed in the hardened paste from the aluminate compounds and gypsum into ettringite. Lea considers these explanations incomplete,[12] and suggests that the improved sulphate resistance results mainly from the greater inhibition of the sulphate reaction by formation of protective calcium silicate hydrate films over the aluminate compounds. The pozzolanas contain alumina which, on hydration, forms products such as hydrated tetracalcium aluminate, i.e. products which are susceptible to sulphate attack. Apparently, the susceptibility of the pozzolanas aluminate products to sulphate attack is lower than that of Portland cement components. Consequently, in ordinary Portland cement, the protective effect of the increased CSH gel content outweighs the effect of the increased content of the hydrated aluminates, and the addition of pozzolanas therefore improves sulphate resistance of such cement. In sulphate resisting cement, however, the adverse effect of the increased content of hydrated aluminates may outweigh the increased protective effect of the CSH gel, and in such cement the addition of pozzolanas may result in inferior sulphate resistance. This will be the case when the added pozzolana is rich in alumina and poor in silica because the addition of such pozzolana will increase the hydrated aluminate content to a greater extent than that of the CSH gel. This explains the previous observation that fly ash, which has a low SiO_2/R_2O_3 ratio, does not improve sulphate resistance of sulphate resisting cement.

The addition of calcareous filler, for reasons which are not fully understood as yet, was also found to improve sulphate resistance of mortars and concretes.[15–18] It was suggested at the time that this improvement could be due to the decreased permeability of the concrete.[15,16] Later, however, the formation of calcium carboaluminate ($C_3A \cdot CaCO_3 \cdot 12H_2O$), as a result of chemical reaction between calcium carbonate and C_3A and C_4AF in the cement,[19] was considered in relation to sulphate resistance of Portland cements. It was even suggested that, due to the ability of the carboaluminate to combine with sulphate to give ettringite and due to the higher solubility of carboaluminate in saturated lime solutions than that of sulphoaluminate, the addition of calcareous filler may adversely affect sulphate resistance of Portland cement,[20] a suggestion which is not in accord with experimental data. Chatterji and Jeffery[17] suggested that, although the addition of calcium carbonate will not affect the formation of ettringite, it will decrease the amount of the monosulphate which may form as an intermediate step. This, in turn, should reduce the extent of sulphate attack because, as was suggested by them earlier,[21] sulphate expansion of Portland cement is mainly due to the conversion of C_4AH_{13} into monosulphate rather than to the formation of ettringite. As already mentioned, this hypothetical explanation for sulphate expansion is somewhat debatable. In any case, the fact remains that the addition of calcareous fillers does improve the sulphate resistance of Portland cement.

Summing up, it may be said that sulphate resistance of concrete can be significantly improved by preparing a concrete with low *W/C* ratio (i.e. 0.40 to 0.50 depending on particular conditions) and by use of sulphate resisting cement. Under extreme conditions, however, this may not be enough, and the concrete must be protected by a coating. In CP 110 (Table 10.1) such a coating is recommended when total sulphate concentration in soils exceeds 2% and that in ground-water 0.5%.

10.2.3 Tests for sulphate resistance

Sulphate resistance of concrete is usually determined by immersing test specimens in 5% sodium or magnesium sulphate solution and observing the effect of such immersion on the performance and properties of the concrete over a period of time. To speed up the test, the specimens are sometimes subjected to alternate cycles of immersion and drying. Sulphate resistance can be evaluated from the expansion of the test specimens, from the change in their dynamic modulus of elasticity, or from visual observation of the intensity of cracking and of deterioration. Generally, concrete strength decreases with increasing sulphate attack. The change in concrete strength can be used to evaluate sulphate resistance of concrete. Strength tests being destructive involve a considerable number of specimens. Hence, measurement of the dynamic modulus of elasticity or the expansion test, which are non-destructive, are usually preferred. Moreover, in some cases, the strength of the concrete was found to increase,[7] apparently because of crystallisation of reaction products in the concrete pores. This effect is sometimes suggested as a reason why strength tests should not be used in determining sulphate resistance.

Another method has been developed in the USA in which the potential sulphate resistance of Portland cement is determined from the expansion in water of mortar bars made from a mixture of Portland cement and gypsum in such proportions that the mixture has a SO_3 content of 7% by weight (ASTM C452). The bars are 1 × 1 × $11\frac{1}{4}$ inches in size, and the mortar is made of one part of the mixture of cement and gypsum and $2\frac{1}{2}$ parts sand. At an age of 22-23 hours, the bars are immersed in water at 23°C, and the expansion over the period from 24 hours to 14 days (or longer) is taken as a measure of potential sulphate resistance of the tested cement.

10.3 Concrete in sea water

It was explained in Chapter 6 that the chemical corrosion of concrete in sea water is due mainly to the presence of sulphates, particularly magnesium sulphate. Hence, generally speaking, all factors which improve sulphate resistance of concrete, i.e. low *W/C* ratio and the use of sulphate resisting cement, will also improve performance in sea water. On the other hand, the deterioration of concrete in sea water is not necessarily characterised by the expansion observed in concretes exposed to sulphate solutions, but rather takes the form of erosion and loss of some constituents.[13] The reason for the reduced expansion is not clear and is sometimes attributed to the greater solubility of calcium hydroxide and ettringite in the presence of chlorides. In any case, as mentioned earlier, the chemical attack on concrete in sea water is less than what might be expected from the SO_3 concentration.

Concrete in sea water may also be damaged by crystallisation of salts inside the mass in zones where the concrete is subjected to alternate wetting and drying. Deterioration can also be caused by erosion and frost action. All the above effects are porosity-related and accordingly, a dense concrete will suffer less deterioration.

Experience has shown that the most severe damage occurs just above high water level where sea water tends to enter the concrete due to capillary action, and damage is accentuated by crystallisation of salts within the mass. At this level, the concrete is also subject to frost action and is most open to erosion effects. Less damage occurs between high and low water levels, and hardly any in completely and continuously immersed concrete provided that the concrete is of adequate quality.

In summing up, it may be said that the durability of concrete in sea water is dependent mainly on its density and less on the particular type of the cement involved. The required density can be attained by using a maximum *W/C* ratio of 0.45-0.50[10] provided, of course, that the concrete is properly placed and compacted (Chapter 11). The low *W/C* ratio improves, not only concrete resistance to chemical attack but also its ability to withstand frost action and erosion effects.

Reinforced concrete is much more open to damage than plain concrete due to possible corrosion of the reinforcement, which is intensified in the presence of salts. As the formation of corrosion products involves volume increase, the concrete covering the reinforcement tends to crack and expose the steel to further attack. A dense concrete cover prevents sea water from penetrating into the concrete and thereby protects the steel against corrosion. Hence, again, the need to use concrete of low *W/C* ratio. Extra protection is provided by increasing the thickness of the concrete covering of the reinforcement to 60 (CP 110) or 75 mm,[4] or sometimes even to 100 mm.[22] Further discussion of the performance of concrete in sea water can be found in reference 23.

10.4 Concrete in acidic environments

Portland cement can suffer severe attack in acidic environments and, in this respect, different types of Portland cement behave very similarly. Accordingly, CP 110 (Table 10.1) requires that, in acidic conditions for which the pH is six or less, concrete is protected by a suitable coating. Alternatively, the use of non-Portland cements, such as high-alumina or supersulphated cement, may be considered.

The occurrence of acid solutions in nature is limited as compared to that of sulphate containing solutions. Water in peat areas may be acid.* The decay of peat involves the formation of organic acids, though these acids are usually neutralised by the lime present in soil. In many cases peat soils contain iron sulphides, such as pyrites and marcasite† which, on oxidation, produce free sulphuric acid. Again this acid is usually neutralised by the bases present in soil giving sulphate salts. In some cases, however, the production of sulphuric acid occurs at such a high rate that some acid remains free in the water and this accounts for its acidity. The process requires the presence of oxygen and it will not occur therefore in areas where the soil is permanently covered with water.

Water may be acidic due to the presence of dissolved carbon dioxide. It was explained earlier (Chapter 6) that only carbon dioxide which is not combined as calcium bicarbonate or is not required for stabilisation of this carbonate, is aggressive. Hence, for a given carbon dioxide concentration the acidity of the water depends on its hardness, and increases with decrease in hardness. Consequently, under these conditions, the pH value is not an adequate measure of the aggressiveness of the water, i.e. water of very low temporary hardness may be aggressive at pH values up to 7, or even 7.5, whereas water of higher hardness may not be aggressive down to pH values of 6.5 to 6.0.[24] In any case, the attack of naturally occurring acidic solutions, which result from the presence of organic acids or carbon dioxide, is normally limited to the surface of the concrete and causes limited damage. Appreciable damage may, however, occur when the aggressive water is under pressure, when the concrete is permeable, or when thin sections (e.g. concrete pipes) are involved.

Normal domestic sewage is alkaline. In some cases, however, considerable evolution of hydrogen sulphide (H_2S) may occur due to the action of anaerobic bacteria on sulphur containing compounds.‡ The production of hydrogen sulphide occurs mainly in the slime deposit on the sewer walls. It is affected by the temperature and the pH of the sewage, and the bacteria become virtually inactive below 10°C and at pH values below five and above ten.[25] Hydrogen sulphide itself does not attack concrete but it may cause damage if it oxidises to sulphuric acid. This process occurs when the hydrogen sulphide, which accumulates in the air space in the upper part of the sewer, dissolves in the moisture present on the sewer walls and undergoes oxidation by aerobic

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*Peat is the name given to layers of dead vegetation, in varying degrees of decomposition, resulting from the accumulation of the remains of marsh vegetation in swampy hollows in cold and temperate regions. Geologically, peat may be regarded as the youngest member of the series of coals, including brown coal, lignite, and bituminous coal, which range from peat to anthracite.[14]

†Sulphides are salts of hydrogen sulphide, H_2S. Iron pyrites and marcasite are both disulphides of iron (FeS_2). The pyrites crystallises in the cubic system and is of a brassy-yellow colour. Marcasite crystallises in the orthorhombic system and is white.

‡Anaerobic bacteria are those whose life processes require no oxygen. Facultative anaerobes can use free oxygen whereas obligate anaerobes are poisoned by it.

bacteria.† It follows that corrosive conditions in sewers can be avoided by preventing the formation of the sulphuric acid. Chlorination of sewage has been successfully used for this and ventilation of sewers may be of some help provided it dries the walls of the pipes, thereby preventing the dissolution of the hydrogen sulphide. The type of cement used has not been found to affect the resistance of concrete to sewer corrosion. The use of limestone aggregate, however, was found to improve the resistance of Portland cement concrete to attack by sulphuric acid.[26] Apparently, the calcareous aggregate neutralises some of the acid thereby reducing the amount which can react with the cement. It was also found that such an aggregate reduces sulphate expansion of concrete in acidic environments. The reaction between acids and calcium carbonate generates carbon dioxide, and it was suggested the presence of carbon dioxide retards the formation of ettringite: hence, the reduced sulphate expansion.[26]

Generally speaking, with dense concrete, normal sewage will only mildly attack it with the damage being mostly limited to the exposed surfaces. Industrial sewage, on the other hand, may be highly corrosive and protection of the concrete will therefore require the application of suitable coatings. Although pH is not always a suitable measure of aggressiveness, it may be used as a practical guideline. Accordingly, concrete must be protected by a coating when the pH of its surroundings is lower than six (Table 10.1). Further details about coatings suitable for various conditions of exposure can be found in references 4 and 27.

10.5 Frost resistance

Concrete which is exposed to freezing temperatures may suffer severe damage. Such conditions prevail in cold regions, particularly those where the temperature fluctuates about 0°C many times during the year. Under such conditions the durability of concrete is mostly determined by its frost resisting properties. Hence, frost resistance of concrete is a very important practical problem in cold climates.[28,29]

Frost resistance of concrete depends on the frost resisting properties of the cement paste and of the aggregate. Frost resistance of the paste can be improved by lowering the *W/C* ratio, and by the entrainment of air in an amount giving a spacing factor not greater than 0.25 mm. As can be expected, these factors both affect frost resistance of concrete in a similar way and, indeed, good frost resisting properties are characteristic of air-entrained concrete of low *W/C* ratio.

10.5.1 Effect of W/C ratio

The effect of *W/C* ratio on frost resistance of concrete is shown in Figure 10.3[30] where the resistance is represented as the number of freezing and thawing cycles which cause a weight loss of 25% in the specimens. It can be seen that frost

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† Aerobic bacteria are those which require oxygen.

resistance of both ordinary and air-entrained concrete is improved with decrease in *W/C* ratio. The effect, however, is significant only for *W/C* ratios lower than 0.45; the use of higher ratios resulted in poor frost resisting properties regardless of the exact value of the *W/C* ratio. Accordingly, a maximum ratio of 0.45 is recommended for concretes which are to be exposed to frost action (Table 10.5).

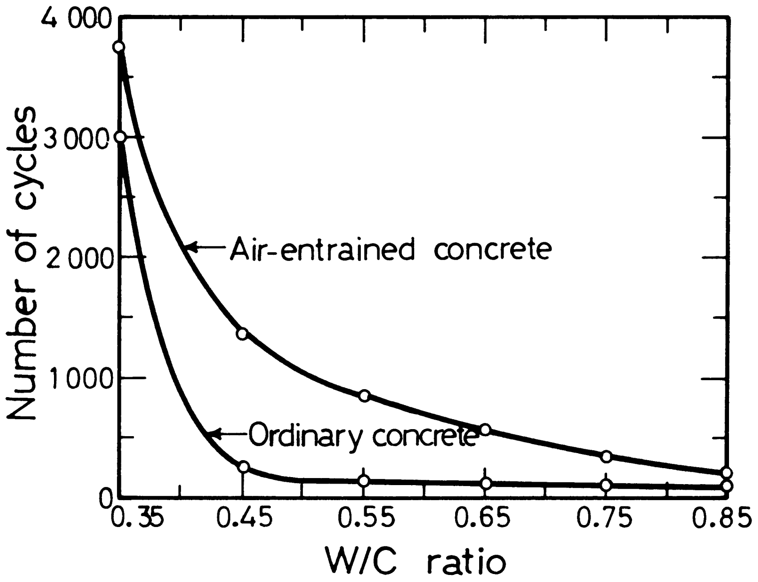

Figure 10.3 *Effect of W/C ratio on frost resistance of concrete (after US Bureau of Reclamation*[30]*)*

10.5.2 Effect of concrete strength

It is to be expected that strong concrete will exhibit better frost resistance than its weaker counterparts. This conclusion is implied from the effect of the *W/C* ratio (Figure 10.3), and is particularly evident when the concrete is exposed to frost action at an early age, i.e. when its strength is rather low. This is shown in Figure 10.4 which describes the volume increase in concrete exposed to freezing-thawing cycles after being allowed to harden for various periods of time.[31] As a longer prehardening period involves greater strength, it is clear that the time of exposure significantly affects frost resisting properties.

It may be concluded from Figure 10.4 that in practice to avoid possible damage, the exposure of concrete to frost action should be delayed as long as possible. In this context, reference is made to 'prehardening period', and to produce a concrete of the required frost resistance, a minimum prehardening period is recommended. Relevant experimental data are presented in Figure 10.5,

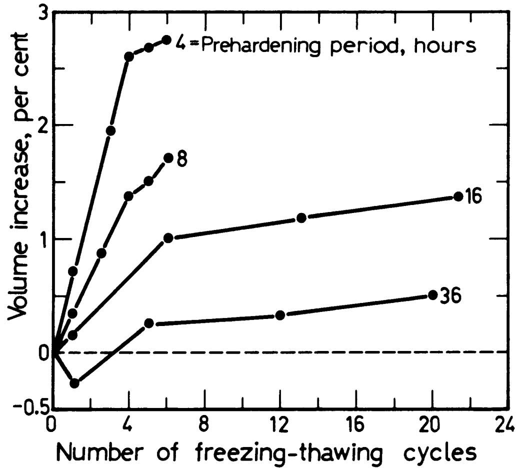

Figure 10.4 *Effect of prehardening period on volume increase of concrete exposed to frost action (after Möller*[31]*)*

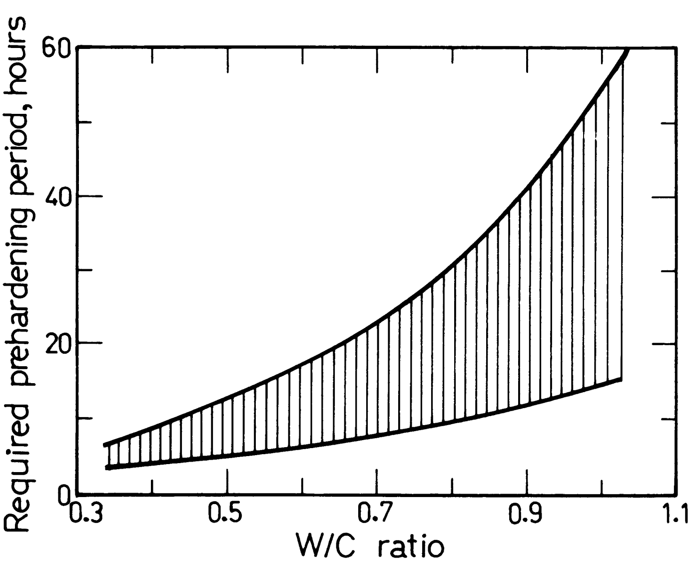

Figure 10.5 *Effect of W/C ratio on the required prehardening period (after various authors*[33]*)*

Table 10.3 Recommended prehardening periods for concretes made with ordinary Portland cement without accelerators[32]

Characteristic strength, N/mm^2	*Minimum prehardening period,* hours			
	5°C	10°C	15°C	20°C
20	71	46	32	24
25	65	42	30	22
30	59	38	27	20
40	50	33	23	17
Absolute minimum	36	24	16	12

and the recommended periods, in accordance with British practice, are in Table 10.3.[32]

The rate of strength development in concrete depends on curing temperature, and is slower the lower the temperature. It follows, therefore, that lower curing temperatures will necessitate longer prehardening periods. This conclusion is reflected in the recommended values which are presented in Table 10.3. The values in question are applicable to concretes made of ordinary Portland cements. When rapid-hardening cement is used or when accelerators are added to the mix, the recommended values may be reduced by half. Under no circumstances, however, should shorter prehardening periods than the indicated absolute minima be used.

Calcium chloride is sometimes used to accelerate the hardening of concrete and to reduce the required prehardening period. Recently, however, there has been a tendency to avoid the use of calcium chloride in reinforced concrete because its presence may promote corrosion of the steel. Generally speaking, an anhydrous calcium chloride content not exceeding 1.5% of the cement weight is not considered harmful in dense concrete.[34] On the other hand, it is somewhat difficult to ensure an even distribution of the calcium chloride throughout the concrete. Consequently, high local concentrations are likely to occur even when the total salt content does not exceed the maximum of 1.5% as specified, for example, in CP 110.* Such local concentrations may cause excessive corrosion and this explains the tendency to avoid the use of calcium chloride altogether. In any case, see CP 110, calcium chloride should not be used in prestressed concrete, where the problem is augmented by possible stress corrosion,[36] unless contact between the tendons and the concrete is prevented by means of an impermeable and durable barrier. The risk of corrosion is further increased when concrete is cured at elevated temperatures or subsequently exposed to warm moist conditions. Accordingly, CP 110 prohibits the curing of reinforced concrete containing calcium chloride at temperatures greater than 60°C.

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*Calcium chloride flakes contain about 30% water. Hence, the maximum of 2% of the cement weight is specified for flakes.[35]

10.5.3 Effect of air entrainment

As with its effect on cement paste, air entrainment improves frost resistance of concrete. This is clearly evident from the data of Figure 10.6, which also indicate that an increase of the spacing factor beyond, say, 0.25 mm (0.01 inch) adversely and significantly affects frost resistance of concrete. The value of 0.25 mm is to be expected in view of Powers' previously mentioned conclusion that such a limiting value will result in frost resistant pastes.[56] In later work, however,

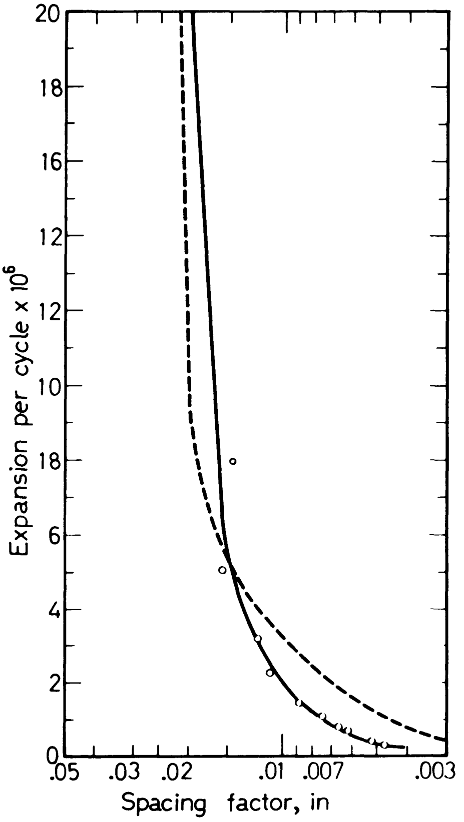

Figure 10.6 *Effect of spacing factor on expansion of concrete due to frost action (after Backstrom et al.*[37])

Backstrom *et al.*[37] concluded that the spacing factor in frost resistant concrete may vary from 0.10 to 0.20 mm. Accordingly, a spacing factor of 0.20 mm is recommended by ACI Committees 201 and 212 for frost resistant concrete.[4,35]

In practice air entrainment is specified and controlled by the air content rather than by the spacing factor. The amount of air which is required to produce a given spacing factor depends, under otherwise similar conditions, on the concentration of the paste in the concrete and on the size of the air bubbles. The concentration of the paste varies from about 15% in concrete made of 150 mm maximum size aggregate to about 30% in concrete made of 12 mm maximum size aggregate.[38] The diameter of the air bubbles generally varies from 0.5 to 1.25 mm with an average of, say, 0.5 mm. Accordingly, the values presented in Table 10.4 are recommended in the USA for frost resistant concrete.[4]

Table 10.4 Recommended air contents for frost resistant concrete (after ACI Committee 201[4]*)*

Maximum size of aggregate, mm (inch)	*Air content,* vol. %	
	Design average	*Minimum*
12 (½)	8	7
19 (¾)	7	6
25 (1)	6	5
38 (1½)	5½	4½
50 (2)	5	4
75 (3)	4½	3½
150 (6)	4	3

10.5.4 Effect of aggregate quality

The porosity of the aggregate normally used for ordinary concrete is much lower than that of the cement paste and only rarely exceeds one per cent. Nevertheless, the aggregate may be susceptible to frost action to an extent which causes deterioration of the concrete as a whole. According to Rhoades and Mielnez[39] the most important factor in this respect is the extent to which the aggregate can reach a high degree of saturation when being embedded in the paste. A similar conclusion was reached by Lewis and Dolch[40] who found that the lack of frost resistance is characteristic of aggregates which reach saturation, and remain saturated, inside the concrete mass. That is, the most susceptible aggregate is aggregate in which the pores are large enough to allow easy entry of water but not that large as to allow easy removal of the water.

The mechanism of frost action in aggregate varies according to the specific nature of its pore system and its other properties, such as strength and modulus of elasticity. The nature of the damage depends, for example, on the magnitude of the hydraulic pressure which is generated due to the formation of ice relative to the strength of the aggregate. If the aggregate is strong enough to withstand the pressure, an elastic volume increase will occur without damaging the aggregate. In most cases, however, the cement paste is weaker than the aggregate, and is not sufficiently strong to withstand expansion of the aggregate. Consequently, under these conditions the concrete will be damaged due to deterioration of the paste and not of the aggregate. On the other hand, if the hydraulic pressure exceeds the strength of the aggregate, deterioration will occur in the aggregate and not in the paste.

Also, some excess water may be expelled from the aggregate into the paste. In the presence of air voids in the paste, the hydraulic pressure may be relieved without causing damage as the water flows into the voids. However, in the absence of such voids deterioration of the paste adjacent to the aggregate-paste interface may occur. In this case, the size of the aggregate particles is important because it determines the distance which the expelled water has to travel, and thereby also the magnitude of the generated hydraulic pressure. In other words, an aggregate may be characterised by a certain critical size, above which the damaging effect of hydraulic pressure will occur in the aggregate and not in the paste immediately adjacent to it.[41]

The aggregate may absorb water from the surrounding paste causing the growth of the ice bodies already present in its pores. The expansion caused by the growth of the ice may damage the aggregate by a similar mechanism to that which was described for the growth of ice in the capillaries of the cement paste. Apparently, this mechanism is not significant in frost resistance of aggregates.[42]

Frost action in aggregates is rather complicated being related to many factors which, in some cases, are interdependent. Consequently, as yet, it is impossible to define quantitatively a quality of the aggregate which will produce frost resistant concrete. As explained earlier, absorption is not a suitable parameter because frost resistance is much more dependent on the nature of the pore system rather than on its content, as such. Accordingly, a porous aggregate may exhibit good frost resisting properties if the pores are large and resist the flow of water to a limited extent only. Small pores, on the other hand, resist the flow of water to a greater extent. Hence, the generated pressure will be higher, and the susceptibility of the aggregate to frost damage will be correspondingly increased.

Aggregates may be subjected to freezing-thawing tests. The results of such tests, however, cannot be used to determine whether or not the tested aggregate will produce frost resistant concrete.[43] Strong aggregates, for example, or those from which the water is easily removed, give good results in such tests. However, in view of the preceding comments, such aggregates will produce concrete of poor frost resistance. As mentioned earlier, as yet no satisfactory method is available for determining whether or not an aggregate will produce frost resistant concrete by testing the aggregate alone. Consequently, relevant specifications and recommendations are usually not specific and generally state that the aggregate should be of the 'durability adequate for the exposure to be encountered'.[44] Whether or not the aggregate has adequate durability can only be determined by testing the frost resistance of air-entrained concrete which is made from the aggregate in question. The use of air-entrained concrete (4-5% air) is required to produce frost resistant paste so that test results will reflect the quality of the aggregate without being obscured by that of the paste.

10.5.5 Freezing–thawing tests

In such tests, concrete specimens are exposed to specified freezing–thawing cycles, and the resulting change in concrete properties is determined. To this end volume and weight changes, as well as changes in strength and modulus of elasticity of the concrete, may be used as test criteria.

The effect on the dynamic modulus of elasticity probably constitutes the preferred criterion for evaluating frost resistance of concrete and, indeed, such a criterion is included in ASTM standard C666. According to this standard, concrete prisms should be subjected to repeated freezing and thawing cycles between 40 and 0°F (+4.4 and −17.8°C) by one of two different procedures, namely, freezing and thawing in water, or freezing in air and thawing in water. The dynamic modulus of elasticity is determined at intervals not exceeding 36 cycles until the specimen has been subjected to 300 cycles or until its relative dynamic modulus of elasticity reaches 60% of the initial modulus, whichever occurs first. Test results are expressed by the 'durability factor', DF, which is given by

$$DF = PN/300$$

where P is the relative dynamic modulus of elasticity after N cycles and N is the number of cycles at which P reaches the minimum value for discontinuing the test or is the specified 300 cycles, whichever is less.

The use of the dynamic modulus of elasticity to determine frost resistance of concrete is generally preferred because it involves non-destructive testing. Moreover, the dynamic modulus, being dependent on the tensile strength of the concrete, is closely related to frost resistance. The test in question is also affected by internal damage in the concrete which cannot be observed by visual inspection. Nevertheless, no direct correlation exists between the durability factor, and indeed between any other factor, and the durability of concrete exposed to frost under actual service conditions. This lack of correlation is attributable to the difference between test conditions and the conditions which prevail under actual exposure. The rate of cooling, for example, is considerably higher under test conditions than under service conditions. Saturation of the concrete does not necessarily always occur in practice. Moreover, in any test the adopted criterion for evaluating frost resistance is somewhat arbitrary. Consequently, freezing and thawing tests are more useful for comparing frost resisting properties of concretes rather than for predicting their performance under service conditions. Nevertheless, some reasonable predictions can be made if the tested concrete is compared with a concrete of known and proved frost resistance.

10.6 Fire resistance

The term 'fire-resisting' is usually applied to structural elements and not to a material as such (BS 476, ASTM C119). The general subject of fire resistance is outside the scope of the present discussion, and consequently the foregoing term is used hereafter to describe the ability of concrete as a material to withstand the effects of high temperatures.

Concrete is incombustible and has good fire resisting properties, i.e. when exposed to fire it continues to perform satisfactorily for a reasonable period of time. Nevertheless, with time, the high temperature gradient, brought about by the fire, causes cracking and spalling. Further deterioration and loss of strength are caused by gradual dehydration of the cement paste.

The rise in temperature causes normal thermal expansion in the cement paste. This expansion, however, is opposed by shrinkage which takes place as water is driven from the paste. At early stages, the thermal expansion exceeds the drying-shrinkage and the paste expands. At later stages, however, drying-shrinkage becomes greater than the thermal expansion and the paste begins to contract. The aggregate, on the other hand, continues to expand, opposing and restraining the shrinkage of the paste. The opposing volume changes produce tensile stresses in the concrete which, in turn, cause cracking and weaken the paste-aggregate bond.[45] Hence, the strength of the concrete is reduced. With wet concrete, the high temperatures may also result in spalling to a depth of 10 mm and more.[46] As this type of damage is usually associated with the presence of moisture, it was suggested that spalling takes place when the vapour pressure in the concrete pores exceeds its tensile strength. Such a situation may occur when the vapour pressure increases at a higher rate than the rate of its relief due to diffusion into the atmosphere.[47]

As mentioned earlier, concrete may also be damaged by dehydration of the cement paste. Complete and rapid dehydration of the paste occurs at about 900°C, but some dehydration takes place at temperatures as low as 250°C.

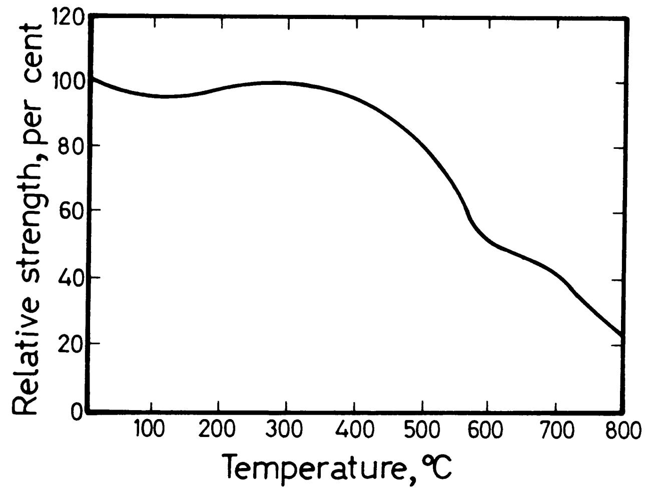

Figure 10.7 *Effect of temperature on concrete compressive strength (after Zoldners*[49]*)*

Complete dehydration can take place even at 500°C if the concrete is exposed to this temperature level for a long period of time.[46]

The effects of high temperatures are reflected in concrete strength. Apparently, up to 250-300°C, strength is hardly affected.[48,49] However, further rise in temperature causes a progressive decrease in strength, and at about 800°C the concrete loses most of its strength and deteriorates completely (Figure 10.7). High temperatures affect the modulus of elasticity of concrete in a similar way. The modulus, however, also decreases in the temperature range up to 250-300°C.[48,50]

The effect of high temperatures on concrete strength is independent of the *W/C* ratio at least within the range 0.40 to 0.65. On the other hand, the effect is related to the cement content, and lean concretes are damaged less than cement-rich concretes.[51] The quality of the aggregate significantly affects fire resisting properties of concrete. Very finely crystalline, or non-crystalline, basic igneous rocks such as dolerites and basalts, are good fire resisting aggregates. Quartz containing aggregates produce less resistant concretes due to the transformation of the quartz from α to β form which occurs at about 570°C.* The transformation involves a sudden expansion of 0.85% which damages the concrete.[52]

10.7 Abrasion resistance

In certain applications, such as floors, pavements, roads, etc., concrete is subjected to wear and its resistance to abrasion becomes an important factor in determining its durability. A similar problem is the erosion of concrete surfaces in hydraulic structures which takes place when abrasive solids are carried by the water. In water flowing at high velocity, the concrete may be severely damaged when cavitation occurs i.e. in the presence of vapour bubbles (cavities) which are formed in the water under certain conditions. The cavities collapse with a high impact and the resulting pressure may cause pitting in the exposed surface of the concrete.

Abrasion resistance of the concrete is improved with decrease in the *W/C* ratio and with the use of hard aggregates. Erosion resisting properties are further improved by use of large aggregates. To improve resistance to cavitation, however, the maximum size of aggregate near the surface should preferably not exceed 20 mm because cavitation tends to remove the large particles rather than the small ones. The hardness of the aggregate is not that important when resistance to cavitation is considered, and good aggregate-paste bond is much more important.[53]

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*Quartz (i.e. crystalline silica) occurs either as prisms capped by rhombohedra or as hexagonal bipyramid crystals. The former is known as low temperature quartz or α-quartz, and the latter as high-temperature or β-quartz. As mentioned, the transformation of α to β quartz occurs at 573°C, and involves an increase in volume.

Several tests are available for determining the resistance of concrete to abrasion. In such tests the concrete is subjected, one way or another, to abrasion, and its resistance is measured as the resulting weight-loss or as the decrease in the thickness of the tested specimen. In any case, the assessment of wear properties from such tests is rather doubtful and due caution should be exercised in the evaluation of abrasion test results. In practice, many modes of abrasion occur while the available test methods simulate, at best, only one or two of these. It is not surprising, therefore, that in most cases only a poor correlation, if any, exists between test results and the performance of concrete in practice. Moreover, in some cases two different tests may produce contradictory results. Such a case is shown in Figure 10.8, in which the resistance of concrete to abrasion (weight-loss), determined by three different methods, is plotted against W/C ratio.[54] In the steel-ball abrasion test (plot 1) the concrete is subjected to abrasion for five minutes in circulating water by 41 balls of one inch (25 mm) diameter. The balls are pressed against the concrete through a rotating head (60 r.p.m.) on which a load of 454 kg is applied. In the dressing-wheel test (plot 2), 32 dressing wheels are rotated 5000 times on the surface of the concrete, with silicon carbide being used as the abrasive material. Finally, in the shot-blast test (plot 3), 2000 pieces of broken steel shot are fired under pressure at the surface of the test specimen which is placed 10 cm from the head of the

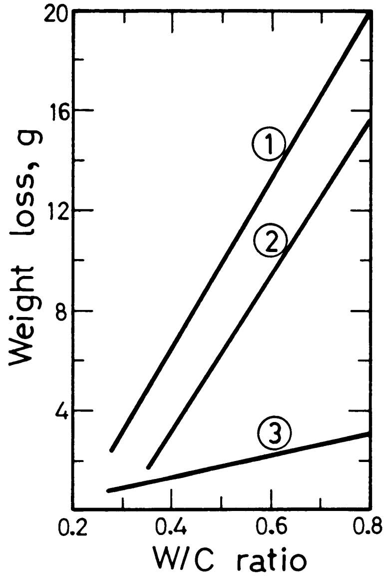

Figure 10.8 *Effect of W/C ratio on weight-loss of concrete subjected to abrasion (after Smith[54]).* (1) *Steel-ball test*; (2) *dressing-wheel test*; (3) *shot-blast test* ejecting nozzle. It can be seen that, in the first two methods (plots 1 and 2), the weight-loss (i.e. abrasion resistance) is highly dependent on *W/C* ratio, whereas in the third method, the *W/C* ratio affects only slightly, if at all, the abrasion resistance of the concrete. The latter conclusion is, of course, not correct because experience has demonstrated repeatedly that the *W/C* ratio significantly affects and determines wear properties of concrete.

The possible lack of correlation between test results and wear properties of concrete is also shown in Figure 10.9, where abrasion resistance of concrete

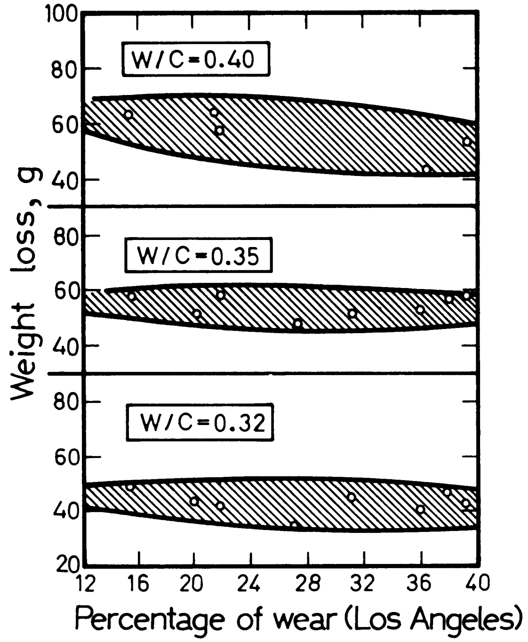

Figure 10.9 *Effect of aggregate hardness on concrete abrasion loss (steel-ball test) (after Smith[54])*

(steel-ball test) is plotted against the hardness of the aggregate expressed as 'percentage of wear' determined by the Los Angeles test in accordance with ASTM standard C131.* The data clearly indicate that, under the specific test conditions, the weight loss is unrelated to the hardness of the aggregate, suggesting, in turn, that this latter property does not affect abrasion resistance of

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*In this test an aggregate sample of specified grading is placed in a horizontally mounted cylindrical drum together with a charge of steel balls. The drum is rotated a specified number of times, and the resulting amount of material passing ASTM Standard sieve No. 12 (1.70 mm), expressed as percentage of the original weight of the test samples, is defined as the percentage of wear.

concrete. This misleading conclusion may be attributed to the specific test conditions under which, apparently, only the quality of the paste (i.e. *W/C* ratio), and not that of the aggregate (i.e. hardness), is reflected. In other tests, however, the expected effect of aggregate hardness on abrasion resistance of concrete is clearly indicated. Such tests results are presented in Figure 10.10, where abrasion resistance is expressed as the reduction in the thickness of a concrete specimen when tested using the Bohme machine in accordance with German standard DIN 52108.[55] In this test a concrete specimen is rotated against a steel plate a specified number of times with emery sand being used as abrasive material. It can be seen here that the abrasion resistance of concrete is related to the hardness of the aggregate, and significantly increases with increase in hardness.

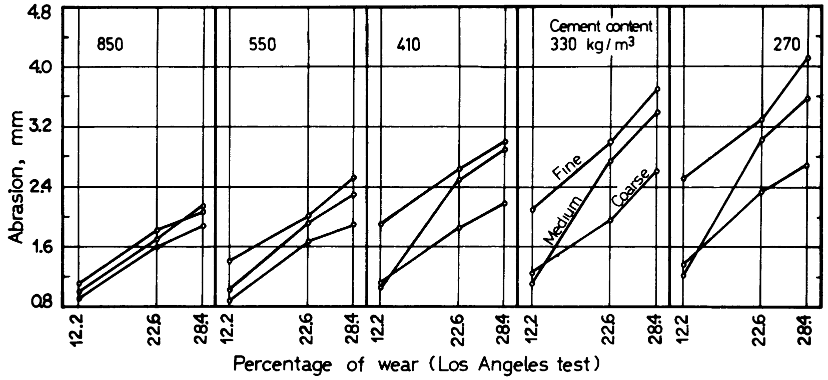

Figure 10.10 *Effect of aggregate hardness on concrete abrasion loss (Bohme machine) (after Soroka*[55]*)*

The difference in the sensitivity of the various testing methods to the different factors which affect abrasion resistance, limits their use for assessing the performance of concrete under service conditions. Figure 10.11, for example, summarises test data which relate the resistance to abrasion of concrete (Bohme machine) to its cement content.[55] The concretes involved were of the same consistence requiring roughly the same amount of mixing water. Hence, the variations in the cement content in Figure 10.11 represent the variations in the corresponding *W/C* ratios which decrease with the increase in cement content. It can be seen that fairly high abrasion resistance was obtained for relatively lean concretes when hard aggregates (i.e. basalt) were used and, accordingly, it may be concluded erroneously that such concretes have good wear properties. Experience has shown, however, that in practice such concretes deteriorate fairly rapidly due to disintegration of the weak paste.

As mentioned earlier, none of the available tests is satisfactory for assessing wear properties of concrete which, in turn, explains the considerable number of existing tests (see also BS 368 and ASTM C418). In practice, abrasion resistance can be

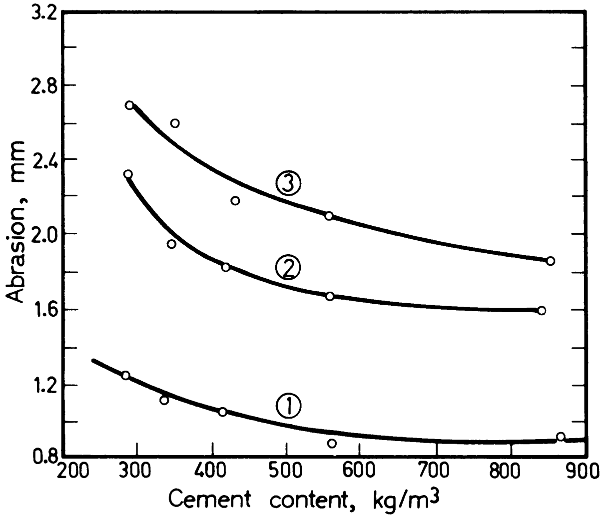

Figure 10.11 *Effect of cement content on abrasion resistance of concretes (Bohme machine) made of different aggregates (after Soroka*[55]*). (1) Basalt; (2) hard limestone; (3) soft limestone*

considerably improved by preparing the concrete with a low *W/C* ratio of 0.40–0.45, and with a hard aggregate.

10.8 Summary and concluding remarks

The ability of a concrete to withstand the effects of destructive agents, and perform satisfactorily over a period of time, is referred to as its 'durability'. The durability of concrete depends on environmental conditions, on the one hand, and the quality of the concrete, on the other.

10.8.1 Concrete in sulphate-containing soils and solutions

The intensity of sulphate attack on concrete depends on many factors. The intensity of attack increases with increasing sulphate concentration (Table 10.1), and depends on the sulphate involved. Magnesium sulphate, for example, is more aggressive than sodium sulphate. Reasonably good sulphate resisting properties can be obtained by making the concrete with sulphate resisting cement and with a low *W/C* ratio of 0.40–0.45. The addition of pozzolana, and probably also of calcareous fillers, to some extent improves sulphate resistance of concrete. Under severe conditions (Table 10.1), however, the concrete must be protected by a suitable coating.

10.8.2 Concrete in sea water

Chemical corrosion of concrete in sea water is due mainly to the presence of magnesium sulphate and gypsum. Hence, all means which improve sulphate resistance of concrete also improve its performance in sea water. Additional damage may be caused due to leaching out of the calcium hydroxide, or the crystallisation of salts in the concrete pores. Further damage may be caused due to erosion and frost action. Dense concrete, having a W/C ratio of 0.40–0.45 is reasonably durable in sea water. The use of sulphate resisting cement is useful but not an absolute requirement.

10.8.3 Concrete in acidic solutions

The occurrence in nature of acidic solutions, such as marsh water and soft water containing dissolved carbon dioxide, is limited. Under certain conditions domestic sewage may give acid reactions, but this is not generally the case. Concrete is highly susceptible to acid attack, and must be protected by suitable coatings if the pH of the environment is lower than six.

10.8.4 Frost resistance

Concrete subjected to repeated cycles of freezing and thawing may be severely damaged. The extent of the damage depends on many factors, but damage occurs only in saturated or nearly saturated concrete. The stronger the concrete, the greater its resistance to frost action. Hence, the exposure of fresh concrete to freezing temperatures should be delayed as long as possible. Frost resistant concrete must be prepared with a low W/C ratio of 0.40–0.45. In this respect, however, the most important single factor is the presence of air voids in the cement paste. Generally, an air content of 4 to 8% (Table 10.4) will produce frost resistant concrete. The quality of the aggregate also affects frost resistance of concrete, but this property cannot be quantitatively defined.

10.8.5 Fire resistance

Concrete is incombustible. It can be damaged, however, when exposed to high temperatures owing to cracking, spalling, and the dehydration of the cement paste. Little damage occurs up to 250–300°C. At higher temperatures, however, strength progressively decreases and complete deterioration occurs at about 900°C. Fire resistance is apparently unrelated to W/C ratio. Lean concretes exhibit higher fire resistance than cement-rich concretes. The use of quartz containing aggregates reduces fire resistance.

10.8.6 Abrasion resistance

In certain applications (floors, pavements, etc.) concrete is subjected to abrasion. A similar effect may be produced by erosion in hydraulic structures. The use of

Table 10.5 ***Maximum permissible water/cement ratios for different types of structure and degrees of exposure*** (*after* ACI committee 201[4])

Type of structure	*Exposure conditions**					
	Severe wide range in temperature or frequent alternations of freezing and thawing (air-entrained concrete only)			Mild temperature rarely below freezing, or rainy, or arid		
	In air	At the water line or within the range of fluctuating water level or spray		In air	At the water line or within the range of fluctuating water level or spray	
		In fresh water	In sea water or in contact with sulphates†		In fresh water	In sea water or in contact with sulphates†
Thin sections, such as railings, curbs, sills, ledges, ornamental or architectural concrete, reinforced piles, pipe, and all sections with less than one inch concrete cover over reinforcing	0.49	0.44	0.40‡	0.53	0.49	0.40‡

Moderate sections, such as retaining walls, abutments, piers, girders, beams	0.53	0.49	0.44‡	§	0.53	0.44‡
Exterior portions of heavy (mass) sections	0.58	0.49	0.44‡	§	0.53	0.44‡
Concrete deposited by tremie under water	–	0.44	0.44	–	0.44	0.44
Concrete slabs laid on the ground	0.53	–	–	§	–	–
Concrete protected from the weather, interiors of buildings, concrete below ground	§	–	–	§	–	–
Concrete which will later be protected by enclosure or backfill but which may be exposed to freezing and thawing for several years before such protection is offered	0.53	–	–	§	–	–

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*Air-entrained concrete should be used under all conditions involving severe exposure and may be used under mild exposure conditions to improve workability of the mixture.

†Soil or ground water containing sulphate concentrations of more than 0.2%.

‡When sulphate resisting cement is used, maximum water/cement ratio may be increased by 0.04.

§Water/cement ratio should be selected on basis of strength and workability requirements.

low W/C ratio of 0.40–0.45 and hard aggregate produces concrete of high abrasion resistance.

10.8.7 Overall durability

It may be noted that, in most cases, the required durability of the concrete can be attained by producing a concrete with low W/C ratio. The practical implication of this conclusion is shown in Table 10.5 which summarises American recommendations for the maximum W/C ratio to be adopted under various conditions of exposure.[4] As expected, the recommended ratio is lower the more severe are the exposure conditions, and also when thin sections are involved. The table includes some recommendations concerning the type of cement to be used. Similar recommendations are incorporated in Table 10.1 and further details can be found in reference 4.

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11 Effect of technical factors on properties of concrete

11.1 Introduction

In previous chapters the properties of concrete were discussed with respect to composition and the properties of the individual constituents. The production of concrete, however, involves various stages, and the treatment of the concrete at each stage affects its properties and determines its quality. The effect of steam-curing and autoclave treatment, for example, was discussed in some detail. Nevertheless, the discussion was incomplete because the effects of the specific technical factors involved were not considered. In fact, none of the technical factors associated with concrete production have yet been discussed in relation to their possible effects on properties of concrete. Such a discussion is presented here. It is assumed that the reader is familiar with these factors and concrete production is, therefore, not treated here. In any case, relevant information can be found elsewhere.[1,2]

11.2 Mix proportions

The porosity of the cement paste plays a very important part in determining the properties of the concrete. The many factors which determine the porosity of the paste have been discussed in some detail. Yet, in practice, the porosity of concrete, and its associated properties, also depend on the extent to which consolidation of the fresh concrete has been achieved, i.e. on the effectiveness of the compacting operation. Compaction of concrete is separately discussed later. However, satisfactory consolidation can only be achieved when the content of fine material in the mix is sufficient to fill the space between the particles of the coarse aggregate. Hence, the provision of the required amount of fine material is a basic principle of concrete mix design. (Concrete mix design is outside the scope of the present discussion, and the available methods can be found elsewhere.[3,4]) Essentially, mix design involves the economic selection of concrete ingredients and mix proportions which will impart to the concrete the required properties and durability. The economic aspect usually implies a minimum cement content, and in this respect the ratio of fine to coarse aggregate is also of some importance. In any case, producing good quality concrete is conditional on selecting a mix proportion which, among other things, facilitates the production of fully compacted concrete.

11.3 Batching

For materials of a given quality, the properties of the concrete are determined by actual mix proportions, and particularly by the W/C ratio. Concrete is produced in batches the size of which depends on the size of the available mixer. Hence, variation in the quality of the concrete produced will depend on the accuracy of the batching operation, i.e. on the extent to which mix proportions and quality of the ingredients are kept the same in all batches. The accuracy of the batching operation, and the resulting variation in the quality of the concrete, depend mainly on the degree of supervision exercised throughout the production process rather than on the type of equipment employed.

Under normal conditions, compressive strength is used to define concrete quality because, for most applications, strength is the most important property. Moreover, most of the other properties of concrete (i.e. permeability, durability, etc.) are strength-related. Hence, the variation in concrete quality is generally measured by the variation in its compressive strength. Apparently, the distribution of concrete strength is logarithmic-normal.[5,6] In practice, however, a normal distribution is usually assumed.[7] Accordingly, the variation in concrete strength can be given as an estimate of the standard deviation, S,

$$S = [\Sigma (x_i - \bar{X})^2/(n - 1)]^{1/2}$$

where x_i is an individual test result, n, is the number of tests, and $\bar{X}$ is the mean of the n tests.

Variations in mix proportions between the different batches are not the only reason for variation in concrete strength. Also contributing are possible variations in the quality of the materials involved, particularly in that of the cement. Testing error does not affect the variation in concrete strength, but is anavoidably included in the standard deviation. The relative contribution of the foregoing effects are presented in Table 11.1.[8] It can be seen that most significant in this respect is the batching operation which accounts for 53 to 78% of the variation in concrete strength, when measured as the standard deviation. Note also that the variation increases as the batching method becomes less accurate, i.e. when weight batching is replaced by volume batching. It should be noted that volume batching is not necessarily less accurate than weight batching. In practice, however, this is usually the case.

Table 11.1 Effect of various factors on the variation in concrete compressive strength (after Erntroy[8])

Method of batching	*Standard deviation** N/mm^2	*Relative contribution (%) to standard deviation*		
		Testing error	*Variations in cement quality*	*Batching*
Cement and aggregate by weight	4.8	9	38	53
Cement by bags, aggregate by weight	5.6	7	25	68
Cement by weight or bags, aggregate by volume	6.1	6	20	74
Cement and aggregate by volume	6.6	5	17	78

*In concretes having mean compressive strength of 35 to 55 N/mm^2.

11.4 Mixing

The efficiency of the mixing operation, i.e. the extent to which the mixing produces a homogeneous mix, is an additional factor contributing to variation in the properties of concrete. The homogeneity of the mix is determined mainly

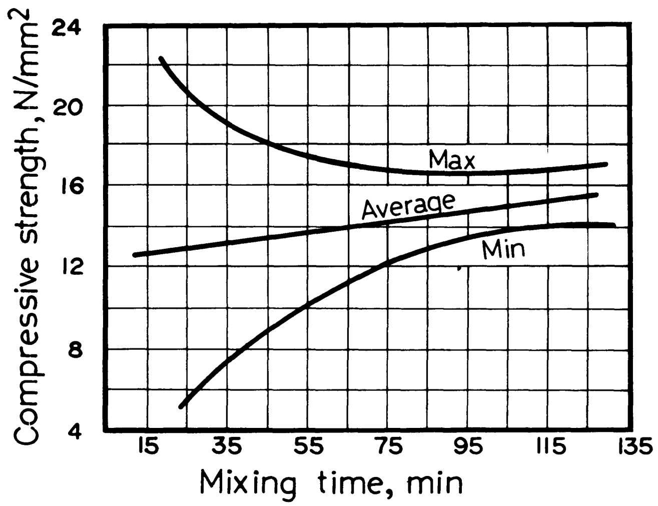

Figure 11.1 *Effect of mixing time on concrete strength (after Shalon and Reinitz[9])* by the efficiency of the mixer, and concrete mixers must satisfy certain requirements with respect to uniformity of the concrete produced in each batch (ASTM C94 and BS 3963). The efficiency of mixing is also related to the length of mixing time, and for each type of mixer there exists a certain minimum which must be followed in order to impart to the mix the required homogeneity. The effect of mixing time is demonstrated in Figures 11.1 and 11.2[9] for a free-fall mixer. In these tests, the uniformity of the mix was measured as the within batch variation in concrete compressive strength. It can be seen (Figure 11.1) that the mean strength of the concrete was only slightly affected by the length of mixing time. It is evident, however, that the uniformity of the mix was considerably affected and increased with increase in length of mixing time. This is indicated by the decreasing difference between maximum and minimum strength (Figure 11.1), and even better by the effect of mixing time on the coefficient of variation of the strength data (Figure 11.2). Note that, up to a mixing time of about 75 s, the coefficient progressively decreases from about 40 to 8%. On further increase in mixing time, however, the coefficient remains unchanged, implying that longer mixing will not further improve the homogeneity of the mix.

In view of these data a minimum mixing time of 75 s should be used for free-fall mixers. In practice, the specified minimum for such mixers is usually 60 s, provided the capacity of the mixer is not greater than about 0.75 m^3.[10] Mixers of greater capacity require longer mixing times (ASTM C94-72). On the other hand, pan-type mixers are more efficient than free-fall mixers and usually require shorter mixing times.

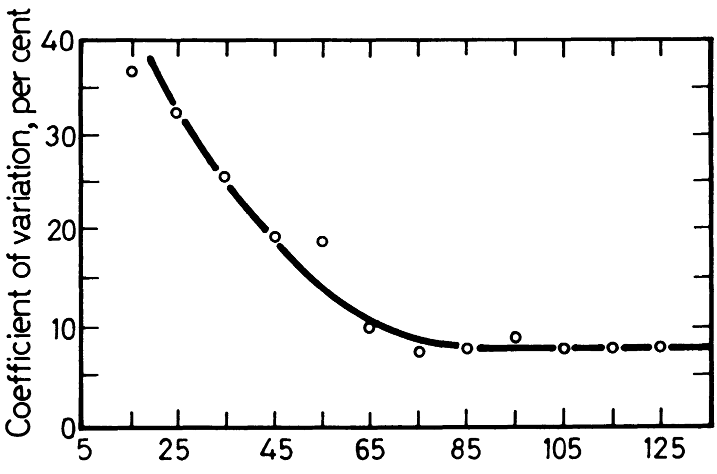

Figure 11.2 *Effect of mixing time on the coefficient of variation of concrete strength (after Shalon and Reinitz*[9]*)*

11.5 Segregation

The fresh concrete tends to segregate due to differences in the specific weights of its ingredients. In a mix without excessive water, and containing sufficient fine material, this tendency is generally low and of limited practical importance. Careless handling and the use of inadequate methods of transporting and placing, however, may aggravate the problem. Considerable segregation may occur, for example, when the concrete is allowed to flow at high velocities or when the direction of the flow is abruptly changed. Such conditions may occur at the end of a chute and at such sites considerable segregation occurs (Figure 11.3). In free flowing concrete the coarse aggregate particles tend to travel a longer distance when discharged from a chute, and separation is likely to occur. A baffle will not prevent segregation but merely change its direction (Figure 11.3B). Discharging the concrete through another chute, at least 60 cm long, is the correct solution which will prevent segregation (Figure 11.3A).

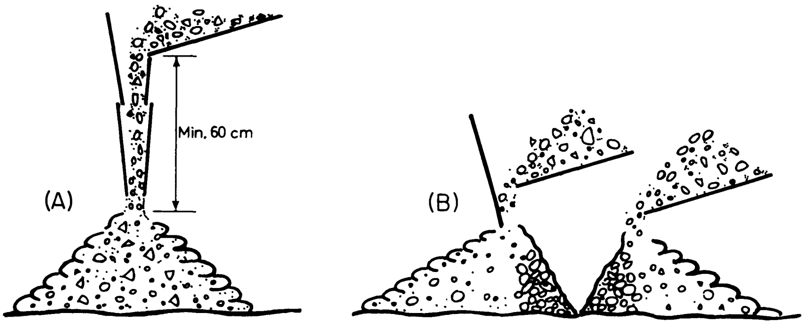

Figure 11.3 *Segregation of concrete at the end of chutes (after ACI Committee* 614[10]). (A) *Correct: discharge of concrete through a short chute, at least* 60 cm *long, prevents segregation.* (B) *Incorrect: uncontrolled discharge of concrete at the end of chutes causes segregation. A baffle merely changes direction of separation*

Vertical dropping of concrete without a drop-chute may cause segregation in a way similar to that occurring during uncontrolled discharge of concrete at the end of a chute (Figure 11.3B). Consequently, a vertical chute is usually provided in practice when concrete is to be dropped from a height exceeding, say, 2 m. The same applies when concrete is placed into narrow and high forms. The direct discharge of concrete into such forms causes segregation and a honeycomb to form at the bottom (Figure 11.4B); this can be avoided by the use of a drop-chute (Figure 11.4A).

Shovelling of concrete promotes segregation because water and fine material tend to separate out and be left behind. This is particularly true case when wet mixes are involved and when the concrete is shovelled over a long distance.

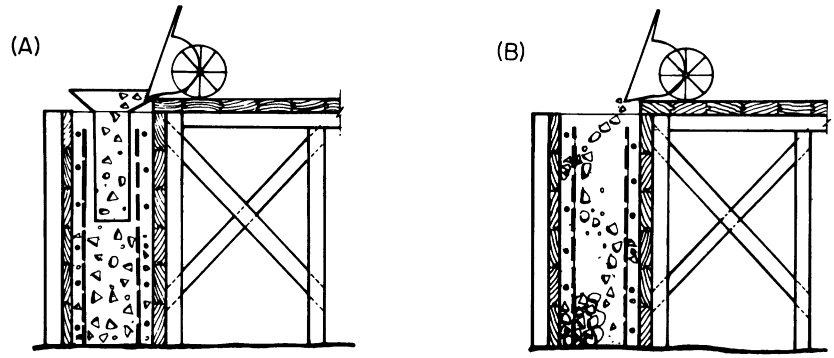

Figure 11.4 *Placing concrete in a narrow and high form (after ACI Committee* 614[10]). (A) *Correct: concrete discharged through a drop chute.* (B) *Incorrect: the directly discharged concrete strikes the form and ricochets from bars and faces causing segregation and producing a honeycomb at the bottom*

Hence, the shovelling of concrete over a distance exceeding about 2 m is usually to be avoided.

There are some additional situations where segregation of concrete may occur, but a complete discussion of the subject is outside the scope of this book. It is evident, however, that segregation will adversely affect concrete quality and, generally speaking, should be avoided.

11.6 Consolidation

The porosity of the cement paste is probably the most significant single factor determining the properties of concrete. The porosity is determined by the W/C ratio, the degree of hydration, and the presence of air voids due either to accidentally trapped or intentionally entrained air. Additional voids may be present in the concrete due to incomplete compaction and these will affect its properties. Hence, compaction plays an important role in determining concrete quality.

In discussing the effect of W/C ratio on concrete strength (i.e. Abrams' law), it was stressed that the suggested relation between the two is valid provided the concrete is fully compacted. In dry mixes, where full compaction cannot be achieved, voids are left within the mass. Consequently, the concrete strength will be lower than that which would be expected from the W/C ratio law. This effect is demonstrated in Figure 11.5, where the compressive strength of 1:5 cement to aggregate concrete is plotted against the W/C ratio.[11] It can be seen, that, for W/C ratios of down to about 0.45, the method of compaction does not affect concrete strength. Apparently, at these ratios the consistence of the mix allows the concrete to be fully compacted either by hand or by mechanical

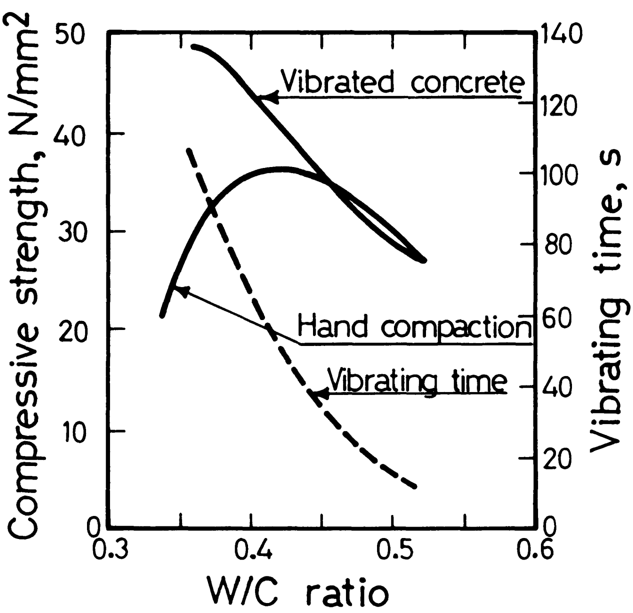

Figure 11.5 *Effect of method of compaction on concrete compressive strength (after Dutron*[11]*)*

vibration. At lower *W*/*C* ratios, however, due to the stiffness of the mix, full compaction could not be achieved by hand. Hence, the retrogression in strength of hand compacted concretes. The difference in the strength between the vibrated and the hand compacted concretes increases with decrease in the *W*/*C* ratio. This is due to the increased stiffness of the mix making hand compaction progressively less efficient while the use of vibrators still allows full compaction of the drier mixes if vibration time is increased (Figure 11.5). Nevertheless, it can be expected that at some *W*/*C* ratio, mechanical vibration will also result in incomplete compaction and concrete strength will start to decrease.

Generally speaking, full compaction by hand can be achieved only in wet mixes characterised by a minimum slump of 7-8 cm. Drier mixes require the use of mechanical means, and failure to use such means will result in concrete of inferior quality.

11.7 Curing

Under otherwise similar conditions, the properties of concrete are determined by the degree of hydration. The porosity of the concrete decreases as hydration proceeds, and its quality is therefore improved. Hydration is conditional on the presence of moisture, and such presence can be maintained by adequate treatment of the finished concrete, i.e. by proper curing. Sometimes the curing is also used to accelerate hardening of the concrete and, accordingly, this is referred to as 'accelerated curing'. When accelerated curing is not required, normal curing can be effected by immersion of the concrete in water or by intermittent and systematic wetting. Alternatively, curing can be achieved by preventing the concrete from drying out by covering its exposed surfaces with polyethylene sheeting or by spraying the surfaces with a sealing compound.

The complete hydration of Portland cement requires about 40% of its weight of water. About 23% of the water is chemically combined in the hydration products and the rest is physically adsorbed onto the surfaces of the gel particles. Usually, concrete is made with a *W/C* ratio exceeding 0.4 and contains therefore more water than required for the complete hydration of the cement. Hence, under these conditions, hydration will proceed uninterrupted, provided that the concrete is not allowed to dry. As will be seen later, due to self-desiccation in the hardened paste, the foregoing conclusion is actually applicable to concretes for which the *W/C* ratio exceeds 0.5. Figure 11.6 shows the amount of hydration, expressed as chemically combined water, in cement pastes cured for six months

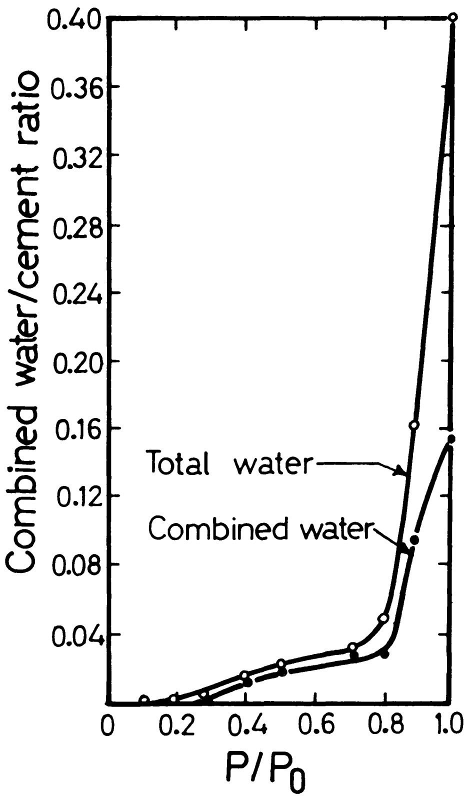

Figure 11.6 *Effect of ambient relative humidity on the hydration of Portland cement paste (after Powers*[12]*)* at different relative humidities.[12] It can be seen that curing below 80% relative humidity significantly reduces hydration, which virtually ceases when curing takes place below approximately 30% relative humidity.

It is implied therefore, that for hydration to proceed, the moisture content of the cement paste must exceed that which is reached on equilibrium with water vapour at about 80% relative humidity. During hydration of the cement some of the water present in the paste becomes chemically combined, and in a closed system the water content of the paste is thus decreased, i.e. self-desiccation occurs. It may happen that, as a result of self-dessication, the water content of the paste will fall below the water content at 80% relative humidity, and consequently the hydration process will be considerably reduced (Figure 11.6). Accordingly, if such is the case, wet-cured concrete will be stronger than otherwise similar concrete which is simply not allowed to dry. This is the case, however, only for concrete made with a *W*/*C* ratio lower than 0.5, because the initial water content of concrete made with a higher *W*/*C* ratio is sufficiently high to prevent the effect of self-desiccation. Indeed, it has been observed that, when the *W*/*C* ratio exceeds 0.5, the strength of concrete not allowed to dry is roughly equal to that of concrete cured by immersion in water.[13] In practice, however, this is usually not the case because the curing methods employed do not completely prevent drying of the concrete. Hence, generally speaking, wet-cured concrete is stronger than concrete which is not allowed to dry.

In view of the preceding discussion, it may be concluded that curing affects concrete strength through its affect on the rate of hydration which, in turn, is related to the availability of free water. Accordingly, maximum strength is to be expected in concrete which is kept wet, and minimum strength in concrete which, immediately after placing, is allowed to dry. This conclusion is reflected in the data of Price[14] presented in Figure 11.7. It can be seen that, up to an age

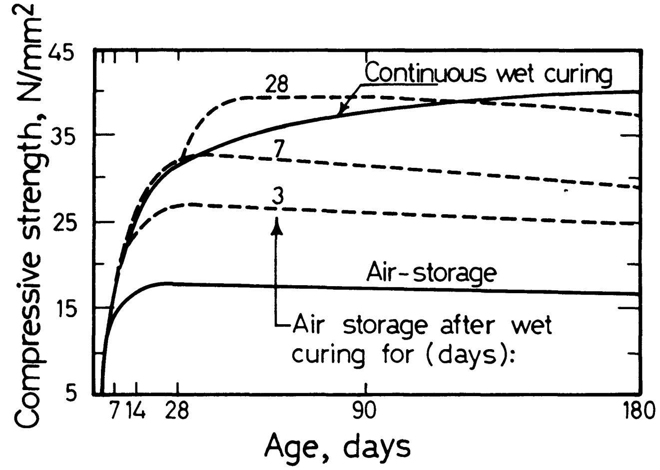

Figure 11.7 *Effect of curing on concrete strength* [*after Price* (*W*/*C* = 0.5)[14]] of about three days, strength development in concrete allowed to dry is the same as that of water-cured concrete. It is implied, therefore, that up to this age, drying of the concrete in the laboratory was not sufficient to affect the development of strength. However, beyond this age the strength difference between the two concretes becomes noticeable, and whereas strength development in the concrete allowed to dry stops at an age of about 14 days, strength development in the water-cured concrete continues to an age of 180 days. At this age the strength of the water-cured concrete is about 2.5 times greater than the strength of its air-cured counterpart.

So far we have not considered the effect of ambient temperature on concrete strength and other properties. It was shown earlier that a rise in temperature increases the rate of hydration (Figures 2.8 and 2.9) and thereby also the rate of strength development in the cement paste. This temperature effect is sometimes made use of in accelerating hardening: the concrete is exposed to water vapour with or without pressure, i.e. by subjecting the concrete to 'steam-curing under atmospheric pressure' or 'steam-curing under pressure' (autoclave treatment), respectively. The effect of these two curing methods on properties of concrete is discussed here.

11.7.1 Steam-curing under atmospheric pressure

Generally speaking, steam-curing consists of the four stages illustrated in Figure 11.8. The first stage, A, known as the 'delay period', is the period of time between casting of the concrete and its exposure to steam. The second stage, B, is the heating period, the third stage, C, is the curing period, and the fourth stage, D, is the cooling period. A fifth stage may be added in which the concrete is

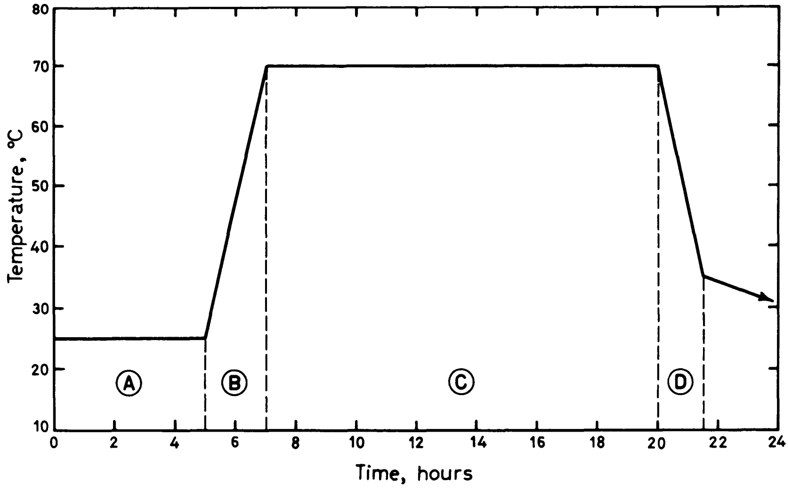

Figure 11.8 *Schematic description of a steam curing regime under atmospheric pressure* subjected to supplementary curing by wetting, etc. In practice, however, curing does not necessarily consist of all these stages. Usually, the concrete is not subjected to supplementary curing, and in many cases steam-curing begins as soon as casting is complete. Sometimes, the concrete is exposed immediately to steam at the curing temperature, i.e. both the delay and the heating periods are virtually eliminated.

Steam-curing accelerates the hardening of concrete to an extent which depends on many factors, such as the properties of the cement involved and the specific parameters of the curing regime. Generally, however, up to about 50% of the 28 day standard compressive strength of concrete can be reached at the end of the curing period. On the other hand, steam-curing adversely affects the ultimate strength of concrete. This effect is demonstrated in Figure 11.9, which

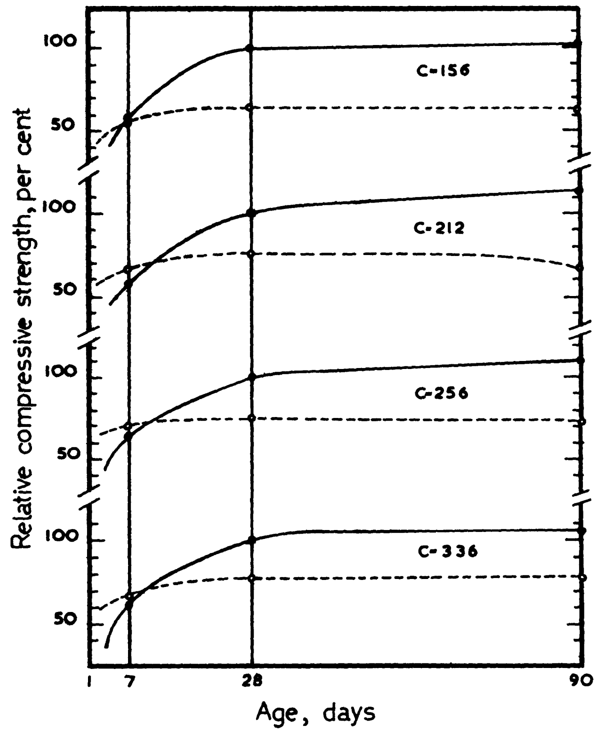

Figure 11.9 *Effect of steam curing on development of concrete strength (after Soroka et al.*[15]*). (C is the cement content in* kg/m^3)

presents data for concretes made with different cement contents, *C*, and cured at 70°C.[15] It can be seen that, beyond the age of 7-10 days, the strength of the steam-cured concrete gradually becomes lower than that of normally cured concrete, and at the age of 90 days the difference between the strengths of the two reaches 26 to 40%. The magnitude of this adverse effect depends on many factors, particularly on the specific parameters of the curing regime. Consequently, the relevant available data[16–18] vary quantitatively from that presented in Figure 11.9. Nevertheless, in most cases, steam-curing is associated with a significant reduction in ultimate strength of concrete.

11.7.1.1 Effect on strength

Strength development of steam-cured concrete is related to the type of cement involved and other factors such as the *W/C* ratio. It was found, for example, that, particularly when the initial strength is considered, the best results are obtained for cements high in C_3S and moderate in C_3A (i.e. 8 to 10%) are used.[19,20] It was also found that the fineness of the cement affects the development of strength, and that the initial strength of steam-cured concrete is roughly proportional to the specific surface area of the cement used.[20] It may be noted that essentially the same effects are observed when concrete is cured at normal temperatures. These effects were discussed earlier, so the following discussion is limited to the effect of the technical parameters of the steam-curing treatment. In this discussion a distinction is made between the effect of these parameters on the initial strength, i.e. the strength at the end of the steam curing regime, and the final or ultimate strength, i.e. the strength at ages exceeding, say, 28 days. Such a distinction is necessary because the various factors involved affect the initial and final strengths differently.

11.7.1.1 (a) Initial strength Under otherwise similar conditions, concrete strength differences are determined by the extent to which the cements have hydrated, i.e. by the degree of hydration. As the latter increases with rise in temperature and the increase in length of curing period, a corresponding increase in concrete strength is to be expected. The effect of temperature and curing period on the initial strength is shown in Figure 11.10,[21] and is supported by the data of others.[20] On the other hand, the semi-logarithmic nature of the relation in Figure 11.10 implies that the beneficial effect of steam-curing on the initial strength gradually decreases with increase in length of the curing period. In practice, such a tendency implies that prolonged curing will not be economical because at some stage further increase in length of curing period will produce only insignificant increase in concrete strength. Moreover, the increase in strength with rise in curing temperature does not take place over the whole range up to 100°C, and at some temperature further rise in temperature results in decreased strength. This effect of curing temperature is shown in Figure 11.11.[17] It can be seen that for a given curing period there exists an optimum curing temperature which is lower the longer is the curing period. Essentially, the same tendency has been observed by others.[21,22]

It was shown earlier (Figure 11.9) that curing at elevated temperatures adversely affects concrete ultimate strength, and it was explained that this

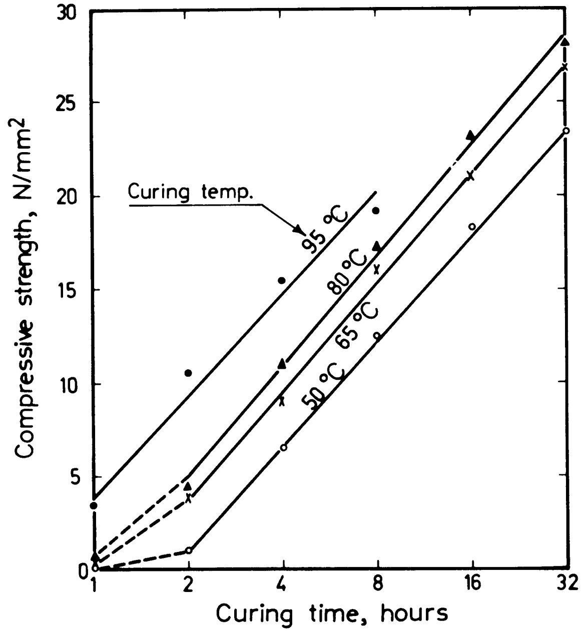

Figure 11.10 *Effect of curing temperature and length of curing period on initial strength of concrete (after Nurse and Whitaker*[21]*)*

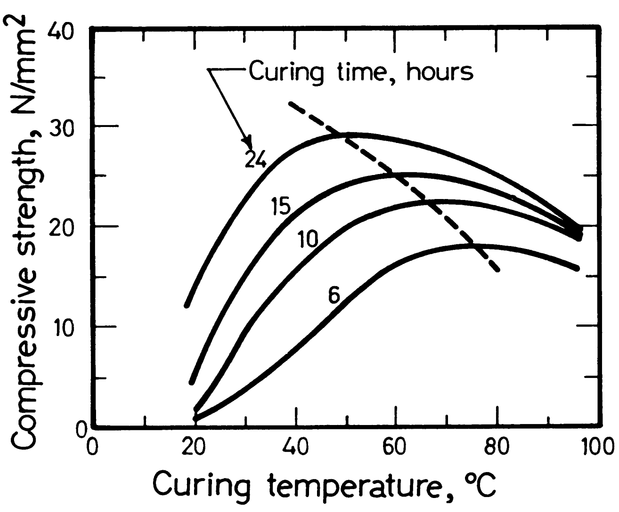

Figure 11.11 *Effect of curing temperature on concrete initial strength (after Mamillan*[17]*)* effect may be attributed to differential thermal expansion of the constituents of concrete. The greater expansion of air and water (Figure 4.21) increases porosity and results in internal stresses which, in turn, may cause cracking. In other words, the strength of concrete cured at elevated temperatures is determined by two opposing effects, i.e. concrete strength is increased due to increased hydration and is reduced due to increased porosity and internal cracking. At early stages the effect of increased hydration is predominant, and the strength of the concrete is therefore increased. At later stages, however, the rate of hydration decreases, and the adverse effect of increased porosity and internal cracking gradually becomes greater than the beneficial effect of increased hydration. The ultimate concrete strength is therefore reduced. Apparently, at higher curing temperatures, and particularly when longer curing periods are involved, the adverse effect of internal cracking becomes predominant at earlier ages explaining, in turn, the reduction in the initial strength of concrete with the rise in curing temperature beyond the optimum. The same explanation is applicable to the decrease in optimum temperature with the increase in length of curing period (Figure 11.11).

The concrete is most likely to be damaged by differential thermal expansion of its constituents during the very early stages of heat curing because, at these stages, the concrete is rather weak and may crack even when the induced stresses are low. Accordingly, it is to be expected that concrete which is allow-

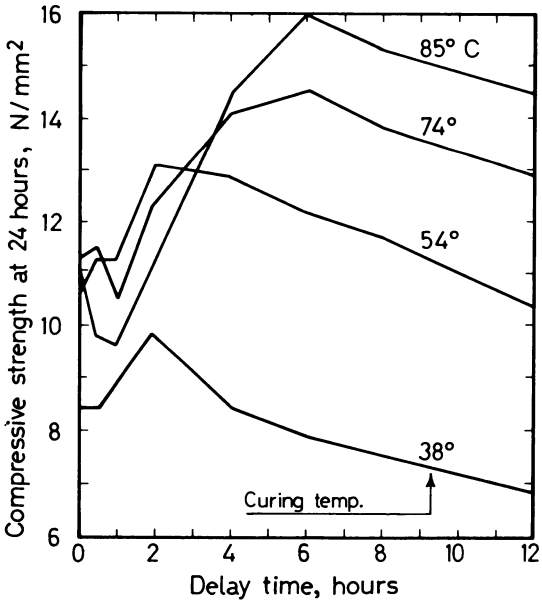

Figure 11.12 *Effect of delay period on 24 hour strength of steam-cured concrete (after Shideler and Chamberlin*[16]*)* ed to harden before being exposed to elevated temperatures will be damaged to a lesser extent than concrete which is exposed to such temperatures immediately after casting. This is confirmed by the data of Figure 11.12, which also suggest that there is an optimum delay period the length of which increases with increasing curing temperature, i.e. from two hours at 38 and 54°C to six hours at 74 and 85°C.[16] Similar results have been obtained by others[22] but not always. It can be seen, for example, from the data presented in Figure 11.13 that the length of the delay period hardly affects the initial strength of steam-cured concrete.[21] Nevertheless, it is generally accepted that, in practice, a delay period of a few hours will improve concrete strength.[23]

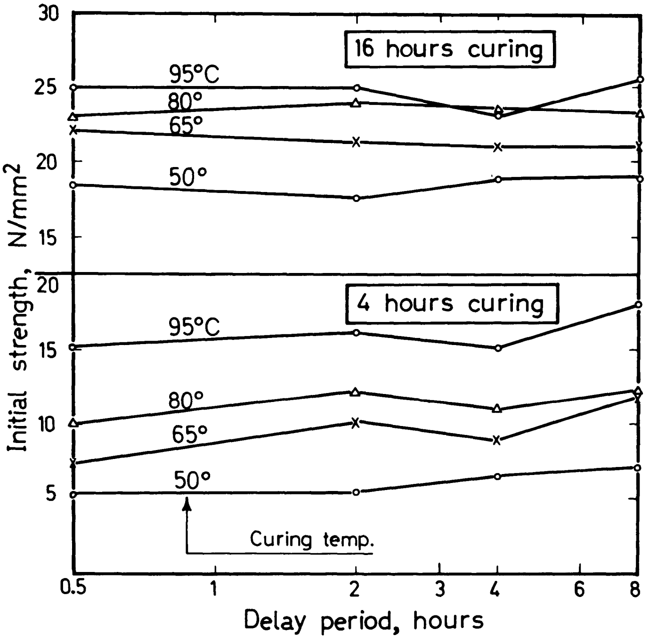

Figure 11.13 *Effect of delay period on the initial strength of steam-cured concrete (after Nurse and Whitaker*[21]*)*

The rate of heating also affects concrete strength. A high rate increases thermal stress as a result of an increased temperature gradient between the surface of the concrete and its interior. The increased stress results in more intensive cracking and therefore in reduced strength. This expected effect is demonstrated by the data of Hanson[22] which are presented in Figure 11.14. Note, however, that there exists an optimum heating rate which imparts to the concrete maximum strength, particularly when short delay periods are employed. This optimum is about 20°C per hour and accordingly this value is usually recommended in practice.[23]

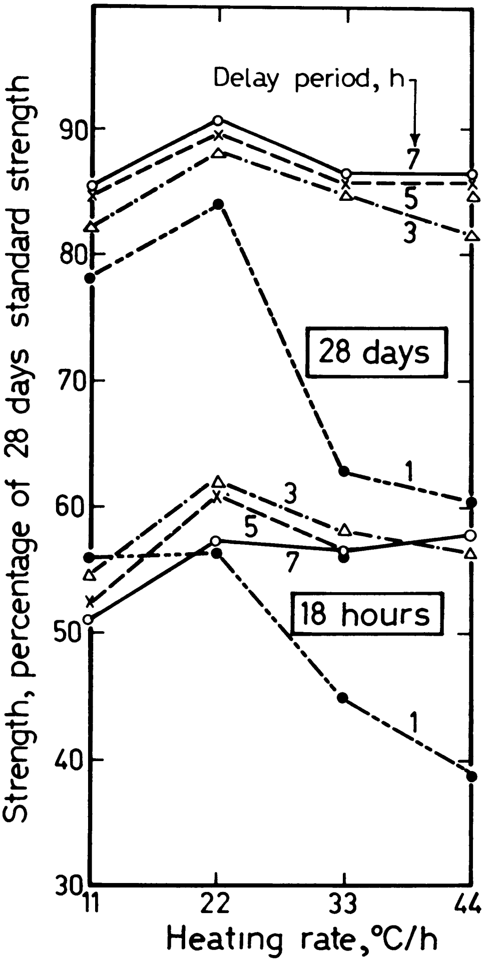

Figure 11.14 *Effect of rate of heating on concrete strength (after Hanson*[22]*)*

11.7.1.1 (b) Later-age strength It was demonstrated earlier that heat curing adversely affects the later-age strength of concrete (Figure 11.9), and it was explained that this effect may be attributed to increased porosity and possible internal cracking brought about by the differential thermal expansion of the concrete's constituents. It was also explained that the intensity of such cracking increases with rise in curing temperature and heating rate, and with decrease in delay period. As cracking is related to strength, it is to be expected that the strength of steam-cured concrete will be affected by the foregoing factors. This conclusion is confirmed by the experimental data presented in Figure 11.15, as well as by other tests.[14,17,24] It may be noted from this figure that, as expected, the strength of the concrete decreases as curing temperature is raised.

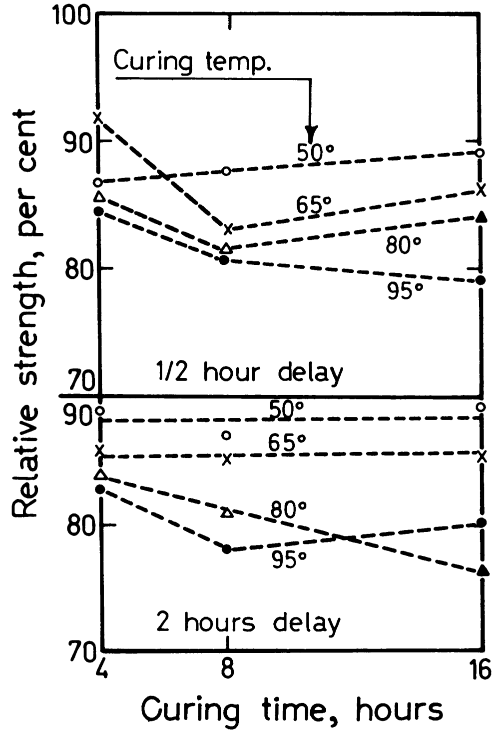

Figure 11.15 *Effect of curing temperature on 28-day concrete strength for different curing and delay periods (after Nurse and Whitaker[21])*

According to the data of Figure 11.15 the length of the curing period hardly affects the 28-day strength. This observation is somewhat unexpected because longer curing periods increase the degree of hydration and should result, therefore, in higher strength. In this particular case, however, the test specimens were stored in water until the age of testing. Apparently, this extra wet-curing caused all specimens to reach essentially the same degree of hydration, and the expected effect of the length of curing period was, thereby, eliminated.

There is an optimum curing temperature for maximum later-age strength. Hence, in practice, curing at the optimum temperature is usually preferred because such curing results in maximum initial strength combined with minimum reduction in later-age strength. Depending on the specific parameters of the curing regime, this optimum temperature lies between 66 and 82°C.[23]

The increase in length of the delay period reduces the adverse effect of steam-curing on later-age strength (Figure 11.16), particularly when the heating rate exceeds 22°C per hour (Figure 11.14). The optimum delay period depends on the *W/C* ratio and decreases with decrease in the latter (Figure 11.16). A decreased *W/C* ratio implies a higher rate of strength development.

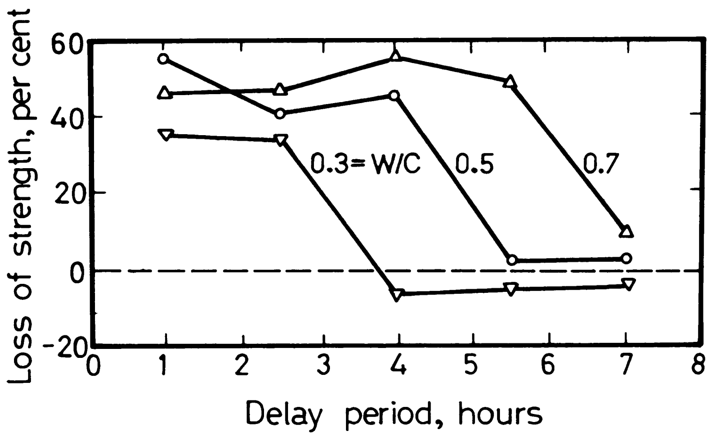

Figure 11.16 *Effect of delay period on reduction in concrete* 28-*day strength* (*after Alexanderson*[18])

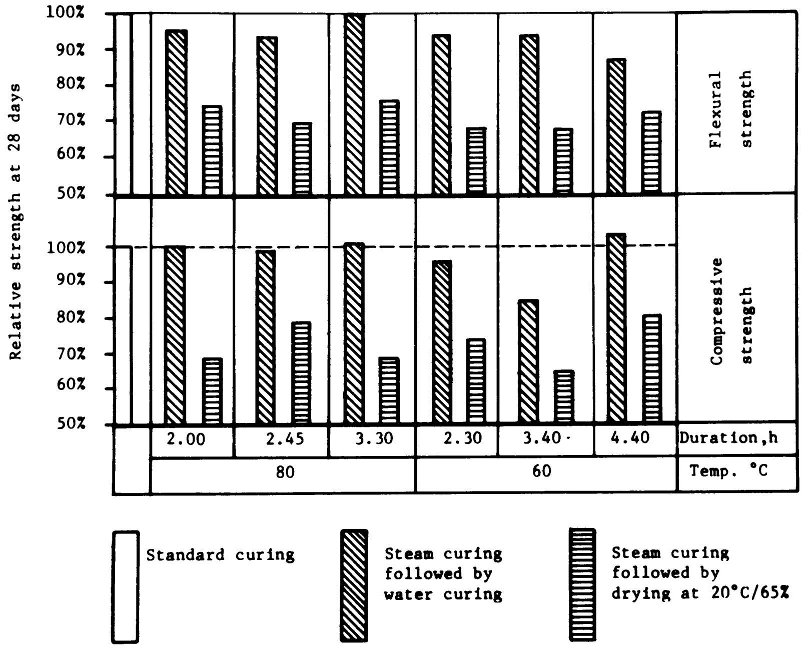

Figure 11.17 *Effect of supplementary wet-curing on* 28-*day strength of steam-cured concrete* (*after Jaegermann and Bentur*[15,26])

Hence, such concrete is able to resist thermal stress after a shorter delay period without being significantly damaged.

It may be noted from Figure 11.16 that delaying the exposure of the concrete to the elevated temperatures eliminates the reduction in later-age strength. In the tests considered the concrete was subjected to supplementary wet-curing, and the elimination of the adverse effect on later-age strength can be attributed to such curing. The same effect was observed by others^{25} and is further confirmed by the data presented in Figure 11.17. These data clearly indicate that later-age strength of steam-cured concrete is only slightly affected if the concrete has undergone supplementary wet-curing. On the other hand, the absence of such curing results in a considerable reduction in later-age strength.^{26} It should be noted, however, that supplementary wet-curing will not necessarily completely eliminate the adverse effect of steam-curing on concrete later-age strength. The adverse effect will, however, be reduced considerably if such curing is employed.

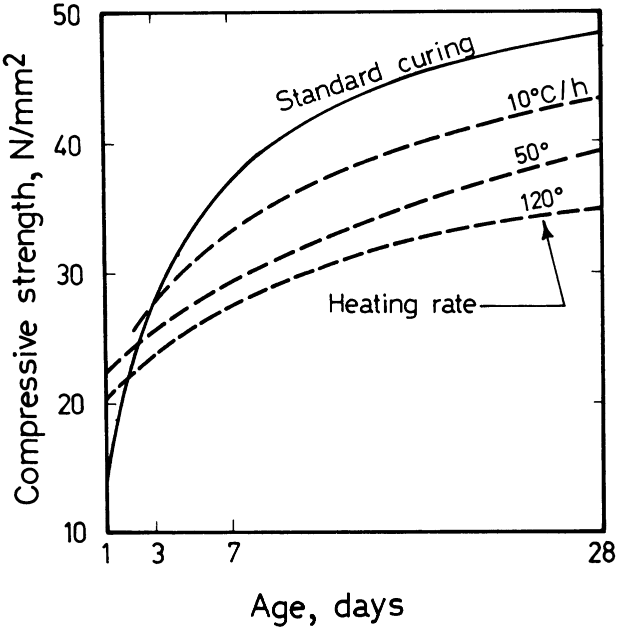

Figure 11.18 *Effect of rate of heating on* 28*-day strength of steam-cured concrete (after Nurse and Whitaker*^{21}*)*

Finally, as expected, the reduction in concrete later-age strength is increased with increase in the rate of heating (Figure 11.18).

11.7.1.1 (c) Prediction of strength It may be appreciated from the foregoing discussion that strength of steam-cured concrete is determined by many factors. On the other hand, particularly when curing is under optimum conditions, the strength of the concrete will be determined mainly by curing temperature and length of curing period. In an attempt to measure the combined effect of these two factors, the concept of concrete 'maturity' was introduced.[27–29] Maturity is defined as the product of the length of curing period, t, and curing temperature, T, measured with respect to –10°C, i.e. with respect to the temperature at which hydration may be assumed to stop completely. Accordingly, the maturity, M, is given by

$$M = t(T + 10)$$

where t is measured in hours or days and T is in °C.

As maturity measures the combined effect of temperature and curing time, it is to be expected that the strength of concrete will be related to this parameter. Experience has shown that such a relation exists, and for a concrete of a given quality (i.e. of a particular cement and W/C ratio, etc.) and made with non-reactive aggregate, this relation takes the form which is schematically described in Figure 11.19. It is implied by this relation that, for a given maturity, concrete will reach a certain strength which is independent of the curing conditions, i.e. regardless of whether curing has taken place for a short period at a high temperature or for a longer period at a lower temperature. In view of the preceding discussion, it may be realised that this is not necessarily correct. Indeed, the suggested relation is only valid for a limited range of ages and curing temperatures, and varies with the quality of the concrete. A more general relation is obtained when the relative strength of the concrete is considered with respect to, say, its 28-day standard strength. Plowman, for example, concluded that

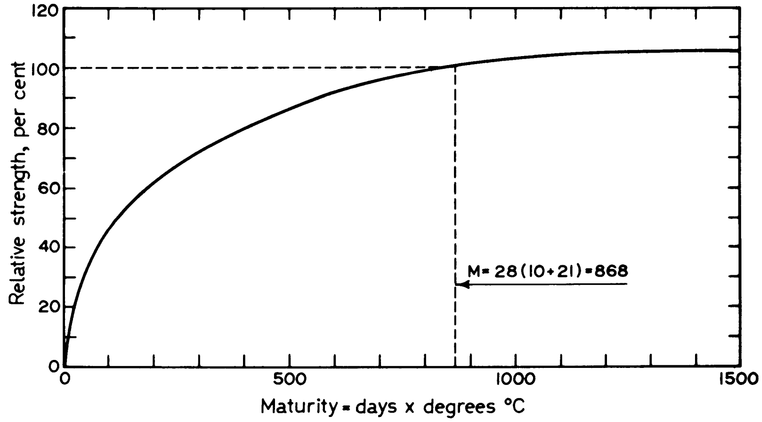

Figure 11.19 *Schematic relation between maturity and concrete relative strength*

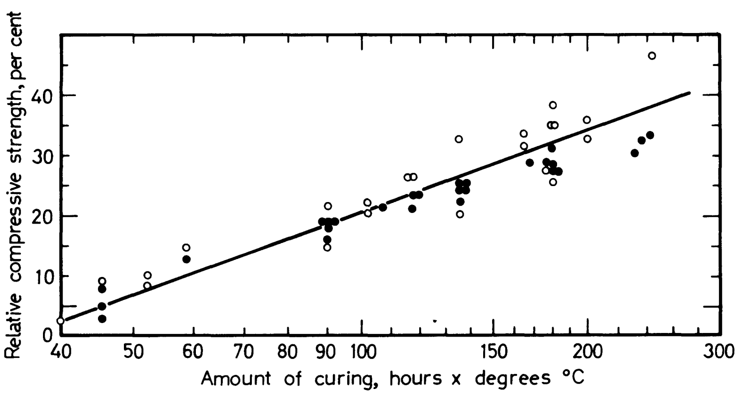

Figure 11.20 *Effect of amount of curing on initial strength of concrete (expressed as percentage of 28-day standard strength) (after Soroka and Jaegermann[25]).* ○, *ordinary concrete;* ●, *lightweight-aggregate concrete*

the relation between relative strength and maturity is independent of the type of cement, mix proportions, curing temperature below 38°C, and shape of test specimen.[30] Figure 11.20 presents data of another study in which the curing temperatures were 60 and 80°C, and the tests included ordinary and lightweight-aggregate concretes containing 275 to 400 kg cement per m^3.[25] It can be seen that these data confirm Plowman's conclusion and imply that it is applicable over a wider temperature range and to concretes made of different aggregates.

11.7.1.2 Effect on drying-shrinkage

Steam-curing reduces drying shrinkage. Higginson's tests, for example, indicate that drying shrinkage of concrete decreases with increase in the length of curing period and with rise in curing temperature, i.e. with the amount of curing.[31] This indication is confirmed in Figure 11.21, which presents the data of another study.[25] Higginson concluded that the reduced shrinkage of steam-cured concrete cannot be attributed to changes in the rate of drying of such concretes. It is also not attributable to changes in the morphology or composition of the cement gel because, as explained earlier, such changes are not brought about by steam-curing. The difference in shrinkage between normally and steam-cured concretes can be explained, however, from the difference between their moduli of elasticity. On exposure to drying conditions, the steam-cured concrete is usually stronger than its normally-cured counterpart, i.e. it has a higher modulus of elasticity and exhibits therefore lower shrinkage. As the strength of steam-cured concrete increases with the amount of curing (i.e. maturity), a corresponding decrease in drying shrinkage is to be expected with increase in the length of curing period and with rise in curing temperature. This expected effect is confirmed by the data of Figure 11.21.

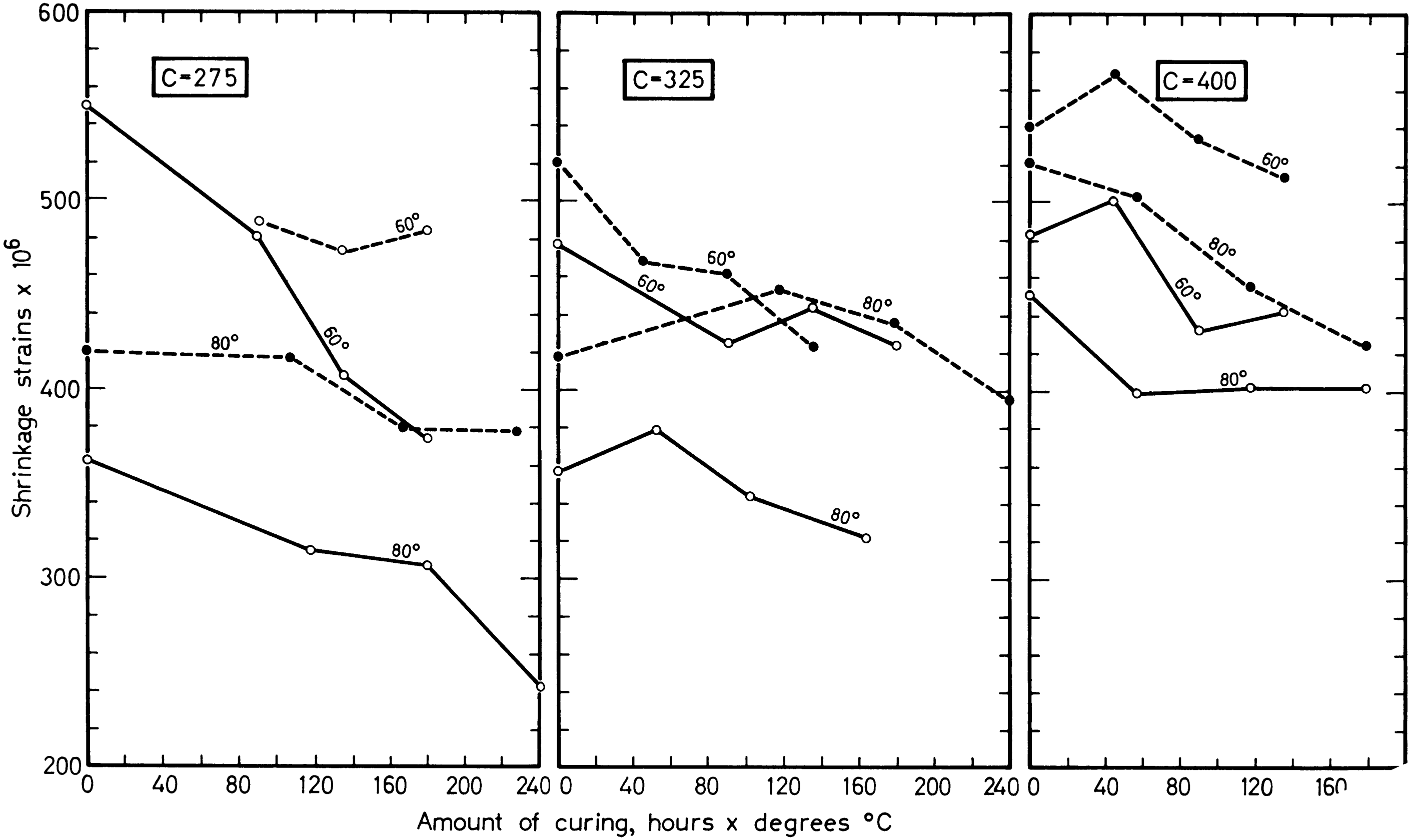

Figure 11.21 *Drying shrinkage of steam-cured concrete of different cement contents* C, *at the age of* 180 *days* (*after Soroka and Jaegermann*[25]). ——, *Ordinary concrete*; – – –, *lightweight-aggregate concrete*

11.7.1.3 Effect on creep

Considering the similarity in the mechanisms of shrinkage and creep, it may be expected that steam-curing will reduce creep. This is confirmed by the data of Figure 11.22[32] and Table 11.2.[33] The data of Table 11.2 also confirm that steam-curing reduces drying shrinkage of concrete.

As in ASTM C150, I is ordinary Portland cement and III rapid-hardening Portland cement.

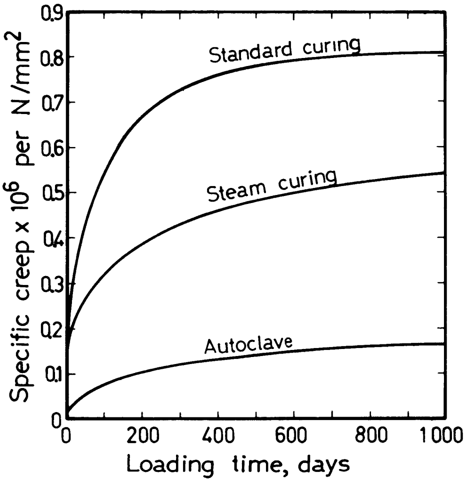

Figure 11.22 *Effect of steam curing on creep of concrete (after ACI Committee* 517[32])

Table 11.2 Effect of steam-curing and autoclave treatment on shrinkage and creep of concretes of equal strength and made with different aggregates (after Hanson[33])

Type of aggregate	*Relative creep**				*Relative shrinkage**			
	Steam-curing		*Autoclave*		*Steam-curing*		*Autoclave*	
	I	III	I	III	I	III	I	III
Expanded blast furnace slag	70	62	24	24	84	74	28	20
Expanded shale	80	70	38	24	90	74	26	21
Normal sand and gravel	82	66	24	18	70	61	26	22

*Percentage of the corresponding creep or shrinkage of normally cured concrete.

11.7.1.4 Effect on permeability

The data of Higginson, which are presented in Figure 11.23, indicate that steam-curing increases water permeability of concrete. Indeed, such a result would be expected from the fact that steam-curing is associated with increased porosity and internal cracking. On the other hand, the same data also indicate that supplementary wet-curing significantly reduces permeability implying that, to a considerable extent, the reduction in the permeability is due to the reduced hydration which is brought about without supplementary curing. This conclusion is supported by the observed decrease in permeability with increase in length of curing period and rise in curing temperature. In any case, however, for the previously mentioned reasons, the permeability of steam-cured concrete is greater than that of normally-cured concrete.

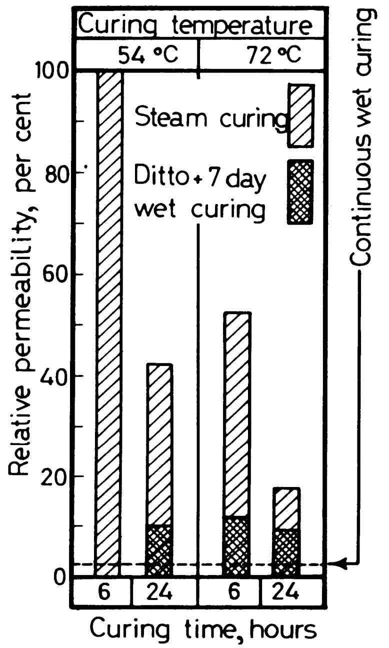

Figure 11.23 *Effect of steam curing on permeability of concrete (after Higginson*[31]*)*

11.7.1.5 Effect on sulphate resistance

According to Lea[34] steam-curing does not improve sulphate resistance of concrete which, under certain conditions, may be adversely affected. Biczok[35] also suggested that sulphate resistance of concrete is not improved by steam-curing. Higginson,[31] however, found that steam-curing improved sulphate resistance of concrete and that, in some cases, this improvement was very significant indeed.

Higginson attributed his findings to the fact that the concrete in his tests was dry when exposed to sulphate attack. Drying is known to improve sulphate resistance of concrete, apparently due to the simultaneous carbonation which takes place.[36] Hence, the improved performance of the steam-cured specimens in Higginson's tests.

11.7.2 Steam-curing under pressure (autoclave treatment)

As explained earlier, cement paste which is treated in an autoclave is characterised by a coarser structure, i.e. by a lower specific surface area (Table 3.4) and by bigger pores (Figure 3.7), than normally-cured paste. Autoclave treatment is also associated with changes in the composition of the paste, i.e. in the formation of $C_2SH(A)$ (Figure 4.22) in place of the CSH gel. Also, the density of the hydration products in autoclave treated paste is greater than that of normally cured paste. Hence, for the same degree of hydration, the porosity of the paste treated in an autoclave is greater than that of the normally cured paste. As may be expected, the foregoing changes in structure and composition are reflected in the properties of the concrete.

11.7.2.1 Effect on strength

The hydrate $C_2SH(A)$ has poor cementive properties. Consequently, and because of the coarser structure of the cement paste, autoclave treated concrete is weaker than its normally-cured counterpart. Addition of silica in an amount

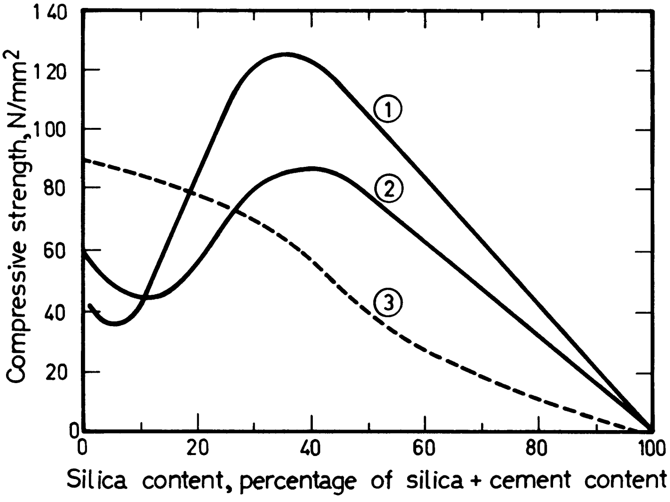

Figure 11.24 *Effect of silica content on strength of concrete (after Gonnerman*[37]*). (1) Autoclave treatment at* 177°C *for* 14 *hours; (2) as (1) but for* 3 *hours; (3) wet curing for* 28 *days* giving a C/S molar ratio equal to about one counteracts the adverse effect of autoclave treatment on strength. In a cement + silica mixture with such a ratio tobermorite, which possesses strong cementive properties, is formed instead of $C_2SH(A)$ (Figure 4.22). Consequently, concrete strength is increased to an extent which offsets the adverse effect of autoclave treatment. The effect is demonstrated in Figure 11.24, from which it can be concluded that, strengthwise, the optimum silica content is 30 to 40% of the combined weight of the silica and the cement.

It may be noted from Figure 11.24 that the addition of silica not only offsets the adverse effect of autoclave treatment on strength but, with the addition of the optimum amount, autoclave treated concrete is actually stronger than normally cured concrete. Also, it may be noted that concrete strength is increased with the length of the autoclave treatment. The same conclusion is indicated by the data of Menzel[38] which are presented in Figure 11.25. These data also indicate that strength is related to autoclave temperature and increases with the rise in the latter.

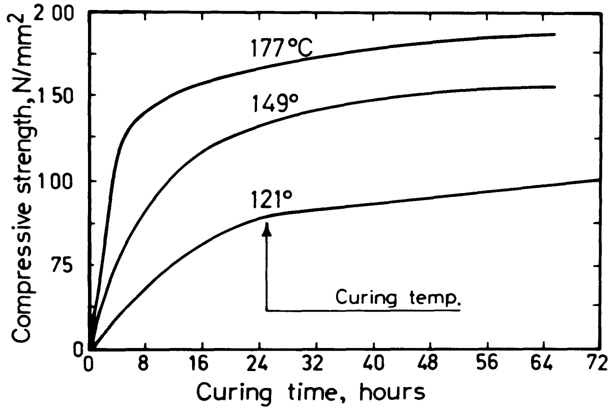

Figure 11.25 *Effect of autoclave temperature and length of curing period on strength of cement paste (after Menzel*[38]*)*

11.7.2.2 Effect on drying-shrinkage and creep

The use of an autoclave considerably reduces shrinkage of cement pastes. As the shrinkage of concrete is related to that of the paste, it is to be expected that shrinkage of concrete will also be reduced. This conclusion is confirmed by the data of Table 11.2, in which the shrinkage of autoclave treated concrete is only about 25% of that of normally cured concrete. In another study the shrinkage of autoclave treated concrete was found to be somewhat higher, namely, 50 to 65% of the shrinkage of its normally cured counterpart.[39]

11.7.2.3 Effect on sulphate resistance

Autoclave treated concrete has better sulphate resistance than normally cured concrete. Such concrete resists the attack of gypsum and sodium sulphate almost completely, and its resistance to magnesium sulphate is considerably better than that of normally cured concrete.

A few suggestions can be offered to explain the improved sulphate-resiting properties of autoclave treated concrete. Such concrete does not contain calcium hydroxide which is reacted upon by sodium and magnesium sulphates. Hence, the absence of calcium hydroxide may explain the improved resistance of autoclaved concrete to the attack of sodium and magnesium sulphates but not to that of calcium sulphate (gypsum) because the latter does not react with calcium hydroxide. Magnesium sulphate also reacts with the hydrates of calcium silicates. The crystalline hydrates of dicalcium and tricalcium silicate, which are formed in autoclaved concrete, are, however, less reactive than those formed when the concrete hydrates under normal conditions. The reduced reactivity of the hydrated calcium silicates may further explain the improved resistance of autoclaved concrete to the attack of magnesium sulphate. Finally, it is also sometimes assumed that the aluminates and the ferrites appear in autoclaved concrete in less reactive forms, i.e. as $\dot{C}_3AH_6$ or as a solid solution having the general formula $3CaO{\cdot}(A\ell, Fe)_2{\cdot}O_3\,[(H_2O)_2, SiO_2]$. Hence the improved resistance of autoclaved concrete to sulphates in general. It is not quite clear, however, to what extent the foregoing compounds are actually formed in autoclaved concrete.[34]

11.8 Summary and concluding remarks

The properties of concrete are affected by the following technical factors.

11.8.1 Mix proportions

The effect of quality of concrete constituents and their concentration in the mix was discussed in previous chapters. In this discussion it was assumed that the paste content is sufficiently high to allow the concrete to be fully compacted so that no voids or cavities are left within the mass. Otherwise, the presence of such voids will reduce concrete strength and adversely affect its other properties. This will be the case when the concrete mix is deficient in fine material. In practice such a deficiency is avoided by selection of an optimum ratio of fine to coarse aggregate with the aid of suitable mix design procedures. Details of the available procedures can be found elsewhere.[3,4]

11.8.2 Batching

The accuracy of the batching operation determines the uniformity of the produced concrete and thereby also its quality. The accuracy of the batching is determined by the batching method (i.e. by weight or volume), the batching equipment, and to a much greater extent, by the degree of supervision exercised during the operation. The variation in concrete properties is also determined by the variation in the quality of ingredients, etc. In this respect, however, the accuracy of the batching operation is the most important factor.

11.8.3 Mixing

Insufficient mixing adversely affects the homogeneity of the concrete produced. Consequently, in practice a minimum mixing time is specified. This minimum depends on type of mixer used and on its capacity. For a free-fall mixer of capacity not exceeding 0.75 m^3, a minimum of 60 s is usually specified.

11.8.4 Segregation

Transporting and placing of concrete may cause segregation, which adversely affects quality. Uncontrolled discharge of concrete from a height of, say, 2 m or an abrupt change in direction of its flow, are two factors which promote segregation.

11.8.5 Consolidation

Concrete which is not fully compacted is inferior concrete due to the presence of voids and cavities within the mass. Wet mixes can be adequately compacted by hand. Stiffer mixes, however, require the use of mechanical means such as vibrators.

11.8.6 Curing

Keeping the concrete moist, either by wetting or by preventing it from drying, enables hydration to continue, thereby improving concrete quality. The efficiency of the various curing methods is determined by the extent to which they prevent the concrete from drying and facilitate continued hydration. Generally speaking, better results are obtained in practice by wetting the concrete rather than by preventing it from drying.

11.8.7 Steam-curing under atmospheric pressure

Steam-curing under atmospheric pressure accelerates hydration and thereby increases the initial strength of concrete, which may reach some 50% of its 28-day standard compressive strength. On the other hand, steam-curing adversely affects concrete ultimate strength which, under certain conditions, may be considerably reduced. This adverse effect is mainly attributable to differential thermal expansion of concrete constituents, rather than to chemical or structural changes in the cement paste. The thermal expansion of air and water, being greater than that of the solid constituents, increases the porosity of the concrete and promotes internal cracking, hence the decreased strength. This adverse effect on strength can be considerably reduced by delaying exposure of the fresh concrete to the steam for a few hours, by raising curing temperature at a rate not exceeding 20°C per hour, and by subjecting the steam-cured concrete to supplementary wet curing. Steam-curing reduces drying shrinkage of concrete but increases its permeability. Sulphate resistance of concrete is virtually unaffected by steam-curing.

11.8.8 Steam-curing under pressure (autoclave treatment)

Autoclave treatment involves mineralogical and structural changes in the cement paste which, in turn, are reflected in the properties of the concrete. Autoclave treatment considerably accelerates the hardening process, and consequently concrete can reach its ultimate strength after 24 hours. The ultimate strength of the concrete, however, is significantly reduced and may reach only 50% of the 28-day strength of otherwise similar concrete which is normally cured. The addition of about 50% of the cement weight of silica counteracts this adverse effect on ultimate strength. Autoclave treatment considerably reduces shrinkage and creep of concrete and improves its sulphate resistance.

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*Page numbers not in parentheses refer to the text in the usual way. References such as Aardt, J.H.P. van, ref. 26 (271, 289) indicate that Aardt is an author of reference 26 which appears on pages 271 and 289; the author's name does not necessarily appear in the text.

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