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Sustainable Construction Materials: Copper Slag

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This book is dedicated to

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Our families
for their unwavering support

Author Profiles

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Jorge de Brito is a full professor of civil engineering in the Department of Civil Engineering, Architecture and Georesources, Instituto Superior Técnico, University of Lisbon. His main research topic is sustainable construction, particularly on the use of recycled aggregates in concrete and mortars. He has participated in 20 competitively financed research projects (four as the principal investigator) and supervised 20 PhD and 150 MSc theses. He is the author of 3 previous books, 20 book chapters, 250 journal and 450 conference papers. He is the editor-in-chief of the *Journal of Building Engineering*, an associate editor of the *European Journal of Environmental and Civil Engineering*, a member of the editorial boards of 15 other international journals and a member of the CIB, FIB, RILEM, IABMAS and IABSE organisations.

Raman Mangabhai is director of Mangabhai Consulting and vice president of the Institute of Concrete Technology. He graduated in applied chemistry from Salford University in 1978. He has worked in various positions at Salford University, King's College London, Queen Mary and Westfield College, Kvaerner Technology, Cementitious Foundations Skanska and Flexcrete Technologies, dealing with polymer modified cements, cementitious materials, grouts, permeability of concrete and instrumentations. He was Hon Sec of the SCI Construction Materials Group and an active member of the Institute of Materials, Minerals and Mining.

Chao Qun Lye is a graduate from the National University of Singapore and previously an assistant concrete quality control manager, for ready-mix concrete, with the G&W Group in Singapore. He is currently a PhD doctoral researcher at the University of Birmingham, United Kingdom, working in the area of sustainable construction materials. He holds a strong interest in sustainability and innovation, applying it to the use of cement additions such as fly ash and ground granulated blast furnace slag and the use of recycled and secondary materials in concrete, geotechnics and road pavements.

Preface

Sustainability is now commonly referred to in the construction sector, zero waste scenarios are frequently floated, a great deal of research has been undertaken in the use of recycled and secondary materials (RSM) and standards and specifications are becoming more sympathetic to their adoption; however, a clear view of the potential for the use of RSM and how this may affect performance remains to be established. This is important and needed to absorb RSM within the present hierarchy of construction materials.

The use of RSM demands a clear understanding of their characteristics and their potential for use in required applications. This can be problematic as the variability of the material can be high, though this is not unusual, as well-established materials such as Portland cement, naturally occurring sand and gravel and crushed-rock aggregates are also known for their high variation at individual plants and even more so between plants. Material processing and design procedures can help to minimise variability. Why then is the construction industry slow to adopt the use of the new breed of waste materials, such as recycled aggregates arising from demolition and excavation waste, copper slag from metal extraction processes, incinerated bottom ashes from municipal solid waste and sewage sludge and glass cullet from used domestic and industrial waste? It can be argued that the inertia in accepting the use of RSM is due mainly to two reasons: first, research has not come together to exploit the present knowledge of RSM and their potential use and, second, a robust case for the value-added use of RSM has not yet been made.

This book, as part of a series of five, brings together the global research information published in English that deals with copper slag production and properties and its potential for use as cement and aggregate components in concrete, geotechnical and road pavement applications, including related case studies, standards and environmental impacts. The data analysed and evaluated for the book were sourced from 400 publications, contributed by 712 authors, from 337 institutions in 40 countries, over a time period from 1964 to 2015.

The main purpose of the book, which is aimed at academics, researchers, design engineers, specifiers and contractors and is structured in an incisive and easy to follow manner, is to bring out what is known, how the material can be potentially used and at the same time avoid unnecessary repetitive research and wasting of resources.

In completing this work, the authors gratefully acknowledge the help of many individuals at different stages of the work, but would like particularly to thank Edwin Trout of the Concrete Society, UK, for his help with sourcing of the literature, Abdurrahaman A. Elgalhud and Ciaran J. Lynn of the University of Birmingham, UK, for their help with analysis and evaluation of some of the data in Chapter 3 and Rui V. Silva of the Instituto Superior Technico, Universidade de Lisboa, Portugal, for his help with preparing Chapter 5.

Ravindra K. Dhir OBE
Jorge de Brito
Raman Mangabhai
Chao Qun Lye

Introduction

1

Main Headings

- Sustainable construction materials
- Copper slag
- Layout and contents

Synopsis

Experience, collaborative industrial research projects and their dissemination to the point of use have established the grounds for this series of five books and are described in this chapter. The role of sustainable construction materials in achieving sustainable development is highlighted. This book, the first in the series, deals with copper slag. The main aspects of the material are provided in this chapter, along with a brief description of the novel procedure of systematic analysis and evaluation that has been used in developing the work. The structure of the book, in terms of the layout and contents, is also described.

Keywords: Sustainable development, Sustainable construction materials, Copper slag, Book layout and contents.

1.1 Background

The basis of this book stems from years of active research in close collaboration with industry and commitment to dissemination, as well as an active and decisive involvement in promoting the use of waste materials in the construction sector. The work has involved the undertaking of carefully planned and focused research to address some of the major and challenging issues over the years. Amongst the topics the research addressed were those connected to sustainability in construction in general (Whyte et al., 2005), the sustainable use of natural resources to reduce CO_2 emissions (Dhir et al., 2004a; Dhir et al., 2006) and the use of recycling of waste materials to conserve natural resources (Limbachiya et al., 2000; Dyer and Dhir, 2001; Paine et al., 2002; Dhir, 2006; Dyer et al., 2006; Paine and Dhir, 2010a). Of particular note, an outreach programme was launched to share and transfer knowledge, in the form of organising seminars, workshops and conferences (Dhir and Green, 1990; Dhir et al., 2008), and in doing so, a centre for the advancement of small- to medium-size

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enterprises in the construction sector was established. This also included the initiation of the globalisation of concrete research and the forming of the UK–India (Newlands and Dhir, 2011) and Ireland–India research collaboration groups in 2008 and 2012, respectively.

Working at the forefront of the cutting-edge research, undertaken in close partnership with a wide industrial base, also brought to light the fragmented and therefore often ineffective nature of the research undertaken. Indeed, in the area of sustainable construction materials, this has stifled the rate of progress in realising the potential for developing greater adoption of these materials. As a response to this, an approach has been developed to bring together and systematically analyse and evaluate the published data in the global literature, to better understand and utilise the information.

Using this systematic approach, the following selected few successful studies were found:

- On the carbonation and carbonation-induced corrosion of steel reinforcement of concrete made with cement incorporating fly ash and complying with European Standard EN 197-1 (2011), the analysis and evaluation of global data revealed some challenging facts about the performance of concrete and its sustainability impact that had hitherto not generally been appreciated (Lye et al., 2015).
- Similarly, another classic study (Lynn et al., 2016) based on systematic analysis and evaluation of globally published data confirmed the fitness for use of municipal solid waste incinerated bottom ash as an aggregate in road pavement and geotechnical applications.
- A study undertaken by Silva et al. (2014) on a similar basis, using the globally published literature, provided a method for classifying recycled aggregates derived from construction demolition waste for use in concrete, which could help with their certification and boost stakeholders’ confidence in their use.

The process of bringing together globally published literature on recycled and secondary materials and undertaking a systematic analysis and evaluation of the data is undoubtedly a very powerful tool for characterising the materials and establishing their potential applications and engineering performance across disciplines, as well as addressing the important environmental impacts and sustainability issues. This approach has been adopted to develop this book as part of a series of five dealing with sustainable construction materials.

This work should serve as a useful resource for academics, researchers and practitioners, providing an up-to-date, comprehensive view of the research on the subject of copper slag (CS) and its use in construction, in concrete, geotechnics and road pavement applications, as well as the associated environmental impacts, case studies and issues related to standards and specifications, where necessary. Of equal importance, this work should help to reduce wasteful repetitive studies and also potentially spark new ideas and useful projects in areas of need.

1.2 Sustainable Construction Materials

Whilst it could be argued that the term ‘sustainability’ is now generally recognised, the wider implications of this are still difficult to comprehend. Alternatively, ‘sustainable development’ appears to be a much more straightforward and graspable expression which is easier to appreciate and numerate. It is defined in the prominent United Nations’ Brundtland report (1987) as ‘development which meets the need of the present without compromising the ability of the future generations to meet their own needs’.

In this context, the ever growing demand for building of infrastructure is fast assuming a central stage in national development, as a major consumer of natural sources of non-renewal materials and energy. This development is expected to increasingly affect the environment in terms of CO_2 emissions, which can lead to subsequent climate change and temperature increases at the earth’s surface, as well as having a major influence on social and economic conditions. The possible consequences in this respect are frightening, potentially leading ultimately to famine, floods, mass movement of people and the destruction of species (Stern, 2006). As such, it is not surprising that governments across the world look to the construction industry to play a major role in addressing the issues relating to sustainable development, and therefore sustainability.

Along with the more efficient design, construction and operation of buildings, the growing use of recycled and secondary materials, which, for obvious reasons, are increasingly being addressed as sustainable construction materials, can also help to lower the environmental impact of construction work. For example, minimising the use of Portland cement, for which the current annual global production is around 4.1 billion tonnes (see Figure 1.1), can lead to significant reductions in CO_2 emissions. The use of CS as part of the raw feed in the production of Portland cement clinker and in ground form as a component of cement is discussed in Chapter 5. Whilst this can make a modest contribution to reducing CO_2 emissions, the similar use of other waste materials can collectively make a significant contribution. Indeed, in this respect, EN 197-1 (2011) on common cements recognises several by-product materials as constituent materials of cement. Furthermore, it is interesting to note the total cement production in China, shown in Figure 1.1; it brings home the threat to sustainability as the development of infrastructure in emerging countries, which accounts for nearly two-thirds of the world, begins to move full speed ahead.

As another example, minimising the consumption of natural aggregates, for which the annual global production is around 50 billion tonnes as of this writing and forecasted to increase further at the rate of 5% per annum, can be realised by developing the use of recycled and secondary aggregates (RSAs) in construction. Whilst this is perhaps generally appreciated, the pertinent question is how to change the mindset and accelerate the process of routinely specifying RSAs in the construction industry. Figure 1.2 clearly emphasises the need to develop the use of RSA materials. In this context, the quantity of manufactured aggregates used in 38 European nations amounts to only 1.5% of the total estimated production of RSAs. The numbers become even

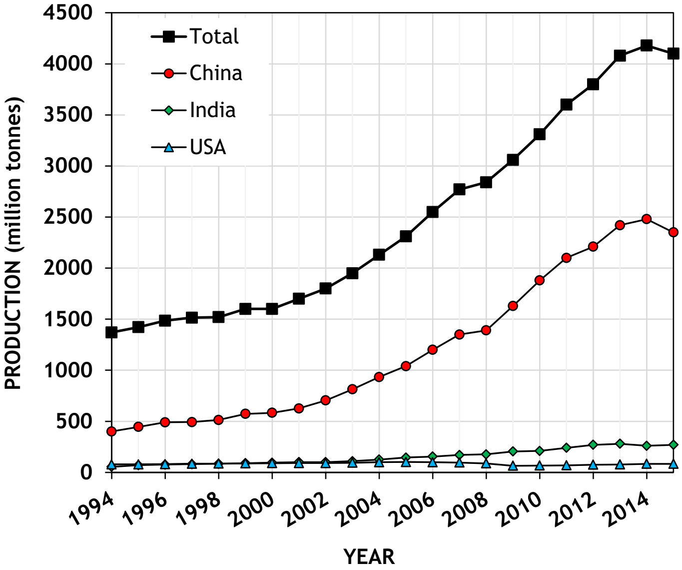

Figure 1.1 World cement production from 1994 to 2015.
Data taken from USGS (2016).

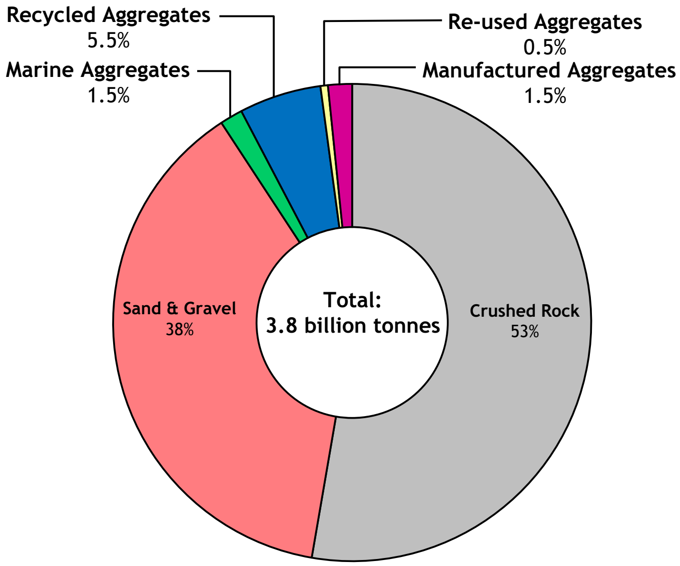

Figure 1.2 Aggregate production in 38 European countries and Israel in 2014.
Data taken from UEPG (2016).

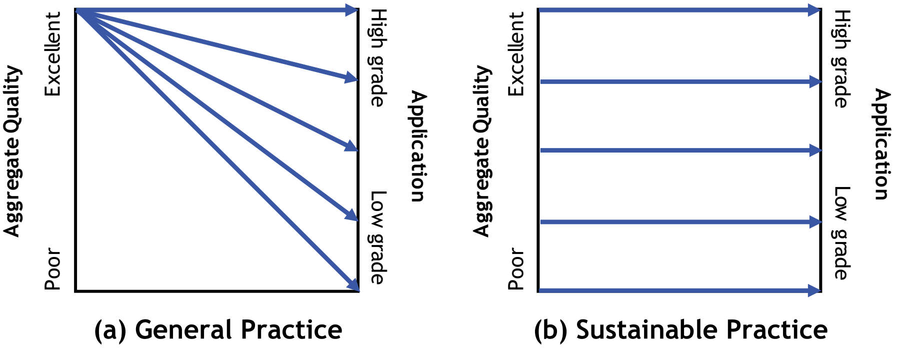

Figure 1.3 General and sustainable practices in dealing with aggregates. (a) General practice. (b) Sustainable practice.
Adapted from Dhir et al. (2004b).

more daunting when one considers that the corresponding share of recycled aggregates arising from construction demolition and excavation waste used in this region stands at only 5.5%.

It is recognised that national standards the world over are moving towards facilitating the use of RSAs in construction and the performance-based approach is being advanced (Paine and Dhir, 2010b; Collery et al., 2015). Figure 1.3 emphasises the pertinent point of sustainability as a simple workable philosophy that is easy to understand and points the way forward in adopting the sustainable use of construction materials by matching the material quality with the application demands.

1.3 Copper Slag

CS is a by-product resulting from the production of copper metal. Whilst not in the same league, in terms of volume, as ferrous slag in the form of iron and steel slag, with an estimated annual production of about 40 million tonnes (figure projected from ICSG, 2015), CS still presents the challenging environmental issue of diverting the material away from landfills and preferably developing it as a valuable resource.

The production of CS, on a sizeable scale, is in the main confined to a few countries. On the basis of 2014 figures (ICSG, 2015), China is estimated to have the highest CS production, with an annual figure in the region of 14 million tonnes. This gives China 35% of the total world CS production. China is followed, in the top 10 group of CS producers, by Japan, Chile, Russia, India, Korea, Poland, Zambia, the United States and Germany. On a regional basis, using the source from ICSG (2015), it would appear that over half of the CS world production in 2014 came from Asia (Figure 1.4).

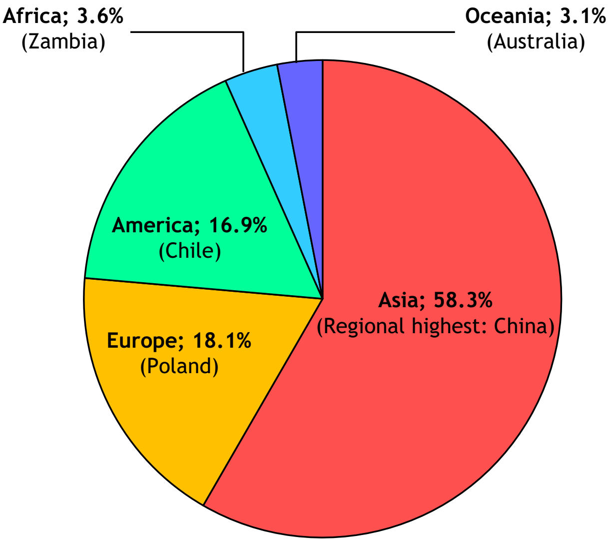

Figure 1.4 Copper slag production in 2014.

The production of CS on a regional basis has varied over the years, with the figures for Asia showing an exponential increase since 1990. The second place in CS production was initially enjoyed by America, but in 2014, this production dropped slightly below that of Europe. The production figures for Africa and Oceania have remained essentially similar and well below those of the other regions.

The nature of CS in its final form can vary depending on the cooling process applied, and although the individual quantities of the different types of slag are hard to know, slag is essentially produced in air-cooled and water-quenched forms. The latter comes as a granular material similar to sand and can also be used as an abrasive material for surface cleaning purposes. The residue from the abrasive process is in the form of spent slag and, as mentioned in Chapter 3, can be cleaned and reused as washed CS in the construction industry, particularly in concrete as a partial sand replacement. Both the physical and the chemical characteristics of CS make the material potentially suitable for use in various applications in the construction industry, namely in cement, concrete, geotechnical and road pavement applications, and these are discussed in Chapters 4–8.

1.4 Layout and Contents

Chapter 1 introduces the nature and purpose of the work undertaken for this book. Details of the methodology adopted in accomplishing the work, which involved bringing together the global knowledge on the characteristics of CS and its potential use in construction, are described in Chapter 2. This chapter explains how the exhaustive search of globally published literature in the English medium, consisting mainly, but not exclusively, of journal papers, conference papers and reports produced by public and private bodies, has been carried out. The manner in which the systematic analysis, evaluation and structuring of the published information therein were conducted, dealing with the use of CS in various construction applications, is also described.

Chapter 3 deals with the production and classification of CS, as well as its chemical, mineralogical and physical properties, indicating, where possible, the potential for use of CS in construction. Chapter 4 deals with the use of CS as sand in concrete, which is seen as its natural application, covering its effects on the performance of concrete, in both the fresh and the hardened states, as well as the durability performance and its specific use in developing high-performance concrete. The potential for use of CS, both as part of the raw feed in the manufacture of Portland cement and in a ground form as a component of cement in concrete, is examined in Chapter 5.

The use of CS in geotechnical and road pavement applications in the form of unbound, hydraulically bound and bituminous bound mixtures is considered in Chapters 6 and 7, respectively. Although environmental issues, case studies and standards are briefly discussed separately in each chapter, a comprehensive coverage of the subject matter in this respect is provided in Chapter 8. Each chapter also includes information on the use of copper tailings. Conclusions are presented at the end of each chapter, along with a list of the thoroughly sourced relevant references. The epilogue, presented in Chapter 9, provides the salient closing points emerging from this work.

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Methodology

2

Main Headings

- Sourcing and appraisal of literature
- Building the data matrix
- Analysis, evaluation and modelling of data
- Dissemination

Synopsis

For the reader to fully benefit from this work, the methodology adopted in preparing the base material for writing this book is described. This consists of three distinct tasks, undertaken in sequence. First, the globally published literature on the subject of copper slag and its use in construction is sourced thoroughly and appraised. This is followed by the next stage of sorting the literature and mining the data from the sourced publications and parking them in Excel to build the data matrix. The final part of the work involved the analysis and evaluation of the data and, where possible, the development of models.

Keywords: Analysis, Copper slag, Data matrix, Evaluation and modelling of data, Literature sourcing and appraisal.

2.1 Introduction

The work described in this book has been developed using an approach that is different to the norm and is best suited to establishing what is already known, and how well it is known. It can further the value-added sustainable use of copper slag (CS) in construction and minimise repetitive research to better channel the resources to further advance the material. To realise this, a robust and clearly structured methodology has been designed. For readers, academics, researchers and practitioners to understand and achieve the full benefit of this work, a detailed description of the methodology is provided.

Figure 2.1 outlines the four main stages of the work, beginning with the sourcing and assembling of the base information from the published literature. As an indication of the sheer scale of the work, it is useful to consider the effort required to produce a single publication. Each is likely to involve, on average, two experts in the field,

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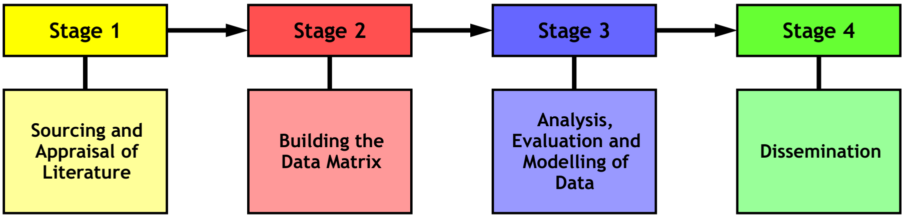


Figure 2.1 Outline of the main stages of the methodology.

working over a prolonged time period. With this book based on 400 publications on the subject of CS and its use in construction, it is clear that there is a large amount of information to be managed. Every publication has to be vetted and sorted and the data therein extracted, to construct the complete data matrix. Thereafter, with the combined pool of extracted experimental results in hand, a fresh analysis, evaluation and modelling of the knowledge are undertaken. To finish, the findings are structured in the final book in a manner that would facilitate effective dissemination.

The book is split into nine chapters, covering the characteristics and use of CS in various construction applications. Each chapter has been assigned its own Excel file, containing as many as 25 separate sheets for different subheadings. Individual sheets were subsequently populated with the extracted data, each containing hundreds to thousands of distinct data points. These sheets then formed the basis of the novel analysis, evaluation and modelling work undertaken.

2.2 Sourcing and Appraisal of Literature

Whilst it is recognised that literature has been published on the subject in many languages, for practicality, the global sourcing was limited to literature published in English. The main contribution has come from peer-reviewed journal papers, which provided a reputable source of information, covering most of the research subject areas. Conference papers have also been sourced, though these were more difficult to obtain and typically contained less robust information. The inclusion of postgraduate theses was not considered a requirement, though a small number have been used. Reports produced from government bodies and private organisations have also been included, where available.

2.2.1 Identifying and Sourcing of Literature

The process of sourcing the literature was wide reaching and thorough. A list of the relevant keywords, covering the scope of the work, along with a comprehensive list of search engines and websites used for sourcing the literature is provided in Table 2.1.

Table 2.1 Keywords and search engines and websites used

(a) Keywords Used

- Copper slag
- Properties
- Characteristics
- Production
- Processing
- Aggregate
- Concrete
- Cement
- Pozzolanic
- Geotechnical applications
- Road pavements
- Unbound
- Hydraulically bound
- Bituminous bound
- Leaching
- Environment
- Case studies

(b) Search Engines and Websites Used

- Academic Search Complete
- American Concrete Institute
- American Society of Civil Engineers
- ASTM
- BASE
- British Standards Online
- EBSCOhost
- Engineering Village
- Google
- Google Scholar
- JSTOR
- Inderscience Online
- Ingenta Connect
- Institute of Civil Engineering
- Construction Information Service
- ProQuest
- Researchgate
- RILEM
- Sagepub
- ScienceDirect
- Science.gov
- Scientific.net
- Scopus
- SpringerLink
- Taylor & Francis Online
- Web of Knowledge
- Web of Science
- Wiley Online Library

The literature search was undertaken until no further publications could be sourced and the search could be assertively judged to be exhausted. This search policy proved to be rewarding, though a challenging and time-consuming exercise.

To catalogue the sourced literature, and thereafter the information extracted from the publications, in an orderly manner, a data matrix was created in Excel, containing all the various relevant topics. Once the literature search was concluded, the initial background information was logged to determine the nature of the sourced literature, including the year of publication, the details of the authors in the form of their affiliated institution and country and the publication type. A few points of interest emerging from this exercise are discussed below.

2.2.2 Publication Timeline

In total, 400 publications were sourced, published over a period of 52 years, from 1964 to 2015. The first work on this subject was a joint paper by Gerritsen from The Netherlands and Bruun from the United States (Gerritsen and Bruun, 1964), dealing

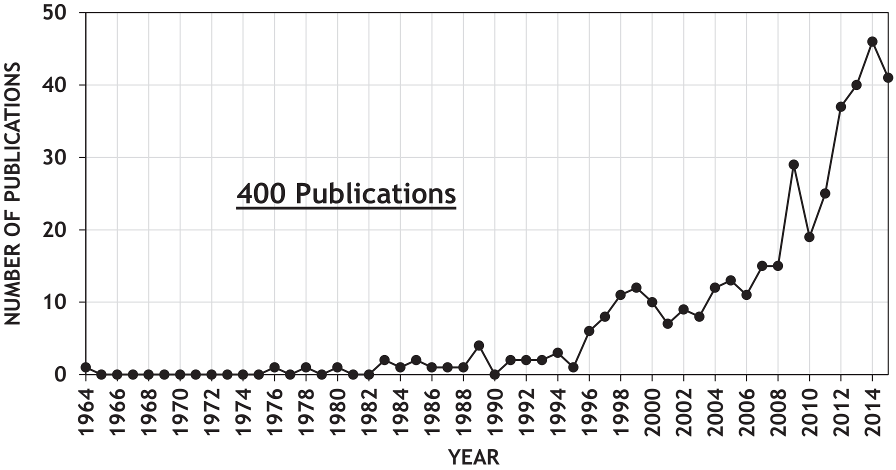


Figure 2.2 Distribution of publications by year.

with the design of revetments in which CS was used. The paper was presented at the Ninth Conference on Coastal Engineering held in Lisbon, Portugal, in 1964. However, as Figure 2.2 shows, up until 1995, there was little work published on the subject of CS use in construction, though there are some signs that the research interest in this area was starting to pick up during the period 1989–95. The real interest in this research and its publication began to grow in 1995, and from 2013 onwards, it has reached an average rate of 40 publications per year. This sudden surge of interest in developing the recycling of CS in construction may have been influenced by the introduction of environmental legislations to promote the use of waste materials to improve sustainable development.

2.2.3 Global Publication Status

The country-wise distribution of the published literature, based on all the authors of each publication, not only the first author, has been logged and this information is presented in Figure 2.3. It can be seen that the spread of publications has tended to concentrate in a few countries, with India alone accounting for over one-third of the total publications, and the top 10 countries, India, Singapore, the United States, Iran, Japan, Oman, Canada, China, the United Kingdom and Belgium, making up 75% of the total publications sourced. Furthermore, the slag production of countries is not reflected in their rate of publications, as many countries that do not produce CS, such as Singapore and the United Kingdom, are amongst the top 10 countries publishing on the subject.

Another interesting point to emerge is that the foremost contributors to the process of knowledge dissemination through publishing in the area of CS, since 1995, have remained the same, with the top 10 countries listed in Table 2.2. India has contributed

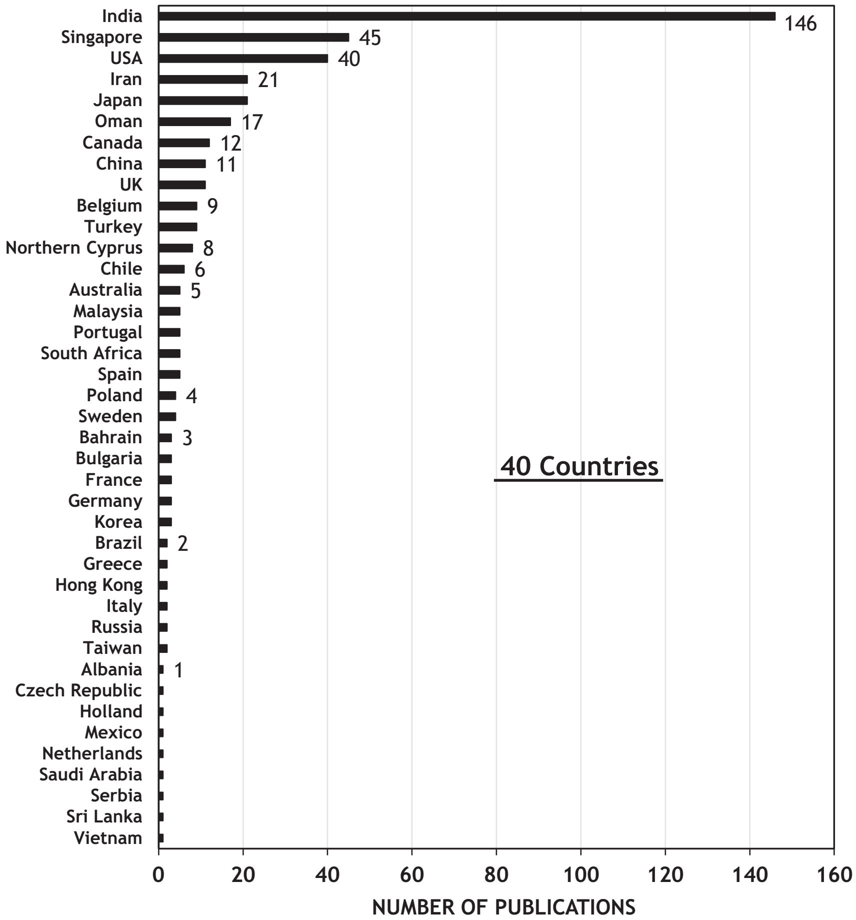


Figure 2.3 Distribution of publications by country.

at the fastest average rate of 10.4 papers per annum since it started publishing in 2002, followed by Singapore at a rate of 2.4 papers per annum and Belgium at the third best rate of 1.8 papers per annum, though it started to publish relatively recently in 2011. Table 2.2 also shows that Japan has not published in this subject area since 2009. It was also found that despite China producing CS more than any other country, their publication rate is considerably low.

2.2.4 Publication Types

Knowing where the sourced literature has been published is another important part of the process of evaluating the overall credentials of the research. As can be seen from Figure 2.4, nearly two-thirds of the publications on CS are journal papers, though there

Table 2.2 Top 10 countries for publications

Country	Period	Number of Publications
India	2002–2015	146
Singapore	1997–2015	45
United States	1976–2014	40
	1996–2014	34
Iran	1999–2015	21
Japan	1997–2009	21
Oman	2002–2014	17
Canada	1984–2013	12
	2000–2013	8
China	1993–2014	11
	1998–2014	10
United Kingdom	2001–2015	11
Belgium	2011–2015	9

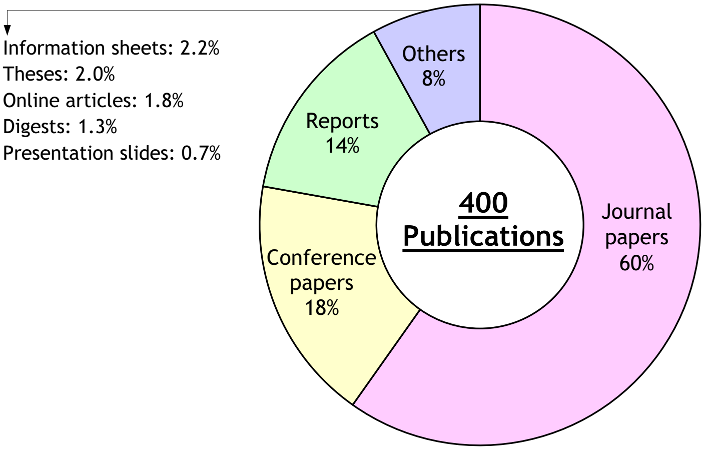


Figure 2.4 Distribution of publications by nature.

are still a good number of conference papers and reports published. Together, these three types of publications accounted for 92% of the total literature sourced. It would be expected that the research published in these three source types would generally be of reasonably high standard. There were also smaller amounts of additional research information found in the form of digests, information sheets, presentation slides, postgraduate theses and online articles.

Table 2.3 Most published journals for copper slag

Journal	Number of Publications	Years
Construction and Building Materials	16	1992–2015
Resources, Conservation and Recycling	10	1997–2011
Waste Management & Research	8	1992–2009
Cement and Concrete Research	5	1994–2012
Int. J. of Engineering Research and Technology	4	2012–2014
Int. J. of Research in Engineering and Technology	4	2014–2015
Int. J. for Research in Applied Science and Engineering Technology	3	2013–2015
Int. J. of Civil and Structural Engineering	3	2010–2012
Int. J. of Civil and Structural Engineering Research	3	2014
Int. J. Civil Engineering &Technology	3	2013–2014
Journal of Hazardous Materials	3	2007–2011
Magazine of Concrete Research	3	2011–2015

Int. J., International Journal.

Investigating further into the nature of the biggest publication type, a staggering number of 139 journals were found to contain information on the subject of CS. This stretched across the fields of engineering, material science and environmental sciences. Journals with a minimum of three papers are listed in Table 2.3. There are 47 and 80 further journals that have published two papers and one paper each, respectively.

2.2.5 Researchers Involved

The background information gathered from the literature on the subject of CS and its use in construction showed that over 700 authors have published in this area, though Table 2.4 has been limited to only those who have contributed a minimum of four publications. In addition to these, there are 30 authors who have contributed three publications, 112 authors with two publications and 543 with one. Al-Jabri (2002–14) from Sultan Qaboos University in Oman has been a consistent researcher over the years and has the highest number of publications. There are a considerable number of researchers from India actively working in this field. Some authors, such as Douglas (1985–87) of Canada, Mobasher (1996–99) of the United States, Mohsenian (2009) and Sohrabi (2009) of Iran and Prasad (2006–09) of India, published rapidly during short time spells and then stopped abruptly. It should be mentioned that two of the top five on the list, Onuaguluchi (2010–14) and Eren (2011–13), have worked on copper tailings.

Table 2.4 Key researchers on copper slag

Author	Country	Years	Number of Publications
Al-Jabri K.S.	Oman	2002–2014	10
Onuaguluchi O.	Northern Cyprus	2010–2013	8
Brindha D.	India	2010–2012	6
Eren O.	Northern Cyprus	2011–2013	6
Taha R.	Oman	2002–2011	6
Behnood A.	Iran	2004–2009	5
De Belie N.	Belgium	2012–2015	5
De Schepper M.	Belgium	2012–2015	5
Ganesan K.	India	2013–2014	5
Havanagi V.G.	India	2007–2012	5
Mathur S.	India	2006–2012	5
Mohsenian H.	Iran	2009	5
Sakthieswaran N.	India	2013–2014	5
Shoya M.	Japan	1997–2004	5
Sohrabi M.R.	Iran	2009	5
Thomas B.S.	India	2012–2013	5
Van Driessche I.	Belgium	2012–2015	5
Biswas S.	India	2009–2014	4
Boakye D.M.	South Africa	2013–2014	4
Coruh S.	Turkey	2006–2011	4
Douglas E.	Canada	1985–1987	4
Gupta R.C.	India	2012–2013	4
Mobasher B.	United States	1996–1999	4
Nagan S.	India	2010–2011	4
Prasad P.	India	2006–2009	4
Sanchez M.	Chile	2004–2013	4
Tsukinaga Y.	Japan	1997–2004	4

2.2.6 Institutions and Organisations Involved

A staggeringly high number of institutions and organisations, of the order of 300 worldwide, have been involved in research in the area of CS characteristics and applications relating to construction since 1990. India dominates the list, with 107 institutions and organisations having worked in this field during 2002–15; the next highest number is 28 for the United States (1976–2014), followed by 17 for Japan

(1997–2009), 14 for Singapore (1997–2015) and China (1993–2014) and 10 for Canada (1984–2013) and the United Kingdom (2001–15). All other institutions have fewer than 10, many with just a single publication.

Table 2.5 provides a list of the main institutions and organisations that have engaged in research in the area of CS and its use in construction. The listing of institutions has been limited to a minimum of four papers, with only two institutions having double-digit numbers of publications. The dominance of Indian research on this specific subject is clearly visible in this respect.

Table 2.5 Institutions/organisations with a minimum of four publications

Institution/Organisation	Country	Number of Publications
Anna University	India	14
Sultan Qaboos University	Oman	14
Building and Construction Authority	Singapore	9
Eastern Mediterranean University	Northern Cyprus	8
CSIR—Central Road Research Institute	India	8
Iran University of Science and Technology	Iran	8
Nanyang Technological University	Singapore	7
Malaviya National Institute of Technology	India	6
National University of Singapore	Singapore	6
Thiagarajar College of Engineering	India	6
Arizona State University	United States	5
Ghent University	Belgium	5
Hachinohe Institute of Technology	Japan	5
Islamic Azad University of Zahedan	Iran	5
National Institute of Technology, Rourkela	India	5
Sudharsan Engineering College	India	5
University of Atacama	Chile	5
University of Sistan and Baluchestan	Iran	5
Eduardo Torroja Institute for Construction Science	Spain	4
Energy, Mines and Resources Canada	Canada	4
Holcim (Singapore)	Singapore	4
Jawaharlal Nehru Technological University Hyderabad	India	4
National Institute of Technology Karnataka	India	4
National Metallurgical Laboratory	India	4
Ondokuz Mayis University	Turkey	4
Sterlite Industries	India	4
University of the Witwatersrand	South Africa	4

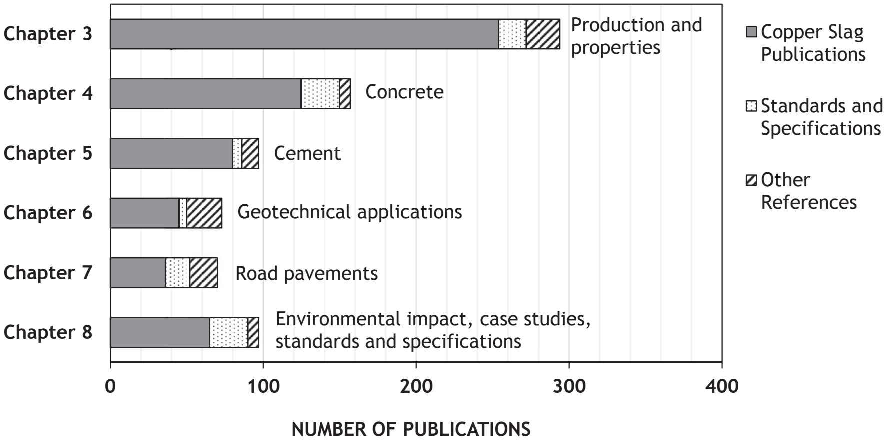


Figure 2.5 Publications, standards and references used in Chapters 3–8.

2.2.7 Subject Area Distribution

In the main, the sourced literature was categorised under six main subject areas (Figure 2.5). On the production and properties of CS, data were sourced from 255 publications and the analysis, evaluation and synthesis work made reference to 21 standards and specifications and 18 other supplementary publications. As CS can be produced in a sand like form, there has been a natural tendency to develop its use as a granular material in the areas of concrete, geotechnics and road pavements, with primary preference as a component of sand in concrete. This is reflected in the number of research publications (125) produced in the area of concrete, which exceeds the combined numbers in the areas of geotechnics (45) and road pavements (36). The chemical composition and amorphous nature of quenched CS appear to have made the material a sufficiently attractive option to explore its potential use both as a component of the raw feed for the manufacture of Portland cement and as a component of cement, with 80 publications, 6 standards and 11 other references used in Chapter 5. Environmental issues and case studies relating to the material account for 65 publications, 25 standards and specifications and 7 other supplementary references, which are also discussed in Chapter 8. The epilogue brings the book to a close.

2.3 Building the Data Matrix

This work consists of two main tasks required to facilitate the subsequent process of systematic analysis and evaluation of the experimental data, as well as the structuring and modelling of the analysed work. Similar to laying the foundation of a building, it is extremely important to set a solid base for this work. This was done through the initial sorting of the literature and the meticulous data mining and parking of the experimental results. Although it may be seen as repetitive and, at times, laborious and tiresome because of the sheer size of the work involved, it demands a keen attention to detail, as the thoroughness of the process can greatly affect the quality and reliability of the later findings.

2.3.1 Initial Sorting of Literature

This stage of the work is very much like the post office sorting the mail to deliver letters. It serves as the foundation and needs to be carried out correctly. Each publication must be thoroughly vetted and allocated to specific relevant subject areas, such as concrete and geotechnics. The publications are then sorted into further subdivisions in each subject area; an example of this is shown in Figure 2.6, on the use of CS as sand in concrete.

2.3.2 Data Mining and Parking

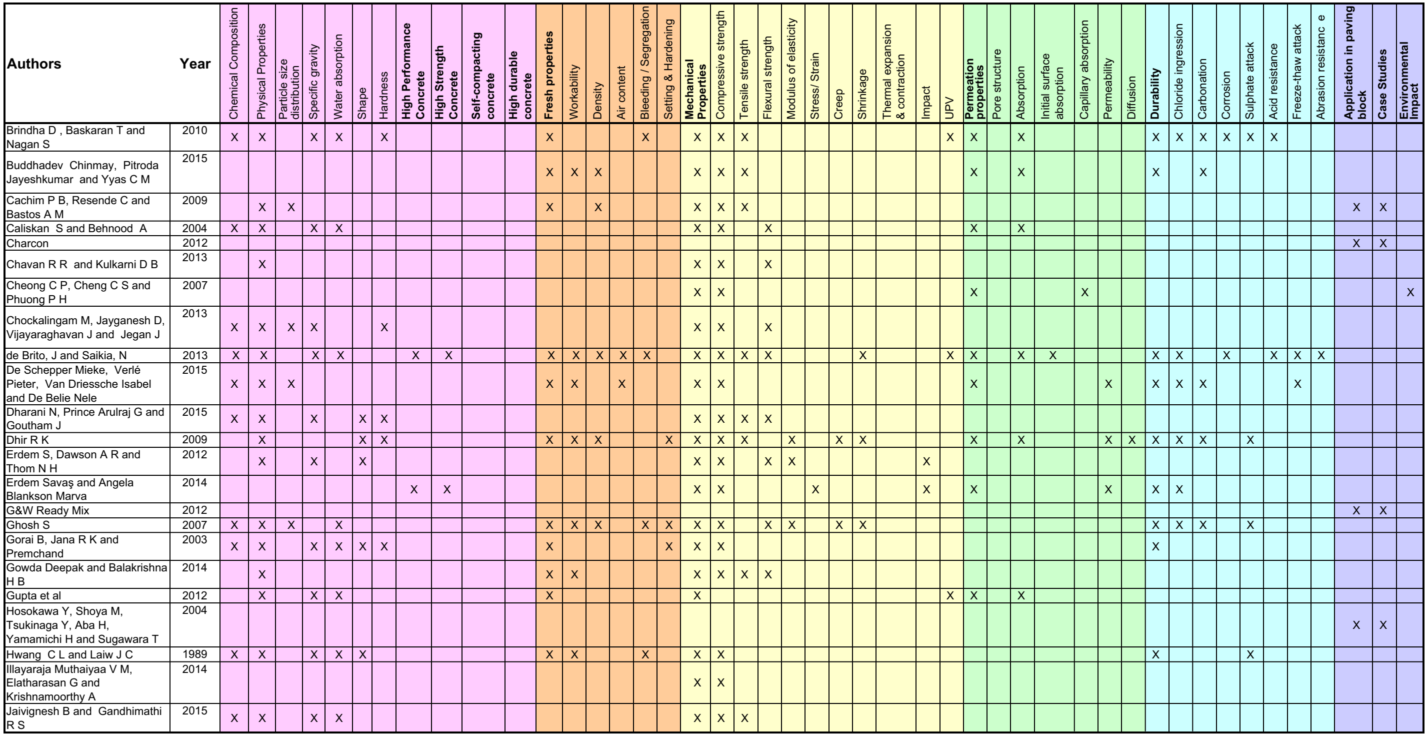
The next stage consists of identifying and extracting both qualitative descriptive information in the text and quantitative results in tables and figures, making use of the software package Plot Digitizer when required, from the sourced publications, for each subject area. The data matrix was formed through this process of mining and parking of the data. A sample of a partial screen capture of the data matrix is shown in Figure 2.7.

2.4 Analysis, Evaluation and Modelling of Data

2.4.1 Analysis and Evaluation

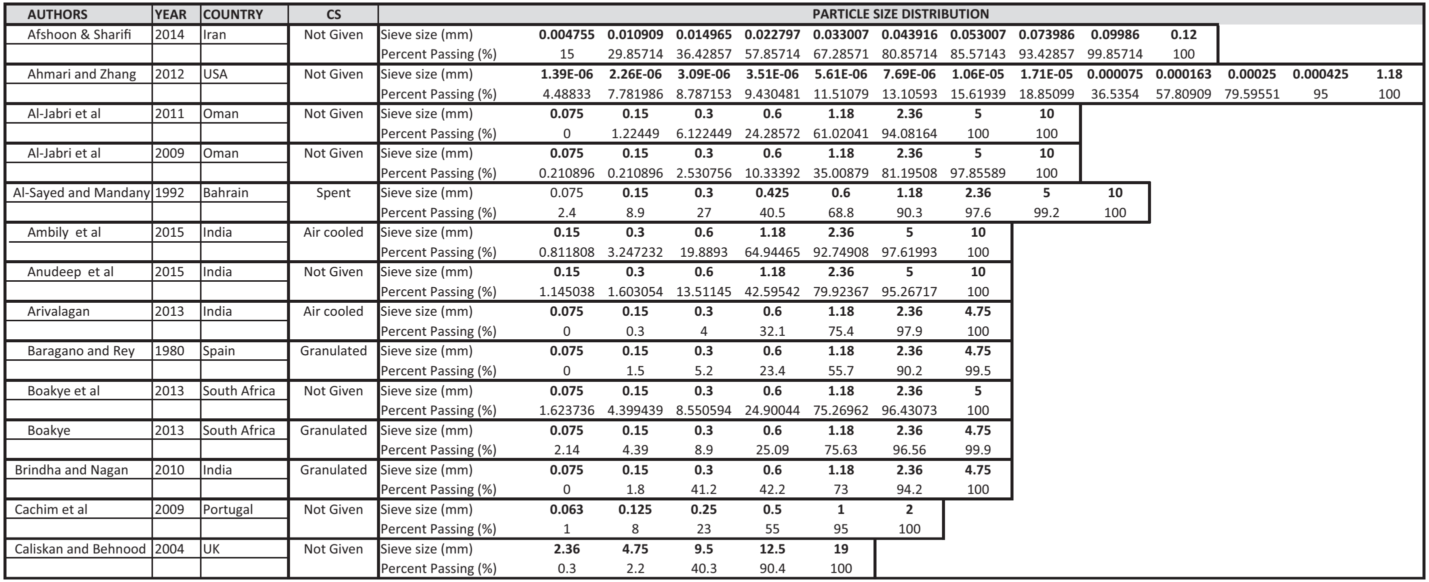
This step involves critical assessment of the globally published experimental results on CS and its use in construction. Using Excel, the data were assembled in a manner allowing a great deal of flexibility in the analysis and evaluation, whilst retaining a very close connection with the results. The analysis and evaluation process proved to be very demanding as there was no magic recipe or straightforward set strategy. The exercise was very much dependent on the nature of the available results and the knowledge and experience of the assessor, requiring great sensitivity and attention to detail in the handling of the data, whilst retaining a pragmatic, imaginative and innovative touch.

The immediate problem one faces with the analysis and evaluation of the global data is the large amount of variation in the test results obtained by different researchers, and this must be assessed carefully. This variability can be controlled, to some extent, by working with relative values, with respect to the reference test material, usually involving the comparison of CS to accepted construction materials. The data were analysed systematically using varying approaches depending on the volume of data,



Authors	**Year**	Chemical Composition	Physical Properties	Particle size distribution	Specific gravity	Water absorption	Shape	Hardness	**High Performance Concrete**	**High Strength Concrete**	**Self-compacting concrete**	**High durable concrete**	**Fresh properties**	Workability	Density	Air content	Bleeding / Segregation	Setting & Hardening	**Mechanical Properties**	Compressive strength	Tensile strength	Flexural strength	Modulus of elasticity	Stress/ Strain	Creep	Shrinkage	Thermal expansion & contraction	Impact	UPV	**Permeation properties**	Pore structure	Absorption	Initial surface absorption	Capillary absorption	Permeability	Diffusion	**Durability**	Chloride ingression	Carbonation	Corrosion	Sulphate attack	Acid resistance	Freeze-thaw attack	Abrasion resistanc e	**Application in paving block**	**Case Studies**	**Environmental Impact**
Brindha D , Baskaran T and Nagan S	2010	X	X		X	X		X					X				X		X	X	X								X	X		X					X	X	X	X	X	X					
Buddhadev Chinmay, Pitroda Jayeshkumar and Yyas C M	2015												X	X	X				X	X	X									X		X					X		X								
Cachim P B, Resende C and Bastos A M	2009		X	X									X		X				X	X	X																								X	X	
Caliskan S and Behnood A	2004	X	X		X	X													X	X		X								X		X															
Charcon	2012																																												X	X	
Chavan R R and Kulkarni D B	2013		X																X	X		X																									
Cheong C P, Cheng C S and Phuong P H	2007																		X	X										X				X													X
Chockalingam M, Jayganesh D, Vijayaraghavan J and Jegan J	2013	X	X	X	X			X											X	X		X																									
de Brito, J and Saikia, N	2013	X	X		X	X			X	X			X	X	X	X	X		X	X	X	X				X			X	X		X	X				X	X		X		X	X	X			
De Schepper Mieke, Verlé Pieter, Van Driessche Isabel and De Belie Nele	2015	X	X	X									X	X		X			X	X										X					X		X	X	X				X				
Dharani N, Prince Arulraj G and Goutham J	2015	X	X		X		X	X											X	X	X	X																									
Dhir R K	2009		X				X	X					X	X	X			X	X	X	X		X		X	X				X		X			X	X	X	X	X		X						
Erdem S, Dawson A R and Thom N H	2012		X		X		X												X	X		X	X					X																			
Erdem Savaş and Angela Blankson Marva	2014								X	X									X	X				X				X		X					X		X	X									
G&W Ready Mix	2012																																												X	X	
Ghosh S	2007	X	X	X		X							X	X	X		X	X	X	X		X	X		X	X											X	X	X		X						
Gorai B, Jana R K and Premchand	2003	X	X		X	X	X	X					X					X	X	X																	X										
Gowda Deepak and Balakrishna H B	2014		X										X	X					X	X	X	X																									
Gupta et al	2012		X		X	X							X						X										X	X		X															
Hosokawa Y, Shoya M, Tsukinaga Y, Aba H, Yamamichi H and Sugawara T	2004																																												X	X	
Hwang C L and Laiw J C	1989	X	X		X	X	X						X	X			X		X	X																	X				X						
Illayaraja Muthaiyaa V M, Elatharasan G and Krishnamoorthy A	2014																		X	X																											
Jaivignesh B and Gandhimathi R S	2015	X	X		X	X													X	X	X																										

Figure 2.6 A partial screen capture of the initial sorting of literature showing the research subjects covered in Chapter 4.



AUTHORS	YEAR	COUNTRY	CS	PARTICLE SIZE DISTRIBUTION													
Afshoon & Sharifi	2014	Iran	Not Given	Sieve size (mm)	0.004755	0.010909	0.014965	0.022797	0.033007	0.043916	0.053007	0.073986	0.09986	0.12			
				Percent Passing (%)	15	29.85714	36.42857	57.85714	67.28571	80.85714	85.57143	93.42857	99.85714	100			
Ahmari and Zhang	2012	USA	Not Given	Sieve size (mm)	1.39E-06	2.26E-06	3.09E-06	3.51E-06	5.61E-06	7.69E-06	1.06E-05	1.71E-05	0.000075	0.000163	0.00025	0.000425	1.18
				Percent Passing (%)	4.48833	7.781986	8.787153	9.430481	11.51079	13.10593	15.61939	18.85099	36.5354	57.80909	79.59551	95	100
Al-Jabri et al	2011	Oman	Not Given	Sieve size (mm)	0.075	0.15	0.3	0.6	1.18	2.36	5	10					
				Percent Passing (%)	0	1.22449	6.122449	24.28572	61.02041	94.08164	100	100					
Al-Jabri et al	2009	Oman	Not Given	Sieve size (mm)	0.075	0.15	0.3	0.6	1.18	2.36	5	10					
				Percent Passing (%)	0.210896	0.210896	2.530756	10.33392	35.00879	81.19508	97.85589	100					
Al-Sayed and Mandany	1992	Bahrain	Spent	Sieve size (mm)	0.075	0.15	0.3	0.425	0.6	1.18	2.36	5	10				
				Percent Passing (%)	2.4	8.9	27	40.5	68.8	90.3	97.6	99.2	100				
Ambily et al	2015	India	Air cooled	Sieve size (mm)	0.15	0.3	0.6	1.18	2.36	5	10						
				Percent Passing (%)	0.811808	3.247232	19.8893	64.94465	92.74908	97.61993	100						
Anudeep et al	2015	India	Not Given	Sieve size (mm)	0.15	0.3	0.6	1.18	2.36	5	10						
				Percent Passing (%)	1.145038	1.603054	13.51145	42.59542	79.92367	95.26717	100						
Arivalagan	2013	India	Air cooled	Sieve size (mm)	0.075	0.15	0.3	0.6	1.18	2.36	4.75						
				Percent Passing (%)	0	0.3	4	32.1	75.4	97.9	100						
Baragano and Rey	1980	Spain	Granulated	Sieve size (mm)	0.075	0.15	0.3	0.6	1.18	2.36	4.75						
				Percent Passing (%)	0	1.5	5.2	23.4	55.7	90.2	99.5						
Boakye et al	2013	South Africa	Not Given	Sieve size (mm)	0.075	0.15	0.3	0.6	1.18	2.36	5						
				Percent Passing (%)	1.623736	4.399439	8.550594	24.90044	75.26962	96.43073	100						
Boakye	2013	South Africa	Granulated	Sieve size (mm)	0.075	0.15	0.3	0.6	1.18	2.36	4.75						
				Percent Passing (%)	2.14	4.39	8.9	25.09	75.63	96.56	99.9						
Brindha and Nagan	2010	India	Granulated	Sieve size (mm)	0.075	0.15	0.3	0.6	1.18	2.36	4.75						
				Percent Passing (%)	0	1.8	41.2	42.2	73	94.2	100						
Cachim et al	2009	Portugal	Not Given	Sieve size (mm)	0.063	0.125	0.25	0.5	1	2							
				Percent Passing (%)	1	8	23	55	95	100							
Caliskan and Behnood	2004	UK	Not Given	Sieve size (mm)	2.36	4.75	9.5	12.5	19								
				Percent Passing (%)	0.3	2.2	40.3	90.4	100								

Figure 2.7 A partial screen capture of data mining and parking showing the copper slag particle size distribution results taken from different studies.

nature of the subject (e.g., chemical composition of CS, deformation of concrete, hydration of cement, compactability of soil, rutting of road pavements and leaching tests), application of the material and test parameters involved. Additionally, reference was made to the current standards and specifications, when necessary, to assess the products for compliance.

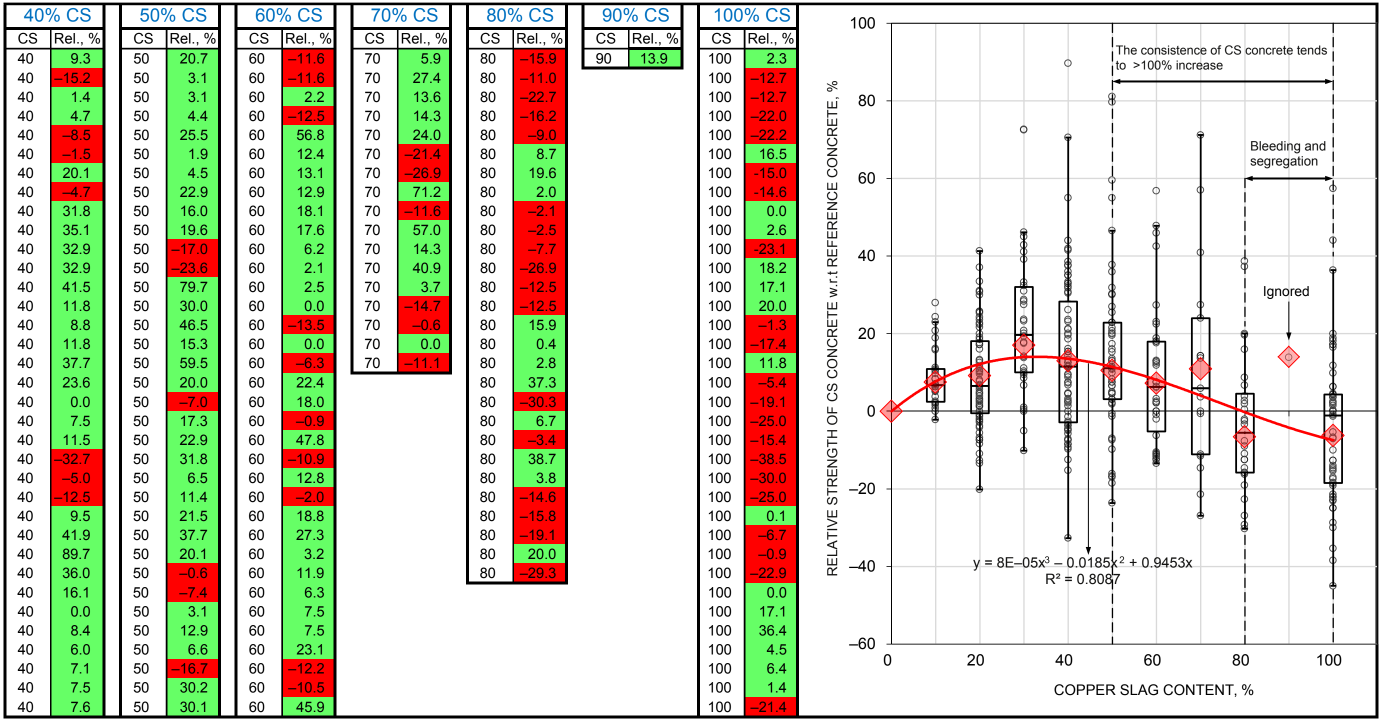
One example of this work is shown in Figure 2.8, in which a total of 626 compressive strength results for concrete made with CS were considered and box-and-whisker plots were adopted to identify the outliers and show their distribution. A trendline was obtained for CS replacement levels from 0% to 100% using polynomial regression analysis. The fresh concrete properties of each mix were examined, and it was found that mixes containing more than 50% CS tended to increase their consistence by more than 100% of the their original value. Additionally, mixes containing CS as a sand component at 80% and above were prone to becoming unstable, experiencing bleeding and segregation.

2.4.2 Modelling

Although in many cases there were not sufficient data for modelling to be carried out with a high degree of confidence, an example of an empirical model that was developed is illustrated in Figure 2.9. This model, which was first introduced by Lye et al. (2015), is based on the experimental data sourced from a single study (Koh and Lye, 2012). The test programme in this study covered concrete mixes designed with 0–100% CS contents in increments of 20% as a component of sand, with water/cement ratios ranging from 0.33 to 0.67 and tested at the ages of 1, 3, 7, 28, 60 and 90 days. The steps taken to develop this model are outlined in Figure 2.9. The model shown in Step 4 allows for the estimation of the additional strength which can be expected at later ages from concrete designed on an equal strength basis at a given age, when 40% CS is used as sand.

2.5 Dissemination

The findings emerging from the analysis, evaluation and modelling of the combined experimental results are structured in an incisive and easy-to-digest manner that can be useable for researchers and practitioners. The work is disseminated in written form as part of a series of books on sustainable construction materials published by Elsevier. With the novel approach undertaken, it is hoped that this book can contribute towards establishing a more widespread practical use of CS as a sustainable construction material, stimulating forward-thinking research and reducing repetitive work.



40% CS	
CS	Rel., %
40	9.3
40	–15.2
40	1.4
40	4.7
40	–8.5
40	–1.5
40	20.1
40	–4.7
40	31.8
40	35.1
40	32.9
40	32.9
40	41.5
40	11.8
40	8.8
40	11.8
40	37.7
40	23.6
40	0.0
40	7.5
40	11.5
40	–32.7
40	–5.0
40	–12.5
40	9.5
40	41.9
40	89.7
40	36.0
40	16.1
40	0.0
40	8.4
40	6.0
40	7.1
40	7.5
40	7.6

50% CS	
CS	Rel., %
50	20.7
50	3.1
50	3.1
50	4.4
50	25.5
50	1.9
50	4.5
50	22.9
50	16.0
50	19.6
50	–17.0
50	–23.6
50	79.7
50	30.0
50	46.5
50	15.3
50	59.5
50	20.0
50	–7.0
50	17.3
50	22.9
50	31.8
50	6.5
50	11.4
50	21.5
50	37.7
50	20.1
50	–0.6
50	–7.4
50	3.1
50	12.9
50	6.6
50	–16.7
50	30.2
50	30.1

60% CS	
CS	Rel., %
60	–11.6
60	–11.6
60	2.2
60	–12.5
60	56.8
60	12.4
60	13.1
60	12.9
60	18.1
60	17.6
60	6.2
60	2.1
60	2.5
60	0.0
60	–13.5
60	0.0
60	–6.3
60	22.4
60	18.0
60	–0.9
60	47.8
60	–10.9
60	12.8
60	–2.0
60	18.8
60	27.3
60	3.2
60	11.9
60	6.3
60	7.5
60	7.5
60	23.1
60	–12.2
60	–10.5
60	45.9

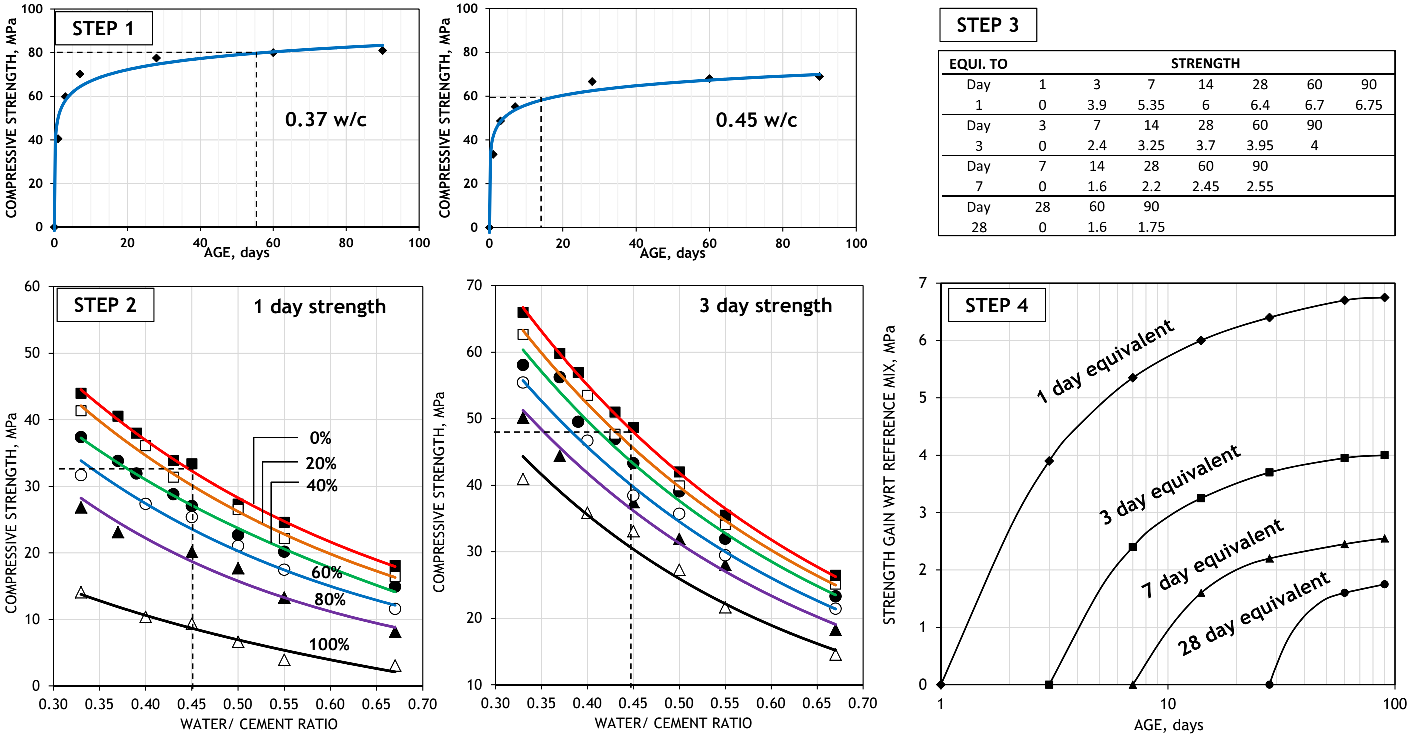
70% CS	
CS	Rel., %
70	5.9
70	27.4
70	13.6
70	14.3
70	24.0
70	–21.4
70	–26.9
70	71.2
70	–11.6
70	57.0
70	14.3
70	40.9
70	3.7
70	–14.7
70	–0.6
70	0.0
70	–11.1

80% CS	
CS	Rel., %
80	–15.9
80	–11.0
80	–22.7
80	–16.2
80	–9.0
80	8.7
80	19.6
80	2.0
80	–2.1
80	–2.5
80	–7.7
80	–26.9
80	–12.5
80	–12.5
80	15.9
80	0.4
80	2.8
80	37.3
80	–30.3
80	6.7
80	–3.4
80	38.7
80	3.8
80	–14.6
80	–15.8
80	–19.1
80	20.0
80	–29.3

90% CS	
CS	Rel., %
90	13.9

100% CS	
CS	Rel., %
100	2.3
100	–12.7
100	–12.7
100	–22.0
100	–22.2
100	16.5
100	–15.0
100	–14.6
100	0.0
100	2.6
100	–23.1
100	18.2
100	17.1
100	20.0
100	–1.3
100	–17.4
100	11.8
100	–5.4
100	–19.1
100	–25.0
100	–15.4
100	–38.5
100	–30.0
100	–25.0
100	0.1
100	–6.7
100	–0.9
100	–22.9
100	0.0
100	17.1
100	36.4
100	4.5
100	6.4
100	1.4
100	–21.4

Figure 2.8 A partial screen capture of analysis and evaluation showing the effect of copper slag as a natural sand replacement on the compressive strength of concrete. *CS*, copper slag; *w.r.t.*, with respect to.



EQUI. TO	STRENGTH						
Day	1	3	7	14	28	60	90
1	0	3.9	5.35	6	6.4	6.7	6.75
Day	3	7	14	28	60	90	
3	0	2.4	3.25	3.7	3.95	4	
Day	7	14	28	60	90		
7	0	1.6	2.2	2.45	2.55		
Day	28	60	90				
28	0	1.6	1.75				

Figure 2.9 A partial screen capture of structuring and modelling showing the strength gain when copper slag concrete is designed on an equal strength basis at different ages. *w/c,* water/cement ratio; *w.r.t.*, with respect to.

2.6 Conclusions

So that the reader can understand and benefit from this work, a clearly structured methodology has been adopted to develop the base material for writing this book. This methodology has three distinct parts as described below.

- The first part deals with the procedures used in sourcing and appraising the literature on the subject of CS and its use in construction.
- The next step involves sorting of the literature, mining of the data from the published literature and parking it in Excel in a well-defined and orderly manner.
- Finally, the data are analysed, evaluated as part of the critical assessment of the combined experimental results to determine the emerging findings and presented in a manner that can be clearly understood and disseminated.

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Production and Properties of Copper Slag

3

Main Headings

- Production of copper and copper slag
- Chemical properties
- Physical properties
- Comparison with typical natural aggregate
- Potential use and applications
- Environmental considerations

Synopsis

This chapter deals with the production, chemical and physical properties and potential applications of copper slag (CS), as well as its associated environmental impact. Air-cooled and quenched slags are the outcomes of different cooling rates applied during the production of copper. Spent CS is a reuse material from its application as an abrasive. CS is an angular, smooth, hard, dense and low-absorption material, composed mainly of iron oxide and silicon dioxide. It has low loss on ignition, has low chloride and sulphate contents and is innocuous to alkali–silica reaction. Air-cooled slag can be crushed to coarse and fine aggregate fractions, whilst quenched slag is granular, similar to sand. The impact and crushing values and friction angle of slag are similar to or better than those of the natural aggregate.

Keywords: Copper slag, Production, Chemical properties, Mineralogy, Physical properties, Applications, Environmental consideration.

3.1 Introduction

About 2.2 tonnes of slag is generated as a by-product for every tonne of copper metal produced (Gorai et al., 2003). The nature and characteristics of copper slag (CS) can vary with the method used during the cooling process. There are two main types of CS produced, namely air-cooled and granulated. The former is a product of cooling the slag slowly to ambient temperature and as a consequence it takes the form of a dense, crystalline product that is usually used as coarse aggregates, similar to crushed rock, in the construction industry. The latter is cooled rapidly through water quenching in a granulator and takes the form of a sandlike material with a large proportion in the amorphous phase. It is suitable for use as an abrasive material and as a fine aggregate in concrete, geotechnical and road pavement applications. Additionally, the ground form, granulated CS, because of its pozzolanic nature can

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be used as a component of cement. There is a third type; when quenched, CS is used as an abrasive and the spent material is collected, cleaned and reused as a fine aggregate. CS can also be used as a raw material in the glass-ceramics and ceramics industry and in other applications.

This chapter mainly discusses the chemical, mineralogical and physical properties of CS and its potential applications. This work is largely based on the in-depth analysis and evaluation of the vast amount of data sourced from 254 publications, originating from 30 countries, published since 1980. The view is also taken that the information in this chapter should provide a basis for the application of CS in concrete, geotechnical and road pavement applications discussed in Chapters 4–7. The environmental impacts that may give rise to concern through the potential for element leaching from CS have also been included.

3.2 Production of Copper

Copper can be found in more than 200 minerals, but only about 10% of this occurs in the form of sulphide minerals (e.g., chalcopyrite, bornite and chalcocite) or oxidized minerals (e.g., cuprite), which are of significance as copper ores (Lossin, 2001). Depending mainly on the ore type, as well as the geographical, economic and environmental considerations, copper can be extracted through:

(i) pyrometallurgy, which involves thermal treatment, predominantly used for copper–iron–sulphide minerals as they do not dissolve easily;

(ii) hydrometallurgy, which involves a leaching operation, commonly used for oxidized minerals.

Pyrometallurgy is largely used in copper production as the main source of the mineral copper–iron–sulphide ores (Schelesinger et al., 2011). There are a wide variety of wastes generated, arising from different stages of pyrometallurgy of copper, among which CS is important to the industry as it contains an appreciable amount of copper, as well as other valuable metals that can be recovered. Figure 3.1 illustrates the main processes involved in extracting copper from sulphide ores using the pyrometallurgical process, with some basic information presented as follows:

- **Mining:** Copper ores are extracted from copper mines.
- **Comminution:** The lumpy ores are crushed and ground into fine particles of size smaller than 100 μm.
- **Flotation:** Copper–sulphide minerals are separated from the finely ground ores by creating a water-repellent film on the minerals using chemicals. The particles become hydrophobic and attach to the rising air bubbles in a flotation cell and go into a collection tank. The final product is known as a concentrate with a typical copper content of 20–30%. Sometimes, the concentrates may be treated with roasting for oxidation, depending on the type of furnace used in the smelting process.

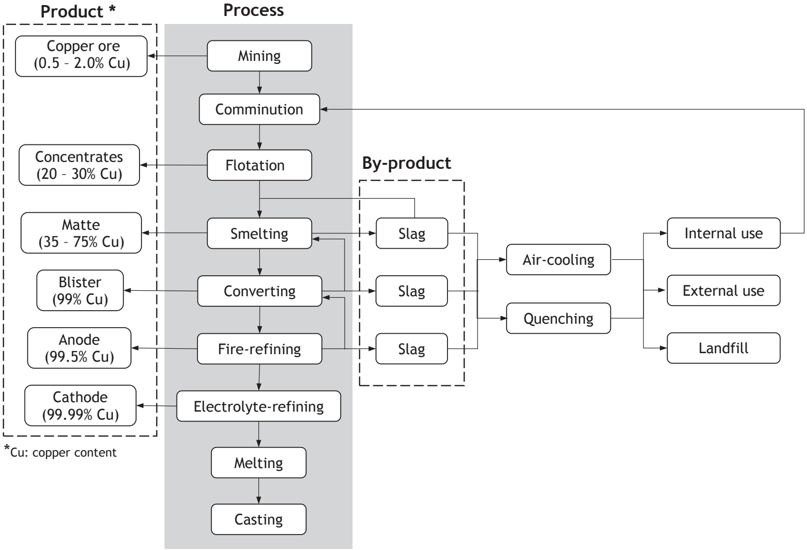

Figure 3.1 Copper and copper slag production in the pyrometallurgical process.

- **Smelting:** The concentrates are subjected to heating, oxidizing and fluxing (using silica) in a furnace at a high temperature to separate copper from iron and other impurities. The two molten materials thus produced from the smelting process are: (i) sulphide matte, which contains a mixture of copper and iron sulphides, and (ii) oxide slag, which contains iron oxides, silicates and other impurities. The matte is subsequently treated to recover its copper, whilst the slag may be treated or disposed of depending on its copper content. Different industrial techniques for matte smelting have been developed, such as flash, reverberatory and blast furnace. The details of the processing of slag are provided in Section 3.2.1. Additionally, the silica dioxide-rich gas generated from the process is collected and sent to a sulfuric acid plant.
- **Converting:** The iron and sulphur of the molten matte from smelting are removed in two stages. In the first stage, the iron is oxidized and silica flux is added to help the formation of iron–silica slag (also known as converter slag), until the iron content of the matte is very low and slag is skimmed off. In the second stage, the sulphur is removed through continuous oxidation to silica dioxide, leaving behind blister copper, which contains 99% copper.
- **Fire refining:** This is the final copper pyrometallurgical process. The molten blister copper is blown with oxygen gas to oxidize and remove its sulphur content as sulphur dioxide gas. Subsequently, its oxygen content is reduced with reducing gas or natural gas. The impurities are also removed as slag. This molten copper is then cast into thin, flat and smooth-surface anodes for electrolytic refining.
- **Electrolytic refining:** After cooling down, the anodes are installed in electrolysis tanks containing acidic copper sulphate solutions. The anodes are dissolved electrochemically and the copper is electroplated onto stainless steel sheets, producing highly pure copper cathodes.
- **Melting and casting:** The cathodes are melted and cast into various products such as wires, rods and sheets.

3.2.1 Production of Copper Slag

About 2.2 tonnes of slag is generated for every tonne of copper produced (Gorai et al., 2003). As shown in Figure 3.1, slags are generated during smelting, converting and fire-refining processes and they contain appreciable copper content, which increases as the purity of the matte increases. Slag that contains more than 1% copper is treated for copper recovery through: (i) smelting molten slag in a separate slag-cleaning furnace, (ii) recycling molten slag back to the previous process or (iii) processing of solidified air-cooled slag in the same manner as ores. On the other hand, slag that contains less than 1% copper is cooled and subsequently sent for other use or disposed of.

Depending on the operation setup, the cooling process has an influence on the properties of the hardened slag. When the molten slag is cooled slowly to the ambient temperature, it solidifies in a large rock-like material that is dense and crystalline. Rapid cooling, by subjecting the molten slag to water quenching, results in amorphous granulated slag. The mineralogy, chemical and physical properties of air-cooled and quenched CS slag are discussed in detail in Sections 3.4 and 3.5 of this chapter.

3.2.2 Processing of Spent Copper Slag

One of the common applications of CS is its use as an abrasive grit for blast cleaning applications, especially in countries with abundant copper production. After blasting operations, the spent CS can be reused as a construction aggregate instead of being sent to the landfill. Such a practice has been promoted by the Building and Construction Authority in Singapore, to reduce the impact on landfill capacity and dependence on imported construction materials (BCA, 2012). Figure 3.2 shows the process flow chart of treating spent CS in Singapore.

Typically, spent CS is collected and sent to a processing plant for treatment. The spent CS is screened and washed to reduce the impurities such as rusts, paints and marine fouling to an acceptable level. After air-drying, the material is stockpiled and ready for reuse as construction aggregate or sent to a landfill if no suitable application can be found.

3.3 Chemical Properties

The chemical composition is a fundamentally important aspect to consider in characterization of the material. Indeed, chemical properties have a strong determining influence on both the physical makeup of the material and its resultant mechanical strength, durability and environmental performance. This section assesses the oxide and mineralogical composition of CS, as well as its cementitious properties.

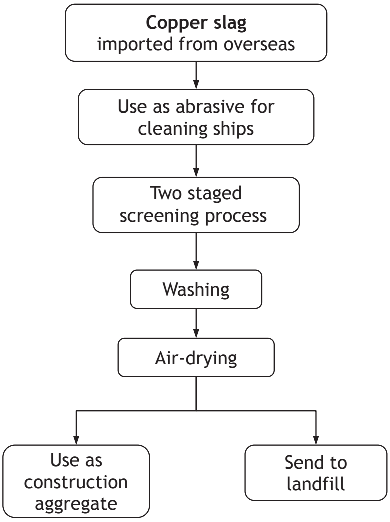

Figure 3.2 Processing of spent copper slag in Singapore.
Based on Kua (2012, 2013).

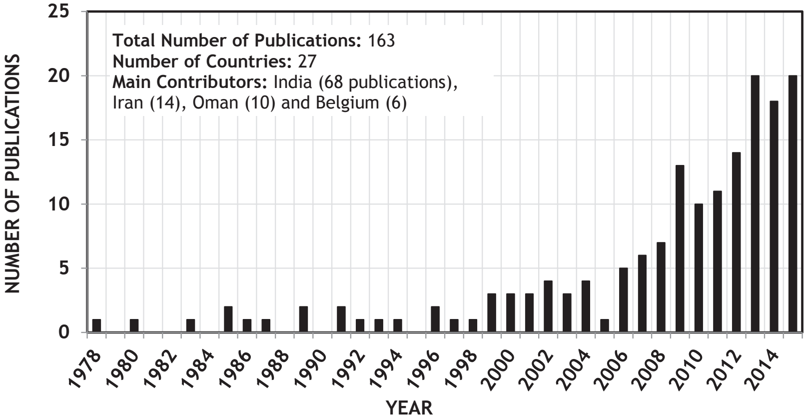

Figure 3.3 Yearly breakdown of publications on the chemical composition of copper slag.

3.3.1 Oxide Analysis

The oxide composition of CS has been examined as a matter of routine in much of the work with this material, resulting in a large stock of data from 163 publications, from 27 countries worldwide, published since 1980. The yearly breakdown of the literature is provided in Figure 3.3 and it shows that there has been a clear growing interest in the material since 1999. The majority of the research has been undertaken in Asian countries, with the main contributions coming from India (68 publications), Iran (14), Oman (10), Belgium (6), Canada (5), China (5), Japan (5) and Turkey (5).

Table 3.1 Analysis of the chemical composition of copper slag

Oxide/ Element	Copper Slag Chemical Composition				
	No. of Samples	Average, %	Std. Dev., %	CV	Range
Fe_2O_3	107	45.4	13.9	30.5	0.8–68.4
SiO_2	106	30.4	9.51	31.3	2.9–71.5
Al_2O_3	101	5.93	9.42	158.8	0.22–89.7
CaO	103	4.77	5.08	106.5	0.15–25.29
ZnO	37	2.32	2.23	96.4	0–8.9
MgO	89	1.85	2.0	110.6	0.008–11.92
SO_3	34	1.06	0.915	86.4	0.045–3.26
K_2O	55	0.821	0.647	78.7	0–3.08
Na_2O	47	0.868	0.793	91.3	0–4.12
CuO	61	0.932	0.657	70.5	0.16–5.07
S	25	0.659	0.427	64.8	0.012–1.5
MnO	39	0.465	1.307	281.0	0.03–8.05
Pb	22	0.340	0.424	124.7	0.034–2.03
TiO_2	28	0.304	0.218	71.6	0–0.98
P_2O_5	12	0.243	0.231	94.7	0.02–0.82
Cr_2O_3	13	0.193	0.225	116.7	0.004–0.73
BaO	6	0.118	0.056	47.0	0.08–0.23
CoO	7	0.109	0.084	77.1	0.02–0.21
Cl	16	0.090	0.245	271.2	0–1
SrO	4	0.018	0.017	97.6	0–0.04
Mo	2	0.225	0.247	110.0	0.05–0.40
NiO	7	0.029	0.021	71.8	0.002–0.06
Cd	3	0.011	0.016	142.6	0.002–0.03
As	3	0.068	0.059	86.7	0.004–0.12
Free silica	2	0.50	0	0.0	0.50
Insoluble residue	2	20.26	3.23	16.0	17.97–22.54

Note: Data include both oxides and elements (e.g., Zn and ZnO results). All iron oxides, including occasional FeO and Fe_3O_4 results, are presented as Fe_2O_3.

Data from Afshoon and Sharifi (2014), Agrawal et al. (2004), Ali et al. (2013), Al-Jabri and Shoukry (2014), Al-Jabri et al. (2002, 2006, 2009a,b, 2011), Alexandrova et al. (2014), Alnuaimi (2012), Alp et al. (2008), Al-Rawas et al. (2002), Amarnaath et al. (2015), Ambily et al. (2015), Anudeep et al. (2015), Arivalagan (2013), Ayano and Sakata (2000), Ayano et al. (2000), Ayres et al. (2002), Bahadur and Nayak (2012), Baragano and Rey (1980), Behnood (2005), Boakye et al. (2013), Boakye (2014), Boakye and Uzoegbo (2014), Brindha et al. (2010), Brindha and Nagan (2010a,b, 2011), Brindha and Sureshkumar (2010), Busolic et al. (2011), Cachim et al. (2009), Caliskan and Behnood (2004), Chandrshekhar et al. (2015), Cheong et al. (2007), Chew and Bharati (2009), Chockalingam et al. (2013), Coruh et al. (2006), Coruh (2008), De Brito and Saikia (2013), De Schepper et al. (2013, 2014a, 2015), Deja and Malolepszy (1989), Deja and Malolepszy (1994), Dharani et al. (2015), Douglas and Mainwaring (1985), Douglas and Malhotra (1987), Douglas et al.

It should be noted that, from the total of 163 publications, many included repeated data, which somewhat lowers the available sample size. A statistical analysis of the composition of the distinctive CS samples is presented in Table 3.1, with the oxides sorted from most to least abundant, based on the average content.

Iron oxide (Fe_2O_3) and silicon dioxide (SiO_2) are the two main components present in CS, making up approximately three-quarters of the material. SiO_2 is commonly present as one of the major components in many traditional construction materials such as Portland cement, sand, fly ash, silica fume, clay and glass. The high Fe_2O_3 content is less common and given the high specific gravity of this oxide (5.2–5.3), its abundant presence in CS contributes to a higher overall material density.

Aluminium oxide (Al_2O_3) and calcium oxide (CaO) are the next most significant oxides found in CS, with average contents of 5.9% and 4.8%, respectively. It is evident that the coefficients of variation are much greater for these components compared to Fe_2O_3 and SiO_2. A large number of additional oxides and elements have also been found at lower content levels in CS, including trace amounts of toxic elements such as Pb, Cd, Zn, Cr and As. The environmental impact associated with the potential release of these elements is dealt with in Section 3.7.

The variability of the composition of CS is further assessed from the individual sample results presented in Figure 3.4(a–d) for the main oxides (a) Fe_2O_3, (b) SiO_2, (c) Al_2O_3 and (d) CaO. The samples have been divided into three groups, based on how the CS has in each case been processed, i.e., air-cooled, quenched (granulated) and the remaining unspecified samples. It should be noted that a small number of studies did not report the contents for all of the four main oxides and this has resulted in some slight discrepancies in the total number of results for each oxide.

Examining the Fe_2O_3 contents in Figure 3.4(a), it appears that there is quite an even spread of samples above and below the average content of 45%. There are a small number of samples with very low iron contents that would not appear to be

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(1985, 1986), Dung et al. (2014), Fadaee et al. (2015), Gaud et al. (2013), Gorai et al. (2003), Gujar and Chohan (2012), Gupta et al. (2012a,b), Hassan and Al-Jabri (2011), Havanagi et al. (2006, 2008, 2009, 2012), Hwang and Laiw (1989), Lim and Chua (2000), Jaivignesh and Gandhimathi (2015), Kajal et al. (2007), Kalinkin et al. (2012), Karamanov et al. (2007), Karthick et al. (2014), Kayathri et al. (2014), Khanzadi and Behnood (2009), Kharade et al. (2013), Kikuchi (2001), Kitazume et al. (1998a), Kiyak et al. (1999), Kumar (2012), Lakshmanan et al. (2014), Lam et al. (2010), Lavanya et al. (2011, 2012, 2013), Lee (2008), Lee et al. (2003), Lorenzo et al. (1991), Lowinska-Kluge et al. (2011), Madany and Raveendran (1992), Madany et al. 1991, Madheswaran et al. (2014), Manasse et al. (2001), Marghussian and Maghsoodipoor (1999), Medina et al. (2006), Meenakashi and Ilandgovan (2011), Merinkline et al. (2013), Mesci et al. (2009), Mihailova and Mechandjiev (2010), Mithun and Narasimhan (2016), Mithun et al. (2015a), Mobasher et al. (1996), Mohsenian and Sohrabi (2009a,b,c,d,e), Monosi et al. (2001), Moosberg et al. (2003), Moura et al. (2007, 1999), Murari et al. (2015), Naganur and Chethan (2014), Najimi and Pourkhorshidi (2011), Najimi et al. (2011), Nataraja et al. (2014a), Nazer et al. (2012, 2013), Ozel et al. (2006), Pappu et al. (2007), Patnaik et al. (2015), Poozvizhi and Kathirvel (2015), Prakash and Brindha (2012), Rajaselvi and Beatrice (2015), Khan et al. (2015), Roper et al. (1983), Sahu et al. (2011), Sanchez et al. (2004), Sanchez de Rojas et al. (2004, 2008), Saraswathy et al. (2014), Sathya and Shanmugavalli (2014), Saxena (2015a,b), Shahu et al. (2012), Sharifi and Kaafi (2013), Sharma et al. (2013a,b), Shi and Qian (2000), Shi et al. (2008), Shoya et al. (1999), Singh and Bath (2015), Singh et al. (2014), Singh and Garg (2002), Siva et al. (2014), Snellings et al. (2012), Song (2013), Spitzner (1978), Srinivas and Muranal (2015), Sterlite Industries (2012), Sudarvizhi and Ilandgovan (2012), Supeaker (2007), Suresh et al. (2013), Sushma et al. (2015), Taeb and Faghihi (2002), Taha et al. (2004), Tandel and Patel (2009), Tiwari and Bhattacharya (2013), Tixier et al. (1997, 1999), Tokuhashi et al. (2001), Wang et al. (2011a,b), Weicai and Tiandi (1993), Wu et al. (2010a,b), Yang et al. (2010), Yogendra (2008), Yucel et al. (1999), and Zain et al. (2004).

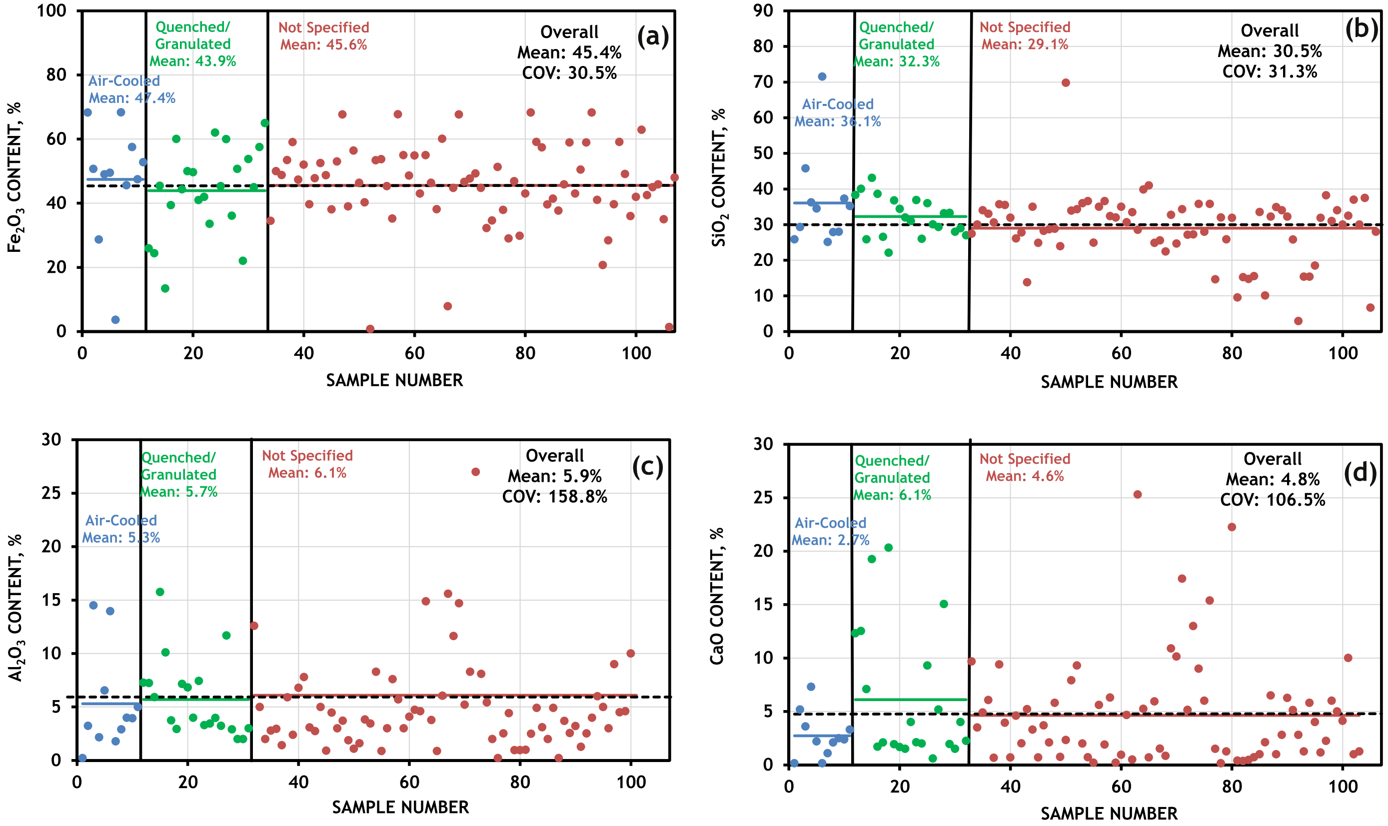

Figure 3.4 (a) Chemical composition of copper slag samples for Fe_2O_3. (b) Chemical composition of copper slag samples for SiO_2. (c) Chemical composition of copper slag samples for Al_2O_3. (d) Chemical composition of copper slag samples for CaO. *COV,* coefficient of variation.

representative of the typical CS characteristics. The nature of the processing, either air-cooled or quenched, does not seem have an overly significant effect on the Fe_2O_3 composition.

SiO_2 contents, Figure 3.4(b), for the most part, are distributed closely around the average; indeed, 83% of samples are within 10% percentage points of the 30.5% average value. The SiO_2 content is, on average, the highest for air-cooled samples, though this is mainly due to one exceptionally high value of 72% rather than a consistently higher trend.

The Al_2O_3 content, Figure 3.4(c), is the most variable of the four main oxides, with a calculated coefficient of variation of 159% (based on 101 CS samples). It is evident that a greater part of the samples, 71 of 101, are below the average value of 5.9%. The average value is somewhat bloated because of a smattering of particularly high values, ranging up to a peak content of 27%. No significant difference is evident in the average Al_2O_3 contents of the air-cooled, quenched or unspecified CS samples.

The CaO data, Figure 3.4(d), follow a pattern similar to that of Al_2O_3, as the average value of 4.8% is slightly skewed by a small number of especially high CaO contents. Approximately 63% of samples had contents lower than the average value of 4.8%. CS was found to have a median CaO content of 2.8%. The CaO contents of the air-cooled samples are lower than those of the quenched samples, ranging from 0.2% to 3.3%, with an average value of 2.7% (air-cooled), compared to 0.6–20.3%, with an average value of 6.1% (quenched).

It is regrettable that many authors did not specify the processing method, as more data would have been useful for further verification of these indications. For use as a cementitious component, the higher CaO content may benefit the potential latent hydraulic properties of CS. It is also expected that quenching would deliver a more suitably reactive material, because of the higher amorphous phases present after rapid cooling.

3.3.2 Mineralogy

The mineralogical composition is a key determining factor in the microstructure of CS and its potential reactivity when used as a cementitious component in concrete, road pavements, geotechnical applications and ceramics. The mineralogy of the material has commonly been assessed using X-ray diffraction, scanning electron microscope and differential thermal analysis methods.

In most cases, the researchers simply identified the main minerals found in CS. A list of these minerals, sorted according to the frequency at which they have been found, is provided in Figure 3.5. Not surprisingly, given the high Fe_2O_3 oxide content (see Table 3.1), the material is dominated by iron oxide minerals including fayalite, magnetite, hematite and wuestite. Quartz is another of the more common minerals in CS, found in 10 of 38 samples. Fayalite has been identified as the principal mineral in the vast

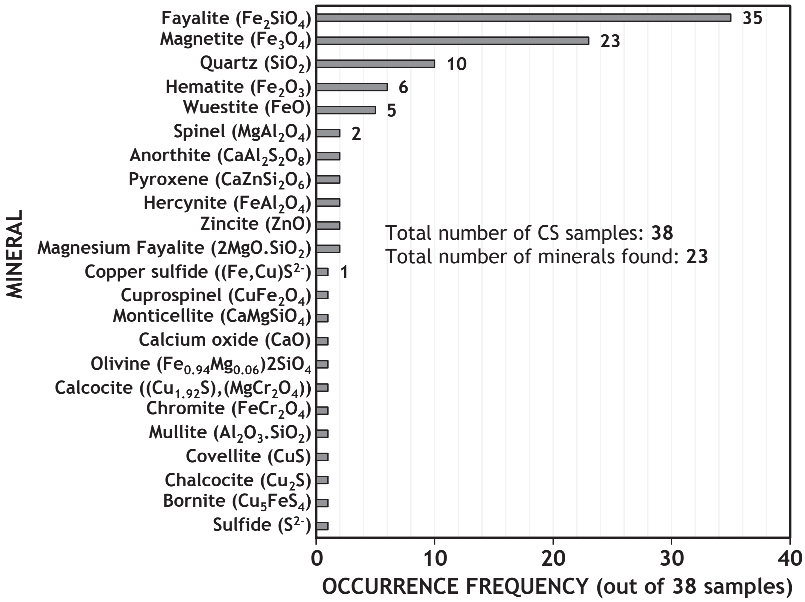

Figure 3.5 Frequency of occurrence of the minerals in copper slag (CS).
Data from Alp et al. (2008), Baragano and Rey (1980), Busolic et al. (2011), Coruh et al. (2006), Coruh (2008), De Schepper et al. (2015), Douglas and Mainwaring (1985), Douglas et al. (1986), Karamanov et al. (2007), Lorenzo et al. (1991), Mihailova and Mechandjiev (2010), Moura et al. (1999, 2007), Murari et al. (2015), Najimi and Pourkhorshidi (2011), Najimi et al. (2011), Nazer et al. (2012), Sterlite Industries (2012), Ozel et al. (2006), Roper et al. (1983), Sanchez and Sudbury (2013), Sanchez de Rojas et al. (2004, 2008), Sahu et al. (2011), Suresh et al. (2013), Tixier et al. (1997, 1999), Wang et al. (2011a,b), and Weicai and Tiandi (1993).

majority of CS samples and occurs in the form of crystalline tubular needles. The mineral is part of the olivine group of minerals and is known to have quite a high hardness, reaching 6.5 on the Mohs scale.

The specific quantities of these crystalline phases present in CS have, on occasion, been determined and the results are presented in Table 3.2 for both air-cooled and quenched samples. Fayalite is clearly the most abundant mineral present in CS, with contents ranging from 45% to 57% in the air-cooled samples. However, the quantities of this mineral are considerably reduced in the two quenched samples, with contents of 4% and 15%, respectively. The rapid cooling during quenching does not allow time for crystallization to occur, which leads to the segregation of Al_2O_3, SiO_2, CaO and K_2O and the presence of a much greater proportion of amorphous phases.

The amorphous fraction, also known as the glass content, affects the material reactivity and as such can have important implications on the potential suitability of CS for use as a cementitious component. Data on the glass content of air-cooled and quenched CS samples is given in Table 3.3, along with additional remaining results.

Table 3.2 Quantitative data on the crystalline mineralogical composition of copper slag

		Crystalline Phases, %							
References	**Process**	**Fayalite (Fe_2SiO_4)**	**Magnetite (Fe_3O_4)**	**Wuestite (FeO)**	**Hematite (Fe_2O_3)**	**Zincite (ZnO)**	**Hercynite ($FeAl_2O_4$)**	**Magnesium Fayalite ($2MgO·SiO_2$)**	**Spinel ($MgAl_2O_4$)**
De Schepper et al. (2015)	AC	45.5	–	0.4	0.8	0.6	3.9	–	–
	Q	4.1	–	1.6	–	0.4	4	–	–
Douglas and Mainwaring (1985)	AC	57	–	–	–	–	–	–	5
	Q	15	–	–	–	–	–	–	10
Nazer et al. (2012)	AC	51	38.8	–	–	–	–	10.2	–
Wang et al. (2011b)	AC	53	12	–	–	–	–	–	–

Note: *AC,* air cooled; *Q,* quenched.

Table 3.3 Glass content of copper slag samples

	Glass Content, %		
References	**Air Cooled**	**Quenched**	**Other**
De Schepper et al. (2015)	49	90	–
Douglas et al. (1986)	37–45	75–95	41–47[a]
Roper et al. (1983)	–	50	–
Sahu et al. (2011)	–	–	13.2[b]
Sánchez de Rojas et al. (2008)	–	–	60[b]
Suresh et al. (2013)	–	–	≈20[b]
Wang et al. (2011a)	35	–	–
Weicai and Tiandi (1993)	–	85	87–89[c]

[a] Activated, remelted, quenched and granulated.
[b] Processing method not identified.
[c] Activated and quenched.

With the exception of the result from Roper et al. (1983), there is a clear difference between the air-cooled samples and the quenched samples, with the latter found to have significantly higher glass fractions, as is to be expected. In particular, the results from De Schepper et al. (2015) and Douglas et al. (1986) provide a useful comparison of the effects of air-cooling versus quenching, as the CS samples for each have been collected from the same sources. The glass content of ground granulated blast furnace slag (GGBS), an established cementitious material (permitted for use as up to 95% of the cement mix according to BS EN 197-1, 2011), is usually above 70% and indeed frequently exceeds 90% (Poole and Sims, 2016) and as such is comparable to quenched CS in this regard.

3.3.3 Cementitious Properties

The chemical composition of CS has a major influence on its suitability in a variety of construction applications, in particular when used in a reactive form, i.e., as raw feed in cement clinker production, as a cementitious component in mortars, concrete and road pavements and as a clay or filler component in ceramics production.

The cement clinker production process involves a series of chemical reactions of the calcium, silicon, alumina and iron oxides present in the raw feed. The quantities of each of the oxides needed to achieve the desired cement properties have been well established and it is possible that CS could be used as a cheap and environmentally friendly source of these oxides. The material has been tested for use in small quantities up to 10%.

The viability of CS as a cementitious component in cement pastes, mortars, concrete and cement-bound road pavement layers and geotechnical applications is dependent on the reactivity of the material, either from pozzolanic activity or as latent hydraulic properties. Dealing first with the glass content, the results in Table 3.4 indicate that quenched CS is the more appropriate choice for use as a cementitious component. The

Table 3.4 Soluble chlorides, sulphates and alkali–silica reactivity of copper slag for use in mortar and concrete

References	Results	Requirements
Water-Soluble chlorides		
SETSCO (from Dhir, 2009)	<0.01%	BS EN 12620:2002+A1 (2008); aggregate for concrete; water-soluble chlorides <0.01%
Ghosh (2007)	<0.01%	
Wee et al. (1996)	0.003%	
Song (2013)	<0.005%	
Dharani et al. (2015)	0.0011%	
Sushma et al. (2015)	0.0011%	
Soluble sulphate		
SETSCO (from Dhir, 2009)	Acid soluble: <0.13%	Most stringent soluble sulphate category limit of <0.2% in BS EN 12620:2002+A1 (2008)
Ghosh (2007)	Acid soluble: 0.09%	
Wee et al. (1996)	Water soluble: 0.016%	
Alkali–Silica reaction		
Ghosh (2007)	Innocuous; non-damaging mortar bar results	ASTM C33 (2016) classifications: innocuous, potentially deleterious, deleterious Mortar bar test classifications: damaging or non-damaging
Pubaalan and Low (2000)	Innocuous	
Tam (2001)	Innocuous; no reactivity in mortar bar test	

air-cooling process also tends to produce a coarser material and as such, these samples may be more naturally suited to use as a coarse aggregate component, potentially in concrete, road pavements or geotechnical applications.

Regarding the oxide composition requirements, it is known that SiO_2, CaO and Al_2O_3 are the main components present in established cementitious materials, such as Portland cement (PC), pulverised fuel ash (PFA) and GGBS. As such the CaO–SiO_2–Al_2O_3 system is often used to provide an indication of the suitability of emerging materials as a cementitious component. The contents of the CS samples in this CaO–SiO_2–Al_2O_3 system are presented in Figure 3.6, along with the typical compositions of PC, PFA, GGBS, silica fume (SF) and metakaolin and the established pozzolanic, latent hydraulic and hydraulic regions. It should be noted that only CS samples with results provided for all three of the oxides are included in Figure 3.6.

It is evident that the CS samples lie mainly in the upper portion of the ternary diagram, close to PFA and SF, because of their significantly higher SiO_2 content relative to CaO and Al_2O_3. However, the problem is that the total sum of the SiO_2, Al_2O_3 and CaO contents of CS, on average, make up less than half of the overall composition of the material and as such the above SiO_2–Al_2O_3–CaO system is less suitable for assessing this particular material.

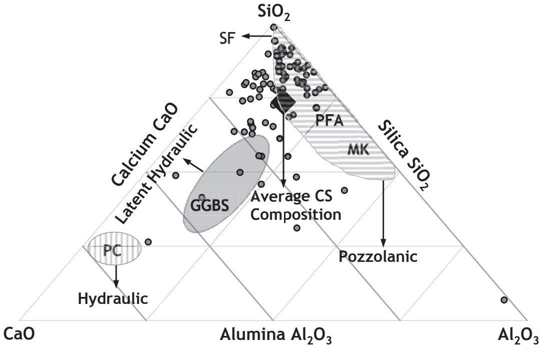

Figure 3.6 Ternary plot of the SiO_2, Al_2O_3 and CaO contents of copper slag in comparison to established construction materials. *CS,* copper slag; *GGBS,* ground granulated blast furnace slag; *MK,* metakaolin; *PC,* Portland cement; *PFA,* pulverised fuel ash; *SF,* silica fume.

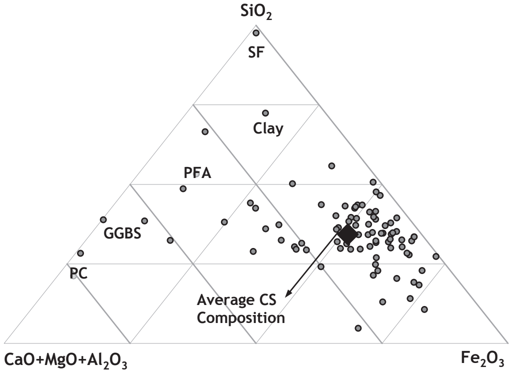

Figure 3.7 Ternary plot of composition of copper slag samples in the ($CaO+MgO+Al_2O_3$)–SiO_2–Fe_2O_3 system, compared to established cementitious materials. *CS,* copper slag; *GGBS,* ground granulated blast furnace slag; *PC,* Portland cement; *PFA,* pulverised fuel ash; *SF,* silica fume.

The material does not fit with many of the chemical classifications outlined for established materials such as PC clinker, fly ash and GGBS in EN 197-1, though it does meet requirements for coal fly ash and raw or calcined natural pozzolana use in concrete in ASTM C618 (2015), specifying that the SiO_2+Al_2O_3+Fe_2O_3 content must exceed 50% (class C fly ash) or 70% (pozzolana and class F fly ash).

To take into consideration the unusually high iron oxide content of CS (average of 45%) compared to other cementitious materials, the composition of the CS samples is presented in an alternative ($CaO+MgO+Al_2O_3$)–SiO_2–Fe_2O_3 system in Figure 3.7. The sum of these five oxides makes up, on average, about 90% of the total composition of CS.

It is evident from Figure 3.7 that the composition of the CS samples is considerably different to the other cementitious materials, mainly because of its Fe_2O_3 content, as discussed previously. As such, there does not appear to be much sign of pozzolanic activity or latent hydraulic properties, based on the chemical composition of the material. However, it is still of interest to assess the performance of the material when used in cementitious products, as the material may have value in other ways, perhaps as a water-reducing material.

Excessive chloride and sulphate contents present in the mix constituents can potentially compromise the durability performance of mortar and concrete products. Alkali–silica reactivity is an additional durability concern to consider when introducing a new material. CS results for each of these three parameters are presented in Table 3.4 and suggest that the material should not lead to undue durability problems. It has been found that:

- The water-soluble chloride content of all tested CS samples fell below the 0.01% limit outlined for aggregate use in concrete in BS EN 12620:2002+A1 (2008). The average total chloride content of 0.09% (see Table 3.1) is also below the 0.1% limits specified for cement according to BS EN 197-1 (2011).
- The soluble sulphate contents of CS are all below the most stringent limit of 0.2% specified in BS EN 12620:2002+A1 (2008). The total sulphate content (as SO_3), ranging from 0.045% to 3.26% for all CS samples (see Table 3.1) is below the 3.5% limit for cement outlined in BS EN 197-1 (2011).
- Alkali–silica reactivity has been assessed using two methods, one recording the reduction in alkalinity with dissolved silica and the other noting expansion damages in a mortar bar test. CS has been categorized as an “innocuous” aggregate and no damaging expansion occurred in the mortar bars, indicating that the material does not contain reactive silicates.

The ceramics production process typically involves heating a clay-based mixture to very high temperatures to produce a mechanically strong, highly resistant and durable product. Fe_2O_3 is renowned for its fluxing properties and as such, because of its considerable presence in CS, the slag may have value as a fluxing agent in ceramics production that may lead to reductions in the energy requirements in the thermal treatment process.

In addition, as discussed previously in Section 3.4.1, the high Fe_2O_3 is likely to contribute to a high overall density for CS and this can have important implications on the batching process and transportation costs when considering the use of the material in all types of applications.

3.3.4 Loss on Ignition

Loss on ignition (LOI) is usually considered as the presence of inorganic material in PC and determined as the weight loss with heating of cement to 1000°C, as in the case of BS EN 197 (2011) and ASTM C150 (2016). Figures for LOI have been given in studies where CS is used in the ground form as a component of cement and the

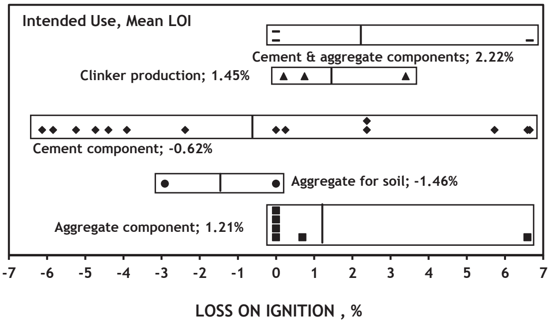

Figure 3.8 Loss on ignition from 10 countries published during 1985–2015.
Data taken from Al-Jabri et al. (2006, 2009a), Al-Rawas et al. (2002), Alp et al. (2008), Amarnaath et al. (2015), Brindha and Sureshkumar (2010), Brindha and Nagan (2010a), Boakye et al. (2013, 2014), Boakye (2014), De Schepper et al. (2014b, 2015), Douglas et al. (1985), Fadaee et al. (2015), Havanagi et al. (2006), Karthick et al. (2014), Kharade et al. (2013), Kikuchi (2001), Lam et al. (2010), Mithun and Narasimhan (2016), Peyronnard and Benzaazoua (2011), and Siva et al. (2014).

unground form as a component of raw feed in the manufacture of cement clinker, and as aggregate for use in concrete and geotechnical applications. The LOI values have been found to range from 0% to a maximum of 6.65% (Figure 3.8).

The maximum permissible value for LOI is 5% for PC in the form of CEM I in BS EN 197 (2011) and 3% for Type I cement in ASTM C150 (2016), and Figure 3.8 suggests that only few results cross the maximum LOI limits of European and American standards in this respect. In some cases, a negative LOI value can be obtained because of a gain in weight after ignition by oxidation of iron oxide and sulphide. A significant proportion of the data obtained, shown in Figure 3.8, appears to be affected in this manner.

3.4 Physical Properties

3.4.1 Particle Shape, Surface Texture and Colour

Although often not appreciated, the shape and surface texture of an aggregate can influence its performance and that of the end product it is used with, for example, in the case of concrete, its properties in both the fresh state (consistence and stability), due to its water demand effect, and the hardened state (strength), due to the aggregate–cement paste bond effect (Jackson and Dhir, 1996). On the other hand, whilst the colour of aggregate in fine fractions is likely to affect only the exposed aggregate concrete finishes, in the ground form it may affect the tint of the concrete produced, depending upon its content and the nature of the constituents of the cement.

Table 3.5 Summary of the particle shape, surface texture and colour information on copper slag from the literature published during 1980–2015

Property	Description	References
Particle shape	Angular	JPL Industries (1997), Lavanya et al. (2013), Lavanya et al. (2012), Potana (2005), Salleh et al., (2014), and Wu et al. (2010b)
	Irregular	Ambily et al. (2015), Arivalagan (2013), Baragano and Rey (1980), and Hwang and Laiw (1989)
	Multifaceted	Anudeep et al. (2015)
Surface texture	Glassy	Ambily et al. (2015), Anudeep et al. (2015), Arivalagan (2013), Brindha and Sureshkumar (2010), Douglas et al. (1985), Salleh et al. (2014), and Wu et al. (2010a)
	Smooth	Anudeep et al. (2015), Baragano and Rey (1980), and Wu et al. (2010a,b)
	Granular	Brindha and Sureshkumar (2010)
	Rough	Hwang and Laiw (1989) and Salleh et al. (2014)
Colour	Black	Ambily et al. (2015), Arivalagan (2013), Brindha and Sureshkumar (2010), Douglas et al. (1985), JPL Industries (1997), Salleh et al. (2014), and Wu et al. (2010a)
	Blackish grey	Anudeep et al. (2015)
	Brown with green, red or black tint	Lewowicki and Rajczyk (1997)

Descriptions of the particle shape, texture and colour of CS have been reported in the literature as summarised in Table 3.5. The time range of these studies is 1980–2015 and the information provided suggests that the particle shape of CS in general can vary between angular and irregular, but there is nothing to suggest in the literature whether any of these characteristics have changed over the time duration for which the information is available. With few exceptions, the texture of CS, based on visual impression, has generally been described as between glassy and smooth and the colour commonly as black (Table 3.5).

3.4.2 Particle Size Distribution

The particle size distribution (PSD) of a granular material, directly associated with its packing, can also be a major influencing factor in affecting its performance, as well as that of the end product produced with its use. For example, in the manufacturing of concrete, the grading of the aggregate used can influence its consistence and stability through the aggregate specific surface, affecting the water demand and cohesion of the mix, as well its strength development and durability through the porosity and permeation effect.

Likewise, in the case of asphalt mixes, PSD can influence its internal packing, permeability and durability (Greene et al. 2011). In the field of geotechnics, PSD can influence the rate of fluid movement through a soil and affect its compaction, strength and load-bearing properties (Das and Sivakugan, 2014). Thus, it is of paramount importance that the PSDs of granular recycled and secondary materials are addressed carefully in developing their potential use in construction.

Information on the PSD of CS available in the literature dating back to 1980 was sourced from 63 reported studies and no specific evidence of change with time period was detected. However, depending on the type of cooling process used for the slag during production, the particle size fraction can differ widely. Basically, there are two cooling processes, air cooling and quenched/granulated, with the former, with its slow cooling, resulting in a mass which is later crushed to produce aggregates of usually coarse fraction and the latter, with its rapid cooling, producing a sandlike material. In addition, the size fraction of these two types can be altered by an additional process of using CS as an abrasive material, where the spent material is collected, washed and recycled for use again in the construction industry. This is applicable only to quenched slag as being more suitable for use as an abrasive material and the spent material is commonly known as spent CS (or washed CS in Singapore). Furthermore, the CS could be ground to cement fraction fineness for potential use as a cement component material.

With the wide variations in the nature of the material, it would be a preferred option that the data available on the PSD of CS be analysed separately in four categories of slags associated with the process used in the cooling of the slag, namely: (i) air cooled, (ii) quenched, (iii) spent and (iv) ground/milled. In addition, though an abundance of information on the PSD of CS is available in the literature, in a large proportion of cases the cooling process adopted for the CS samples tested was not clearly made known. These publications are listed here for completeness and as they also provide a useful source of reference for the reader: Al-Jabri et al., 2011, 2009a,b; Anudeep et al., 2015; Boakye et al., 2013; Mir, 2015; Cachim et al., 2009; Caliskan and Behnood, 2004; Chavan and Kulkarni, 2013; Havanagi et al., 2006, 2007, 2008, 2009, 2012; Kharade et al., 2013; Kitazume et al., 1998a,b; Lee et al., 2003; Mahmood and Hashmi, 2014; Mithun and Narasimhan, 2016; Mithun et al., 2015a,b; Nataraja et al., 2014b; Patel et al., 2007; Patil 2015; Resende et al., 2008; Sabarishri et al., 2015; Sharma et al., 2013a,b; Singh et al., 2014; Sudarvizhi and Ilangovan 2012; Tiwari and Bhattacharya 2013; Vamsi and Kishore 2013; Vamsi et al., 2013; Velumani and Nirmalkumar 2014; Yildrim et al., 1993; Yogendra, 2008.

However, to avoid confusion, such data for which the process of cooling of the slag was not been made known could not be considered further, even if the results of this category of CS were compared with the PSD of spent and quenched CS and the results were within the overall grading boundaries of quenched CS.

Air-Cooled Copper Slag

The collected data for the grading of air-cooled CS (Figure 3.9) suggest that the material, as in the case of air-cooled blast furnace aggregate, could be produced, by varying the process of crushing, in different size fractions as required. The limited information available on the material suggests little scope for research and development work. However, it is clear from Figure 3.9 that the material has been studied as coarse aggregate, as coarse sand and, in one case, in dust form, which in terms of PSD is similar to pond fly ash.

Quenched and Spent Copper Slag

These two types of CS have been commonly used in the construction industry and much of the research has been carried out in identifying and developing their applications within the construction sector. Such efforts have usually been undertaken using the material in as-received form with no further processing undertaken to modify their original size fractions. In this section, for obvious reasons, the information available on the PSD of the material is examined with respect to the use of CS in concrete, geotechnical and road pavement applications.

(a) Copper Slag for Concrete Applications

The results of the quenched and spent CS taken from the widely sourced data are collectively presented in Figure 3.10 together with the BS EN 12620:2002+A1 (2008) limits for fine aggregates. These limits describe the degree of fineness of the material based on the percentage passing the 0.5-mm sieve. It can be seen that all the results lie in the size of sand fraction and the particles of spent CS are finer than the quenched. Few of the quenched CS results show that the material can be gap-graded, but the data population suggests that this is not likely to be the norm with this material and

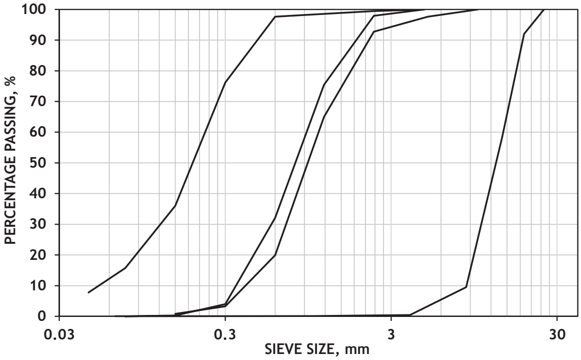

Figure 3.9 Particle size distribution of air-cooled copper slag in different particle size fractions.
Data taken from Ambily et al. (2015), Arivalagan (2013), De Schepper et al. (2015), and Gupta et al. (2012a).

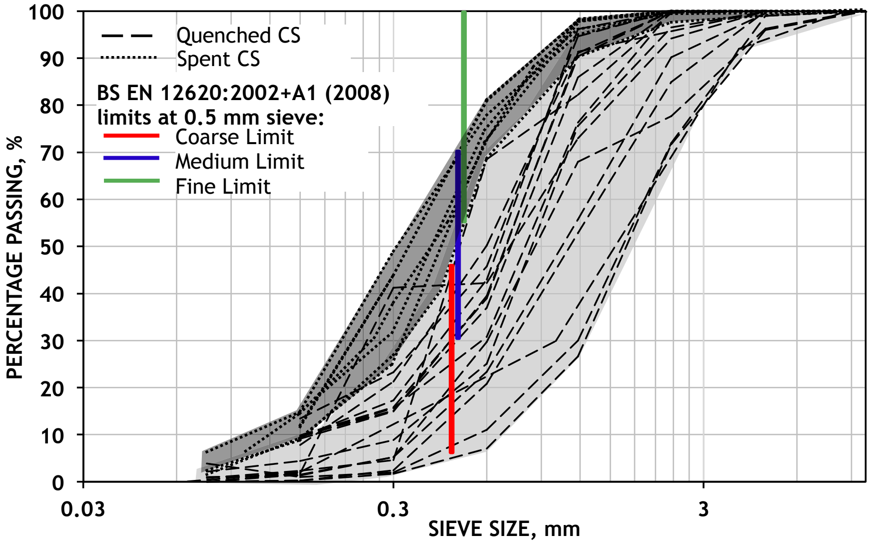

Figure 3.10 Particle size distribution of quenched and spent copper slag (CS) as sand fraction with the BS EN 12620:2002+A1 (2008) limits for fine aggregates.
Data taken from Baragano and Rey (1980), Boakye (2014), Brindha and Nagan (2010a), De Schepper et al. (2015), Hassan and Al-Jabri (2011), Kumar (2012), Meenakashi and Ilangovan (2011), Priyanka and Thahira (2013), Selvanambi et al. (2011), Shoya et al. (1997, 1999), Tokuhashi et al. (2001), Al-Sayed and Mandany (1992), Koh and Lye (2012), Wee et al. (1996), Ping (2011), Remade Scotland (2001), Resende et al. (2008), and Tam (2001).

therefore may, for all practical purposes, be disregarded. On the whole, it emerges from Figure 3.10 that the PSD of spent CS varies from medium to fine grading but is mostly located in the overlap of the fine–medium zone, whilst in the case of the quenched CS, the results range from coarse to medium, with the majority being in the coarse zone.

On the other hand, for those who are used to working with BS 882 (1992) the results in Figure 3.10 have been plotted in Figure 3.11 with the sand zones of BS 882 modified (Cui and Dhir, 2005) to take account of the PSD limits defined for the fine aggregates in BS EN 12620:2002+A1 (2008).

This approach of merging the requirements of the two standards was considered to be more useful in classifying the PSD of the material than opting for the new standard. It can be seen that in general, the majority of the results lie in the zone of medium to coarse grading. The particle size of spent CS still varies from medium to fine, whilst most of the quenched CS results still range from medium to coarse grading. The facts that it was not possible to detect any sign of PSD of CS varying with time and that the data collected globally fall within the fine–medium grading range for the spent slag and medium–coarse grading range for the quenched slag can be useful in developing the use of the material in concrete construction. Very few

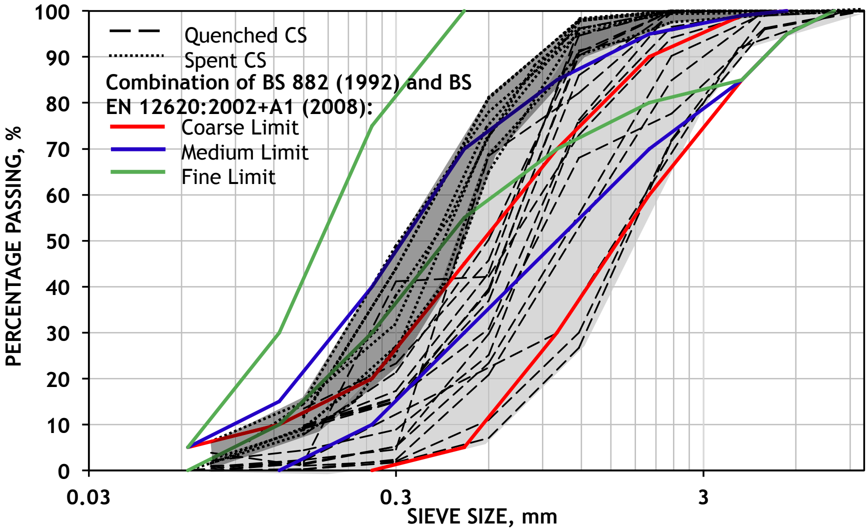

Figure 3.11 Particle size distribution of quenched and spent copper slag (CS) as sand fraction with the combined limits of BS EN 12620:2002+A1 (2008) and BS 882 (1992) for fine aggregates. Data taken from Baragano and Rey (1980), Boakye (2014), Brindha and Nagan (2010a), De Schepper et al. (2015), Hassan and Al-Jabri (2011), Kumar (2012), Meenakashi and Ilangovan (2011), Priyanka and Thahira (2013), Selvanambi et al. (2011), Shoya et al. (1997, 1999), Tokuhashi et al. (2001), Al-Sayed and Mandany (1992), Koh and Lye (2012), Wee et al. (1996), Ping (2011), Remade Scotland (2001), Resende et al. (2008), and Tam (2001).

studies have reported quenched CS showing very coarse grading, where the results partially fall outside the coarse limits. This is an unusual occurrence and for all practical purposes can be ignored.

(b) Copper Slag for Geotechnical Applications

For geotechnical applications, the classification of soil materials takes a very different approach to that of sand for use in the production of concrete. BS 1377-2 (1990) provides a classification for different types of soils depending on their grain size and the classifying limits. These together with the PSD results of quenched and spent CS are plotted in Figure 3.12.

Overall, it is shown that in general CS particles have grain sizes ranging between fine sand to medium gravel particle size fractions, with a split between spent CS lying within the fine–coarse sand particle size fractions and quenched CS dominantly lying within the medium–coarse sand particle size fractions. Again, this is very helpful as both the materials can, in general, be usefully applied in geotechnical applications.

In accordance with BS 5930 (2015), soils containing gravel-size and sand-size particles could be described as a ‘sand’ or a ‘gravel’, depending on which of the constituents predominates by mass, and the term for the mixture soil is selected based

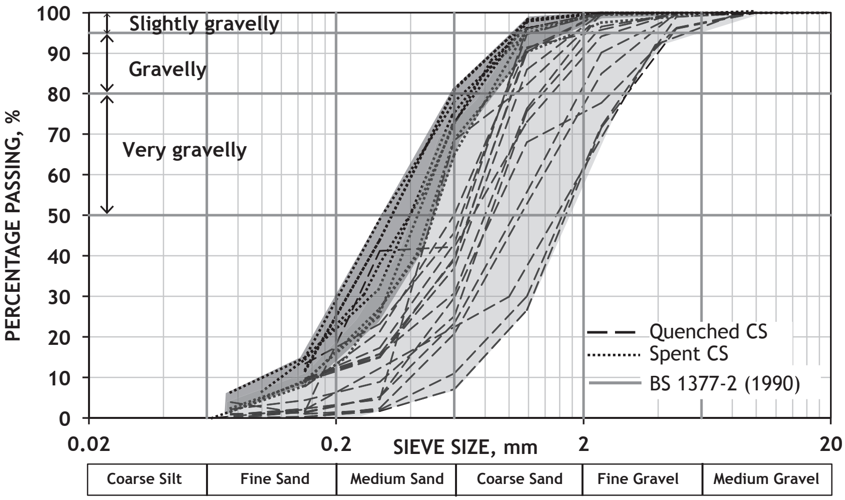

Figure 3.12 Particle size distribution of quenched and spent copper slag (CS) as sand fraction with the classification of BS 1377-2 (1990) for different types of soils.
Data taken from Baragano and Rey (1980), Boakye (2014), Brindha and Nagan (2010a), De Schepper et al. (2015), Hassan and Al-Jabri (2011), Kumar (2012), Meenakashi and Ilangovan (2011), Priyanka and Thahira (2013), Selvanambi et al. (2011), Shoya et al. (1997, 1999), Tokuhashi et al. (2001), Al-Sayed and Mandany (1992), Koh and Lye (2012), Wee et al. (1996), Ping (2011), Remade Scotland (2001), Resende et al. (2008), and Tam (2001).

on the percentage passing of 2-mm sieve size as illustrated by the horizontal lines in Figure 3.12. The grain size of the majority of spent CS could be described as slightly gravelly, fine–coarse sand. Similarly, the grain size of the majority of the quenched CS could be identified as gravelly coarse sand.

Coefficients of uniformity (C_U) and curvature (C_C), which are related to PSD of a granular material, can also be used as the basis for classification of CS in accordance with the Unified Soil Classification System. The C_U and C_C of all the PSD curves presented in Figure 3.12 were calculated for quenched CS to be within the ranges 1.62–7.56 and 0.38–2.02, respectively, and for spent CS within the ranges 2.50–4.38 and 0.90–1.40, respectively. With the exception of one sample of CS tested by De Schepper et al. (2015) which was considered to be well graded, all CS samples were found to be poorly graded in accordance with ASTM D2487 (2011).

Copper Slag for Road Pavement Applications

In road pavement applications, the requirements set out for aggregates to be used depend upon the type of bitumen mix adopted. To illustrate this point, requirements for asphaltic concrete, considered as one of the most commonly used asphalt mixes, have been selected as an example. The limits of the fine aggregates for this mix, with the results of spent and quenched CS, are plotted in Figure 3.13. This illustrates that both

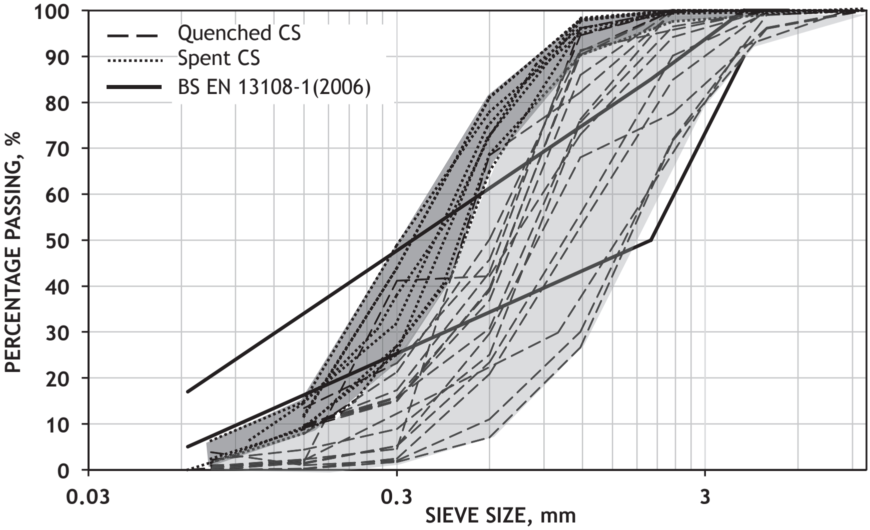

Figure 3.13 Particle size distribution of quenched and spent copper slag (CS) as sand fraction with the BS EN 13108-1 (2006) limits for fine aggregates of asphalt concrete.
Data taken from Baragano and Rey (1980), Boakye (2014), Brindha and Nagan (2010a), De Schepper et al. (2015), Hassan and Al-Jabri (2011), Kumar (2012), Meenakashi and Ilangovan (2011), Priyanka and Thahira (2013), Selvanambi et al. (2011), Shoya et al. (1997, 1999), Tokuhashi et al. (2001), Al-Sayed and Mandany (1992), Koh and Lye (2012), Wee et al. (1996), Ping (2011), Remade Scotland (2001), Resende et al. (2008), and Tam (2001).

the quenched and the spent CS on their own do not comply with the required grading for asphalt concrete mixes. However, it is possible to adopt the use of these materials in the bitumen mixes in combination with other materials, as discussed in Chapter 7. Alternatively, it should be possible to adopt the use of air-cooled CS material, as this can be crushed to produce the material to a required size specification that will comply with the specified grading limits.

Ground Copper Slag

CS has also been ground to determine its suitability for use as a component of cement (regardless of the type of cooling process applied), though information available in this area has often tended to be somewhat problematic (Lorenzo et al., 1991; Tixier et al., 1997; De Schepper et al., 2015). The grading data available have been plotted in Figure 3.14, and this shows that the overall range of particle size fraction varies from 0.001 to 1 mm.

The percentage passing on the 45-μm size sieve (the size fraction used for classifying fly ash) varies from 7% to 82%, whereas the limits specified in BS EN 450-1 (2012) for both fine and coarse fly ash are within 60–100%. The percentage passing on the 63-μm size sieve varies from 15% to 90%, whereas the limits set by BS EN 12620:2002+A1 (2008) for the filler aggregate are 70–100%. Whilst recognizing that the information available is limited, those reported in the literature

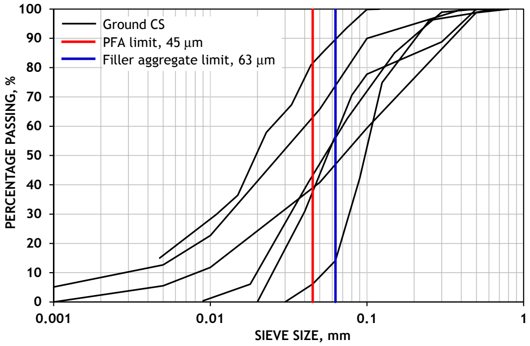

Figure 3.14 Particle size distribution of ground copper slag (CS). *PFA,* pulverised fuel ash. Data taken from Afshoon and Sharifi (2014), Coruh et al. (2006), De Schepper et al. (2015), Lorenzo et al. (1991), and Tixier (1997, 2000).

are coarser than the limits for fly ash and filler aggregate and additional grinding would be required to produce finer CS for considering its use as a component of cement or as filler aggregates.

3.4.3 Fineness Modulus

The significance of fineness modulus (FM) is in specifying the proportions of fine and coarse aggregates when designing concrete mixes. The higher the value of FM, the coarser the aggregate. Generally, a lower FM results in more paste, making the concrete easier to finish. However, FM does not define the grading curve and different gradings could have similar FMs (Suprenant, 1994).

The obtained results for FM for the different CSs as reported in the literature have been summarized and are presented in Table 3.6. This shows that the range of FM for the air-cooled CS is wider than that of the quenched and the spent CS, reflecting the variability of different size fractions that air-cooled CS can have compared to the other two CS types. In addition, the FM results of spent CS indicate that the material possesses a finer fraction than in the case of the quenched CS. Additionally, a very large number of studies did not provide information regarding the cooling process applied to the slags tested, and the materials show a broad range of FM, and as such it would be difficult to come to any specific conclusions about such results.

3.4.4 Fineness of Ground Copper Slag

Depending upon the mineralogical composition, the fineness of ground CS can provide an indication of its potential reactivity, as the higher the fineness the higher the surface area available for reacting, and hence the faster the rate of chemical reaction. As the material in ground form is used as supplementary cementing material, the type of cooling process is not a matter of influence and has been disregarded.

Table 3.6 Fineness modulus of copper slag

	Fineness Modulus		
Copper Slag	**Range**	**Mean**	**References**
Air cooled	3.47–4.90	3.66	Arivalagan (2013), Brindha et al. (2010), Brindha and Nagan 2011, Gaud et al. (2013), Gupta et al. (2012b), Rajaselvi and Beatrice (2015), Karthick et al. (2014), and Sathya and Shanmugavalli (2014)
Quenched	2.20–3.40	3.07	Boakye et al. (2013), Boakye (2014), Nataraja et al. (2014a,b), and Shoya et al. (1999)
Spent	1.78–2.00	1.84	Resende et al. (2008) and Wu et al. (2010a,b)
Unidentified	2.08–8.01	3.31	Ayano and Sakata (2000), Gowda and Balakrishna (2014), Hosokawa et al. (2004), Hwang and Laiw (1989), Jaivignesh and Gandhimathi (2015), Khan et al. (2015), Kharade et al. (2013), Kumar (2012), Lee (2008), Leema and Suganya (2015), Patil (2015), Madhu and Venkataratnam (2015), Mahmood and Hashmi (2014), Meenakashi and Ilangovan (2011), Saxena (2015a), Priyanka and Thahira (2013), Resende et al. (2008), Sabarishri et al. (2015), Sakthieswaran and Ganesan (2014), Shoya et al. (1997), Sudarvizhi and Ilangovan 2012, Suresh et al. (2013), and Vamsi et al. (2013)

The fineness of ground CS samples reported in the literature, presented in Figure 3.15, shows that the range of fineness of the material used in the ground form varies between 125 and 680 m^2/kg, giving a mean of about 315 m^2/kg. The distribution of the results shows that the majority of the material tested was ground to a fineness of 300–400 m^2/kg, which is similar to the range of PC fineness of 325–385 m^2/kg manufactured in the United Kingdom. This is considered to be slightly coarser than the average fineness of GGBS, which is usually above 350 m^2/kg. In addition, the fineness values above 400 m^2/kg are few, while there is a notable amount of fineness values less than 300 m^2/kg.

3.4.5 Specific Gravity

The specific gravity (SG) of a material is an important property and in the case of aggregates it is used to classify the material into lightweight, normal weight, and heavyweight, as well as to find the absolute volume that a given mass of material will occupy, for example, in the mix proportion calculations for a concrete mix. SG aggregate also affects the weight of the final product, whether it is concrete, soil or a bitumen mixture.

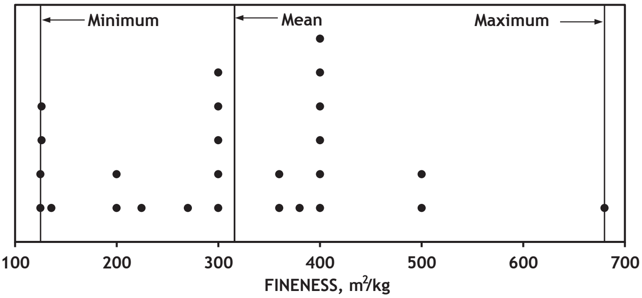

Figure 3.15 Fineness of ground copper slag.
Data taken from Afshoon and Sharifi (2014), Al-Jabri and Shoukry (2014), Al-Jabri et al. (2002, 2006), Ariño and Mobasher (1999), Boakye (2014), Brindha et al. (2010), Brindha and Nagan (2011), Deja and Malolepszy (1989, 1994), Douglas and Mainwaring (1985), Douglas et al. (1985, 1986), Najimi et al. (2011), and Sánchez de Rojas et al. (2008).

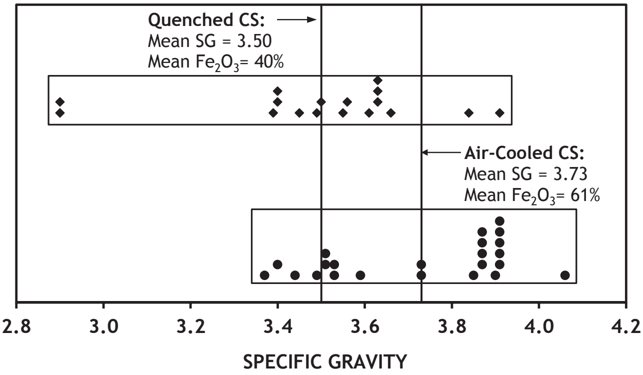

Figure 3.16 Specific gravity (SG) of air-cooled and quenched copper slag (CS).
Data taken from Ambily et al. (2015), Arivalagan (2013), Brindha et al. (2010), Brindha and Nagan (2011), Douglas et al. (1985), Gupta et al. (2012a), Rajaselvi and Beatrice (2015), Kumar and Mahesh (2015), Poozvizhi and Kathirvel (2015), Sathya and Shanmugavalli (2014), Singh and Bath (2015), Singh et al. (2014), Siva et al. (2014), Srinivas and Muranal (2015), Peyronnard and Benzaazoua (2011), Thomas et al. (2012), Tixier (2000), Chandrshekhar et al. (2015), Deja and Malolepszy (1989, 1994), Douglas et al. (1985), Hassan and Al-Jabri (2011), Nataraja et al. (2014a,b), Selvanambi et al. (2011), Shoya et al. (1997, 1999), and Tokuhashi et al. (2001).

The results taken from the published literature for the SG of CS in the air-cooled and quenched forms are presented in Figure 3.16, showing the spread of the data and the mean values. Ignoring the extreme figures in both cases, SG appears to vary from 3.35 to 3.65, with a mean of 3.50, for the quenched slag and 3.30 to 3.90, with a mean value of 3.70, for the air-cooled slag. This difference in SG of the material is due to the cooling process used, with the quenched CS being porous and lighter than air-cooled CS (Shi et al., 2008). This difference might also be attributed to the total iron content (Fe_2O_3), as the mean Fe_2O_3 content of the air-cooled and quenched CS is 61% and 40%, respectively.

On the other hand, data made available during 1992–2014 for spent CS suggest a mean value of 3.53 for a narrowly based range of 3.4–3.7 (Figure 3.17). The SG figures for CS with an unidentified cooling process, which were reported during 1983–2015, are spread over a wide range of 2.7–4.1 with a mean value of 3.51 (Figure 3.17). The fact that the mean SG value for the spent CS (3.53) and that of unidentified CS (3.51) are essentially similar to that of the quenched CS at mean 3.50 tends to suggest that much of the research and development work in developing the use of CS as a valuable resource material within the construction industry has been based on the use of quenched CS.

In general, the fact that the SG of all forms of CS shows values higher than the conventional aggregates (SG = 2.6) suggests that CS is a relatively heavyweight material, and if it is not taken into consideration at the design stage, this could lead to the segregation of composite mixtures.

3.4.6 Water Absorption

The water absorption property of a material is indicative of its total pore volume accessible to water and can be used to determine its possible potential durability, such as the freeze and thaw resistance (Neville, 1994). In dealing with concrete, water absorption is used to calculate the amount of water that is likely to be absorbed by the aggregates during the concrete mix preparation, which can, if not accounted for, disturb the effective water/cement ratio of the mix (Jackson and Dhir, 1996).

In the case of bitumen mix, it is desirable to avoid a highly absorptive aggregate in hot mix asphalt, as asphalt binder absorbed by the aggregate is not available for coating the aggregate particle surface and is therefore not available for bonding. Thus, highly absorptive aggregates require more asphalt binder to develop the same film thickness as less absorptive aggregates, making the resulting asphalt mix more expensive (Transportation Research Board, 2011).

The water absorption data available in the literature is presented in Table 3.7, with the data separated based on the type of cooling process used in the handling of slag, even though a very large proportion of the studies failed to provide such information. The analysis of the data (Table 3.7), as to be expected, gives the range and mean value for the air-cooled CS (dense and crystalline) as appreciatively lower than those for the quenched CS (granulated and porous texture). The corresponding figure for the spent CS, though it has a higher variable range, is essentially similar to that of the quenched CS, which is commonly adopted in the first instance as an abrasive material for ship cleaning. As to be expected, for the large volume of the data for which the cooling process has not been identified, the variability range of the CS absorption value is enormously wide and, consequently, the mean value is the highest.

Notwithstanding this, in general, comparing the water absorption of all CS types with those of the materials commonly used in the construction sector as aggregates, such as granite (0.3% absorption), limestone (0.9%) and sandstone (1.8%), CS could be considered a low-absorptive and heavyweight material. This can be taken as a good indication of the potential scope for using CS in the construction industry.

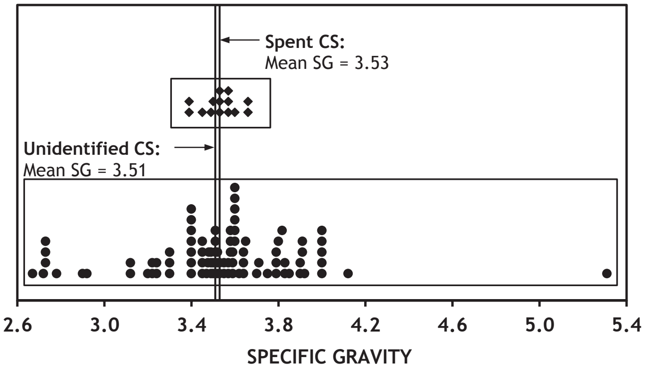

Figure 3.17 Specific gravity (SG) of spent and unidentified copper slag (CS).
Data taken from Al-Sayed and Mandany (1992), Chew and Bharati (2009), Ghosh (2007), Goi et al. (2003), Lim and Chu 2006, Madany et al. (1991), Wee et al. (1996), Ping (2011), Salleh et al. (2014), Tam (2001), Wu et al. (2010a,b), Zain et al. (2004), Afshoon and Sharifi (2014), Al-Jabri et al. (2002, 2006, 2009a,b, 2011), Amarnaath et al. (2015), Anjana et al. (2015), Anudeep et al. (2015), Ayano and Sakata (2000), Behnood (2005), Boakye et al. (2013), Boakye (2014), Brindha and Nagan (2010a), Brindha and Sureshkumar (2010), Cachim et al. (2009), Caliskan and Behnood (2004), Das et al. (1983), Dharani et al. (2015), Erdem et al. (2012), Gowda and Balakrishna (2014), Havanagi et al. (2006, 2007, 2009, 2012), Hosokawa et al. (2004), Hwang and Laiw (1989), Jaivignesh and Gandhimathi (2015), Kang et al. (2013), Kayathri et al. (2014), Khanzadi and Behnood (2009), Kharade et al. (2013), Kitazume et al. (1998a), Kumar (2012), Lakshmanan et al. (2014), Lavanya et al. (2013), Lavanya et al. (2012), Lee (2008), Leema and Suganya (2015), Madheswaran et al. (2014), Madhu and Venkataratnam (2015), Mahendran and Arunachelam (2015), Mahmood and Hashmi (2014), Meenakashi and Ilangovan (2011), Mithun and Narasimhan (2016), Mithun et al. (2015a,b), Naganur and Chethan (2014), Najimi et al. (2011), Nazer et al. (2012, 2013), Patel et al. (2011), Patil (2015), Patnaik et al. (2015), Priyanka and Thahira (2013), Pundhir et al. (2005), Resende et al. (2008), Khan et al. (2015), Sabarishri et al. (2015), Sakthieswaran and Ganesan (2013, 2014), Saravana et al. (2005), Saxena (2015a,b), Shabbeer et al. (2012), Shahu et al. (2012), Shams (2013), Sharifi and Kaafi (2013), Sharma et al. (2013a,b), Shoya et al. (2003), Singh et al. (2014), Sudarvizhi and Ilangovan (2012), Suresh et al. (2013), Suresh and Kishore (2013), Sureshkumar et al. (2013), Sushma et al. (2015), Tamil et al. (2014), Tiwari and Bhattacharya (2013), Ueno et al. (2005), Vamsi and Kishore (2013), Vamsi et al. (2013), Velumani and Nirmalkumar (2014), Viji (2014), Vimarsh et al. (2014), and Yogendra (2008).

3.4.7 Hardness

Developed by German geologist and mineralogist, Friedrich Mohs, in 1812, the Mohs scale of mineral hardness is a qualitative measure that characterizes the scratch resistance of minerals. It is one of several definitions of hardness in materials science, some of which are more quantitative. The Mohs scale ranges from 1 to 10, with 1 being the softest (talc) and 10 the hardest (diamond).

Information available on the hardness of CS has been compiled in Table 3.8, separately for air-cooled and quenched types, and those for which the process of cooling has not been given. This shows that, with the exceptions of Lakshmanan et al. (2014), Anudeep et al.

Table 3.7 Water absorption of copper slag

Copper Slag	Water Absorption, %		References
	Range	Mean	
Air cooled	0.15–0.40	0.26	Ambily et al. (2015), Arivalagan (2013), Brindha et al. (2010), Brindha and Nagan (2011), Gupta et al. (2012a,b), Rajaselvi and Beatrice (2015), Kumar and Mahesh (2015), Poozvizhi and Kathirvel (2015), Sathya and Shanmugavalli (2014), Siva et al. (2014), Srinivas and Muranal (2015), and Tixier (2000)
Quenched	0.17–0.55	0.37	Hassan and Al-Jabri (2011), Nataraja et al. (2014a), Shoya et al. (1997, 1999, 2003), and Tokuhashi et al. (2001)
Spent	0.10–0.70	0.38	Al-Sayed and Mandany (1992), Ghosh (2007), Koh and Lye (2012), Madany et al. (1991), Ping (2011), Resende et al. (2008), and Tam (2001)
Unidentified	0.13–2.60	0.45	Afshoon and Sharifi (2014), Al-Jabri et al. (2011, 2009a,b), Amarnaath et al. (2015), Anjana et al. (2015), Ayano and Sakata (2000), Behnood (2005), Boakye et al. (2013), Boakye (2014), Brindha and Nagan (2010a), Brindha and Sureshkumar (2010), Cachim et al. (2009), Caliskan and Behnood (2004), Gowda and Balakrishna (2014), Hosokawa et al. (2004), Hwang and Laiw (1989), Ishimaru et al. (2005), Jaivignesh and Gandhimathi (2015), Kang et al. (2013), Khanzadi and Behnood (2009), Kharade et al. (2013), Kumar (2012), Lee (2008), Lee et al. (2003), Leema and Suganya (2015), Mahmood and Hashmi (2014), Meenakashi and Ilangovan (2011), Mithun and Narasimhan (2016), Mithun et al. (2015a,b), Naganur and Chethan (2014), Patil (2015), Saxena (2015a), Pundhir et al. (2005), Resende et al. (2008), Sabarishri et al. (2015), Salleh et al. (2014), Shams (2013), Sharma et al. (2013a,b), Song (2013), Sudarvizhi and Ilangovan (2012), Suresh et al. (2013), Suresh and Kishore (2013), Tamil et al. (2014), Thomas et al. (2012), Ueno et al. (2005), and Vimarsh et al. (2014)

(2015), Potana (2005), and Spitzner (1978), all the results are within 6–7 Mohs hardness and compare well with those reported by Gorai et al. (2003) and Shi et al. (2008). There are no significant differences in the hardness values of air-cooled and quenched slag, and comparisons with other abrasive materials indicate that CS is comparable to quartz (silica sand) (7.0 Mohs hardness), blast furnace slag (7.0) and olivine (6.5).

Table 3.8 Hardness of copper slag

Copper Slag	Hardness, Mohs	References
Air cooled	6–7	Arivalagan (2013), Gaud et al. (2013), Jebitta and Sofia 2015, Poozvizhi and Kathirvel (2015), Singh and Bath (2015), and Singh et al. (2014)
Quenched	6–7	Song (2013) and Sureshkumar et al. (2013)
Not given	6–7	Gorai et al. (2003), Anjana et al. (2015), Brindha et al. (2010), Cachim et al. (2009), Chandrshekhar et al. (2015), Chockalingam et al. (2013), Lavanya et al. (2011, 2013), Prakash and Brindha (2012), Shams (2013), Sushma et al (2015), Tixer (2000), Shi et al. (2008), and de Brito and Saikia (2013)
	6	JPL Industries (1997)
	7	Shabbeer et al. (2012) and Sharifi and Kaafi (2013)
	7–8	Potana (2005)
	8	Spitzner (1978)
	5–7	Lakshmanan et al. (2014) and Anudeep et al. (2015)
	6.5–7	Lavanya et al. (2012)

3.4.8 Soundness

The soundness test determines an aggregate's resistance to disintegration by weathering and, in particular, freeze–thaw cycles (AASHTO T 104, 2003 and ASTM C88, 2013). The test is carried out by repeated immersion in a saturated solution of sodium or magnesium sulphate followed by oven drying to partially or completely dehydrate the salts precipitated in the permeable pore space. The data available (Gorai et al., 2003; Shi et al., 2008; Song, 2013) suggest that the reported soundness measurements of 0.8–0.9% for CS are well below the maximum permissible limits of 15–25% for hot mix asphalt surface course, structural concrete made with marine limestone (BS EN 12620:2002+A1, 2008; BS EN 13242:2002+A1, 2007; SCDOT, 2011). Thus, it may be concluded that CS is a perfectly sound material for use in construction.

3.4.9 Aggregate Crushing Value

Although currently Los Angeles abrasion is the preferred aggregate resistance to fragmentation test required for specifying concrete BS EN 12620:2002+A1 (2008) and asphalt BS EN 13043 (2002) properties and the aggregate crushing value test

BS 812-110 (1990) has been withdrawn, the test has remained in use by researchers (Caliskan and Behnood, 2004), and the results have been reported until recently in the studies undertaken on the use of CS in concrete (Behnood, 2005; Shi et al., 2008; Khanzadi and Behnood, 2009; Song, 2013; Naganur and Chethan, 2014; Saxena, 2015a,b).

The aggregate crushing value (ACV) provides a relative measure of the resistance of an aggregate to crushing under a gradually applied load. The test uses an aggregate sample of definitive size fraction 14–10 mm, though smaller fraction sizes 5.00–3.35 and 3.35–2.36 are permitted according to BS 812-110 (1990). The implied resistance of aggregate to crushing is defined to decrease with increasing ACV measured value, and at the value of above 30% the material is considered to be weak, and in such cases the 10% fines test method is recommended in BS 812-110 (1990).

The ACV of CS has generally been reported to be within the range of 10–21% (Caliskan and Behnood, 2004; Behnood, 2005; Khanzadi and Behnood, 2009) and though not implicitly mentioned, it would appear to be the same as air-cooled slag, as 12.5 mm has been used as coarse aggregate in these studies. An ACV of 26% has also been recorded in studies where CS, probably of similar size range to sand, has been used as partial replacement for fine aggregate (Naganur and Chethan, 2014: Saxena, 2015a,b). Comparison of the ACV of CS, using the values given in BS 812-110 (1990), would rank the material in the form of air-cooled slag somewhere between igneous rock and mixed gravel (16–21%) and of considerably better quality than blast furnace slag (35%) and in the quenched form close to argillaceous limestone (27%). Interestingly, Caliskan and Behnood (2004) have compared it to limestone having a crushing value of 23%.

3.4.10 Aggregate Impact Value

The impact test (BS 812-112, 1990), as in the case of the compaction test (BS 812-110, 1990), has been taken out of the set of standard tests used for determining the physical properties of aggregates for assessing their suitability for use in construction applications. However, the aggregate impact value, together with the ACV, has continued to be included, not surprisingly, by the same researchers in their studies on the use of CS in concrete (Caliskan and Behnood,2004; Behnood, 2005; Shi et al., 2008; Song, 2013; Naganur and Chethan, 2014; Saxena, 2015a,b).

Three sets of aggregate impact values have been reported, namely, (i) 8–16% (Behnood, 2005; Shi et al., 2008; Khanzadi and Behnood, 2009), (ii) 18–26% (Caliskan and Behnood, 2004) in the studies where CS has been used as a coarse aggregate, which is most likely to be obtained from air-cooled slag, and (iii) 31% (Naganur and Chethan, 2014; Saxena, 2015a,b) where it has been used as a component of sand, which is most likely to be obtained from quenched slag. Using the values given in BS 812-112 (1990), air-cooled CS could be ranked somewhere between igneous rock and mixed gravel (15–26%) and quenched CS ranked between argillaceous limestone and blast furnace slag (28–32%).

3.4.11 Angle of Internal Friction

In ground engineering, shear strength assumes particular importance in relation to embankments, slopes and retaining walls. The angle of internal friction, which is commonly known as the friction angle (φ), is the ability of granular material to withstand shear stress. The data available for CS in this respect are summarised in Table 3.9 and show φ to vary greatly depending on how the CS has been processed. Ignoring the spent CS, which is produced in small quantities and is mainly used in the concrete construction industry, the overall range of φ for CS can be taken as 40–53°. This makes it higher than other common soils (Lambe and Whitman, 1979) such as sand and gravel soils (36–48°) and well-graded sand soil (34–46°).

3.4.12 Conductivity

Electrical conductivity measurements have been made to determine water-soluble contaminants in CS which may leach. The studies involved have considered geotechnical, concrete and epoxy composite applications (Gorai et al., 2003; Shi et al., 2008; Lakshmanan et al., 2014; Shabbeer et al., 2012; Song, 2013; Shams, 2013; Anudeep et al., 2015) and, with few exceptions, have reported the electrical conductivity of CS to be about 50 mS/m, irrespective of how the CS was processed.

3.4.13 Plasticity and Swelling Indices

The nature of CS would suggest that, being a granular material, on its own, it is not likely to display any plastic and swelling behaviour. The reported test results confirmed CS to be a non-plastic and non-swelling material (Patel et al., 2007 and Tandel and Patel, 2009). The effect of CS on the Atterberg limits of soils is discussed in Chapter 6 (Section 6.3).

Table 3.9 Angle of friction for copper slag

Copper Slag	Angle of Friction, degree	References
Air cooled	51–53	Brindha and Nagan (2011), Brindha et al. (2010), Gupta et al. (2012a,b), Thomas et al. (2012), Arivalagan (2013), Gaud et al. (2013), Poovizhi and Kathirvel (2015), and Sathya and Shanmugavalli (2014)
Quenched	49	Nataraja et al. (2014a,b)
Spent	29–47	Goi et al. (2003)
Not identified	40–53	Gorai et al. (2003), Lavanya et al. (2012, 2013), and Shams (2013)

3.5 Comparison With Typical Natural Aggregates

Comparison of CS with some of the natural aggregates could be helpful in gaining a better appreciation of the material. In this regard, an attempt has been made to collate the data for CS from the dedicated literature referred to in this chapter, and Neville (1994), Newman and Choo (2003) and Rumbarger and Vitullo (2003) have been used for obtaining the corresponding data for natural sand, limestone and granite materials. The comparison is provided in Table 3.10 for the various properties. Briefly, it can be seen that the particle shape and texture of CS are not dissimilar to the commonly used natural materials. CS, however, has a very distinct black to blackish-grey colour, its SG is the highest compared to the commonly used natural aggregates and its water absorption is the lowest. The impact value is considerably higher than those of limestone and granite, whilst the crushing value is of similar order.

Table 3.10 Comparison of some physical and mechanical properties of copper slag and some common natural aggregates

	Copper Slag[a]			River Sand[b]	Limestone[b]	Granite[b]
Property	**Air Cooled**	**Quenched**	**Spent**			
Particle shape	Angular/irregular			Rounded/ irregular	Angular	Angular
Surface texture	Glassy/smooth/granular			Smooth	Rough	Crystalline
Colour	Black/blackish grey			White-grey	White/grey	Red/grey/ dark blue/ black
Specific gravity	3.37–4.06 (3.73)	2.90–3.91 (3.50)	3.39–3.66 (3.53)	2.60–2.70 (2.65)	2.50–2.80 (2.66)	2.60–3.00 (2.69)
Water absorption, %	0.15–0.40 (0.26)	0.17–0.55 (0.37)	0.10–0.70 (0.38)	1.10–3.15	0.50–0.73	0.20–1.90 (0.60)
Impact value, %	8.2–30.8 (19.6)			–	15.0–20.0 (17.0)	17.0–21.0 (19.0)
Crushing value, %	10.0–26.4 (20.3)			–	19.0–31.0 (24.0)	23.0–30.0 (26.0)

Note: Numbers in parentheses are the average of the overall results in the given range.

[a] Data taken from previous sections of this chapter.

[b] Information taken from Neville (1994), Newman and Choo (2003), Rumbarger and Vitullo (2003), Bell (1993), Jackson and Dhir (1996), Smith and Collis (1993), and Hewlett (1998).

3.6 Potential Use and Applications

3.6.1 Cement

The high iron and silica contents of CS suggest that it is suitable for use as a raw material for providing two of four primary chemical components for the manufacturing of cement clinker (the other two being lime and alumina).

Alternatively, CS can be used as pozzolanic cement as its sum of $SiO_2+Al_2O_3+Fe_2O_3$ components generally exceeds 70%, meeting the requirement of Class F fly ash specified in ASTM C618 (2015). The pozzolanic reaction of CS with calcium hydroxide released from cement hydration can produce calcium silica hydrate, leading to densification of cement paste structure and improving the strength and durability of concrete. A comprehensive analysis and evaluation of the effects on the performance of concrete of using CS as part of the raw feed for PC production and separately as a cement component is presented in Chapter 5.

3.6.2 Construction Aggregate

Crushed air-cooled CS as coarse and fine aggregates and quenched/granulated CS as sand have been used as construction aggregates in real concrete, geotechnical and road pavement applications, as early as the 18th and 19th centuries. In general, similar or better engineering and durability properties can be expected when CS is used as a replacement for natural aggregates in those applications, provided the PSD of the materials are made to conform to relevant specifications currently in use.

Indeed, when designed carefully, the unique inherent characteristics of CS can enhance the performance of the resultant products. For example, its low water demand property makes it suitable for use in high-strength concrete, which has a low water/cement ratio design. As suggested by Lye et al. (2015) and shown in Section 4.3.1, the low water demand characteristic of CS can be used for developing higher strength concrete, without having to increase its cement content, or for reducing cement content without compromising its strength. Additionally, owing to its lower porosity and higher hardness than natural sand, CS offers greater deformation and abrasion resistance in both concrete (see Sections 4.5 and 4.8.8) and road pavement applications (see Sections 7.4.4 and 7.4.5).

Chapters 4 ,6 ,7 provide detailed information regarding the effects of CS as an aggregate on the properties of concrete and geotechnical and road pavement applications.

3.6.3 Abrasive Blasting Medium

CS is commonly used as an abrasive blasting medium in shipyards and refinery industries to remove paint, rust and other contaminations from steel surfaces prior to the application of new coatings. Although its abrasive-related characteristics have been reported not to be comparable to those of the traditionally used silica sand, CS offers a greater advantage of low concentration of respirable free silica, which is hazardous to health (KTA-Tator, 1998a,b). Several models have been developed by Kambham et al. (2007) to select working pressure and feeding rate for maximum efficiency in using CS as an abrasive in such applications.

3.6.4 Ceramic Tiles

Owing to its significant silica content, CS could be an ideal raw material for the ceramic industry. Marghussian and Maghsoodipoor (1999) have investigated the properties of unglazed floor tiles made with clay, sand and CS. It is reported that the addition of CS would have to be limited to 40% content of the raw feed, as higher CS content could result in a bloating effect due to the oxidation of sulphides in CS at the high temperatures used in the ceramic industry. Samples made with 40% CS, which were sintered at 1025°C for 1 h, render a bending strength, water absorption and microhardness that can meet the requirements of a standard unglazed ceramic tile. Additionally, the tiles also show good acid resistance.

3.6.5 Glass-Ceramics

Glass-ceramics are polycrystalline materials formed by controlling the nucleation and growth of crystal phases within the glass. Transition metal oxides and sulphides, such as titanium dioxides (TiO_2) and zirconium dioxides (ZrO_2), are typically used as nucleating agents. Since CS contains iron, its effect on the crystallisation of glass-ceramics, which has not been studied extensively, can be of interest. Iron-rich phases are claimed to impart magnetic, electrical and thermal properties, as well as a brownish shade, to glass-ceramics (Chinnam et al., 2013).

Perhaps the first glass-ceramic made with CS was produced by Yetka et al. (2004) from Iran. Three glass-ceramic samples composed of 16.3%, 28.6% and 56.0% CS content and two other raw materials, quartz and calcium carbonate, were produced. These test specimens were sintered to different peak temperatures ranging from 750 to 1030°C for 60 min. Glass ceramics made with 56.0% CS which was sintered at 865°C were reported to have the highest bending strength, microhardness and density.

As the presence of iron in CS can result in a brownish shade on the glass-ceramics, Yang et al. (2013) prepared light-coloured glass-ceramics made with 61.5% CS. Fluorite was used at 4.6% as a nucleating agent. The glass was quenched, ground and compacted, followed by heat treatment at different peak temperature ranging from 900 to 1100°C for 60 min duration. It was found that optimum material properties, such as high bulk density and hardness and low porosity and water absorption, were obtained when glass-ceramic was sintered at 950°C.

On the other hand, the effect of the iron content of CS on glass-ceramic foam, a porous structure material with thermal and acoustic insulation properties, has been investigated by Mohamed et al. (2015). Two base glass compositions made with 47%

and 32% CS that contained 24% and 16% iron(III) oxide (Fe_2O_3) content, respectively, were prepared and 3% silicon carbide was used as a foaming agent. The glass-ceramic foams were fabricated through a powder-sintering method by heating the powdered glasses to a peak temperature ranging from 800 to 1000°C at 10°C/min for a duration of 25 min. Glass ceramic foam made with 32% CS having 0.18 relative density and 9-MPa compressive strength was obtained when sintered at 950°C. The foaming of sample made with 47% CS was reported to be impossible because of the increase in the intensity of crystallization attributed to its high iron content. However, the thermal and acoustic insulation properties of the resultant glass-ceramic foams have not been assessed.

3.6.6 Polymer Matrix Composites

Polymer matrix composites are made with specific types of fillers and/or fibres, bound together by a polymer matrix to achieve the desired engineering properties, which are important to many industries, including aerospace, automotive, electrical and marine.

The use of ground CS of particle size between 100 and 200 μm as filler has been reported to increase the thermal conductivity of the resultant composites (Shams, 2013). In a study conducted by Biswas and Satapathy (2010), the incorporation of 70-μm CS filler at 10% content in a glass-fibre reinforced epoxy composite has shown to improve its mechanical properties, such as flexural strength, tensile modulus, impact strength and hardness. The maximum wear rate of the composite filled with CS occurs at a 45° impingement angle, indicating semi-ductile behaviour. The resultant composites show semi-ductile erosion behaviour, with maximum erosion rate occurring at a 45° impingement angle. A similar erosion response has also been observed when 10% CS filler is added to bamboo fibre reinforced epoxy composites (Biswas, 2010; 2014; Biswas et al., 2010).

3.6.7 Wastewater Treatment

The heavy metal chromium(IV), discharged from electroplating, leather tanning and wood preservation industries, is known to be environmentally hazardous and carcinogenic. During the wastewater treatment process, chromium(IV) is normally reduced to chromium(III) using suitable reducing agents such as ferrous sulphate, followed by precipitation. The use of CS as an alternative ferrous(II) source in the chromium(IV) reduction process has been undertaken by Kiyak et al. (1999) in Turkey. CS is shown to be effective in reducing chromium(IV) and its effectiveness increases (a) under more acidic conditions, (b) with decreasing particle size of CS and (c) with increasing temperature of the solution.

3.6.8 Other Applications

There are several other applications in which the use of CS, as well as copper tailings and copper flotation waste, has been considered, such as:

- bricks (Ahmari and Zhang, 2012; Kanagalakshmi et al., 2015; Sathish et al., 2014)
- mine backfill (Atkinson et al., 1989; Grice, 1998; Hassani et al., 2001; Petrolito et al., 2005; Peyronnard and Benzaazoua, 2012)
- pigments (Ozel et al., 2006)
- prepacked concrete grout (Murata et al., 1985)

3.7 Environmental Considerations

In 1991, a regulatory determination issued by the US Environmental Protection Agency (US EPA) stated that 20 specific mineral processing wastes, including CS and copper tailings, are considered as special wastes, which are excluded from regulation as hazardous wastes under Subtitle C of the Resource Conservation and Recovery Act (US EPA, 1991).

Later, in 1996, the United Nations Basel Convention on the Transboundary Movement of Hazardous Wastes and Their Disposal also characterised CS as a non-hazardous material (Alter, 2005). The work leading to the acceptance of CS as non-hazardous waste and the approach to clarifying the definition of hazardous waste by the Basel Convention have been published by Alter (2005, 1997), respectively. The background information provided therein could be useful to the reader to gain insight into the size and scale of the relevant research and development work that has been undertaken.

Given that CS has been determined to be a non-hazardous material independently by the US EPA and the Basel Convention, provided that it is in compliance with regulatory requirements, CS can be freely moved internationally and be used as an alternative natural source in many applications, particularly in the construction industry.

3.7.1 Leaching Studies

Leaching tests are frequently used to assess the potential risk of a waste to release organic and inorganic contaminants into the environment. Several leaching protocols have been developed with each differing in terms of leaching solution used, liquid-to-solid ratio, contact time, number of extractions and other testing parameters. The most commonly used leaching protocol is the US EPA Method 1311 for the Toxicity Characteristic Leaching Procedure (TCLP) (US EPA, 1992), which is designed to simulate leaching conditions in municipal solid waste landfills using a laboratory setup. In brief, the test extracts a solid sample of particle size less than 9.5 mm using acetic acid of pH 4.93, at a liquid-to-solid ratio of 20:1, for an extraction period of 18 h.

The leached element concentrations of CS, originating from India (3 samples), Singapore (6 samples) and Chile, Canada and the United States (11 samples in total), obtained using the TCLP test and published since 1983, are given in Table 3.11. The US EPA regulatory levels for metals that are characterised as hazardous are also listed in the same table (US EPA, 2012).

It is evident from Table 3.11 that the leached element concentrations of all CS samples are well below the regulatory limits, even when exposed to a non-standard yet more aggressive environment of pH 3.0 for 24 h duration (Lim and Chu, 2006). Although the concentrations of copper and zinc are not regulated, it should be mentioned that they tend to be high especially under more acidic conditions, as shown in the results of Sarawathy et al. (2014), Supekar (2007) and Lim and Chu (2006). The leaching behaviour of CS does not seem to be affected by its type, such as air cooled, quenched or spent.

Table 3.12 lists the leached element concentrations of CS originating from the Asian and European countries, using methods other than the TCLP, such as the multiple extraction procedure, which is known as a long-term stability test. Although not applicable because of different testing conditions, the US EPA regulatory levels for the contaminants are also given in Table 3.12 for reference purposes. The results in Table 3.12 show that all the leached element concentrations of CS are well below the regulatory limits, except for the CS sample tested by Zain et al. (2004), using standard methods for the examination of water and wastewater, showing that the leaching of lead is higher than the allowable threshold.

Again, the leached concentrations of copper and zinc have shown a considerable increase when CS is tested in an acidic environment (Madany and Raveendran, 1992; Sanchez et al., 2004). Although this is not likely to restrict the use of CS, it is still advisable to check with the local authorities, especially when the applications of CS are made in an acidic environment.

3.7.2 Life Cycle Assessment of Copper Slag

Life cycle assessment (LCA) evaluates the potential environmental impacts associated with a product, being the energy and material consumption and waste generation, from its initial extraction to final disposal. It provides information and guidance to policymakers and industry for better environmental management.

An LCA study on using spent CS as a cement component and natural sand in Singapore was conducted by Kua (2012, 2013). Being an island country without natural resources, Singapore imports CS mostly from Japan for its application in sand blasting of ships. The spent CS after blasting, instead of going straight into a landfill, is normally used as natural sand in the construction industry in Singapore. The studies, however, showed that the net effect of using spent CS as cement and sand replacement does not provide attractive life cycle benefits, which is possibly due to the lack of representative process models and a general absence of regional primary data.

Table 3.11 Leached element concentrations of copper slag using the toxicity characteristic leaching procedure method

References	Copper Slag Type[a]	Element Concentration, mg/L												
		Ag	As	Ba	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Se	Sr	Zn
US EPA regulatory level	–	5.0	5.0	100.0	1.0	5.0	–	0.2	–	–	5.0	1.0	–	–
Das et al. (1983)	AC	0	0	0.5	0.002	0	–	0	–	–	0	0.08	–	–
Shanmuganathan et al. (2008)	Q	–	0.04	–	0.01	0.15	2.20	–	–	0.08	0.10	–	–	0.08
Cheong et al. (2007)	S	–	0.227	0.981	0.068	0.136	23.42	–	0.734	0.064	0.797	–	–	23.32
Ghosh (2007)	S	ND	ND	0.23	ND	0.091	ND	ND	ND	ND	ND	ND	–	0.006
JPL Industries(1997)	S	<0.01	<0.10	<5	<0.05	<0.05	–	<0.01	–	–	<0.20	<0.10	–	–
Lim and Chu (2006)[b]	S	<0.01	0.08	1.2	0.03	0.081	33.6	0.02	–	0.37	0.51	0.05	–	18.5
	S	–	–	–	0.06	0.59	81.6	–	–	7.29	2.96	–	–	54.7
	S	–	–	–	0.032	0.07	2.8	–	–	0.18	<0.01	–	–	1.86
Ling and Thim (1999a)	S	<0.01	<0.05	<0.01	<0.01	<0.01	4.2	<0.01	–	<0.01	<0.05	<0.05	–	0.17
Ling and Thim (1999b)	S	<0.005	<0.01	0.38	<0.001	<0.05	<0.01	<0.001	<0.01	<0.01	<0.005	<0.005	–	<0.01
Alter (2005)[c]	NG	–	<0.52	–	<0.04	<0.06	6.23	–	–	–	<0.84	<0.28	–	0.84
Sharma et al. (2013b)	NG	–	0.39	–	–	0.10	–	–	–	–	1.22	–	–	–
Suresh et al. (2013)	NG	0.2	–	–	0.7	1.35	19.46	–	–	–	1.9	–	–	7.4

[a] Type of CS. *AC,* air cooled; *Q,* quenched; *S,* spent (previously used in blasting); *NG,* not given; *ND,* not detected.

[b] The test conditions for the first to third samples were leachate of pH 5.0 for 18 h, leachate of pH 3.0 for 24 h and leachate of pH 8.0 for 24 h.

[c] Average results of 10 samples collected from the United States, Canada and Chile.

Table 3.12 Leached element concentrations of copper slag using methods other than the toxicity characteristic leaching procedure

References	Copper Slag Type[a]	Leached Element Concentration, mg/L												
		Ag	**As**	**Ba**	**Cd**	**Cr**	**Cu**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Sr**	**Zn**
US EPA regulatory level	–	5.0	5.0	100.0	1.0	5.0	–	0.2	–	–	5.0	1.0	–	–
(a) ASTM D5233 (1995) single-batch extraction method														
Brindha and Nagan (2011, 2010b), and Brindha et al. (2010)	Q	–	0.923	0.258	ND	ND	11.64	–	0.048	0.097	ND	ND	0.046	0.991
(b) Cascade leaching test														
Dung et al. (2014)	S	–	ND	–	0.23	ND	10	–	–	ND	0.2	–	–	–
(c) Multiple extraction procedure														
Shanmuganathan et al. (2008)[b]	Q	–	–	–	–	0.81	2.898	–	–	0.168	0.392	–	–	3.424
Madany and Raveendran (1992)[c]	S	–	–	–	0.001	0.001	0.106	–	–	–	0.005	–	–	0.028
	S	–	–	–	0.005	0.005	0.325	–	–	–	0.010	–	–	0.080
	S	–	–	–	0.006	0.13	99.25	–	–	–	0.500	–	–	29.50
	S	–	–	–	0.008	0.440	128.4	–	–	–	1.330	–	–	37.0

(d) Spanish ministerial order method														
Sanchez et al. (2004)[d]	NG	–	–	0.04	0.01	0.01	0.12	0	0.01	0.01	0.10	–	–	0.27
	NG	–	–	0.12	0.02	0.06	52.8	0	0.06	0.12	0.32	–	–	5.5
(e) Standard methods for the examination of water and wastewater														
Zain et al. (2004)	NG	–	–	–	–	–	15.49	–	–	1.218	8.793	–	–	12.07
(f) Sulphuric acid leaching test														
Shanmuganathan et al. (2008)[e]	Q	–	–	–	–	0.16	1.15	–	–	–	–	–	–	0.078
	Q	–	–	–	–	0.24	1.55	–	–	–	–	–	–	0.083
(g) Other method														
Sarawathy et al. (2014) and Supekar (2007)[f]	Q	ND	0.389	ND	0.029	ND	0.107	ND	–	–	ND	–	–	–
	Q	ND	0.334	ND	0.003	ND	0.931	ND	–	–	ND	–	–	–
	Q	ND	0.745	ND	0.007	ND	0.239	ND	–	–	ND	–	–	–

[a] Type of CS. *AC,* air cooled; *Q,* quenched; *S,* spent (previously used in blasting); *NG,* not given; *ND,* not detected.

[b] Nine batch extractions using leachate of pH 3.0 based on US EPA Method 1311 (1992).

[c] Six batch extractions. The test conditions for the first to fourth samples were distilled water for 1 h, distilled water for 24 h, acid solution of pH 4.5 for 24 h and synthetic leachate of pH 4.5 for 24 h.

[d] The pH of leachate used for the first and second samples was 6.7 and 5.0, respectively.

[e] The pH of leachate used for the first and second samples was 7.0 and 5.0, respectively. Tests were conducted in a 45°C environment for 250 min.

[f] The leachate used for the first to third samples was tap water, acid rainwater (pH 2–4) and seawater (pH 8.68).

Another LCA study was conducted by De Schepper et al. (2014b) regarding the environmental benefits of concrete made with fly ash and GGBS as cement components and CS as a natural sand. It was shown that the resultant concrete significantly reduced the global warming potential, but that was mainly from the reduction in the use of Portland clinker, rather than use of the natural sand.

3.8 Conclusions

Slag is an important by-product, generated during pyrometallurgical processing of copper. Typically, CS is classified based on its cooling process, namely air-cooled CS, formed through slow air cooling, and quenched/granulated CS, resulting from rapid water quenching. Another type is called spent CS, which is a quenched CS previously used as an abrasive. The chemical, mineralogical and physical properties of CS are largely influenced by its cooling rate.

The chemical and mineralogical analyses of CS suggest that the material is suitable for use as a component of either raw feed for cement clinker production or cement as a pozzolanic material. In general, CS contains about 75% iron oxide and silicon dioxide and 10% aluminium and calcium oxides, meeting the oxide requirement for fly ash specified in ASTM C618 (2015). Air-cooled CS is essentially a crystalline material with predominant phases of fayalite and magnetite. whereas quenched CS contains a high proportion of glass, which makes it suitable for use as a pozzolanic material. The LOI of CS is normally less than 3% but a value of up to 6.65% has been reported. CS has fairly low soluble chloride and sulphate contents and it is innocuous to alkali–silica reaction.

CS is an angular, glassy and smooth material. Air-cooled CS can be crushed into various sizes for use as coarse, fine and filler aggregate. The particle size and distribution of quenched and spent CS resemble those of natural sand normally used in concrete, geotechnical and road pavement applications. However, quenched CS tends to have a coarser grading than spent CS. When used as a filler or cement component, CS needs to be ground to meet the standard requirement. In general, air-cooled CS is denser than the quenched/spent CS, having SG of 3.73 and water absorption of 0.26% compared to 3.50 and 0.37% for the latter. Both the air-cooled and the quenched CSs are hard (with 6 to 7 Mohs hardness), sound, non-plastic and non-swelling materials, having aggregate crushing and impact values lower than or similar to those of natural aggregate. These materials have an angle of internal friction ranging from 40 to 53°, which is higher than the common natural soils. The electrical conductivity of CS is about 50 mS/m.

Both the chemical and the physical properties of CS have been applied for their use in several potential applications and some have been successfully implemented. Its iron and silica contents make the material suitable for use in the manufacture of cement, ceramics and polymer matrix composites and in wastewater treatment. Because of its excellent hardness and low water absorption properties, CS is an ideal material for use as an abrasive grit and aggregate in concrete, geotechnical and road pavement applications. CS is non-hazardous and its leached element concentrations are lower than the US EPA regulatory limits.

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Use of Copper Slag as Concrete Sand

4

Main Headings

- Fresh properties
- Strength
- Deformation
- Non-destructive tests
- Permeation
- Durability
- High performance concrete
- Copper tailings
- Environmental impact
- Case studies

Synopsis

Consolidating 125 studies undertaken since 1989, the effects of copper slag (CS) used as sand on concrete properties are discussed. CS increases the consistence of concrete but, if uncontrolled, this may affect its stability. The setting times and early strength development are retarded. It has been commonly reported that concrete containing up to 50% CS shows improvement in strength properties, modulus of elasticity, creep and shrinkage. The permeation of concrete could be reduced because of an improvement in particle packing. The durability of concrete is generally not affected. The material shows potential for use in self-compacting, high-strength and high-durability concrete. Its use in concrete does not present a threat to the environment and the material is used in the concrete construction industry. The study of copper tailings is discussed.

Keywords: Copper slag, Concrete, Fresh properties, Strength, Deformation, Permeation, Durability, Environmental impact, Case studies.

4.1 Introduction

Concrete is one of humankind's most important technological innovations and was invented during the Roman Empire. Being the most widely used construction material, with an estimated annual global production of 25 billion tonnes (WBCSD, 2009), concrete is made entirely with a mixture of natural resources, such as cement, aggregates and water, and its manufacturing process has always been known not to be environmentally friendly. Whilst the production of cement is mainly responsible for carbon dioxide

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emission, the use of the non-renewable natural aggregates, which occupies about three-fourths of the concrete volume, is not sustainable. By 2020, a projected figure of 35.1 billion tonnes of aggregates is needed to meet the global construction demand.

With increasingly stringent environmental regulations, the search for alternative sources to natural aggregates in concrete applications has intensified. In general, these alternative materials can be broadly categorised into two groups: (1) recycled aggregates, which are derived from excavation, construction and demolition waste, and (2) secondary aggregates, which are normally by-products of power station coal ash, ferrous metal, non-ferrous metal, foundry, mining and quarry industries. However, the use of secondary aggregates has not been well accepted in real practice, and among them, only blast furnace slags are recognised as a concrete aggregate in BS EN 12620:2002+A1 (2008). Clearly, many of the other valuable secondary aggregates, whose properties have been established, are underappreciated and go into the landfill every day. These materials include copper slag (CS), which is another metallurgic slag like blast furnace slag, but originates from copper smelting and refining processes.

Because of its low water absorption, low porosity and moderate hardness characteristics, CS can be used as a viable material to replace natural sand in concrete, offering some desirable engineering properties such as greater resistance against deformation and abrasion. Indeed, the study of Lye et al. (2015) shows that if the concrete mix is designed properly, CS can result in potential water saving, as well as cement saving, thereby improving the green image of concrete.

In this assessment of the effects of CS on the fresh and hardened concrete properties, the analysis and evaluation are based on data extracted from 125 publications, originating from 15 countries, with a large contribution from the Asian countries, among which India has the highest number of publications (79), followed by Singapore (13) and Japan (8). The relevant research was first published in 1989, but CS did not begin to attract significant research attention until the end of the first decade of the 21st century, but this attention continues to soar today (Figure 4.1).

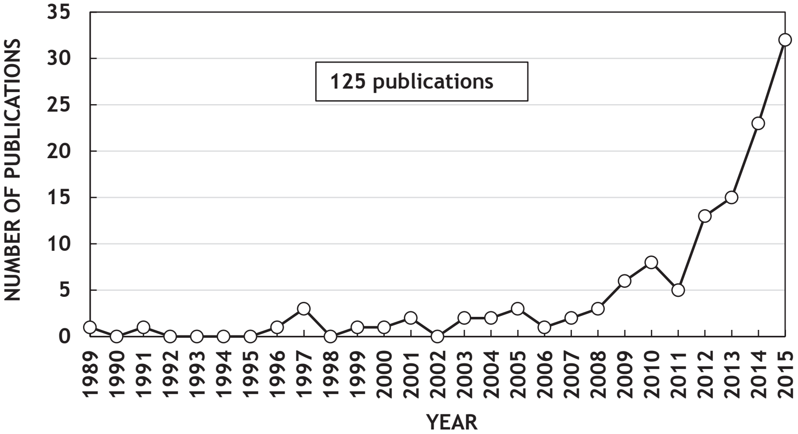

Figure 4.1 Distribution by year of publication.

4.2 General Information

Whilst the use of CS as sand in concrete continues to receive research attention, some authors have published papers reviewing, to varying extents, the existing literature relating to the properties of CS concrete. This information is examined in this section and the main potential benefits and concerns arising from the use of CS as a natural sand replacement in concrete are briefly summarised in Table 4.1, and discussed below.

- **Consistence (workability)**: Whilst many have reported that the addition of CS increases the consistence of concrete, Lye et al. (2015) have developed a simple model for estimating the potential water savings of concrete made with different CS contents in different consistence classes.
- **Strength**: Compressive, tensile and flexural strength of concrete generally increases with increasing CS content, and some studies have suggested an optimum CS replacement level at around 40–50% (Buddhadev et al., 2015; De Brito and Saikia, 2013; Lye et al., 2015; Madhavi, 2014; Milena, 2013; Mir, 2015).
- **Deformation resistance**: The use of CS tends to increase the resistance of concrete against deformation.
- **Permeation**: The water absorption of concrete decreases with increasing CS content, up to about 40% replacement level.
- **Durability**: The addition of CS increases the abrasion resistance of concrete, but its effects on other durability properties, such as chloride ingress, sulphate resistance and freeze–thaw attack, do not show a consistent trend.
- **Bleeding and setting time concerns**: A number of studies have reported that the use of CS increases the bleeding rate and delays the setting time of concrete.

In summary, the use of CS as a sand can improve many properties of concrete, particularly its workability, strength, deformation and permeation. Whilst as an inert and low-porosity material, it may be thought that with CS the durability of concrete would be similar to or better than that of concrete with natural sand, the research findings have not been conclusive, suggesting a need for further work in this area. Additionally, the bleeding and delay of setting time attributed to the use of CS should be taken into consideration when designing concrete mixes.

4.3 Fresh Concrete Properties

Fresh concrete in a construction process is important as it can affect the performance of the resulting hardened concrete, in terms of both its engineering properties and its durability performance. The main properties of fresh concrete are its workability [now termed consistence in BS EN 206 (2013)] and its stability. Each, for a given mix, together with other constituent materials, is affected by the nature of the coarse and fine aggregates used. Thus, in evaluating the use of CS as a replacement for

Table 4.1 The potential benefits of and concerns about using copper slag as sand in concrete

References	No. of Refs. Used	Potential Benefits								Concerns	
		Workability	Compressive Strength	Tensile Strength	Flexural Strength	Deformation Resistance	Permeation	Durability[a]	Abrasion Resistance	Bleeding	Setting Time
Buddhadev et al. (2015)	11	↑	↑	↑	↑		↑				
Chockalingam et al. (2013)	17	↑	↑	↑	↑		↑	↕		↑	↑
De Brito and Saikia (2013)	15	↑	↑	↑	↑	↑	↑	↕	↑	↑	↑
Gorai et al. (2003)	5		↑								
Lye et al. (2015)	68	↑	↑	↑	↑	↑	↑	↕	↑	↑	↑
Madhavi (2014)	6	↑	↑		↑			↕		↑	↑
Milena (2013)	2		↑								
Mir (2015)	2		↑	↑	↑						
Murari et al. (2015)	5	↑	↑					↕			↑
Ramesh et al. (2014)	2		↑	↑							
Shi et al. (2008)	8		↑	↑				↕	↑		↑

↑, increase; ↕, may be increase, decrease or no change.

[a] Excluding abrasion resistance.

normal sand in any proportion, it would be necessary to know how this may affect the properties of fresh concrete, how its use in concrete can be further exploited and how the use of sustainable materials in construction can be promoted.

4.3.1 Consistence (Workability)

Workability is the most commonly specified property of fresh concrete for its intended placing requirement onsite in a structure. Normally, consistence is measured in slump, but depending upon the consistence level, it may have to be determined by other measurements such as compacting factor test (low–high consistence), Vebe test (very low–low consistence) and flow table test (very high consistence as with self-levelling concrete). There are a number of controlling factors that may determine the consistence of concrete, and for given mix proportions, its aggregate properties such as particle size and distribution, particle shape, surface texture and water absorption can play a significant role.

The effects of CS on the consistence of normal, high-strength and self-compacting concrete have been studied in terms of its replacement level for natural sand since 1989 in Taiwan (Hwang and Laiw, 1989). The various studies undertaken have shown a three-way effect of CS inclusion on consistence at a fixed water content as stated below.

- Consistence increases with increasing CS content (Al-Jabri, 2006; Al-Jabri et al., 2009b, 2011; Gowda and Balakrishna, 2014; Hwang and Laiw, 1989; Jebitta and Sofia, 2015; Kharade et al., 2013; Mahmood and Hashmi, 2014; Mithun and Narasimhan, 2016; Mithun et al., 2015a; Patil, 2015; Priyanka and Thahira, 2013; Khan et al, 2015a; Sabarishri et al., 2015; Sakthieswaran and Ganesan, 2014c; Shoya et al., 1999, 2003; Singh et al., 2014; Srinivas and Muranal, 2015; Sudarvizhi and Ilangovan, 2011, 2012; Tamil et al., 2014; Tiwari and Bhattacharya, 2013; Ueno and Uji, 2009; Velumani and Nirmalkumar, 2014; Wu et al., 2010a,b).
- Consistence changes inconsistently with CS content (Anudeep et al., 2015; Bahadur and Nayak, 2012; Kumar and Mahesh, 2015).
- Consistence decreases as CS content is increased (Asotha and Mala, 2014; De Schepper et al., 2015; Lewowicki and Rajczyk, 1997; Resende et al., 2008).

Of the three possible effects shown, the first effect has been by far the most commonly observed and is most likely to be the outcome associated with the smooth surface texture of CS. It was noted that the second effect shows an inconsistent change in consistence with CS content, i.e., the consistence first increases/decreases with CS addition but it decreases/increases later at higher CS content, and the third effect (consistence decreasing with increasing CS content) has been observed in only a few studies. As such, behaviour cannot be explained in terms of material characteristics of CS; these results can only be ignored.

The workability improvement in CS concrete under the first effect mentioned has been categorised into two groups based on the consistence class of reference natural sand concrete in accordance with BS EN 206 (2013) and the effect is briefly illustrated in

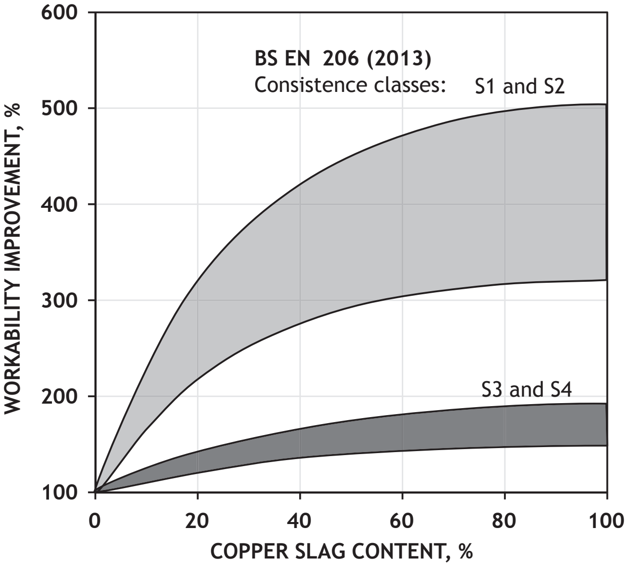

Figure 4.2 Influence of specified slump class on improvement of workability using copper slag sand for a given water/cement ratio.

Figure 4.2. As to be expected, low specified workability in the region of slump classes of S1 and S2 experiences a greater increase in consistence with the addition of CS as sand, whereas with specified consistence in the region of slump classes of S3 and S4, the increase in consistence is considerably less.

The observed improvement in workability of concrete with the use of CS offers an opportunity to design concrete mixes for a given workability with reduced water content. Indeed, some studies have reduced the water content of concrete when CS is used, to keep the slump of the resultant concrete similar to the corresponding reference concrete (Al-Jabri et al., 2009a; Arivalagan, 2013; Madheswaran et al., 2014; Pazhani and Jeyari, 2010). Dedicated work in an attempt to determine the potential water savings with the use of CS has been undertaken by Koh and Lye (2012) and a simple model thus developed by Lye et al. (2015) for use in practice is illustrated in Figure 4.3.

As with any other development of concrete mixes, the proposed model may be used as a guide in designing concrete mixes where it is intended to use CS as a natural sand replacement. For example, Lye et al. (2015) showed that concrete mixes made with 50% washed copper slag (WCS) of slump class S2 can be designed using the proposed model, and that furthermore this could be used for (1) developing higher concrete strength without having to increase the cement content or (2) reducing the cement content without compensating for concrete strength, as illustrated in Figure 4.4.

The cement savings in the latter effect can also lead to several benefits such as reduction in carbon dioxide emissions, reduction in production cost and improvement in durability of the concrete, due to its reduction in cement paste (Dhir and Hewlett, 2008).

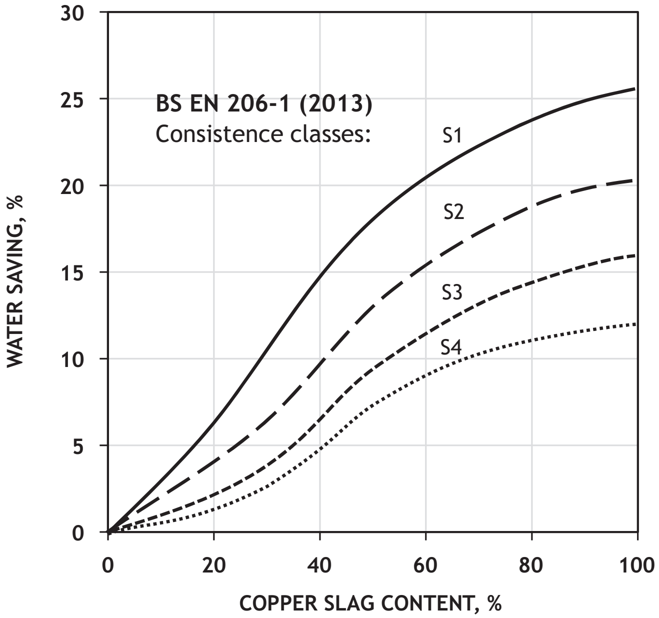

Figure 4.3 Potential water savings with the use of copper slag.
After Lye et al. (2015).

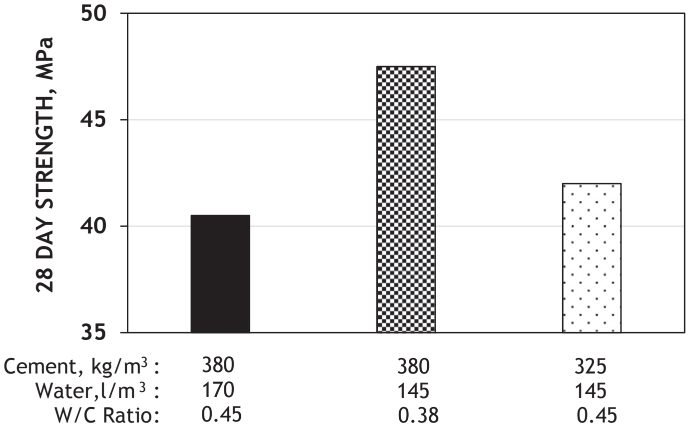

Figure 4.4 Concrete made with washed copper slag using the proposed model in Figure 4.3. *W/C*, water/cement ratio.

Additionally, the water savings potential of WCS can be used in conjunction with other recycled and secondary materials in concrete mixes, such as sewage sludge incinerated bottom ash and recycled concrete aggregate, to improve the strength of the resulting concrete mixes, without having to increase their cement content (see Figure 4.4), thereby facilitating the use of such materials in making concrete and at the same time enhancing the sustainability credentials of concrete construction.

In summary, incorporating CS as a component of natural sand in concrete mixes, provided it is properly used, should help to achieve improved workability, reduced use of admixture or reduced water content of a mix, which should result in an additional gain in strength for a given cement content. However, above all, the use of CS will also help to promote the use of other recycled materials and thereby enable the concrete construction industry to further embrace the global sustainability agenda.

4.3.2 Stability

As the specific gravity of CS is higher than that of natural sand, if not taken into account in designing a concrete mix, as with any other material, this may additionally affect the stability of the concrete mix. As the lack of stability is characterized by the mix becoming prone to bleeding and segregation, the performance of the concrete in the hardened state could also be adversely affected.

(i) Bleeding

Bleeding in concrete refers to the seepage of water to the surface of the concrete in the fresh state. Normal bleeding is desirable as it helps to prevent plastic shrinkage cracking of concrete, but excessive bleeding can create localised weak zones in concrete due to a high water/cement ratio.

The lack of an adequate proportion of fines content in the total aggregate content of a concrete tends to make the mix more prone to bleeding. Therefore, in comparing the bleeding of CS concrete with natural sand concrete, it is important to keep the aggregate grading, particularly the fines content, similar in both mixes. Additionally, the use of an air entrainment agent is known to reduce bleeding of concrete, thus its dosage should also be kept the same between the two mixes. Whilst the effect of CS on bleeding of concrete/mortar mixes has not been the subject of an exclusive study, Table 4.2 summarises the relevant data available where bleeding has been recorded.

The main points arising from Table 4.2 are:

- When the CS sand content is high, particularly at 100%, CS concrete tends to show more bleeding than the corresponding reference concrete (Al-Jabri, 2006; Bahadur and Nayak, 2012; Brindha and Nagan, 2010a; Ueno and Uji, 2009), even when the fineness moduli of the CS and natural sand are the same (Nataraja et al., 2014b; Ueno et al., 2005).
- As to be expected, replacing reference natural sand with coarser CS leads to higher bleeding (Kumar, 2012; Sudarvizhi and Ilangovan, 2011), whilst the opposite is reported when finer CS is used (Hwang and Laiw, 1989).

Table 4.2 Effect of copper slag on bleeding of concrete/mortar

References	Mix Design Parameters	Main Observation
Al-Jabri (2006)	CS, 0–100%; FM, not given; AE, not used; W/C, 0.50, 0.35	Concrete containing high CS showed more bleeding
Bahadur and Nayak (2012)	CS, 0–100%; FM, not given; AE, not used; W/C, 0.40, 0.46, 0.55	Concrete made with 100% CS showed more bleeding
Brindha and Nagan (2010a)	CS, 0–50%; FM, not given; AE, not used; W/C, 0.50	Concrete made with 50% CS showed more bleeding
Ghosh (2007)	CS, 0 and 50%; FM, not given; AE, not used; W/C, 0.47 (NS), 0.45 (CS)	No unusual bleeding was observed
Hwang and Laiw (1989)	CS, not given; FM, 3.01 (NS), 2.21 (CS); AE, not used; W/C, not given	CS reduced the bleeding rate of mortar
Kumar (2012)	CS, 0–100%; FM, 1.62 (NS), 3.87 (CS); AE, not used; W/C, 0.40	The bleeding rate and amount increased with CS
Sudarvizhi and Ilangovan (2011)	CS, 0–100%; FM, 2.27 (NS), 3.40 (CS); AE, not used; W/C, 0.50	Concrete made with 100% CS showed more bleeding
Nataraja et al. (2014b)	CS, 0–100%; FM, 3.14 (NS), 3.17 (CS); AE, not used; W/C, 0.80–1.70	Mortar made with 100% CS showed more bleeding
Shoya et al. (1997)	CS, 0 and 100%; FM, 2.75 (NS), 2.21–2.59 (CS); AE, 0.034% (NS), 0.017–0.030% (CS); W/C, 0.60	The bleeding amount of CS concrete was higher
Shoya et al. (1999) and Tokuhashi et al. (2001)	CS, 0, 50, 100%; FM, 2.57 (NS), 2.20 (CS); AE, 0.40% (NS), 0.20 and 0.45% (CS); W/C, 0.55	The bleeding rate of CS concrete was less than 0.003 mL/cm^2
Ueno and Uji (2009)	CS, 0–100%; FM, 3.24 (NS), 1.96–2.47 (CS); AE, not used; W/C, 0.60 (designed) but water content of CS mortar was adjusted for target slump	The bleeding amount of CS mortar was similar to the reference up to 50% CS, and 100% CS showed more bleeding
Ueno et al. (2005)	CS, 0 and 100%; FM, 2.60 (NS), 2.60 (CS); AE, not used; W/C, 0.45, 0.55, 0.65	The bleeding amount of CS mortar was higher than the reference mortar

AE, air entraining admixture; *CS*, copper slag; *FM*, fineness modulus (higher value indicates coarser sand); *NS*, natural sand; *W/C*, water/cement ratio.

- In one case, Shoya et al. (1997), although the CS used was finer than the natural sand, the bleeding of CS concrete was higher than that of the reference concrete. This was considered to be the outcome of the air entrainment dosage of CS concrete being less than that of the natural sand concrete to maintain the same slump.
- Ueno and Uji (2009) showed that the use of finer CS, with the water content reduced to maintain the target slump, resulted in bleeding similar to that of the reference mortar for up to 50% CS content, but CS mortar showed more bleeding at 100% CS content.
- The effects of CS on the bleeding of concrete with water/cement ratio varying from 0.35 to 0.65 have been studied by Al-Jabri (2006), Bahadur and Nayak (2012) and Ueno et al. (2005). Only the test results of Ueno et al. (2005) have been made available, showing that the use of CS as sand increases the bleeding of concrete (as shown by others) and that this effect increases with increasing water/cement ratio of the mix. This suggests that to avoid problems associated with bleeding, greater care would be required in designing a concrete mix when using CS sand.
- A more dedicated investigation on the effects of CS (together with other slags, namely, blast furnace slag, ferronickel slag and electric arc furnace oxidising slag) on bleeding of mortar undertaken by Ueno et al. (2005), in Japan, produced some specific observations of practical value, showing that the bleeding of a mortar mix is affected by: (i) the specific gravity of the replacement aggregate, and bleeding was found to increase with its specific gravity, and (ii) its maximum size, and in the case of CS replacing sand, it was found that up to 0.30 mm the aggregate size would not affect the bleeding of mortar.

Overall, the use of high CS content, particularly at 100%, is likely to make the concrete sensitive to bleeding. This effect may be controlled by revising the mix design in terms of limiting the CS content, increasing the fines fraction of the aggregate or reducing the water content, as the workability is improved with the use of CS.

(ii) Segregation

The separation of aggregate and cement paste causing non-uniform distribution of constituents in concrete is known as segregation. This is normally caused by a number of factors such as poor aggregate grading, large differences in the specific gravity of the constituent materials used in the mix and/or poor handling of concrete.

Although not a common problem, when due care is not taken, concrete can suffer from segregation and also show signs of excessive bleeding. Thus, it is not surprising that the concrete mixes tested with CS have been reported to suffer from such an effect in a few cases, particularly at high CS content (Al-Jabri, 2006; Bahadur and Nayak, 2012; Brindha and Nagan, 2010a). On the other hand, however, work undertaken by Ghosh (2007) monitoring the consistency performance in terms of consistence (workability) and strength of concrete made with 50% WCS over a period of 3 months reported that no unusual bleeding or segregation was observed.

A dedicated study on the segregation of concrete has been undertaken by JPL Industries (1997) in Singapore using WCS as sand, which was CS that had been previously used in blasting. The WCS content was kept at 15% as it was conceived at that time that the national specifications were unlikely to permit the use of more than this content of WCS in structural concrete. The two sets of mixes with and without WCS, with their sand content adjusted for the difference in the densities between the natural sand and the WCS, having a water/cement ratio of 0.5, were placed in a pipe of 200 mm diameter and 4 m height. The pipes were cut before the mixes were set into 20 equal-length sections in each pipe. The portions of concrete were washed thoroughly and the sieve analysis of the aggregates of each set of mixes showed essentially similar gradings, providing very clear proof that when the mixes are designed carefully, taking into account the densities and particle size distribution of their constituents, such mixes should not suffer from bleeding and segregation.

The results of JPL Industries (1997) confirm that properly designed concrete mixes with characteristics, such as shape, surface texture, particle size and distribution, density and water absorption, of the constituent materials taken into consideration, irrespective of the nature of the materials used, should not normally suffer from bleeding and segregation. In the case of CS, additional effects arising from its reduced water demand would also need to be taken into consideration in the design of concrete mixes.

4.3.3 Density

The specific gravity of CS is reported to be around 3.6 compared to natural sand being about 2.6 (Chapter 3). This is based on the data reported in various studies (Al-Jabri, 2006; Al-Jabri et al., 2009a,b, 2011; Anudeep et al., 2015; Cachim et al., 2009; Ghosh, 2007; Khrade et al., 2013; Mithun and Narasimhan, 2016; Mithun et al., 2015a,b; Resende et al., 2008, Tam, 2001; Tiwari and Bhattacharya, 2013; Wu et al., 2010a,b), and has been calculated to give rise to an increase in the density of concrete at the rate of 1% for every 10% addition of CS. This increase in density should be considered in the design of concrete structures.

4.3.4 Air Content

The presence of air has a dual effect on concrete. It is specified to prevent freeze–thaw attack on concrete, but it reduces its compressive strength as well. The air content of concrete is primarily affected by the characteristics of its constituent materials, admixtures if specified, and the handling of the fresh concrete. For a well-compacted non-air-entrained concrete made with 20-mm maximum size well-graded aggregate, the entrapped air can be expected to be less than 2.0% of the total volume of concrete.

Although the grading of CS used in the studies providing data on the air content of concrete mixes is different to the corresponding reference sand used for making concrete, the air content of non-air-entrained CS concrete mixes (1.2–2.2%) is on the same order as that of normal concrete (1.1–2.8%), and also the mean values of the two sets of concrete with mean air content of 1.93% and 2.03% for normal concrete and CS concrete mixes, respectively, were close to the typical value of 2.0% (De Schepper et al., 2015; JPL Industries, 1997; Shoya et al., 1997). How much air entraining admixture is required for a concrete to have a specified air entrainment can be an important factor in a large construction project, and the data available suggest that CS concrete requires a lower dosage of air entraining admixture to achieve a given level of air content (Ayano and Sakata, 2000). If this can be achieved under site conditions, this will certainly be a positive point in favour of specifying the use of CS.

In general, it should be safe to assume that the use of CS as a component of sand does not significantly affect the air content of non-air-entrained mixes, provided that the aggregate particle packing is unaffected.

4.3.5 Initial and Final Setting and Hardening

Although CS is unlikely to contain organic impurities that are known to delay setting times of cement, the initial and final setting times of mortar made with CS have generally been reported to increase (Ayano and Sakata, 2000; Dhir, 2009; Ghosh, 2007; Resende et al., 2008; Shoya et al., 1997).

The increase in setting times due to CS addition depends on its content, as the initial and final setting times of mortar containing up to 20% are found to be essentially similar to those of the reference mortar (JPL Industries, 1997), whilst the final setting time of mortar made with 100% CS was delayed for about a week (Ayano and Sakata, 2000). Indeed, a similar influence of CS content from 0% to 75% on setting times of mortar at constant 0.50 water/cement ratio has been reported by Resende et al. (2008). The results of this study are presented in Figure 4.5 and show that that both the initial and the final setting times of mortar increase at an increasing rate as CS content increases.

Another study on the effect of CS on setting times of concrete was undertaken by Ayano and Sakata (2000), using concrete with a water/cement ratio of 0.55 and water-reducing and air entraining admixtures, and having a slump of 80 mm and air content of 4.5%. Two different types of CS were used as sand for replacement of natural sand. Mortar was obtained by screening coarse aggregates of the mix for testing for setting times at a constant temperature of 20°C and relative humidity of 80%. The results suggest that the setting times were influenced by:

- source of CS used as sand;
- particle size and distribution of CS, as setting times increased with CS size deceasing from 0.6 to 0.15 mm;
- water-insoluble substances, which were removed during the washing of CS, but modified its effect on the setting times of concrete.

It would be important to establish the setting and hardening times of concrete made with CS, especially when high CS content is used together with a retarding admixture, as the delay in setting and hardening of concrete can affect the formwork striking time. However, arguably, the retardation effect of CS can be beneficial for concreting in hot weather countries, where fast setting and hardening of concrete have always been a concern.

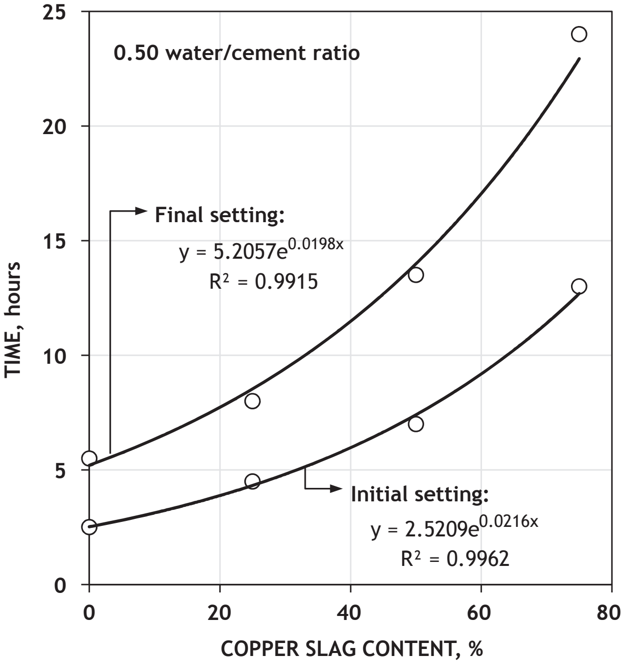

Figure 4.5 Influence of copper slag on the initial and final setting of mortar.

4.4 Strength

4.4.1 Compressive Strength

Compressive strength is one of the three most important properties of concrete that are commonly specified in the design and construction of concrete structures, the other two being its workability and durability. In practice, the compressive strength of concrete is commonly used as a benchmark to assess its quality because, with some exceptions, improvement in the compressive strength of concrete leads to improvement in its other properties.

In this section, the effects of the use of CS as sand replacement on compressive strength will be first discussed, followed by the influence of CS on the water/cement ratio and strength development of concrete. Last, mix design considerations will be addressed.

Effects of Copper Slag Content

The effects of CS replacing sand on the strength of concrete and mortar, with varying strength grade and replacement levels up to 100%, have been investigated in a large number of studies reported since 1989. Before going into detail, it is worth appreciating

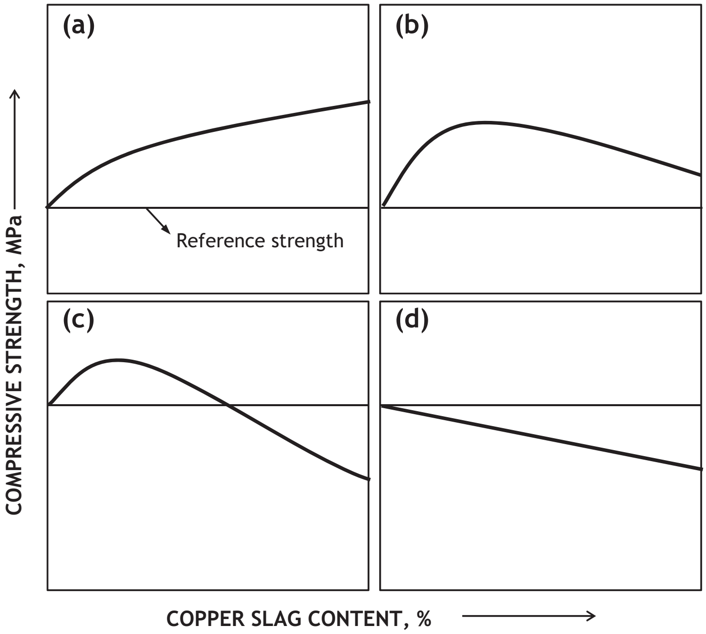

Figure 4.6 Overall impression of the effect of copper slag on the strength of concrete.

that the reported experimental strength data on such a wide scale and over a period of time can, to an extent, vary between studies. General trends observed are summarised in Figure 4.6 and are described below:

- The strength of concrete can increase with CS content, Figure 4.6(a);
- The strength of concrete can increase with CS content up to a varying optimum level and then decrease with increasing CS content, but the strength of CS concrete remains higher than that of normal concrete, Figure 4.6(b), or goes below the normal concrete level, Figure 4.6(c);
- The strength of concrete can decrease with CS content, Figure 4.6(d).

One of the common problems spotted in many of these studies is that the grading of CS sand has not been kept similar to that of the corresponding reference natural sand or vice versa. In such a scenario, the overall particle packing of the test specimen may change with CS content and this can become the main contributing factor that affects the strength of the resultant concrete. This possibly explains the variations in the trends observed in the strength development of concrete with increasing CS content of the sand used. Additionally, the test specimens that have previously been reported to have a stability issue in the fresh state (as discussed in Section 4.3.2) may suffer from poor compaction, and in such a scenario, the strength of concrete is likely to be affected by the inhomogeneity of the mix.

Indeed, this is likely to be the main contributor to the variable trends observed in the strength data provided in the literature, and this can clearly be seen from all the data presented Table 4.3 in two forms, namely the studies where, perhaps prudently, the two sets of mixes, CS mix and the corresponding reference mix without CS, were made to have the same consistence, and these results are presented in Table 4.3(a), and where the water/cement ratio was considered as the prime factor and kept constant, even if the consistence was to vary, and these results are presented in Table 4.3(b).

Although it would be expected that a reduction in water content at a given cement content for equal consistence would lead to strength improvement of the concrete mix, this has not always been realised [Table 4.3(a)]. Because of the limited data available in the literature for this option, no clear optimum level of CS can be identified in Table 4.3(a), but on average, the use of CS as a sand component gives a 5% increase in strength for CS concrete compared to normal concrete.

The number of strength data tabulated in Table 4.3(b) for CS concrete having a water/cement ratio equal to the reference concrete is significantly greater than that in Table 4.3(a) for CS concrete having consistence equal to the reference concrete. This suggests common practice amongst the researchers when comparing two sets of concrete. However, by adopting the equal consistence design basis, the advantage could have been gained by reducing the water/cement ratio, as in this case the consistence has been shown to improve with increasing CS content.

Except for three sets of results showing unduly high values [see footnote of Table 4.3(b)], all the data obtained over the period 1987–2015 given in Table 4.3(b) were used in developing Figure 4.7, with a box-and-whisker plot at each CS level created to visualise data distribution and determine outliers. Overall, a polynomial regression is obtained, giving a correlation of 0.8087. The obtained trendline suggests that the strength of concrete increases with increasing CS content, up to 20%, and reaches a near-plateau situation of average 13% strength increase for 20 to 50% CS, beyond which the strength begins to decrease, and from 80% CS, it falls below that of the corresponding reference concrete.

Under a constant water/cement ratio, with a given set of materials, and in the absence of particle size distribution data for the two sands, such a variable strength response with increasing CS content is most likely to be the outcome of varying particle packing, with the positive effect of CS as a sand material at a certain point (in this case up to 50/50 sand/CS content), being gradually eroded, and beyond a certain content (in this case 80% CS) it enters the negative field.

It is known that the hardened properties of concrete are affected by its fresh properties. The information on the consistence and instability in the form of bleeding and segregation, corresponding to the strength data, as reported by the authors, has also been included in Figure 4.7. This is helpful, as it supports the simple and empirical model used to explain the change in strength with increasing CS content.

Returning to Table 4.3, where all the data have been deliberately presented in some detail so that the reader can perform his or her own analysis and evaluation and develop the use of this information in designing concrete mixes using CS. Whilst it would have

Table 4.3 Analysis of compressive strength data presented in the literature by various studies

REF.	28 Day Compressive Cube Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100
(a) Equal Consistence											
[2]HSC [a]	88.1			87.1		101.3		104.4	101.6		107.4
[b]	0	-	-	-1	-	15	-	19	15	-	22
[11]NSC	30.2	-	32.8	-	35.1	-	21.3	-	20.4	-	20
	0	-	9	-	16	-	-29	-	-32	-	-34
[23]NSC	39.9	-	-	-	-	42.3	-	-	-	-	-
	0	-	-	-	-	6	-	-	-	-	-
[32]NSC	70	-	-	-	-	-	65	-	70	-	72
	0	-	-	-	-	-	-7	-	0	-	3
NSC	67	-	-	-	-	-	69	-	70	-	71.5
	0	-	-	-	-	-	3	-	5	-	7
Ave.[c], %	**0**	**-**	**9**	**-1**	**16**	**11**	**-11**	**19**	**-3**	**-**	**-2**
Individual Ave.[d], %		**5**									
(b) Equal Water/ Cement Ratio											
[1]NSC	44	44.9	48.5	48.9	48.1	53.1		46.6		50.1	45
	0	2	10	11	9	21		6		14	2
HSC	93.9	99.8	95.3		79.6	96.8	83		79		82
	0	6	1		-15	3	-12		-16		-13
[2]NSC	25.6	29.4	32.4	36	39.4	43.7	42.9	48.8	51.6	59.3	66.3
	0	15	27	41	54	71	68	91	102	132	159

REF.	28 Day Compressive Cube Strength [a], MPa										
	Relative Strength of CS Mix W.R.T Reference Mix[b], %										
	Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100
[3]HSC	93.9	99.8	95.3	-	95.2	96.8	83.0	-	83.6	-	82.0
	0	6	1	-	1	3	-12	-	-11	-	-13
[4]NSC	45	46	47		47.1	47	46		34.8		35.1
	0	2	4		5	4	2		-23		-22
[5]NSC	36.6	-	35.0	-	33.4	-	32.0	-	30.6	-	28.4
	0	-	-4	-	-9	-	-13	-	-16	-	-22
[6]NSC	34.4	-	-	-	33.9	-	-	-	31.3	-	-
	0	-	-	-	-1	-	-	-	-9	-	-
[7]NSC	21.8	-	-	37.6	-	-	-	-	-	-	25.4
	0	-	-	72	-	-	-	-	-	-	17
[8]HPC	138	-	-	-	-	-	-	-	-	-	117
	0	-	-	-	-	-	-	-	-	-	-15
HPC	148	-	-	-	-	-	-	-	-	-	126
	0	-	-	-	-	-	-	-	-	-	-15
[9]NSC	22.7	25.1	26.7	27.2	27.2	28.4	35.6	28.9	-	-	-
	0	11	18	20	20	25	57	27	-	-	-
[10]NSC	47.8	-	45.2	-	45.6	48.7	53.8	-	52	-	47.8
	0	-	-6	-	-5	2	12	-	9	-	0
[12]NSC	39	-	-	-	-	-	-	-	-	-	40
	0	-	-	-	-	-	-	-	-	-	3

REF.	28 Day Compressive Cube Strength, MPa											REF.	28 Day Compressive Cube Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %												Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %												Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100		0	10	20	30	40	50	60	70	80	90	100
[12]NSC [a]	39	-	-	-	-	-	-	-	-	-	30	[18] MO	54.6	-	43.6	-	-	41.7	-	39.9	-	-	-
[b]	0	-	-	-	-	-	-	-	-	-	-23		0	-	-20	-	-	-24	-	-27	-	-	-
[13]NSC	44	-	47	-	-	46	-	50	-	-	52	MO	23.6	-	22	-	-	42.4	-	40.4	-	-	-
	0	-	7	-	-	5	-	14	-	-	18		0	-	-7	-	-	80	-	71	-	-	-
NSC	35	-	41	-	-	43	-	40	-	-	41	[19]NSC	30.4	35.2	38.2	42.3	43	39.5	35.9	26.9	-	-	25.1
	0	-	17	-	-	23	-	14	-	-	17		0	16	26	39	41	30	18	-12	-	-	-17
NSC	25	-	27	-	-	29	-	31	-	-	30	[20]NSC	25.5	-	26	-	28.5	-	30	-	30.5	-	28.5
	0	-	8	-	-	16	-	24	-	-	20		0	-	2	-	12	-	18	-	20	-	12
[14]NSC	32.7	-	37.9	40.3	43.1	39.1	-	-	-	-	-	[21]NSC	61.5	-	63.4	-	66.9	-	65.3	-	62.7	-	58.2
	0	-	16	23	32	20	-	-	-	-	-		0	-	3.1	-	8.8	-	6.2	-	2	-	-5
[15]NSC	32.2	39.6	42.1	42.9	43.5	42.5	-	-	-	-	-	NSC	57	-	57.7	-	63.7	-	-	-	-	-	-
	0	23	31	33	35	-	-	-	-	-	-		0	-	1.2	-	12	-	-	-	-	-	-
[16]NSC	35.1	-	43.4	-	46.7	-	39.7	-	-	-	-	[22]NSC	32.9	-	-	43.6	45.3	48.2	-	-	-	-	-
	0	-	24	-	33	-	13	-	-	-	-		0	-	-	32	38	47	-	-	-	-	-
[17]NSC	35	-	43.5	-	46.5	-	39.5	-	-	-	-	[24]NSC	33.3	-	-	33.4	41.1	38.4	-	-	-	-	-
	0	-	24	-	33	-	13	-	-	-	-		0	-	-	0	24	15	-	-	-	-	-
[18]NSC	38.5	-	-	-	-	-	-	-	-	-	38	[25]MO	47	-	46	-	47	-	48	-	46	-	38
	0	-	-	-	-	-	-	-	-	-	-1		0	-	-2	-	0	-	2	-	-2	-	-19
MO	56.5	-	50.3	-	-	46.9	-	44.4	-	-	-	MO	26	-	27	-	29	-	26	-	24	-	22
	0	-	-11	-	-	-17	-	-21	-	-	-		0	-	-3	-	8	-	3	-	-3	-	-25

Continued

Table 4.3 Continued

REF.	28 Day Compressive Cube Strength, MPa											REF.	28 Day Compressive Cube Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %												Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %												Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100		0	10	20	30	40	50	60	70	80	90	100
[25]MO [a]	26	-	27	-	29	-	26	-	24	-	22	[32]NSC	86	-	-	-	86	-	-	-	-	-	-
[b]	0	-	4	-	12	-	0	-	-8	-	-15		0	-	-	-	0	-	-	-	-	-	-
NSC	52	-	45	-	35	-	45	-	38	-	32	NSC	77.5	-	-	-	84	-	-	-	-	-	-
	0	-	-13	-	-33	-	-13	-	-27	-	-38		0	-	-	-	8	-	-	-	-	-	-
NSC	40	-	40	-	38	-	40	-	35	-	28	NSC	75	-	-	-	79.5	-	-	-	-	-	-
	0	-	0	-	-5	-	0	-	-13	-	-30		0	-	-	-	6	-	-	-	-	-	-
NSC	32	-	33	-	28	-	30	-	28	-	24	NSC	70	-	72	-	75	-	-	-	-	-	-
	0	-	3	-	-13	-	-6	-	-13	-	-25		0	-	3	-	7	-	-	-	-	-	-
[26]NSC	35.3	-	-	-	38.7	-	-	-	-	-	-	NSC	67	-	66	-	72	-	-	-	-	-	-
	0	-	-	-	10	-	-	-	-	-	-		0	-	-1	-	7	-	-	-	-	-	-
[27]NSC	31.4	-	39.3	-	44.5	-	38.4	-	36.4	-	31.4	NSC	59.5	-	-	-	64	-	-	-	-	-	-
	0	-	25	-	42	-	22	-	16	-	0		0	-	-	-	8	-	-	-	-	-	-
[28]NSC	25.2	-	-	43.5	47.8	40.2	-	-	-	-	-	NSC	53	-	-	-	59	-	-	-	-	-	-
	0	-	-	73	90	60	-	-	-	-	-		0	-	-	-	11	-	-	-	-	-	-
[29]NSC	25	25.2	30	30.2	34	30	-	-	-	-	-	NSC	42	-	-	-	44	-	-	-	-	-	-
	0	1	20	21	36	20	-	-	-	-	-		0	-	-	-	5	-	-	-	-	-	-
[30]NSC	33	-	28.8	-	-	30.7	-	51.8	-	-	-	[33]NSC	54.5	-	56	-	56	-	54	-	56	-	54
	0	-	-13	-	-	-7	-	57	-	-	-		0	-	2.8	-	2.8	-	-1	-	2.8	-	-0.9
[31]NSC	38.3	41	48.1	40.8	44.4	44.9	45.2	-	38.4	-	35.7	NSC	16.1	-	19.7	-	19.1	-	23.8	-	22.1	-	-
	0	7.1	26	6.7	16	17	18	-	0	-	-7		0	-	22	-	19	-	48	-	37	-	-

REF.	28 Day Compressive Cube Strength, MPa											REF.	28 Day Compressive Cube Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %												Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %												Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100		0	10	20	30	40	50	60	70	80	90	100
[34]NSC [a]	31.4	32.5	33.4	34.4	32	-	-	-	-	-	-	[40]NSC	28.6	30.6	32.4	33.6	37.3	34.4	32.3	-	30.5	-	29.9
[b]	0	4	7	9	2	-	-	-	-	-	-		0	7	13	17	30	20	13	-	7	-	5
[35]NSC	31.8	38.4	43.6	45.4	44.1	-	-	-	-	-	-	[41]NSC	53.6	-	-	-	-	-	-	-	-	-	57
	0	21	37	43	39	-	-	-	-	-	-		0	-	-	-	-	-	-	-	-	-	6
[36]MO	35	-	-	-	-	-	-	-	-	-	27	[42]NSC	62.1	-	60.8	-	-	61.7	-	64.4	-	-	63
	0	-	-	-	-	-	-	-	-	-	-23		0	-	-2	-	-	-1	-	4	-	-	1
MO	33	-	-	-	-	-	-	-	-	-	33	[43]NSC	62.1	-	61.4	-	-	57.5	-	53	-	-	48.8
	0	-	-	-	-	-	-	-	-	-	0		0	-	-1	-	-	-7	-	-15	-	-	-21
[37]GC	58.6	61.8	64.7	66.7	70.1	71.2	-	-	-	-	-	NSC	61.8	-	63.8	-	-	63.7	-	61.4	-	-	64
	0	5	10	14	20	22	-	-	-	-	-		0	-	3	-	-	3	-	-1	-	-	4
GC	28.2	30.6	31.5	33.7	35.6	38.9	-	-	-	-	-	[44]NSC	29.3	29.9	32.1	37.6	39.5	33	28.7	-	-	-	-
	0	8	12	19	26	38	-	-	-	-	-		0	2	10	28	35	13	-2	-	-	-	-
[38]NSC	36.8	37.6	39.1	40.6	41	39.2	-	-	-	-	-	[45]NSC	40.1	-	-	-	-	-	-	-	-	-	41.6
	0	2	6	10	11	7	-	-	-	-	-		0	-	-	-	-	-	-	-	-	-	4
	41.1	43.2	45.6	46.9	47.4	45.8	-	-	-	-	-	NSC	40.1	-	-	-	-	-	-	-	-	-	44.1
	0	5	11	14	15	11	-	-	-	-	-		0	-	-	-	-	-	-	-	-	-	10
[39]NSC	35	-	41	-	-	43	-	40	-	-	41	[46]MO	26.1	-	-	-	-	-	-	-	-	-	29.6
	0	-	17	-	-	23	-	14	-	-	17		0	-	-	-	-	-	-	-	-	-	14
NSC	22	-	27	-	-	29	-	31	-	-	30	MO	20.9	-	-	-	-	-	-	-	-	-	18.8
	0	-	23	-	-	32	-	41	-	-	36		0	-	-	-	-	-	-	-	-	-	-10

Continued

Table 4.3 Continued

REF.	28 Day Compressive Cube Strength, MPa											REF.	28 Day Compressive Cube Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %												Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %												Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100		0	10	20	30	40	50	60	70	80	90	100
[46]MO [a]	12.9	-	-	-	-	-	-	-	-	-	10.5	[55]NSC	35.5	42.2	44.6	46.5	48.8	46.2	-	-	-	-	-
[b]	0	-	-	-	-	-	-	-	-	-	-19		0	19	26	31	37	30	-	-	-	-	-
[47]MO	32.7	-	-	-	-	-	-	-	-	-	47.1	[56]HPC	31	36	43.8	45.3	28.7	26	32	31	-	-	-
	0	-	-	-	-	-	-	-	-	-	44		0	16	41	46	-7	-16	3	0	-	-	-
[48]NSC	36.1	39.1	47.3	39.2	37	38.5	42.9		34.9		31	[57]HPC	59	-	-	-	63	67	66	-	-	-	-
	0	8	31	9	2	7	19		-3		-14		0	-	-	-	7	14	12	-	-	-	-
[49]NSC	36.8	-	-	-	41.1	-	-	-	-	-	-	HPC	63	-	-	-	65	70	67	-	-	-	-
	0	-	-	-	12	-	-	-	-	-	-		0	-	-	-	3	11	6	-	-	-	-
NSC	41.1	-	-	-	47.4	-	-	-	-	-	-	HPC	67	-	-	-	70	72	72	-	-	-	-
	0	-	-	-	15	-	-	-	-	-	-		0	-	-	-	4	7	7	-	-	-	-
[50]NSC	40.6	-	45.9	-	50	-	51.7	-	56.3	-	63.9	HPC	67	-	-	-	70	72	72	-	-	-	-
	0	-	13	-	23	-	27	-	39	-	57		0	-	-	-	4	7	7	-	-	-	-
[51]NSC	40	41	-	-	-	-	-	-	-	-	-	[58]MO	54	-	50	-	-	44	-	48	-	-	-
	0	3	-	-	-	-	-	-	-	-	-		0	-	-7	-	-	-19	-	-11	-	-	-
[52]NSC	33.9	42.1	45.2	-	-	-	-	-	-	-	-	[59]MO	26		28		34	33	32		27		26
	0	24	33	-	-	-	-	-	-	-	-		0		8		31	27	23		4		0
[53]NSC	36	35.2	34.7	34.2	32.5	30	-	-	-	-	-	NSC	41		42		44	43	36		35		34
	0	-2	-4	-5	-10	-17	-	-	-	-	-		0		2		7	5	-12		-15		-17
[54]NSC	22.5		27.4	29	30	29.3	-	-	-	-	-	[60]HPC	56	-	-	-	64	-	-	-	-	-	-
	0		22	29	33	30	-	-	-	-	-		0	-	-	-	14	-	-	-	-	-	-

REF.	28 Day Compressive Cube Strength, MPa											REF.	28 Day Compressive Cube Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %												Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %												Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100		0	10	20	30	40	50	60	70	80	90	100
[61]HPC [a]	50	-	-	50.5	56.3	45.1	-	-	-	-	-	[73]NSC	39.7	41.8	43.7	46.7	48.1	43	-	-	-	-	-
[b]	0	-	-	1	13	-10	-	-	-	-	-		0	5	10	18	21	8	-	-	-	-	-
[62-65]	54.4	-	-	48.9	52.5	53.7	-	-	-	-	-	[74]NSC	23.6	30.2	-	33.3	-	-	-	-	-	-	-
NSC	0	-	-	-10	-3	-1	-	-	-	-	-		0	28	-	41	-	-	-	-	-	-	-
[66]NSC	32.6	36.2	38.6	41.5	46.9	44.2						[75]NSC	21	-	-	-	35.9	38.1	30.7	-	-	-	-
	0	11	19	27	44	36							0	-	-	-	71	81	46	-	-	-	-
[67]NSC	37.9	-	-	-	-	-	-	-	-	-	35.2	[76]NSC	-	-	-	-	-	-	-	-	-	-	-
	0	-	-	-	-	-	-	-	-	-	-7		0	-	-	0	-	-	-	-	-	-	-
NSC	31	-	-	-	-	-	-	-	-	-	31.1	[77]NSC	38.8	-	40.7	-	44	-	34.4	-	31.4	-	27.7
	0	-	-	-	-	-	-	-	-	-	0		0	-	5	-	13	-	-11	-	-19	-	-29
[68]SCC	41.2	-	-	-	-	42.1	-	-	-	-	43.8	[78]NSC	36.3	40.1	43.2	44.9	48	40.3	-	-	-	-	-
	0	-	-	-	-	2	-	-	-	-	6		0	10	19	24	32	11	-	-	-	-	-
[69]SCC	42.3	-	-	-	-	44.4	-	-	-	-	44.1	[79]NSC	38.3	-	40.4	-	-	43.3	-	-	-	-	45.5
	0	-	-	-	-	5	-	-	-	-	4		0	-	6	-	-	13	-	-	-	-	19
[70]NSC	38	-	42	-	37	-	34	-	32	-	31	[80]NSC	42.3	-	-	-	-	-	-	-	-	-	44.1
	0	-	11	-	-3	-	-11	-	-16	-	-18		0	-	-	-	-	-	-	-	-	-	4
[71, 72]	25.2	38.6	39.9	40.1	43.2	45.3	-	-	-	-	-	[81,82]	29.6	32.5	27.4	-	-	-	-	-	-	-	-
NSC	0	53	58	59	71	80	-	-	-	-	-	NSC	0	10	-7	-	-	-	-	-	-	-	-
[73]NSC	34.4	36.7	38.7	40.4	41.7	37.8	-	-	-	-	-	NSC	35.1	37.5	32.2	-	-	-	-	-	-	-	-
	0	7	13	18	21	10	-	-	-	-	-		0	7	-8	-	-	-	-	-	-	-	-

Continued

Table 4.3 Continued

REF.	28 Day Compressive Cube Strength, MPa											REF.	28 Day Compressive Cube Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %												Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %												Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100		0	10	20	30	40	50	60	70	80	90	100
[83]NSC [a]	40	40	52	58	62	62	57	-	48	-	22												
[b]	0	0	30	45	55	55	43	-	20	-	-45												
[84]NSC	33.9	34.4	35.4	37.2	38.1	37.5	-	-	-	-	-												
	0	2	5	10	13	11	-	-	-	-	-												
[85]HSC	99	-	98	-	96	-	88	-	70	-	64												
	0	-	-1	-	−3	-	−11	-	−29	-	−35												
Ave. [c]*,%	**0**	**9**	**9**	**23**	**15**	**15**	**9**	**11**	**-3**	**14**	**-4**												
Individual Ave [d], %		**10**																					
Overall Ave [e], %		**9**																					

Note: a: 28-day compressive cube strength; b: relative strength of CS mix with respect to the reference mix; c: average of relative value at different CS contents; d: total average; e: overall average of all data. *GC*, geopolymer concrete; *HPC*, high-performance concrete; *HSC*, high-strength concrete; *MO*, mortar; *NSC*, normal-strength concrete; *W.R.T*, with respect to.

Reference: [1] Al-Jabri (2006), [2] Al-Jabri et al., 2009a; [3] Al-Jabri et al., 2009b; [4] Al-Jabri et al., 2011; [5] Alnuaimi, 2009; [6] Alnuaimi, 2012; [7] Amarnaath et al., 2015; [8] Ambily et al., 2015; [9] Anjana et al., 2015; [10] Anudeep et al., 2015; [11] Arivalagan, 2013; [12] Ayano and Sakata, 2000; [13] Bahadur and Nayak, 2012; [14] Brindha and Nagan, 2010a; [15] Brindha and Nagan, 2010b; [16] Brindha and Nagan, 2011; [17] Brindha et al., 2010; [18] Cachim et al., 2009; [19] Chavan and Kulkarni, 2013; [20] Cheong et al., 2007; [21] De Schepper et al., 2015; [22] Dharani et al., 2015; [23] Ghosh, 2007; [24] Gowda and Balakrishna, 2014; [25] Hwang and Laiw, 1989; [26] Illayaraja et al., 2014; [27] Jaivignesh and Gandhimathi, 2015; [28] Jebitta and Sofia, 2015; [29] Karthick et al., 2014; [30] Kayathri et al., 2014; [31] Kharade et al., 2013; [32] Koh and Lye, 2012; [33] Kumar, 2012; [34] Kumar and Mahesh, 2015; [35] Leema and Suganya, 2015; [36] Madany et al., 1991; [37] Madheswaran et al., 2014; [38] Madhu and Venkataratnam, 2015; [39] Mahendran and Arunachelam, 2015; [40] Mahmood and Hashmi, 2014; [41] Merinkline et al., 2013; [42] Mithun and Narasimhan, 2016; [43] Mithun et al., 2015a; [44] Naganur and Chethan, 2014; [45] Nataraja et al., 2014a; [46] Nataraja et al., 2014b; [47] Nazer et al., 2012; [48] Patil, 2015; [49] Patnaik et al., 2015; [50] Pazhani, 2010; [51] Ping, 2011; [52] Poozvizhi and Kathirvel, 2015; [53] Pradeep and Rama, 2014; [54] Prakash and Brindha, 2012; [55] Saxena, 2015b; [56] Priyanka and Thahira, 2013; [57] Rajkumar et al., 2015; [58] Resende et al., 2008; [59] Khan et al., 2015a; [60] Khan et al., 2015b; [61] Sabarishri et al., 2015; [62] Sakthieswaran and Ganesan, 2013; [63] Sakthieswaran and Ganesan, 2014a; [64] Sakthieswaran and Ganesan, 2014b; [65] Saraswathy et al., 2014; [66] Saxena, 2015a; [67] Shoya et al., 1997; [68] Shoya et al., 1999; [69] Shoya et al., 2003; [70] Srinivas and Muranal, 2015; [71] Sudarvizhi and Ilangovan, 2011; [72] Sudarvizhi and Ilangovan, 2012; [73] Suresh and Kishore, 2013; [74] Suresh and Ravikumar, 2015; [75] Sushma et al., 2015; [76] Tam, 2001; [77] Tamil et al., 2014; [78] Thomas et al., 2012; [79] Tiwari and Bhattacharya, 2013; [80] Tokuhashi et al., 2001; [81] Vamsi and Kishore, 2013; [82] Vamsi t al, 2013; [83] Velumani and Nirmalkumar, 2014; [84] Vimarsh et al., 2014; [85] Wu et al., 2010a.

Note *: The average data excluded the results of Al-Jabri et al. (2009a) because of a possible compaction problem in concrete due to low slump and Sudarvizhi and Ilangovan (2011, 2012) for using copper slag in conjunction with ferrous slag.

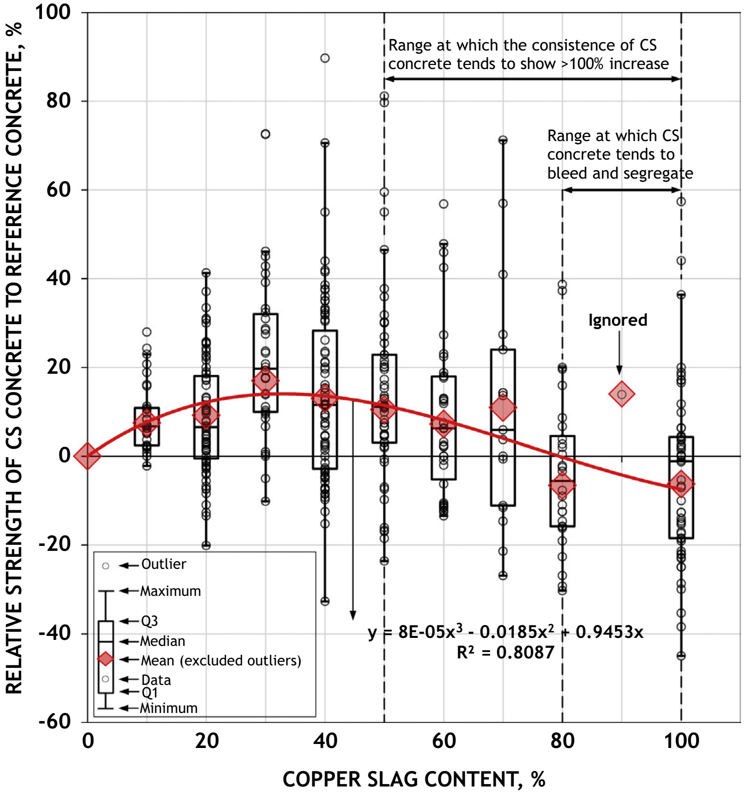

Figure 4.7 Effect of copper slag (CS) on the strength of concrete keeping the water/cement ratio of copper slag concrete similar to that of the corresponding reference concrete [data taken from Table 4.3(b)].

been ideal to develop general rules for the use of CS as sand for practical purposes, to be realistic, it is unlikely that this is possible. However, on the whole, the results do support the viewpoint that concrete designed with CS as sand should develop 5–10% higher strength than the corresponding natural sand concrete. Furthermore, for a given consistence, taking advantage of improved consistence resulting from the use of CS, the material can even be used to develop high-strength concrete and possibly high-performance concrete as well.

Water/Cement Ratio and Strength Relationship

Although important, only limited detailed information is available on the development of strength with water/cement ratio of concrete incorporating CS as a component of sand (Bahadur and Nayak, 2012; Hwang and Laiw, 1989; Koh and Lye, 2012; Nataraja et al., 2014b), except for Koh and Lye (2012), who measured the strength development of concrete made with 0–100% WCS used in increments of 20% with water cement/

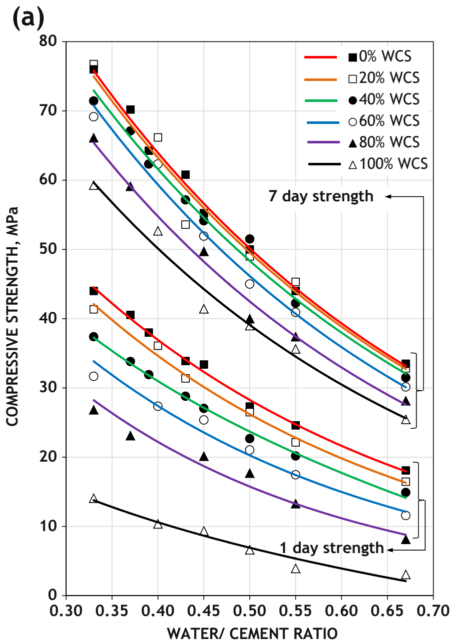

Figure 4.8 (a) Effect of washed copper slag (WCS) on water/cement ratio for 1- and 7-day strength:
After Koh and Lye, 2012.

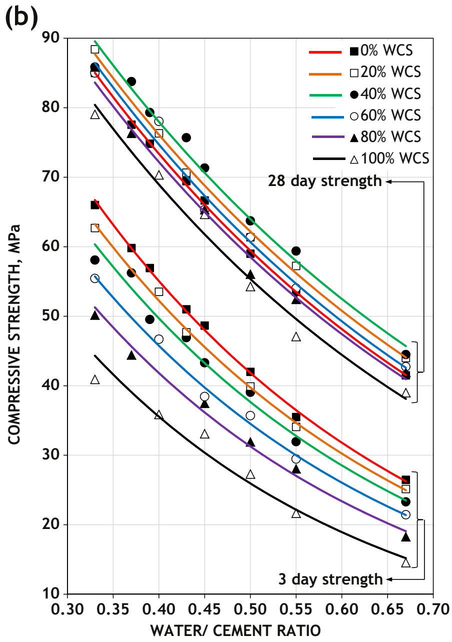

Figure 4.8 (b) Effect of WCS on water/cement ratio for 3- and 28-day strength
After Koh and Lye, 2012.

ratio varied in eight steps ranging from 0.33 to 0.67. The concrete mixes were tested at the ages of 1, 3, 7 and 28 days and their results have been plotted in Figure 4.8(a) for 1 and 7 days and Figure 4.8(b) for 3 and 28 days.

The often-mentioned early age retardation effect due to the use of CS, or WCS as in this case, comes through well from 1-day strength results [Figure 4.8(a)], particularly for the 100% WCS level, but such an effect subsides with time and it is not noticeable at the age of 28 days [Figure 4.8(b)].

The fact that a normal water/cement ratio and strength relationship for WCS/CS concrete is observed at all ages [Figures 4.8(a) and (b)] means that normal mix design procedures can be adopted in practice when planning to use CS/WCS, without requiring any additional step in the mix design procedure. In fact, the development of this water/cement ratio and strength relationship for the CS concrete mixes can help the engineer to decide on a suitable water/cement ratio and CS content, which can be used in concrete for a given strength. For example, to achieve 50-MPa strength at 28 days [Figure 4.8(b)] suggests that the required water/cement ratio of concrete made with 0%, 20%, 40%, 60%, 80% and 100% is 0.58, 0.60, 0.62, 0.59, 0.57 and 0.54, respectively.

Though there is a degree of variability, in general terms, these results show the influence that CS can have on the strength development of concrete mixes using CS at a constant water/cement ratio similar to the empirical model in Figure 4.7.

Given that the water demand of CS for a given consistence can generally be reduced, it is feasible, together with the use of a water-reducing admixture, to produce concrete mixes having considerably higher strength than the reference mix without having to increase the cement content. This is illustrated in Figure 4.9 and clearly shows the advantage that can be taken from the lower water demand of CS, which can be furthered using a superplasticising admixture. Additionally, no ceiling strength has been detected for CS/WCS concrete at low water/cement ratio (Figure 4.8), indicating that this material is potentially suitable for making sustainable high-strength concrete.

Strength Development with Age

Several investigators have studied the development of strength of CS concrete with age (Ambily et al., 2015; Cachim et al., 2009; Cheong et al., 2007; De Schepper et al., 2015; Dharani et al., 2015; Hwang and Laiw, 1989; Hosokawa et al., 2004; Madany et al., 1991; Madhu and Venkataratnam, 2015; Mithun and Narasimhan, 2016; Naganur and Chethan, 2014; Nazer et al., 2012, 2013; Patil, 2015; Pazhani, 2010; Poozvizhi and Kathirvel, 2015; Khan et al., 2015a,b; Sabarishri et al., 2015; Saxena, 2015a,b; Sudarvizhi and Ilangovan, 2011; Tiwari and Bhattacharya et al., 2013; Velumani and Nirmalkumar, 2014; Wu et al., 2010a), but only one study (Hwang and Laiw, 1989) tested concrete made with 0–100% CS up to 1 year. Interestingly, the results of this study, where the type of CS used was different to that used by Koh and Lye (2012) (Figure 4.8), show considerable reduction in strength compared to normal concrete (Figure 4.10).

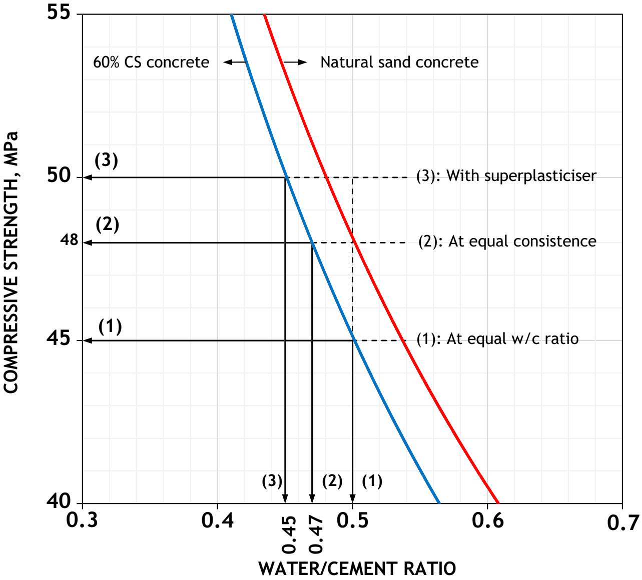

Figure 4.9 Designing concrete made with copper slag (CS). *w/c*, water/cement ratio.

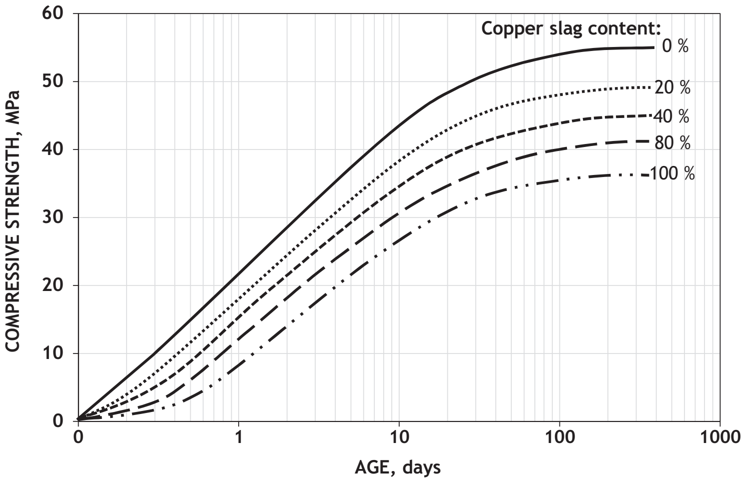

Figure 4.10 Influence of copper slag on strength development with age.
Based on Hwang and Laiw (1989).

It can be seen that other than the depicted early age retardation effect of CS, which increases with increasing CS content, the use of CS does not appear to affect the strength development with time. However, the results make the point that when the early strength requirement is crucial, such as in precast concrete manufacturing, the strength development for a particular CS concrete mix should be first established to determine the appropriate formwork striking time.

Designing Concrete with Copper Slag as Sand

The design process of concrete using CS as sand can be the same as for normal concrete. However, the density of CS should be taken into account, as this can be close to 35% higher than that of natural sand, and can make a difference in the water demand of the mix as well as its workability and stability.

It is also clear from the data presented previously that, depending on the natural sand replacement level, there can be a significant improvement in the consistence of concrete and potentially the strength. These advantages can be taken, leading to a reduction in the water content of concrete, which in turn, for a given consistence, should result in higher strength due to the resulting reduction of water/cement ratio of the mix.

The use of CS tends to prolong the setting times and thereby delay the early age hardening of concrete; this leads to an undesirable effect of strength retardation of concrete at high CS content. Indeed, this can affect concreting work in the construction industry. Certainly, in such cases, the dosage of admixtures such as retarder or superplasticiser with a retarding effect needs to be revised, and to some extent, this shortfall will contribute to a cost savings.

Furthermore, a model developed based on a laboratory trial by Lye et al. (2015) suggests that the strength of CS concrete can be designed to match that of natural concrete at different ages, as early as 1-day strength, and in return, result in higher strength gain than by the natural concrete (Figure 4.11). This has been achieved by reducing the water content for a given cement content, thereby reducing the water/cement ratio as

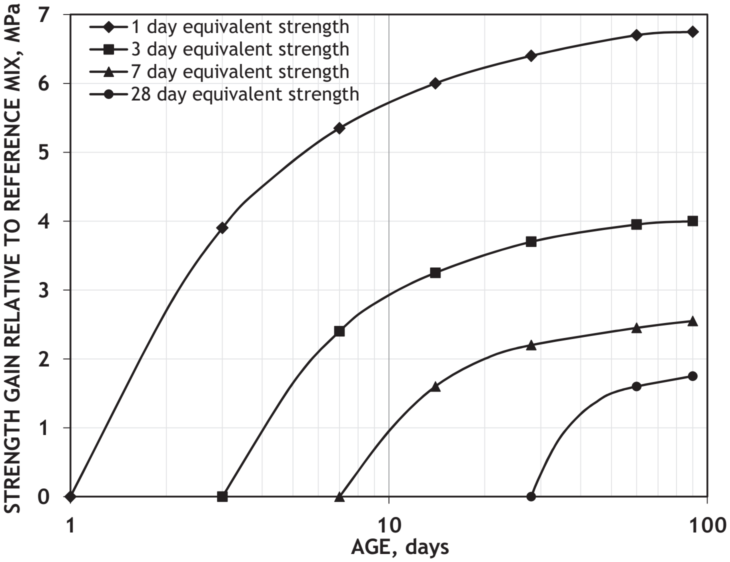

Figure 4.11 Strength gain of equivalent strength at different ages.
After Lye et al. (2015).

explained previously. Depending on the design requirement, Figure 4.11 shows that the magnitude of strength gain decreases with increasing strength matching age. This allows design engineers to estimate the ultimate strength of CS concrete.

Where CS is used as sand for the first time, it is recommended to start with a small amount of natural sand replacement, and thereafter, the replacement level can be increased as experience and confidence in using CS are gained. The use of CS as a natural sand replacement shall not be restricted to a certain level, and rather concrete mixes shall be properly designed based on the specification requirements for concrete, which can help to maximize the performance of CS in concrete.

4.4.2 Tensile Strength

Although in comparison to its strength in compression, concrete is weak in tension and is generally not considered in reinforced concrete structural elements, its tensile strength assumes importance in the design of concrete road pavements and runways at airports, as well as in the resisting of load-independent strains that may develop with time in concrete, such as shrinkage movements and thermal expansion and contraction changes. The standards universally make provision for calculating the tensile strength of concrete, as for example in Table 3.1 of Eurocode 2 (BS EN 1992, 2004), which deals with concrete of up to 105 MPa characteristic cube strength.

In testing concrete for tensile strength generally, two indirect methods are universally adopted, namely splitting cylinder tensile and flexural strength tests. Between the two, splitting cylinder tensile strength, because of its consistent performance, is more generally used, whilst the flexural strength test is more closely linked with the concrete pavement design.

Splitting Cylinder Tensile Strength

Although there can be some exceptions, unlike compressive strength, tensile strength is commonly tested for 28-day strength because it is seldom used to measure the maturity of concrete with time. Table 4.4 has been created to list separately the results as groups of equal (1) consistence and (2) water/cement ratio. All experimental results found published in the literature since 1997, in the individual mix form for CS content ranging from 0% to 100%, have been rounded off in steps of 10. In addition to the actual results, CS concrete results have also been expressed as a relative percentage of the corresponding reference mix with zero CS content. The corresponding compressive strength data of the same mixes are also provided for comparison purposes.

To obtain an overall impression of the CS effect on tensile strength, which is perhaps by far the best approach to handle such information, the data have been plotted in Figure 4.12, together with the plot for the corresponding compressive strength. Interestingly, but not unexpectedly, the inclusion of CS as a component of sand affects similarly both the tensile and the compressive strengths, showing how this effect varies with increasing CS content. The reasons for this are similar to those stated previously in

Table 4.4 Analysis of splitting tensile strength and its corresponding compressive strength of copper slag mixes

REF.	28 Day Compressive Cube Strength, MPa											28 Day Splitting Tensile Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
(a) Equal Consistence																						
[2]HSC [a]	88.1	-	-	87.1	-	101.3	-	104.4	101.6	-	107.4	4.7	-	-	5.2	-	5.5	-	5.3	5.5	-	5.6
[b]	0	-	-	-1	-	15	-	19	15	-	22	0	-	-	11	-	17	-	13	17	-	19
[8]NSC	30.2	-	32.8	-	35.1	-	21.3	-	20.4	-	20	1.6	-	2.2	-	2.9	-	2.5	-	2	-	1.6
	0	-	9	-	16	-	-29	-	-32	-	-34	0	-	45	-	85	-	58	-	29	-	3
Ave. [c], %	**0**	**-**	**9**	**-1**	**16**	**15**	**-29**	**19**	**-9**	**-**	**-6**	0	-	45	11	85	17	58	13	23	-	11
Individual Ave. [d], %	**2**											24										
(b) Equal Water/Cement Ratio																						
[1]NSC	44	44.9	48.5	48.9	48.1	53.1	-	46.6	-	50.1	45	3.0	3.5	3.7	3.2	3.8	4.1	-	3.6	-	3.6	3.4
	0	2	10	11	9	21	-	6	-	14	2	0	17	23	7	27	37	-	20	-	20	13
HSC	93.9	99.8	95.3	-	79.6	96.8	83	-	79	-	82	5.4	5.2	6.2	-	4.6	6.1	4.8	-	4.7	-	4.4
	0	6	1	-	-15	3	-12	-	-16	-	-13	0	-4	15	-	-15	13	-11	-	-13	-	-19
[2]NSC	25.6	29.4	32.4	36	39.4	43.7	42.9	48.8	51.6	59.3	66.3	2.6	2.9	3.1	2.9	3.3	3.5	3.7	3.3	3.8	3.9	4.1
	0	15	27	41	54	71	68	91	102	132	159	0	12	19	12	27	35	42	27	46	50	58
[3]HSC	93.9	99.8	95.3	-	95.2	96.8	83.0	-	83.6	-	82.0	5.4	5.2	6.2	-	6.1	6.1	4.8	-	4.7	-	4.4
	0	6	1	-	1	3	-12	-	-11	-	-13	0	-4	15	-	13	13	-11	-	-13	-	-19
[4]NSC	45	46	47	-	47.1	47	46	-	34.8	-	35.1	3.0	3.5	3.7	-	3.8	4.1	3.6	-	3.6	-	3.4
	0	2	4	-	5	4	2	-	-23	-	-22	0	17	23	-	27	37	20	-	20	-	13
[5]NSC	36.6	-	35.0	-	33.4	-	32.0	-	30.6	-	28.4	2.9	-	3.1	-	2.7	-	2.9	-	2.7	-	2.7
	0	-	-4	-	-9	-	-13	-	-16	-	-22	0	-	5	-	-9	-	-2	-	-7	-	-7

Continued

Table 4.4 Continued

REF.	28 Day Compressive Cube Strength, MPa											28 Day Splitting Tensile Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[6]NSC [a]	34.4	-	-	-	33.9	-	-	-	31.3	-	-	3.2	-	-	-	2.9	-	-	-	2.7	-	-
[b]	0	-	-	-	-1	-	-	-	-9	-	-	0	-	-	-	-9	-	-	-	-16	-	-
[7]NSC	47.8	-	45.2	-	45.6	48.7	53.8	-	52.0	-	47.8	3.2	-	2.9	-	3.5	3.5	3.8	-	3.8	-	3.7
	0	-	-6	-	-5	2	12	-	8.7	-	0	0	-	-10	-	8	10	20	-	18	-	14
[9]NSC	32.7	-	37.9	40.3	43.1	39.1	-	-	-	-	-	3.1	-	5.1	5.4	5.9	4.5	-	-	-	-	-
	0	-	16	23	32	20	-	-	-	-	-	0	-	66	75	92	46	-	-	-	-	-
[10]NSC	32.2	39.6	42.1	42.9	43.5	42.5	-	-	-	-	-	3.1	4.7	5.1	5.4	5.9	4.5	-	-	-	-	-
	0	23	31	33	35	32	-	-	-	-	-	0	54	66	75	92	46	-	-	-	-	-
[11]NSC	35.1	-	43.4	-	46.7	-	39.7	-	-	-	-	3.4	-	4.0	-	4.6	-	3.9	-	-	-	-
	0	-	24	-	33	-	13	-	-	-	-	0	-	18	-	37	-	17	-	-	-	-
[12]NSC	35	-	43.5	-	46.5	-	39.5	-	-	-	-	3.3	-	3.4	-	4.5	-	3.9	-	-	-	-
	0	-	24	-	33	-	13	-	-	-	-	0	-	5	-	38	-	18	-	-	-	-
[13]MO	56.5	-	50.3	-	-	46.9	-	44.4	-	-	-	9.4	-	7.8	-	-	7.8	-	7.3	-	-	-
	0	-	-11	-	-	-17	-	-21	-	-	-	0	-	-17	-	-	-17	-	-22	-	-	-
MO	54.6	-	43.6	-	-	41.7	-	39.9	-	-	-	8.7	-	7.3	-	-	6.9	-	6.8	-	-	-
	0	-	-20	-	-	-24	-	-27	-	-	-	0	-	-16	-	-	-21	-	-22	-	-	-
MO	23.6	-	22	-	-	42.4	-	40.4	-	-	-	8.7	-	7.3	-	-	7.4	-	6.8	-	-	-
	0	-	-7	-	-	80	-	71	-	-	-	0	-	-16	-	-	-15	-	-22	-	-	-
[14]NSC	32.9	-	-	43.6	45.3	48.2	-	-	-	-	-	2.7	-	-	3.0	3.0	2.8	-	-	-	-	-
	0	-	-	32	38	47	-	-	-	-	-	0	-	-	11	13	6	-	-	-	-	-

REF.	28 Day Compressive Cube Strength, MPa											28 Day Splitting Tensile Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[15]NSC [a]	33.3	-	-	33.4	41.1	38.4	-	-	-	-	-	2.8	-	-	3.3	3.3	3.8	-	-	-	-	-
[b]	0	-	-	0	24	15	-	-	-	-	-	0	-	-	17	17	35	-	-	-	-	-
[16]NSC	31.4	-	39.3	-	44.5	-	38.4	-	36.4	-	31.4	5	-	5.7	-	5.3	-	5.1	-	5	-	5.5
	0	-	25	-	42	-	22	-	16	-	0	0	-	14	-	5	-	2	-	1	-	10
[17]NSC	25.2	-	-	43.5	47.8	40.2	-	-	-	-	-	3.8	-	-	4.1	4.5	4.2	-	-	-	-	-
	0	-	-	73	90	60	-	-	-	-	-	0	-	-	8	18	11	-	-	-	-	-
[18]NSC	25	25.2	30	30.2	34	30	-	-	-	-	-	2	2	2.1	2.2	2.7	2	-	-	-	-	-
	0	1	20	21	36	20	-	-	-	-	-	0	1	5	10	33	0	-	-	-	-	-
[19]NSC	33	-	28.8	-	-	30.7	-	51.8	-	-	-	1.7	-	2.6	-	-	1.9	-	3	-	-	-
	0	-	−13	-	-	−7	-	57	-	-	-	0	-	53	-	-	12	-	76	-	-	-
[20]NSC	31.4	32.5	33.4	34.3	32	-	-	-	-	-	-	3.5	3.6	3.7	3.7	3.5	-	-	-	-	-	-
	0	4	7	9	2	-	-	-	-	-	-	0	1	5	6	1	-	-	-	-	-	-
[21]NSC	41.1	-	-	-	47.4	-	-	-	-	-	-	2.9	-	-	-	3	-	-	-	-	-	-
	0	-	-	-	15	-	-	-	-	-	-	0	-	-	-	2	-	-	-	-	-	-
[22]GC	58.6	61.8	64.7	66.7	70.1	71.2	-	-	-	-	-	4.2	4.3	4.6	4.7	4.8	5	-	-	-	-	-
	0	5	10	14	20	22	-	-	-	-	-	0	2	9	13	15	18	-	-	-	-	-
GC	28.2	30.6	31.5	33.7	35.6	38.9	-	-	-	-	-	3	3.2	3.3	3.5	3.7	3.9	-	-	-	-	-
	0	8	12	19	26	38	-	-	-	-	-	0	8	12	17	25	31	-	-	-	-	-
[23]NSC	28.6	30.6	32.4	33.6	37.3	34.4	32.3	-	30.5	-	29.9	2.5	2.7	2.9	2.9	3.1	2.9	3	-	2.9	-	2.8
	0	7	13	17	30	20	13	-	7	-	5	0	7	15	17	24	16	20	-	16	-	12

Continued

Table 4.4 Continued

REF.	28 Day Compressive Cube Strength, MPa											28 Day Splitting Tensile Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[24]NSC ^{a}	62.1	-	60.8	-	-	61.7	-	64.4	-	-	63	4.9	-	4.8	-	-	4.9	-	5	-	-	4.8
^{b}	0	-	-2	-	-	-1	-	4	-	-	1	0	-	-2	-	-	1	-	2	-	-	-1
[25]NSC	62.1	-	61.4	-	-	57.5	-	53	-	-	48.8	4.4	-	4.2	-	-	3.8	-	3.6	-	-	3.3
	0	-	-1	-	-	-7	-	-15	-	-	-21	0	-	-5	-	-	-14	-	-19	-	-	-25
	61.8	-	63.8	-	-	63.7	-	61.4	-	-	64	4.6	-	4.5	-	-	4.6	-	4.5	-	-	4.7
	0	-	3	-	-	3	-	-1	-	-	4	0	-	-2	-	-	0	-	-2	-	-	1
[26]NSC	29.3	29.9	32.1	37.6	39.5	33	28.7	-	-	-	-	2.6	2.9	3.1	3.4	3.5	2.8	2.8	-	-	-	-
	0	2	10	28	35	13	-2	-	-	-	-	0	12	19	31	35	8	6	-	-	-	-
[27]NSC	36.1	39.1	47.3	39.2	37	38.5	42.9	-	34.9	-	31	3.4	5.0	5.7	5.7	5.7	4.3	4.3	4.2	4.1	4.1	3.8
	0	8	31	9	2	7	19	-	-3	-	-14	0	46	68	67	67	27	25	24	20	19	12
[28]NSC	36.8	-	-	-	41.1	-	-	-	-	-	-	2.2	-	-	-	2.2	-	-	-	-	-	-
	0	-	-	-	12	-	-	-	-	-	-	0	-	-	-	1	-	-	-	-	-	-
NSC	41.1	-	-	-	47.4	-	-	-	-	-	-	2.9	-	-	-	3.0	-	-	-	-	-	-
	0	-	-	-	15	-	-	-	-	-	-	0	-	-	-	2	-	-	-	-	-	-
[29]NSC	40.6	-	45.9	-	50	-	51.7	-	56.3	-	63.9	2.2	-	2.5	-	2.5	-	2.7	-	2.9	-	3.2
	0	-	13	-	23	-	27	-	39	-	57	0	-	11	-	13	-	20	-	29	-	47
[30]NSC	33.9	42.1	45.2	-	-	-	-	-	-	-	-	2.4	3.3	3.1	-	-	-	-	-	-	-	-
	0	24	33	-	-	-	-	-	-	-	-	0	35	29	-	-	-	-	-	-	-	-
[31]NSC	36	35.2	34.7	34.2	32.5	30	-	-	-	-	-	3.6	3.4	3.3	3.4	2.3	2.3	-	-	-	-	-
	0	-2	-4	-5	-10	-17	-	-	-	-	-	0	-4	-6	-5	-35	- 36	-	-	-	-	-

REF.	28 Day Compressive Cube Strength, MPa											28 Day Splitting Tensile Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[32]NSC [a]	22.5	-	27.4	29	30	29.3	-	-	-	-	-	3.1	-	4.4	4.6	4.8	4.0	-	-	-	-	-
[b]	0	-	22	29	33	30	-	-	-	-	-	0	-	43	51	57	31	-	-	-	-	-
[33]HPC	31	36	43.8	45.3	28.7	26	32	31	-	-	-	3.2	3.3	3.8	4.2	4	3.7	3.3	2.9	-	-	-
	0	16	41	46	-7	-16	3	0	-	-	-	0	3	19	31	25	16	3	-9	-	-	-
[34]MO	26	-	28	-	34	33	32	-	27	-	26	3.9	-	4	-	4.5	4.4	4	-	3.7	-	3.3
	0	-	8	-	31	27	23	-	4	-	0	0	-	3	-	15	13	3	-	-5	-	-15
NC	41	-	42	-	44	43	36	-	35	-	34	4.6	-	5	-	5.7	5.7	4.6	-	3.9	-	3.5
	0	-	2	-	7	5	-12	-	-15	-	-17	0	-	9	-	24	24	0	-	-15	-	-24
[35]HPC	56	-	-	-	64	-	-	-	-	-	-	4.7	-	-	-	5.8	-	-	-	-	-	-
	0	-	-	-	14	-	-	-	-	-	-	0	-	-	-	23	-	-	-	-	-	-
[36]NSC	50	-	-	50.5	56.3	45.1	-	-	-	-	-	3.7	-	-	3.6	3.8	3.7	-	-	-	-	-
	0	-	-	1	13	-10	-	-	-	-	-	0	-	-	-5	1	-1	-	-	-	-	-
[37]NSC	32.6	36.2	38.6	41.5	46.9	44.2	-	-	-	-	-	7.2	8.3	8.8	9	9.5	9.1	-	-	-	-	-
	0	11	19	27	44	36	-	-	-	-	-	0	14	22	24	31	26	-	-	-	-	-
[38]NSC	37.9	-	-	-	-	-	-	-	-	-	35.2	3.1	-	-	-	-	-	-	-	-	-	3.1
	0	-	-	-	-	-	-	-	-	-	-7	0	-	-	-	-	-	-	-	-	-	-2
NSC	31	-	-	-	-	-	-	-	-	-	31.1	2.8	-	-	-	-	-	-	-	-	-	2.7
	0	-	-	-	-	-	-	-	-	-	0	0	-	-	-	-	-	-	-	-	-	-2
[39,40]	25.2	38.6	39.9	40.1	43.2	45.3	-	-	-	-	-	4.1	6.3	7.3	7.8	8.1	8.2	-	-	-	-	-
NSC	0	53	58	59	71	80	-	-	-	-	-	0	56	80	93	99	101	-	-	-	-	-

Continued

Table 4.4 Continued

REF.	28 Day Compressive Cube Strength, MPa											28 Day Splitting Tensile Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[41]NSC [a]	34.4	36.7	38.7	40.4	41.7	37.8	-	-	-	-	-	3.5	3.7	4.1	4.3	4.6	3.8	-	-	-	-	-
[b]	0	7	13	18	21	10	-	-	-	-	-	0	8	17	25	32	10	-	-	-	-	-
NSC	39.7	41.8	43.7	46.7	48.1	43	-	-	-	-	-	3.7	4.1	4.4	4.8	5	4.2	-	-	-	-	-
	0	5	10	18	21	8	-	-	-	-	-	0	10	18	28	34	12	-	-	-	-	-
[42]NSC	23.6	30.2	-	33.3	-	-	-	-	-	-	-	2.3	2.4	-	2.5	-	-	-	-	-	-	-
	0	28	-	41	-	-	-	-	-	-	-	0	7	-	12	-	-	-	-	-	-	-
[43]NSC	21	-	-	-	35.9	38.1	30.7	-	-	-	-	2.1	-	-	-	3.4	3.5	2.6	-	-	-	-
	0	-	-	-	71	81	46	-	-	-	-	0	-	-	-	67	73	27	-	-	-	-
[44]NSC	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0	-	-	0	-	-	-	-	-	-	-	0	-	-	0	-	-	-	-	-	-	-
[45]NSC	38.8	-	40.7	-	44	-	34.4	-	31.4	-	27.7	2.5	-	2.7	-	3.1	-	2.5	-	2.2	-	1.9
	0	-	5	-	13	-	-11	-	-19	-	-29	0	-	10	-	27	-	0	-	-10	-	-24
[46]NSC	36.3	40.1	43.2	44.9	48	40.3	-	-	-	-	-	3.3	3.6	3.7	4.2	4.5	3.9	-	-	-	-	-
	0	10	19	24	32	11	-	-	-	-	-	0	12	15	28	38	19	-	-	-	-	-
[47]NSC	40	40	52	58	62	62	57	-	48	-	22	4.9	5	6	7	7.5	7	6	-	5	-	3
	0	0	30	45	55	55	43	-	20	-	-45	0	2	22	43	53	43	22	-	2	-	-39
[48]NSC	99	-	98	-	96	-	88	-	70	-	64	5.6	-	5.4	-	5.4	-	5.3	-	4.1	-	4.2
	0	-	-1	-	-3	-	-11	-	-29	-	-35	0	-	-4	-	-4	-	-5	-	-27	-	-25

REF.	28 Day Compressive Cube Strength, MPa											28 Day Splitting Tensile Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
Ave. [c], %	**0**	**8**	**10**	**22**	**21**	**16**	**9**	**8**	**-3**	**14**	**-9**	**0**	**12**	**15**	**25**	**23**	**15**	**9**	**3**	**0**	**19**	**-4**
Individual ave.[d], %		**10**											**12**									
Overall ave. [e],%		**10**											**13**									

Note: a: 28-day compressive cube strength; b: relative strength of CS mix to reference mix; c: average of relative values at different CS contents; d: total average; e: overall average of all data. *GC*, geopolymer concrete; *HPC*, high-performance concrete; *HSC*, high-strength concrete; *MO*, mortar; *NSC*, normal-strength concrete; *W.R.T*, with respect to.

Reference: [1] Al-Jabri (2006), [2] Al-Jabri et al., 2009a; [3] Al-Jabri et al., 2009b; [4] Al-Jabri et al., 2011; [5] Alnuaimi, 2009; [6] Alnuaimi, 2012; [7] Anudeep et al., 2015; [8] Arivalagan, 2013; [9] Brindha and Nagan, 2010a; [10] Brindha and Nagan, 2010b; [11] Brindha and Nagan, 2011; [12] Brindha et al., 2010; [13] Cachim et al., 2009; [14] Dharani et al., 2015; [15] Gowda and Balakrishna, 2014; [16] Jaivignesh and Gandhimathi, 2015; [17] Jebitta and Sofia, 2015; [18] Karthick et al., 2014; [19] Kayathri et al., 2014; [20] Kumar and Mahesh, 2015; [21] Madhu and Venkataratnam, 2015; [22] Mahendran and Arunachelam, 2015; [23] Mahmood and Hashmi, 2014; [24] Mithun and Narasimhan, 2016; [25] Mithun et al., 2015a; [26] Naganur and Chethan, 2014; [27] Patil, 2015; [28] Patnaik et al., 2015; [29] Pazhani, 2010; [30] Poozvizhi and Kathirvel, 2015; [31] Pradeep and Rama, 2014; [32] Prakeash and Brindha, 2012; [33] Priyanka and Thahira, 2013; [34] Khan et al, 2015a; [35] Khan et al., 2015b; [36] Sakthieswaran and Ganesan, 2014a; [37] Saxena, 2015b; [38] Shoya et al., 1997; [39] Sudarvizhi and Ilangovan, 2011; [40] Sudarvizhi and Ilangovan, 2012; [41] Suresh and Kishore, 2013; [42] Suresh and Ravikumar, 2015; [43] Sushma et al., 2015; [44] Tam, 2001; [45] Tamil et al., 2014; [46] Thomas et al., 2012; [47] Velumani and Nirmalkumar, 2014; [48] Wu et al., 2010a.

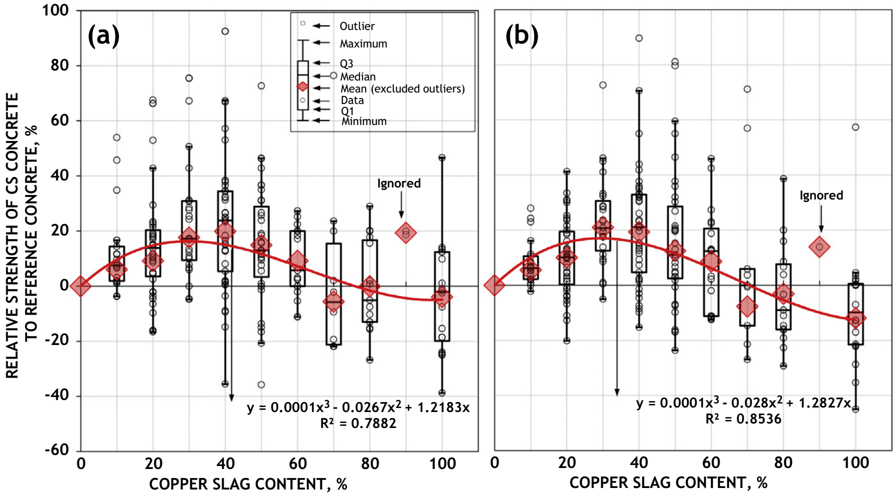

Figure 4.12 Comparison of copper slag concrete and reference concrete in terms of (a) splitting tensile strength and its corresponding (b) compressive strength.

conjunction with Figure 4.3 and in the main points to the aggregate particle packing effect, and in this case suggest that the best results are likely to be obtained when using CS at 20–50% as a component of sand.

To obtain a collective view of all the results, and more importantly to examine whether the current Eurocode 2 (2004) can be used for working with concrete where CS is used as sand, all the results in Table 4.4 are used to establish the relationship between compressive strength and tensile strength of CS concrete, as shown plotted in Figure 4.13. The figures given in Table 3.1 of Eurocode 2 (2004) have also been plotted in the same figure for comparison purposes.

In developing Figure 4.13:

- The measured cube strength values were converted into characteristic cube strength using the coefficient of variation of 6% given in ACI 301-05 (2005) for fair laboratory control as:

  $$f_{\mathrm{ck,cube}} = f_{\mathrm{m}}\ (1 - 1.64v)$$

  where $f_{\mathrm{ck,cube}}$ is the characteristic cube compressive strength, f_{m} is the mean cube compressive strength, 1.64 is the constant for 5% of individual cube strength below the design strength and v is the coefficient of variation.

- The results of 6 of 48 studies were not considered, as they appeared to be at odds with the rest of the data populations (Cachim et al., 2009; Jaivignesh and Gandhimathi, 2015; Saxena, 2015b; Sudarvizhi and Ilangovan, 2011, 2012; Velumani and Nirmalkumar, 2014).
- An attempt was made to analyse the data for different CS content levels, but no clear trend was observed.

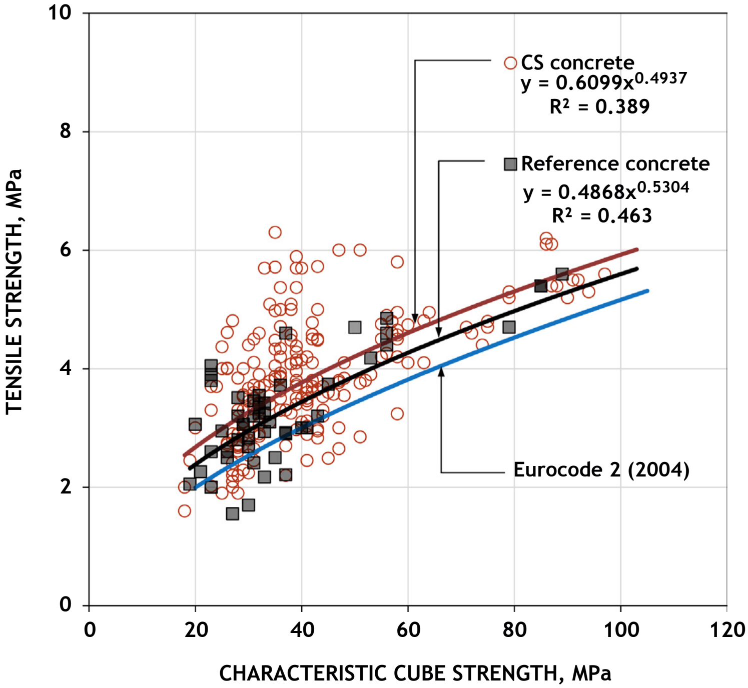

Figure 4.13 Relationship between characteristic compressive strength and tensile strength of copper slag (CS) concrete (data taken from Table 4.4).

Figure 4.13 gives a positive message, showing clearly that, for a given characteristic cube strength, the tensile strength of CS concrete is slightly higher than that of the natural concrete. Although the overall trendline of CS concrete is slightly above that of Eurocode 2 (2004), as a worst case scenario it can be taken as comparable (Figure 4.12), implying that CS can be accepted as a component of sand in concrete and that Eurocode 2 (2004) can be used, without any modification, for estimating tensile strength of such concrete mixes in a normal manner (Figure 4.13).

Flexural Strength

Flexural strength is commonly used in the design of concrete pavement. For its test, a prism specimen is subjected to bending using the third-point loading method, such as specified in ASTM C78 (2015) and BS EN 12390-5 (2009), or centre point loading, such as specified in ASTM C293 (2015), until failure. The latter method is less commonly adopted and is also known to result in a higher value than the former method.

The studies providing information on the flexural strength of CS concrete have covered the effects of CS replacement level from 0% to 100%, with water/cement ratio varying from 0.27 to 0.60. Similar to the analysis adopted for splitting cylinder tensile strength, all the results available for flexural strength in the literature have been analysed together with their corresponding compressive strength values in terms of constant consistence [Table 4.5(a)] and constant water/cement ratio [Table 4.5(b)]. This table has been formatted as the mirror image of that developed for the splitting cylinder tensile strength results (Table 4.4) and it would help the reader to refer to this before going to Table 4.5.

Again, to facilitate the readers in undertaking their own analysis of the data given, a full set of the results found published in the literature since 2006 is given in Table 4.5 and plotted in Figure 4.14. These results show that, overall, the compressive and flexural strengths, for all intents and purposes, are similarly affected by the use of CS as sand in concrete (Table 4.5), with Figure 4.14 suggesting, as for the tensile strength, that the use of CS at 20–50% of the total sand content is most likely to give the best performance, which could also be about 10–15% higher than that of the corresponding normal reference concrete.

Figure 4.15 shows the relationship between the flexural strength and the corresponding characteristic cube strength of concrete for the data given in Table 4.5. The procedure used to calculate the characteristic cube strength for this was the same as previously used for developing Figure 4.13 and explained in the section on splitting cylinder tensile strength. The results of 7 of 40 studies (Ambily et al., 2015; Arivalagan, 2013; Al-Jabri, 2006; Al-Jabri et al., 2009b; Suresh and Kishore, 2013; Poozvizhi and Kathirvel, 2015) have been excluded as they appeared to deviate from the main trend. Eurocode 2 (2004) does not give such a relationship for normal concrete, and instead one proposed by RILEM Technical Committee 162 (2000) was used.

Given the results, the only practical conclusion one can draw from the various relationships in Figure 4.15 is that it can be safely assumed that the use of CS up to 100% should not significantly change the relationship between flexural strength and characteristic cube strength and the latter can, where necessary, be used to estimate the flexural strength of concrete containing CS. In addition, the tensile strength of concrete was also plotted against its corresponding flexural strength, but no clear trend was observed.

4.5 Deformation Properties

The deformation of concrete can be broadly classified based on its time and load dependency, for which three main properties are normally specified for concrete structure design purposes: elastic modulus (instantaneous load-dependent deformation), creep (both time- and load-dependent deformation) and shrinkage (time-dependent but load-independent deformation). Aggregate is known to withstand the deformation of concrete. Given that the hardness of CS is about 6 to 7 Mohs (comparable to that of silica sand) and its porosity is very low, all other things being equal, the use of CS as a sand component should result in concrete having deformation resistance that is similar to or better than concrete made with natural sand.

Table 4.5 Analysis of flexural strength and its corresponding compressive strength of copper slag mixes

REF.	28 Day Compressive Cube Strength, MPa											28 Day Flexural Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
(a) Equal Consistence																						
[2]HSC [a]	88.1	-	-	87.1	-	101.3	-	104.4	101.6	-	107.4	11.4	-	-	13.2	-	14.4	-	14.8	13.9	-	14.5
[b]	0	-	-	-1	-	15	-	19	15	-	22	0	-	-	16	-	26	-	30	22	-	27
[9]NSC	30.2	-	32.8	-	35.1	-	21.3	-	20.4	-	20	1.9	-	2.3	-	2.5	-	2.8	-	2.9	-	2.9
	0	-	9	-	16	-	-29	-	-32	-	-34	0	-	22	-	33	-	48	-	51	-	52
Ave. [c], %	0	-	9	-1	16	15	-29	19	-9	-	-6	0	-	22	16	33	26	48	30	22	-	27
Individual Ave. [d], %		2											28									
(b) Equal Water/Cement Ratio																						
[1]NSC	44	44.9	48.5	48.9	48.1	53.1	-	46.6	-	50.1	45	7.7	7.2	7.2	6.9	6.5	7.3	-	6.3	-	7.2	5.9
	0	2	10	11	9	21	-	6	-	14	2	0	-6	-6	-10	-16	-5	-	-18	-	-6	-23
HSC	93.9	99.8	95.3	-	79.6	96.8	83	-	79	-	82	14.6	13.6	12.4	-	10.8	12.9	11	-	10.3	-	10.1
	0	6	1	-	-15	3	-12	-	-16	-	-13	0	-7	-15	-	-26	-12	-24	-	-29	-	-31
[2]NSC	25.6	29.4	32.4	36	39.4	43.7	42.9	48.8	51.6	59.3	66.3	5.4	5.8	5.9	6.2	6	5.9	6.3	6.4	6.5	6.7	7.2
	0	15	27	41	54	71	68	91	102	132	159	0	7	9	15	11	9	17	19	20	24	33
[3]HSC	93.9	99.8	95.3	-	95.2	96.8	83.0	-	83.6	-	82.0	14.6	13	12.4	-	12.5	12.9	11	-	10.3	-	10.1
	0	6	1	-	1	3	-12	-	-11	-	-13	0	-11	-15	-	-14	-12	-24	-	-29	-	-31
[4]NSC	45	46	47	-	47.1	47	46	-	34.8	-	35.1	7.7	7.2	7.2	6.9	6.5	7.3	6.3	-	7.2	-	5.9
	0	2	4	-	5	4	2	-	-23	-	-22	0	-6	-6	-10	-16	-5	-18	-	-6	-	-23
[5]NSC	36.6	-	35.0	-	33.4	-	32.0	-	30.6	-	28.4	3.9	-	4.0	-	4.5	-	4.6	-	4.4	-	4.5
	0	-	-4	-	-9	-	-13	-	-16	-	-22	0	-	4	-	14	-	18	-	14	-	15

Continued

Table 4.5 Continued

REF.	28 Day Compressive Cube Strength, MPa											28 Day Flexural Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference MIX, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[6]NSC [a]	34.4	-	-	-	33.9	-	-	-	31.3	-	-	4.9	-	-	-	4.3	-	-	-	4	-	-
[b]	0	-	-	-	-1	-	-	-	-9	-	-	0	-	-	-	-12	-	-	-	-18	-	-
[7]NSC	21.8	-	-	37.6	-	-	-	-	-	-	25.4	7.7	-	-	7.3	-	-	-	-	-	-	5.9
	0	-	-	72	-	-	-	-	-	-	17	0	-	-	-5	-	-	-	-	-	-	-23
[8]HPC	138	-	-	-	-	-	-	-	-	-	117	7.5	-	-	-	-	-	-	-	-	-	10
	0	-	-	-	-	-	-	-	-	-	-15	0	-	-	-	-	-	-	-	-	-	33
HPC	148	-	-	-	-	-	-	-	-	-	126	35	-	-	-	-	-	-	-	-	-	35
	0	-	-	-	-	-	-	-	-	-	-15	0	-	-	-	-	-	-	-	-	-	0
[10]NSC	32.7	-	37.9	40.3	43.1	39.1	-	-	-	-	-	3.6	-	5.0	5.1	5.3	5.2	-	-	-	-	-
	0	-	16	23	32	20	-	-	-	-	-	0	-	39	43	48	47	-	-	-	-	-
[11]NSC	30.4	35.2	38.2	42.3	43.0	39.5	35.9	26.9	-	-	25.1	3.5	3.6	4.0	3.6	3.7	3.8	3.6	3.5	-	-	3.8
	0	16	26	39	41	30	18	−12	-	-	−17	0	3	15	4	5	7	2	1	-	-	10
[12]NSC	32.9	-	-	43.6	45.3	48.2	-	-	-	-	-	5.5	-	-	3.5	3	2.5	-	-	-	-	-
	0	-	-	32	38	47	-	-	-	-	-	0	-	-	-36	-45	-55	-	-	-	-	-
[13]NSC	33.3	-	-	33.4	41.1	38.4	-	-	-	-	-	3.6	-	-	4.6	5	5	-	-	-	-	-
	0	-	-	0	24	15	-	-	-	-	-	0	-	-	28	39	39	-	-	-	-	-
[14]NSC	25	25.2	30	30.2	34	30	-	-	-	-	-	7	8	8.1	8.2	9	6.7	-	-	-	-	-
	0	1	20	21	36	20	-	-	-	-	-	0	14	16	17	29	−4	-	-	-	-	-
[15]NSC	38.3	41.0	48.1	40.8	44.4	44.9	45.2	-	38.4	-	35.7	4.2	4.3	4.8	4.4	4.4	4.5	4.3	-	4.2	-	4.2
	0	7	26	7	16	17	18	-	0	-	-7	0	3	15	4	5	7	2	-	1	-	0

REF.	28 Day Compressive Cube Strength, MPa											28 Day Flexural Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[16]NSC [a]	54.5	-	56	-	56	-	54	-	56	-	54	5.1	-	5.2	-	5.4	-	5.6	-	5.9		6.2
[b]	0	-	3	-	2.8	-	-1	-	2.8	-	-1	0	-	2	-	6	-	10	-	16		22
[17]NSC	31.4	32.5	33.4	34.3	32	-	-	-	-	-	-	6.1	6.2	6.3	6.4	6.3	-	-	-	-	-	-
	0	4	7	9	2	-	-	-	-	-	-	0	2	4	5	3	-	-	-	-	-	-
[18]NSC	36.8	-	-	-	41	-	-	-	-	-	-	4.5	-	-	-	4.8	-	-	-	-	-	-
	0	-	-	-	11	-	-	-	-	-	-	0	-	-	-	7	-	-	-	-	-	-
[19]NSC	28.6	30.6	32.4	33.6	37.3	34.4	32.3	-	30.5	-	29.9	3.3	3.5	3.6	3.7	3.9	3.7	3.6		3.6		3.5
	0	7	13	17	30	20	13	-	7	-	5	0	6	9	14	20	12	9		9		8
[20]NSC	62.1	-	60.8	-	-	61.7	-	64.4	-	-	63	7.1	-	7.25	-	-	7.1	-	7.1	-	-	7.3
	0	-	-2	-	-	-1	-	4	-	-	1	0	-	2	-	-	0	-	0	-	-	3
[21]NSC	62.1	-	61.4	-	-	57.5	-	53	-	-	48.8	7	-	6.7	-	-	6	-	5.5	-	-	5
	0	-	-1	-	-	-7	-	-15	-	-	-21	0	-	-4	-	-	-14	-	-21	-	-	-29
NSC	61.8	-	63.8	-	-	63.7	-	61.4	-	-	64	7.2	-	7.2	-	-	7.2	-	7.2	-	-	7.2
	0	-	3	-	-	3	-	-1	-	-	4	0	-	0	-	-	0	-	0	-	-	0
[22]NSC	-	-	-	-	-	-	-	-	-	-	-	7.5	-	-	-	-	7.6	-	-	-	-	7.7
	-	-	-	-	-	-	-	-	-	-	-	0	-	-	-	-	1	-	-	-	-	1
[23]NSC	36	-	-	-	-	-	-	-	-	-	52	6.0	-	-	-	-	-	-	-	-	-	8.2
	0	-	-	-	-	-	-	-	-	-	44	0	-	-	-	-	-	-	-	-	-	37
NSC	50	-	-	-	-	-	-	-	-	-	58	7.0	-	-	-	-	-	-	-	-	-	10.0
	0	-	-	-	-	-	-	-	-	-	16	0	-	-	-	-	-	-	-	-	-	43

Continued

Table 4.5 Continued

REF.	28 Day Compressive Cube Strength, MPa											28 Day Flexural Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[24]NSC [a]	36.1	39.1	47.3	39.2	37	38.5	42.9	-	34.9	-	31	4.1	4.3	4.7	4.3	4.4	4.4	4.2		4.2		4.6
[b]	0	8	31	9	2	7	19	-	-3	-	-14	0	4	15	4	6	8	2		1		12
[25]NSC	36.8	-	-	-	41.1	-	-	-	-	-	-	4.4	-	-	-	4.7	-	-	-	-	-	-
	0	-	-	-	12	-	-	-	-	-	-	0	-	-	-	7	-	-	-	-	-	-
NSC	41.1	-	-	-	47.4	-	-	-	-	-	-	4.9	-	-	-	5.3	-	-	-	-	-	-
	0	-	-	-	15	-	-	-	-	-	-	0	-	-	-	8	-	-	-	-	-	-
[26]NSC	40.6	-	45.9	-	50	-	51.7	-	56.3	-	63.9	5.0	-	5.0	-	5.3	-	5.3	-	5.3	-	5.4
	0	-	13	-	23	-	27	-	39	-	57	0	-	0	-	6	-	6	-	7	-	8
[27]NSC	33.9	42.1	45.2	-	-	-	-	-	-	-	-	9.9	13.3	11.6	-	-	-	-	-	-	-	-
	0	24	33	-	-	-	-	-	-	-	-	0	34	17	-	-	-	-	-	-	-	-
[28]NSC	22.5	-	27.4	29	30	29.3	-	-	-	-	-	2.6	-	3.7	3.8	3.9	4.1	-	-	-	-	-
	0	-	22	29	33	30	-	-	-	-	-	0	-	41	46	50	58	-	-	-	-	-
[29]NSC	35.5	42.2	44.6	46.5	48.8	46.2	-	-	-	-	-	3.8	4.0	4.1	4.4	4.7	4.2	-	-	-	-	-
	0	19	26	31	37	30	-	-	-	-	-	0	5	10	17	24	13	-	-	-	-	-
[30]HPC	59	-	-	-	63	67	66	-	-	-	-	5.6	-	-	-	5.3	5.2	5.1	-	-	-	-
	0	-	-	-	7	14	12	-	-	-	-	0	-	-	-	-5	-7	-9	-	-	-	-
HPC	63	-	-	-	65	70	67	-	-	-	-	5.8	-	-	-	4.8	4.9	5.4	-	-	-	-
	0	-	-	-	3	11	6	-	-	-	-	0	-	-	-	-17	-16	-7	-	-	-	-
HPC	67	-	-	-	70	72	72	-	-	-	-	5.5	-	-	-	5.3	5.7	5.5	-	-	-	-
	0	-	-	-	4	7	7	-	-	-	-	0	-	-	-	-4	4	0	-	-	-	-

REF.	28 Day Compressive Cube Strength, MPa											28 Day Flexural Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[30]HPC [a]	67	-	-	-	70	72	72	-	-	-	-	5.7	-	-	-	5.5	6.2	5.1		-	-	-
[b]	0	-	-	-	4	7	7	-	-	-	-	0	-	-	-	-4	9	-11		-	-	-
[31]MO	54	-	50	-	-	44	-	48	-	-	-	**9.2**	-	8.4	-	-	7.6	-	7.8	-	-	-
	0	-	-7	-	-	-19	-	-11	-	-	-	0	-	-9	-	-	-17	-	-15	-	-	-
[32]HPC	50			50.5	56.3	45.1	-	-	-	-	-	5.8	-	-	6.1	6.1	6.6	-	-	-	-	-
	0			1	13	-10	-	-	-	-	-	0	-	-	6	5	13	-	-	-	-	-
[33]NSC	32.6	36.2	38.6	41.5	46.9	44.2	-	-	-	-	-	3.7	4.0	4.1	4.4	4.7	4.2	-	-	-	-	-
	0	11	19	27	44	36	-	-	-	-	-	0	6	11	18	25	14	-	-	-	-	-
[34]NSC	-	-	-	-	-	-	-	-	-	-	-	5.7	-	6.2	-	6.7	-	6.0	-	5.5	-	5.1
	-	-	-	-	-	-	-	-	-	-	-	0	-	8	-	17	-	5	-	-4	-	-11
[35]NSC	34.4	36.7	38.7	40.4	41.7	37.78	-	-	-	-	-	6.1	6.8	7.2	7.8	8.3	6.2	-	-	-	-	-
	0	5	10	18	21	8	-	-	-	-	-	0	12	19	28	37	2	-	-	-	-	-
NSC	39.7	41.8	43.7	46.7	48.1	42.96	-	-	-	-	-	11.9	12.7	13.6	14.3	15.3	12.2	-	-	-	-	-
	0	5	10	18	21	8	-	-	-	-	-	0	7	14	20	28	3	-	-	-	-	-
[36]NSC	21.0	-	-	-	35.9	38.1	30.7	-	-	-	-	6.9	-	-	-	7.3	8.3	7.5	-	-	-	-
	0	-	-	-	71	81	46	-	-	-	-	0	-	-	-	6	21	10	-	-	-	-
[37]NSC	38.8	-	40.7	-	44.0	-	34.4	-	31.4	-	27.7	4.8	-	7.0	-	7.7	-	6.3	-	5.5	-	4.4
	0	-	5	-	13	-	-11	-	-19	-	-29	0	-	46	-	61	-	31	-	14	-	-8
[38]NSC	36.3	40.1	43.2	44.9	48	40.3	-	-	-	-	-	3.6	4.0	4.4	4.7	5.0	4.6	-	-	-	-	-
	0	10	19	24	32	11	-	-	-	-	-	0	9	20	30	38	26	-	-	-	-	-

Continued

Table 4.5 Continued

REF.	28 Day Compressive Cube Strength, MPa											28 Day Flexural Strength, MPa										
	Relative Strength of CS Mix W.R.T Reference Mix, %											Relative Strength of CS Mix W.R.T Reference Mix, %										
	Copper Slag Content, %											Copper Slag Content, %										
	0	10	20	30	40	50	60	70	80	90	100	0	10	20	30	40	50	60	70	80	90	100
[39]NSC [a]	29.6	32.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
[b]	0	10	-	-	-	-	-	-	-	-	-	0	10	-	-	-	-	-	-	-	-	-
NSC	35.1	37.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	0	7	-	-	-	-	-	-	-	-	-	0	7	-	-	-	-	-	-	-	-	-
[40]NSC	99	-	98	-	96	-	88	-	70	-	64	9.3	-	9.2	-	9.6	-	8.4	-	8.6	-	8.2
	0	-	-1	-	-3	-	-11	-	-29	-	-35	0	-	-1	-	3	-	-10	-	-8	-	-12
Ave. [c], %	**0**	**9**	**11**	**22**	**17**	**15**	**7**	**-5**	**-7**	**14**	**-4**	**0**	**5**	**11**	**12**	**10**	**5**	**0**	**-9**	**-3**	**-6**	**0**
Individual Ave. [d], %		**8**											**3**									
Overall Ave. [e], %		**8**											**4**									

Note: a: 28-day compressive cube strength; b: relative strength of CS mix to reference mix; c: average of relative values at different CS contents; d: total average; e: overall average of all data. *GC*, geopolymer concrete; *HPC*, high-performance concrete; *HSC*, high-strength concrete; *MO*, mortar; *NSC*, normal-strength concrete; *W.R.T*, with respect to.

Reference: [1] Al-Jabri (2006), [2] Al-Jabri et al., 2009a; [3] Al-Jabri et al., 2009b; [4] Al-Jabri et al., 2011; [5] Alnuaimi, 2009; [6] Alnuaimi, 2012; [7] Amarnaath et al., 2015; [8] Ambily et al., 2015; [9] Arivalagan, 2013; [10] Brindha and Nagan, 2010a; [11] Chavan and Kulkarni, 2013; [12] Dharani et al., 2015; [13] Gowda and Balakrishna, 2014; [14] Karthick et al., 2014; [15] Kharade et al., 2013; [16] Kumar, 2012; [17] Kumar and Mahesh, 2015; [18] Madhu and Venkataratnam, 2015; [19] Mahmood and Hashmi, 2014; [20] Mithun and Narasimhan, 2016; [21] Mithun et al., 2015a; [22] Mithun et al., 2015b; [23] Nazer et al., 2012; [24] Patil, 2015; [25] Patnaik et al., 2015; [26] Pazhani, 2010; [27] Poozvizhi and Kathirvel, 2015; [28] Prakash and Brindha, 2012; [29] Saxena, 2015b; [30] Rajkumar et al., 2015; [31] Resende et al., 2008; [32] Sabarishri et al., 2015; [33] Saxena, 2015a; [34] Singh and Bath, 2015; [35] Suresh and Kishore, 2013; [36] Sushma et al., 2015; [76] Tam, 2001; [37] Tamil et al., 2014; [38] Thomas et al., 2012; [39] Vamsi and Kishore, 2013; [40] Wu et al., 2010a.

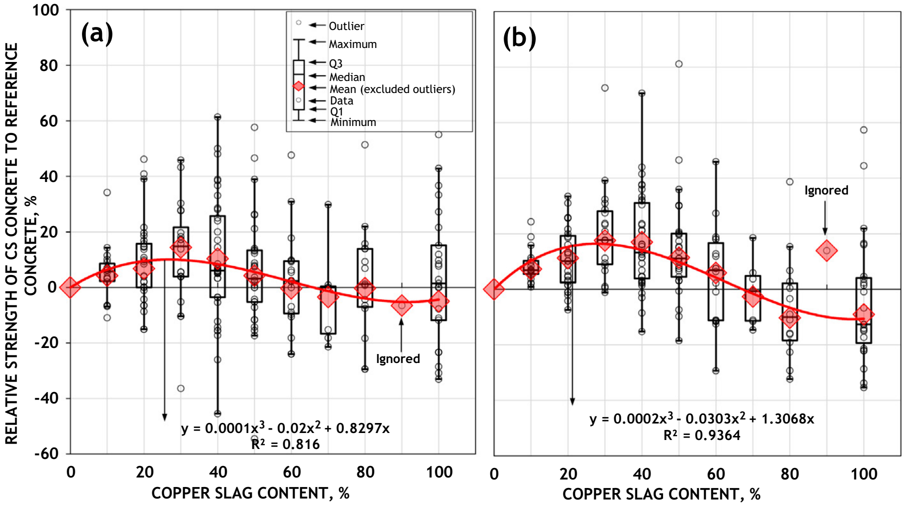

Figure 4.14 Comparison of copper slag concrete and reference concrete in terms of (a) flexural strength and its corresponding (b) compressive strength.

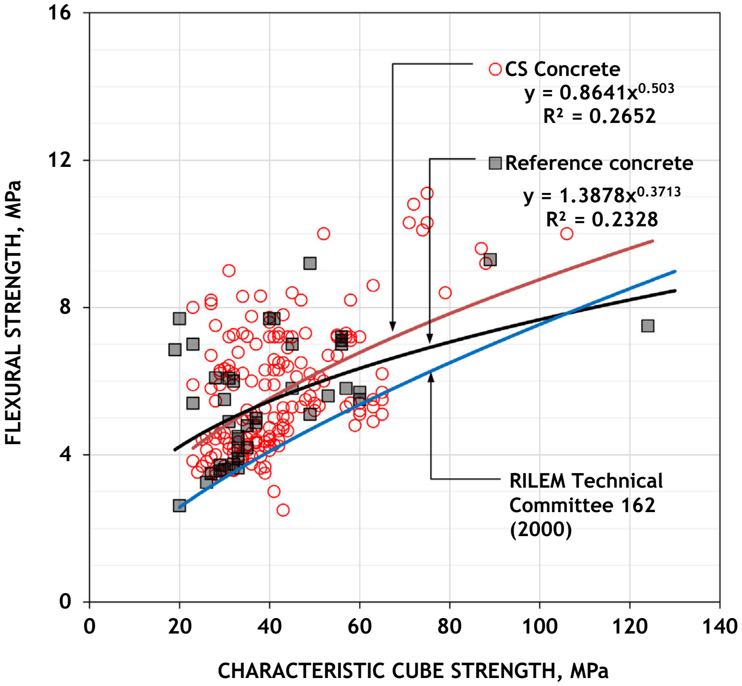

Figure 4.15 Relationship between characteristic compressive strength and flexural strength of copper slag (CS) concrete (data taken from Table 4.5).

4.5.1 Modulus of Elasticity

The slope between two connecting points of a typical stress–strain curve of concrete can define different moduli, initial tangents, tangents, secants or chord moduli. The secant modulus, commonly called the modulus of elasticity in practice, is normally used in designing concrete structures. As a composite material, the modulus of elasticity of concrete is affected by the elastic properties of coarse and fine aggregates, hydrated cement paste and the bonds between the two.

To gauge the effect of CS as sand on the modulus of elasticity of concrete, Figure 4.16 has been developed from the data published recently (Jebitta and Sofia, 2015; Patil, 2015; Mithun and Narasimhan, 2016) and the established relationships between the modulus of elasticity and the characteristic cube strength in Eurocode 2 (2004). The concrete mixes tested all used natural coarse aggregate, and granite aggregate in the case of the mixes is shown within the shaded circle in the figure. The fine aggregate used was river sand in all the studies and was replaced by CS in proportions of 10–100%.

It is evident from Figure 4.16 that the use of CS as sand does not adversely affect the modulus of elasticity of concrete and that Eurocode 2 (2004) can be used when specifying concrete using CS as a component of sand. Two technical review reports by

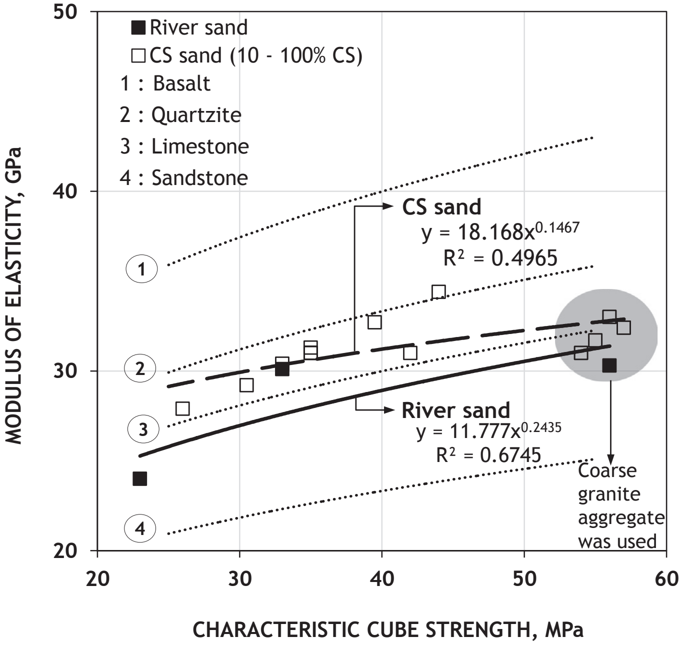

Figure 4.16 Compressive strength and modulus of elasticity of copper slag (CS) concrete. Data taken from Jebitta and Sofia (2015), Patil (2015), and Mithun and Narasimhan (2016).

Dhir (2009) and Tam (2001), based on the experimental work undertaken in Singapore using washed copper as sand, suggest that the modulus of elasticity of concrete with CS sand can be similar to or higher than that of the normal concrete.

4.5.2 Creep

The creep of concrete is the time-dependent deformation in response to sustained load. In concrete, creep takes place in hydrated cement paste owing to its porous structure, and aggregates provide restraint. As the quality assessment of concrete usually utilises strength, and testing for creep requires special facilities, it is seldom reported. However, Tam (2001), in reviewing the results obtained with WCS used as sand at a content of not more than 30%, found that WCS does not affect the creep of concrete in any adverse manner. Because of its higher hardness and stiffness compared to natural sand, the use of CS could be expected to reduce the creep of concrete (Dhir, 2009).

4.5.3 Shrinkage

The shrinkage of concrete is a generic term which implies volume reduction of concrete that may continue in different forms throughout its service life. Studies undertaken on drying shrinkage of concrete made with CS as sand replacement, together with that of the corresponding normal concrete, are summarized in Table 4.6. The results suggest that the use of CS as sand can considerably reduce the shrinkage of concrete. With reference to Section 4.3.1, which discusses the mix water reduction capability of CS, where mixes are designed with reduced water compared to the norm, a further reduction in the shrinkage characteristics of concrete can be achieved.

Table 4.6 Influence of copper slag on the shrinkage of concrete

References	Testing Conditions	W/C	CS, %	Shrinkage, µm
Ayano and Sakata (2000)	Age at test: 14 days	0.55	0	600
	Exposure: 21 ± 1°C, 60 ± 3% RH	0.55	100	400
	Testing period: 100 days			
Shoya et al. (1999)	Age at test: 28 days	0.55	0	510
	Exposure: 20°C, 60% RH	0.55	50	530
	Testing period: 100 days	0.55	100	490
Tam (2001)	Age at test: not given	Not given	0	<60
	Exposure: 30°C, 60% RH		10	<60
	Testing period: 350 days		30	<60

CS, copper slag; *RH*, relative humidity; *W/C*, water/cement ratio.

4.6 Non-destructive Tests

Some studies have used non-destructive tests with concrete made with CS as sand, using rebound hammer and ultrasonic pulse velocity methods, probably because the tests can be performed rapidly and easily and they cost the least. A further attraction of these tests could be in proving their suitability for use in applications where the structural assessment of concrete buildings may require compliance with BS EN 13791 (2007). Two sets of results, using a range of concrete parameters, such as water/cement ratio, aggregate type, different levels of CS sand content and age at test, have been produced and some of this information is plotted in Figures 4.17 and 4.18.

The rebound hammer measurements results in Figure 4.17 mirror the strength development trend observed with CS sand used in the concrete mixes tested, and suggest that the test method is sufficiently sensitive to strength change and can effectively be employed in the in situ non-destructive survey of structural concrete where CS as the sand component may have been used. The results in Figure 4.18 tend to mirror the strength change profile measured with the use of CS as sand varying from 0% to 100% (see Figure 4.7). This level of sensitivity to strength development, like the rebound hammer test, suggests that the ultrasonic pulse velocity test can also be used routinely in undertaking non-destructive structural surveys where CS may have been used as sand.

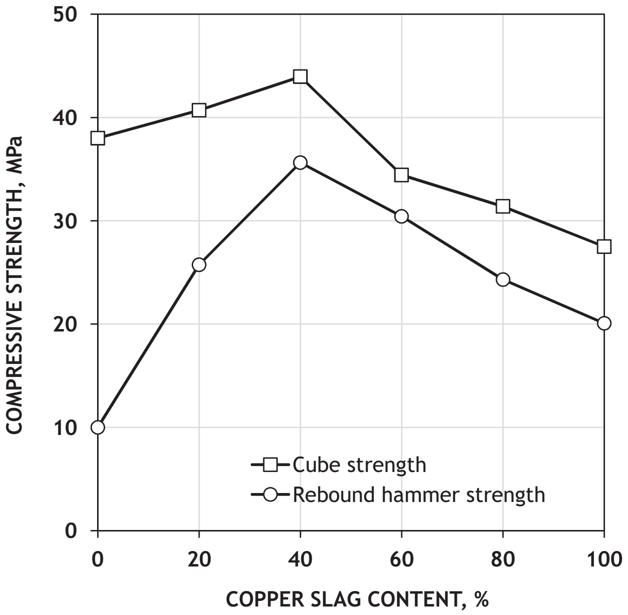

Figure 4.17 Compressive strength of copper slag concrete obtained from rebound hammer test and cube crushing test.
Data taken from Tamil et al. (2014).

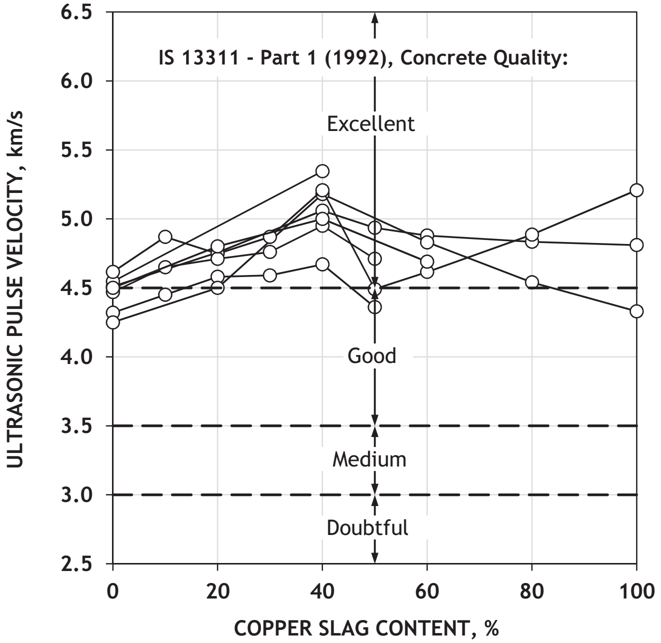

Figure 4.18 Ultrasonic pulse velocity of concrete made with copper slag.
Data taken from Brindha et al. (2010), Gupta et al. (2012), Madhu and Venkataratnam (2015), Khan et al. (2015a,b), Tamil et al. (2014), Thomas et al. (2012), and Velumani and Nirmalkumar (2014).

4.7 Permeation

Permeation, in the form of absorption, permeability or diffusion, plays an important role in determining the resistance of concrete to the potential deterioration from the ingress of water, aggressive ions and gases. Permeation is closely associated with the nature of pore structure, of which the volume and interconnectivity of pores are more important. This means that both the hydrated cement paste and the particle packing of aggregates are the key factors in determining the permeation characteristics of concrete.

A study of the available data on water absorption measurements broadly suggests that the use of CS as a component of sand affects the water absorption of concrete in two different ways: the water absorption decreases with increasing CS content up to 100% (Mithun and Narasimhan, 2016; Pazhani, 2010; Thomas et al., 2012), as shown in Figure 4.19(a), or the improvement is limited to 40% CS content, followed by a sharp increase in water absorption (Brindha et al., 2010; Rajkumar et al., 2015; Velumani and Nirmalkumar, 2014), as shown in Figure 4.19(b). In general terms, this is similar to the behaviour observed with the stability of fresh concrete in the form of bleeding and segregation and the strength of hardened concrete, as described previously in

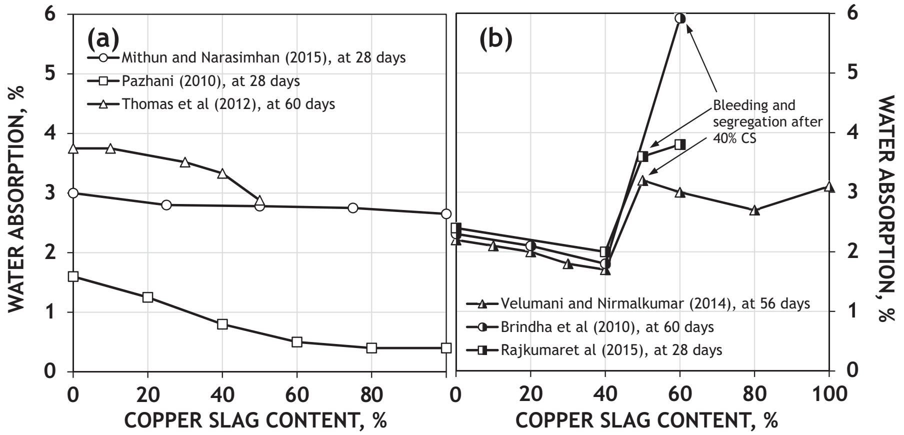

Figure 4.19 Influence of copper slag (CS) on water absorption of concrete showing (a) reduction as CS content is increased and (b) a sharp increase after 40% CS.

Sections 4.3.2 and 4.4, respectively. Other aspects that support the observed water absorption measurements also tend to link them to the manner with which the apparent porosity of the mixes changes with the addition of CS.

The possible explanation for the observed CS effects on the water absorption of concrete is associated with the aggregate particle packing, and this is supported by the study undertaken by Mithun and Narasimhan (2016), which shows little change in water absorption with incremental CS replacement of natural sand up to 100% [Figure 4.19(a)]. In this case, the mixes have been designed on a volume basis, as opposed to the commonly used weight basis; the natural and CS sands essentially have similar grading with fineness moduli of 2.59 and 2.61, respectively, and the porosity of the two concretes measured at the ages of 28 and 90 days was well within the experimental error, as shown in Table 4.7. Although with the other studies in Figure 4.19(a) the relevant supporting data are missing, a small reduction in the water absorption observed with increasing CS content is likely to be due the improvement in the particle packing of aggregates.

Table 4.7 Total porosity of concrete containing copper slag

Copper Slag, %	Total Porosity, %	
	28 days	90 days
0	8.8	8.0
25	8.8	7.9
50	9.0	8.0
75	8.4	8.2
100	8.4	8.0

Based on Mithun and Narasimhan, 2016.

The particle packing in concrete with the introduction of increasing CS content, for several reasons, can vary, and Figure 4.19(b) illustrates a different outcome to that observed in Figure 4.19(a). However, it would appear that the appearance of instability of the mix is a good indication that further increase in CS content is unlikely to be desirable, as can be seen in Figure 4.19(b), where the use of CS in excess of 40% is seen to result in unstable concrete and a sharp decline in its quality.

Initial water absorption measured in accordance with BS 1881-208 (1996) has also been used to assess the effect of CS as sand on concrete, and the absorption measurement taken at 10 min (ISAT-10), which is the most commonly used time interval in practice, has been adopted. Two groups of researchers from Oman and India have provided data with CS content as a component of sand varying from 0% to 100% and with test mixes designed on the basis of equal water/cement ratio (Al-Jabri et al., 2009b, 2011; Khan et al., 2015a,b) and equal consistence (Al-Jabri et al., 2009a), as shown in Figure 4.20. Whilst the variations in ISAT-10 with CS content, in principle, are similar to those discussed previously, the results obtained with the equal consistence mixes (Al-Jabri et al., 2009a) are encouraging in suggesting that CS can be used at up to 100% as a sand component, without negatively impacting the porosity of the concrete, as implied by the initial water absorption measurements.

The sorptivity test measures the rate of capillary rise absorption of a specimen which is partly in contact with water. The sorptivity results of concrete in Table 4.7, taken at the age of 2 and 3 months, with CS content varying from 0% to 100% and water/

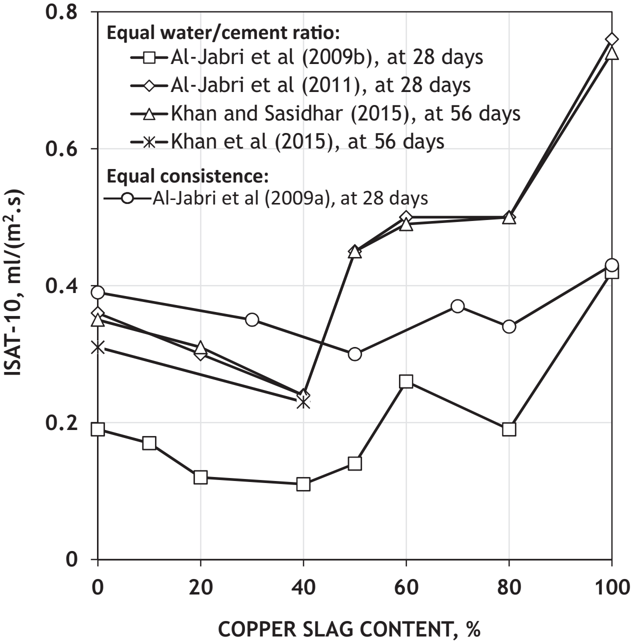

Figure 4.20 Initial surface absorption at 10 min of concrete made with copper slag.

Table 4.8 Influence of copper slag on water permeability of self-compacting concrete

Copper Slag, %	Coefficient of Permeability, $\times 10^{-13}$ m^2/s
0	2.43
50	1.98
100	1.89

cement ratios of 0.40 and 0.45, determined in accordance with ASTM C1585 (2004), are generally similar to those of ISAT-10 and largely reflect the particle packing of the fine aggregate used and how this varies with the introduction of CS as sand.

The transportation of a fluid into concrete under a pressure gradient is referred to as permeability. This mechanism is relevant to marine and dam concrete structures subjected to deep water submersion. Shoya et al. (1999), using self-compacting concrete (SCC) and measuring water permeability, and De Schepper et al. (2015), using normal concrete and measuring air permeability, observed that the use of CS as a sand component up to the full replacement level should not significantly alter the water and air permeability of concrete, as shown in Table 4.8 and Figure 4.21, respectively.

Diffusion refers to the transportation of a fluid into concrete under a concentration gradient. As the test is difficult to perform and most laboratories are unlikely to be equipped with such facilities, it is not surprising that there are no actual test results reported for the diffusion characteristics of concrete made using CS as a sand component. However, it has been suggested by Dhir (2009), in relation to the use of WCS as sand in concrete, that providing that the WCS complies with the concrete sand standard specifications, and the concrete mix is thoughtfully designed, the use of WCS can be treated as natural sand and it should not adversely affect the diffusion of the resulting concrete.

4.8 Durability

In addition to being of sufficient strength to sustain applied loads, concrete is also required to be durable during its service life. Given the physical and chemical nature of CS, and provided that good concrete practice is adopted in the specifying, manufacturing and curing of concrete, the use of CS as sand should not adversely affect the durability of concrete. It would nonetheless be prudent to confirm this before the use of CS in concrete is fully adopted. This section discusses the information available on the durability performance of concrete using CS as the sand component.

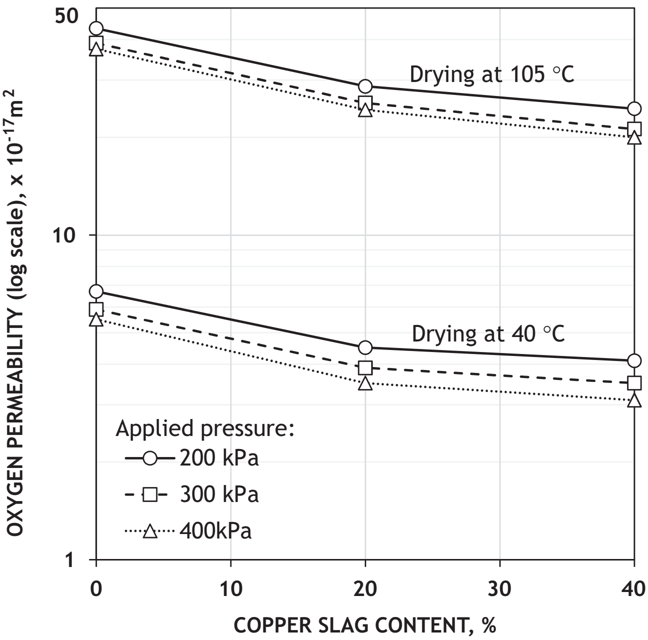

Figure 4.21 Oxygen permeability of copper slag concrete under different pressures at different saturation degrees.
Data taken from De Schepper et al. (2015).

4.8.1 Carbonation

Carbonation reduces the alkalinity of concrete through neutralization of $Ca(OH)_2$ and this can result in the removal of a protective passivation layer of steel reinforcement and eventually lead to its corrosion in the presence of water and oxygen. As carbonation is a slow process, it is commonly measured with accelerated tests using high CO_2 concentration exposure in a controlled relative humidity and temperature environment. The depth of carbonation is determined using phenolphthalein solution.

Studies have been undertaken to measure the carbonation of concrete containing CS up to full replacement of sand, and with water/cement ratio and strength that comply with the mix limitations specified in BS EN 206 (2013) for exposure classes XC1 to XC4. The results are summarised in Table 4.9 and are all very positive for the use of CS as sand in structural concrete. In two cases, CS was the sole sand used, and though some bleeding and segregation at constant water/cement ratio may be expected, because of its reduced water demand, this should not adversely affect the carbonation resistance of the CS concrete mixes.

Table 4.9 Carbonation of concrete made with copper slag and natural sand

References	W/C	Curing, Days	Exposure Conditions	CS, %	Carbonation Depth, mm
Ayano and Sakata (2000)	0.55	14	20% CO_2, 30°C, 60% RH (for 110 days)	0	28.0
				100	20.0
De Schepper et al. (2015)	0.45	26	10% CO_2, 20°C, 60% RH (for 84 days)	0	0.2
				20	Not detected
				40	0.5
Shoya et al. (1999) and Tokuhashi et al. (2001)	0.55	-	5% CO_2, 30°C, 60% RH (for 91 days)	0	7.0
				50	6.8
				100	6.8
Tam (2001) [a]	0.50	-	6% CO_2, temperature not given, 65% RH (for 490 days)	0	-
				30	Up to 5 mm higher than normal concrete

CS, copper slag; *RH*, relative humidity; *W/C*, water/cement ratio.

[a] Data based on Wee et al. (1999).

4.8.2 Chloride Ingress

Chlorides may be present in concrete through its constituent materials and/or the ingress of external media such as seawater and de-icing salt. The presence of chlorides in reinforced concrete can be harmful as it can lead to the corrosion of steel reinforcement and result in concrete cracking, spalling and delaminating and ultimately a loss of structural integrity.

Limits are in place in most national, regional and international standards for the maximum allowable chlorides in both aggregates for concrete and structural concrete, such as BS EN 12620:2002+A1 (2008) and BS EN 206 (2013), respectively. In general, the majority of literature dealing with the use of CS in concrete has reported its water-soluble chloride content to be less than 0.01%, the maximum limit specified in BS EN 12620:2002+A1 (2008). This suggests that the use of CS should not present any concern on the grounds of build-up of chlorides in concrete. For reinforced and prestressed concretes, the maximum chloride limits are 0.2–0.4% and 0.1–0.2%, depending upon the type of cement used (BS EN 206, 2013).

Tests on concrete made with CS as sand have been performed in several studies, mainly using the rapid chloride penetration test (RCPT), in accordance with ASTM C1202 (2012), which is simple and cheap and provides results in 6 h. It is an indirect test and

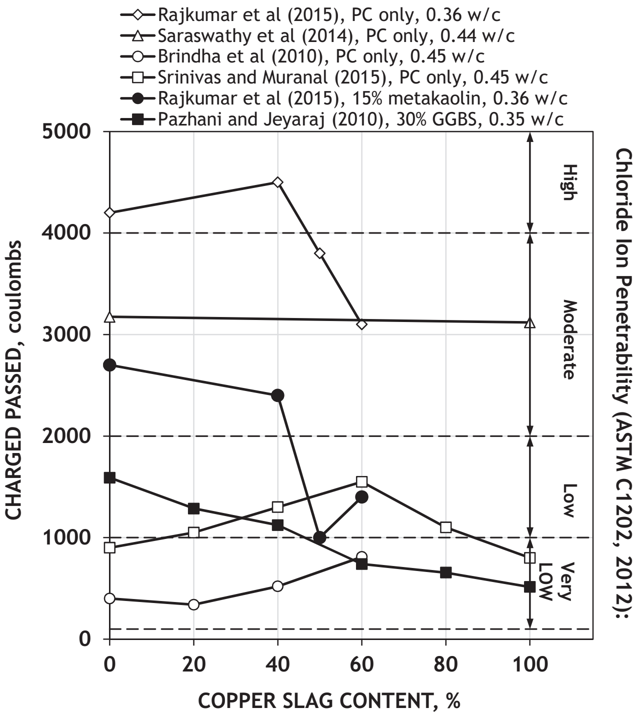

Figure 4.22 Influence of copper slag on chloride resistance of concrete. *GGBS*, ground granulated blast furnace slag; *PC*, portland cement; *w/c*, water/cement ratio.

relies on the correlation between total electric charge passed (in coulombs) through concrete and its resistance to ion penetration. The results obtained for concrete test specimens made with and without pozzolanic cement and water/cement ratios ranging from 0.35 to 0.45, which are well within the limits for the exposure classes XD (chloride-induced corrosion from seawater) and XS (other than from seawater) in BS EN 206 (2013), are shown in Figure 4.22. The results show that for the concrete mixes made with Portland cement (Brindha et al., 2010; Rajkumar et al., 2015; Saraswathy et al. 2014 and Srinivas and Muranal, 2015) the use of CS does not significantly alter the RCPT measurements. However, where pozzolanic cements are used (Pazhani, 2010; Rajkumar et al., 2015) with CS there is a continuous improvement with increasing CS content of the test mixes.

Two studies, De Schepper et al. (2015) and Mithun and Narasimhan (2016), adopted the Nordic chloride ion diffusion test methods, NT Build 492 (1999) and NT Build 443 (1995), respectively, and found that the use of CS up to full replacement of natural sand did not significantly affect the original chloride diffusion coefficient on the order of 10^{-13} m^2/s. This confirmed the earlier results showing that the use of CS as a component of sand is unlikely to change the resistance of concrete to chloride penetration.

4.8.3 Corrosion of Reinforcement

As the resistance of concrete to carbonation and chloride ingress is generally unaffected by the use of CS as a sand component up to full replacement of natural sand, the risk of steel reinforcement in concrete with such an application of CS should also not be affected significantly.

No information could be found to confirm this for carbonation-induced corrosion. In the case of chloride-induced corrosion of reinforcement in concrete, the RCPT results of Brindha et al. (2010) in Figure 4.22 show some increase for concrete mixes having constant water/cement ratio with 40% and 60% CS used as sand whilst remaining within the very low level of chloride ion penetrability classification by ASTM C1202 (1202). Some studies (Brindha et al., 2010; Naganur and Chetan, 2014; Srinivas and Muranal, 2015) show that the reinforcement corrosion rate increases with the incorporation of CS. However, the CS used was coarser and in some cases it was used on a mass replacement basis. This, together with the expected increase in consistence and the risk of bleeding and segregation in concrete mixes using CS with a constant water/cement ratio (Sections 4.3.1 and 4.3.2), particularly with CS being of coarser grading than the natural sand, will adversely affect the porosity of concrete and, in this case, increase the susceptibility of concrete to faster ingress of chlorides and the corrosion of reinforcement. This deviation from the expected outcome of CS concrete is due to the adverse particle packing effect rather than the inherent characteristics of CS.

4.8.4 Acid Attack

Portland cement-based concretes are vulnerable to acid attack and it is generally acknowledged that, for a given acid strength severity of attack, the acid attack resistance is not greatly influenced by the strength of the concrete. The results of various studies, using different cement types, H_2SO_4 acid strengths, water/cement ratios and test durations can be observed in Figure 4.23. With a number of variables involved, the only point that emerges from this figure as common to all is that the depth of attack increases with CS content. The results of Mithun and Narasimhan (2016) are particularly interesting in this respect, as with the modulus of fineness of sand, the porosity of concrete and its strength being constant, the study is able to suggest that the presence of CS increases the intensity of the acid attack. As the sulphuric acid leaching technique has been used in metal recovery from CS (Wang et al., 2013), this probably explains the low resistance of CS to H_2SO_4 acid attack.

4.8.5 Sulphate Attack

Calcium, sodium and magnesium sulphates occur widely in soils, groundwater and seawater. Their contact with concrete foundations and underground and marine structures can be a matter of some concern, as the reactions between sulphates and hydrated cement compounds result in volume increase and build-up of internal stresses, leading to the breakdown of structures.

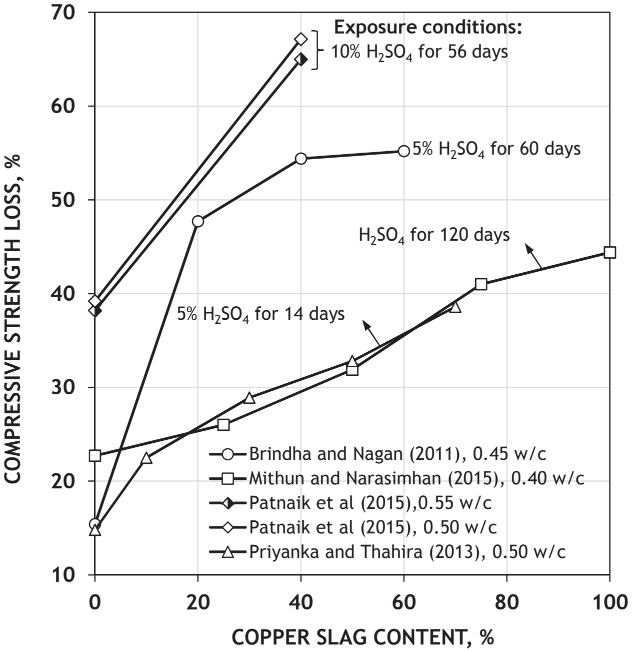

Figure 4.23 Influence of copper slag on acid resistance of concrete. *w/c*, water/cement ratio.

Like most chemical attacks, sulphate attack on concrete is essentially dependent on the type of cement used and the quality of hardened cement paste and, all things being equal, aggregates do not play any part in the process. The results available for specimens tested in up to 10% sodium sulphate and magnesium sulphate solutions are summarized in Table 4.10.

As to be expected, the use of CS as a sand component up to full replacement of natural sand does not adversely affect the resistance of concrete to sulphate attack, even where the test specimens are exposed to the rapid deterioration mode of alternating saturation in sulphate solution and drying [Table 4.10(a)]. The results of Mithun and Narasimhan (2016) are of particular interest, as the fineness moduli of natural sand and CS at full replacement were essentially similar and both sets of concrete mixes showed no sign of bleeding and segregation in the fresh state and had almost similar porosity and strength in the hardened state.

4.8.6 Freeze–Thaw Resistance

Upon freezing, the volume of ice is 9% greater than that of water. For a saturated concrete, this volume expansion creates internal pressure and enlarges the locations where further water can be frozen, and eventually successive freeze–thaw cycles can lead to distress in the concrete, such as surface scaling, pop-outs, D-cracking and internal damage. The use of entrained air in concrete produces protection against freeze–thaw attack.

Table 4.10 Compilation of the studies on sulphate resistance of copper slag concrete

References	Parameters, Testing Conditions, Results
(a) Alternating Saturation in Sulphate Solution and Drying	
Ayano and Sakata (2000)	**Parameters**: 0% and 100% CS; 0.55 w/c **Testing conditions**: Alternate wetting in 5% Na_2SO_4 solution and drying for 48 weeks **Dynamic Young's modulus**: The relative changes in the modulus for both CS and normal concrete were the same **Weight**: Both CS and normal concrete showed almost no change in weight loss
Brindha et al. (2010)	**Parameters**: 0–60% CS; 0.45 w/c **Testing conditions**: Alternate wetting in 5% Na_2SO_4 and 5% $MgSO_4$ solution and drying process for 60 days **Compressive strength**: Although CS concrete showed higher relative strength loss after exposure, the remaining strength was still higher than that of the normal concrete
Hwang and Laiw (1989)	**Parameters**: 0–100% CS; 0.42, 0.51 and 0.62 w/c **Testing conditions**: Alternate wetting in Na_2SO_4 and drying for 10 cycles **Results**: No noticeable sulphate attack was observed
(b) Submerging in Sulphate Solution	
Mithun and Narasimhan (2016)	**Parameters**: 0–100% CS; 0.32 w/c **Testing conditions**: Immersing in two solutions, 10% Na_2SO_4 and 10% $MgSO_4$, for 12 months **Compressive strength**: Both CS and normal concrete showed no strength deterioration in Na_2SO_4 solution but experienced similar strength reductions in $MgSO_4$ solution
Patnaik et al. (2015)	**Parameters**: 0% and 40% CS; 0.55 and 0.50 w/c **Testing conditions:** Immersing in 10% Na_2SO_4 for 2 months **Compressive strength**: Both CS and natural concrete showed no loss in strength **Weight**: Both CS and natural concrete showed no loss in weight
Tam (2001) [a]	**Parameters**: 0% and 30% CS; 0.50 w/c **Testing conditions**: Immersing in Na_2SO_4 for 8 months **Visual observation**: CS had no influence on sulphate resistance

CS, copper slag; *w/c*, water/cement ratio.

[a] Data based on Wee et al. (1999).

The effects of CS as a sand component on the freeze–thaw resistance of concrete have been studied by a few researchers, mainly from Japan, as well as one from Belgium. The relevant information including mix parameters, testing conditions and the experimental results is provided in Table 4.11.

Except for De Schepper et al. (2015), in which the specimens used were non-air-entrained, the level of air entrainment in all other studies was in the range of 3–8%, but predominantly at 5%. No one clear trend could be identified. This is not surprising given the problems that are associated with the process and quality of air entrainment, as well as the variability in the methods used for the measurement of the results.

4.8.7 Abrasion

In some concrete applications, the surface of concrete is subjected to wear damage in the form of rolling, scrapping and sliding, which detaches materials from the surface. This deterioration is common in pavements and industrial floorings that are exposed to abrasion and impact from wheeled traffic and machinery. Similar damage, which is known as erosion, can also occur in hydraulic structures due to the solids content of flowing water.

The abrasion resistance of concrete made with processed and unprocessed CS as a component of sand, measured in accordance with Indian Standard IS 1237 (2012), was found to increase with CS content (Mithun et al., 2015a). As CS is a strong and hard material (6–7 Mohs hardness), its use as a sand replacement can be expected to increase the abrasion resistance of concrete, as shown in Figure 4.24. The presence of weaker friable matter within CS would adversely affect its abrasion resistance.

4.9 High-Performance Concrete

For a normal day-to-day supply of concrete, provided that good concrete practice is adhered to, the concrete is generally of sufficient quality to comply with the main construction requirements. However, in some applications, concrete with special attributes, termed high-performance concrete (HPC), is required to comply with challenging specifications. The materials used in HPC are essentially similar to those of normal concrete, but HPC is normally made with a high proportion of pozzolanic and/or slag cements, good quality aggregate and high-range water-reducing admixtures. The use of CS as a sand component in high-strength, high-durability and self-compacting concrete is discussed in this section.

4.9.1 High-Strength Concrete

Although Eurocode 2 (2004) provides design guidance on the mechanical properties of concrete with characteristic cube strength of up to 105 MPa, there is no definite point at which concrete is considered to have high compressive strength (high-strength

Table 4.11 Compilation of studies on the freeze–thaw resistance of copper slag concrete

References	Parameters, Testing Conditions and Results
Ayano and Sakata (2000)	**Parameters**: 0% and 100% CS; 0.55 w/c; 4.5 ± 1% target entrained air **Testing conditions**: Alternate freezing at −30°C and thawing at 100°C for up to 30 cycles **Dynamic Young's modulus**: CS concrete was broken after 30 cycles whilst normal concrete was broken after 20 cycles
De Schepper et al. (2015)	**Parameters**: 0–40% CS; 0.45 w/c; 2.8% air (normal concrete), 1.2% and 2.2% air (CS concrete) **Testing conditions**: Based on Appendix D of NBN EN 1339 (2003), 28 freeze–thaw cycles, freezing medium contained 3% NaCl de-icing agent **Surface scaling**: The amount of scaled material of both CS and normal concrete exceeded the limit of 1 kg/m^2, as per NBN EN 1339 (2003)
Shoya et al. (2003)	**Parameters**: 0–100% CS; 0.55 w/c; 4% and 5% target entrained air **Testing conditions**: Based on ASTM C666 (1992) Procedure A, 300 freeze–thaw cycles **Dynamic Young's modulus**: The relative reduction of the modulus of CS concrete was greater than that of normal concrete after 300 cycles
Shoya et al. (1997)	**Parameters**: 0% and 100% CS; 0.55, 0.60 and 0.65 w/c; 3, 5 and 8% target entrained air **Testing conditions**: Based on ASTM C666 (1992) Procedure A, 300 freeze–thaw cycles **Durability factor (DF)**: CS concrete showed lower DF due to excessive bleeding
Shoya et al. (1999)	**Parameters**: 0% and 100% CS; 0.55 w/c; 5% target entrained air **Testing conditions**: Based on ASTM C666 (1992) Procedure A, 300 freeze–thaw cycles **Durability Factor**: The DF of CS concrete was higher than that of normal concrete
Tokuhashi et al. (2001)	**Parameters**: 0% and 100% CS; 0.55 w/c; 4 and 5% target entrained air **Testing conditions**: Based on ASTM C666 (1992) Procedure A, 300 freeze–thaw cycles **Durability Factor**: The DF of CS concrete was lower than the natural concrete at 4% target entrained air; however, both concretes showed similar DF at 5% target entrained air

CS, copper slag; *w/c*, water/cement ratio.

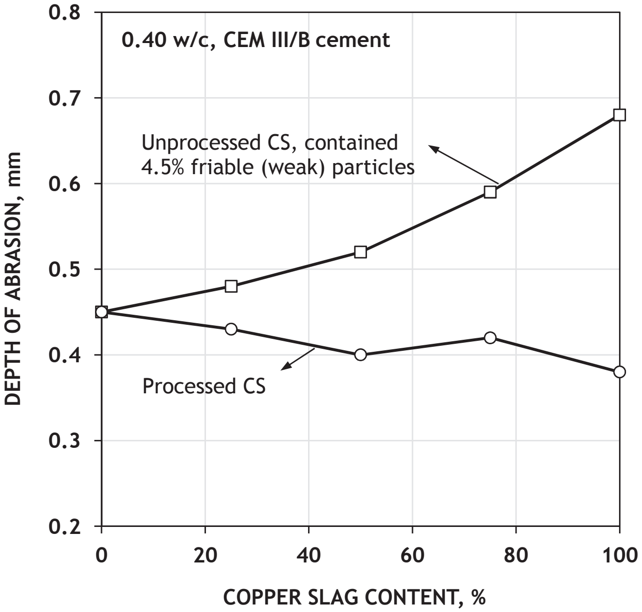

Figure 4.24 Depth of abrasion of concrete made with processed and unprocessed copper slag (CS). *w/c*, water/cement ratio.

concrete; HSC). According to Technical Report 49 of the Concrete Society in the United Kingdom, published in 1998, HSC is to have a characteristic cube strength between 60 and 100 MPa (Concrete Society, 1998). In the United States, ACI CT (2013) defines HSC as having a characteristic strength of 55 MPa or greater.

Attention has been drawn earlier to the ability of CS both to reduce the water demand of concrete mix (Section 4.3.1) and to retard the early age strength development (Sections 4.3.5 and 4.4.1). Both these effects increase as the proportion of CS used as a replacement for sand is increased, and it is the manner in which a concrete mix is designed that virtually determines its potential for developing high strength.

Al-Jabri et al. (2009a,b) carried out two sets of studies using up to 100% CS as sand replacement by keeping the water/cement ratio constant at 0.35 and by keeping the mix consistence constant where the water/cement ratio was reduced to 0.25. With the latter approach to mix design, the 28-day strength increased from 88.0 to 107.5 MPa for 400 kg/m^3 Portland cement and 44 kg/m^3 silica fume. The other mix exhibited an increase in slump from 30 to 150 mm, increase in bleeding and segregation and drop in strength from 88.0 to 78.0 MPa. Similarly, large reductions in strength with the constant water/cement ratio design approach were reported by Wu et al. (2010a,b).

In a 2015 study, Lye et al. (2015) reported the attainment of 100 MPa 28-day strength of concrete having 160-mm slump and made with 465 kg/m^3 Portland cement and full replacement of natural sand with CS.

4.9.2 Self-Compacting Concrete

SCC should flow like a liquid yet maintain its homogeneity and achieve full consolidation without the need for compaction. Such a concrete was known to be first developed in Japan. The three key fresh properties of SCC are filling ability, passing ability and resistance to segregation, and different test methods have been developed to assess the fresh properties of SCC, such as those covered in BS EN 12350-8 (2010), BS EN 12350-9 (2010), BS EN 12350-10 (2010), BS EN 12350-11 (2010) and BS EN 12350-12 (2010).

Table 4.12 summarises the fresh properties of SCC mixes made with 0%, 50% and 100% CS, tested by Shoya et al. (1999, 2003) and Tokuhashi et al. (2001). All the SCC mixes contained 45% limestone powder as filler and had a fixed water/cement ratio of 0.55. The particle size distribution of the aggregates used in all the mixes was, for practical purposes, sufficiently close and they had fineness moduli within the range of 2.20–2.55 and no bleeding and segregation of the mixes was reported. The fresh concrete measurements for the two sets of concrete can be regarded as essentially similar, except for mixes with 100% CS, which showed a little less flowability. The reported strength results of the mixes with and without CS were exceptionally similar within the range of 41–45 MPa.

Additionally, in the hardened state for each specific study, the following observations were made:

(i) Shoya et al. (1999): Concrete mixes made with 0%, 50% and 100% CS as sand had similar drying shrinkage, permeability and carbonation resistance and additionally showed higher durability factors in the freeze–thaw tests.

(ii) Shoya et al. (2003): Concrete mixes made with 0%, 50% and 100% CS had similar tensile strengths and CS concrete had better freeze–thaw resistance than the corresponding concrete made with natural sand.

(iii) Tokuhashi et al. (2001): Concrete mixes made with natural sand and CS sand had similar drying shrinkage, permeability and carbonation resistance. Freeze–thaw resistance was similar for both sets of concrete when entrained air content was 5%, but at the slightly lower value of 4% air entrainment, the concrete made with 100% CS had lower resistance than the corresponding reference concrete.

Table 4.12 Fresh properties of self-compacting concrete made with copper slag

	Copper Slag Content, %		
Property	**0**	**50**	**100**
Slump flow, mm	700	700–710	720
Time taken to reach 500 mm flow, s	7	5	5
V-funnel flow time, s	12–14	11	8–9
Filling height, mm	300	340	340

4.9.3 High-Durability Concrete

Some attempts have been made to test the suitability of CS use in designing high-durability concrete. A study by Khan et al. (2015b) focused on the assessment of the effects of CS use on the permeation characteristics of concrete. The test mixes were designed using 0% and 40% CS as sand, and silica fume as an addition at the rate of 7.5%, on the basis of constant water/cement ratio of 0.40. The results of initial surface absorption and sorptivity tests showed that the use of CS sand does not adversely affect the permeation of concrete.

In another study, Rajkumar et al. (2015), using CS as sand component at 0%, 40%, 50% and 60% with metakaolin addition at rates of 5%, 10% and 15%, the concrete mixes designed at a water/cement ratio of 0.36 showed that CS can be used in producing high-durability concrete. The studies undertaken by Ambily et al. (2015) and Sabarishri et al. (2015), with CS sand content varying from 0% to 100%, also confirmed the suitability of CS use as sand in producing high-durability concrete.

4.10 Copper Tailings

Copper tailings are beginning to draw attention for their possible use as a sand component in concrete. A series of laboratory tests undertaken by Thomas et al. (2013), using up to 60% copper tailings as part of sand, showed that the performance of concrete mixes designed at water/cement ratios of 0.40, 0.45 and 0.50 improved with the use of copper tailings up to 30% for compressive strength, flexural strength, pull-off strength, drying shrinkage, water permeability and abrasion resistance. The durability of concrete in terms of chloride resistance, sulphate resistance and alkalinity was reported not to be affected by the use of copper tailings. As the particle size of copper tailings is generally fine, having a fineness modulus of about 1.60, the material may possibly be used as a filler in concrete and this could open up the scope for further research in this area.

4.11 Environmental Impact

CS is one of the 20 specific mineral processing wastes, including copper tailings and iron blast furnace slag, that have been categorised since 1991 as non-hazardous waste by the US Environmental Protection Agency (US EPA, 1991). Although CS is unlikely to pose any threat to the environment, the understanding of its leaching behaviour when used as a sand component in concrete would help to confirm that CS remains unharmful.

The leached element concentration data for CS in different solutions, namely distilled water, tap water, acid rain and seawater, obtained using the well-known Toxicity Characteristic Leaching Procedure (TCLP) Method 1311 (US EPA, 1992) are presented in Table 4.13, together with the corresponding US EPA regulatory levels given in Document 40 CFR 261.24 (US EPA, 2012) for classification of hazardous waste.

The leached element concentrations of CS in the standard condition are well below the US EPA regulatory limits in Document 40 CFR 261.24 (US EPA, 2012), confirming that the material is non-hazardous (Table 4.13). Similar results were also observed when CS was subjected to a more aggressive condition, namely acid rain and seawater solutions for a 6-month leaching period (Table 4.13).

The leaching of concrete containing up to 100% CS as sand, having a 0.4–0.6 water/cement ratio, and cured for up to 150 days was measured by Cheong et al. (2007), Brindha and Nagan (2010b) and Saraswathy et al. (2014). The experimental variables such as CS content, water/cement ratio, curing age, leaching method and tested elements, as well as the main observations emerging from the tests, are given in Table 4.14. All the leached concentrations of the elements regulated for toxicity characteristics by US EPA (2012), such as As, Ba, Cd, Cr and Pb, were found to be well below the allowable limits regardless of the leaching method used.

Table 4.13 Toxicity characteristic leaching procedure results of copper slag using different solutions

		Leached Concentration, mg/L			
		Cheong et al. (2007)	Saraswathy et al. (2014)		
Element	US EPA Regulatory Level, mg/L	TCLP	In tap water[a]	In acid rain[a]	In seawater[a]
As	**5**	0.227	0.389	0.334	0.745
Ag	**5**	-	N.D.	N.D.	N.D.
Ba	**100**	0.981	-	-	-
Ca	**N.R.**	50.6	-	-	-
Cd	**1**	0.068	0.029	0.003	0.007
Cr	**5**	0.136	N.D.	N.D.	N.D.
Cu	**N.R.**	23.42	0.107	0.931	0.239
Fe	**N.R.**	85.77	-	-	-
Hg	**5**	-	N.D.	N.D.	N.D.
Mn	**N.R.**	0.734	N.D.	N.D.	N.D.
Ni	**N.R.**	0.064	-	-	-
Pb	**5**	0.797	N.D.	N.D.	N.D.
Zn	**N.R.**	23.32	-	-	-

ND, not detected; *NR*, not regulated; *TCLP*, toxicity characteristic leaching procedure.

[a] Copper slag was mixed with the solution and allowed to stand for a 6-month leaching period.

Table 4.14 Leaching studies of concrete made with copper slag

References	Experimental Variables	Main Observations
Cheong et al. (2007)	**Concrete design**: 0–100% CS; 0.4–0.6 w/c; 28, 91 days curing **Method**: TCLP (US EPA, 1992) **Tested elements:** As, Ba, Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb	**Effect of w/c**: Leaching of elements is essentially the same for different w/c **Effect of curing age**: Leaching of Ba and Pb decreases with time, but that of Cu increases with time
	Concrete design: 20, 80% CS; 0.6 w/c; 91 days curing **Method**: modified extraction procedure **Tested elements**: As, Ba, Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb	**Effect of CS**: Leaching of Ba, Cu, Mn and Pb increases when CS is increased from 20% to 80%
Brindha and Nagan (2010b)	**Concrete design**: 20–50% CS; 0.43 w/c; 28 days curing **Method**: ASTM D5233-92 (2009) **Tested elements**: Ca, Cu, Fe	**Effect of CS**: Leaching of Cu increases with increasing CS content
Saraswathy et al. (2014)	**Concrete design**: 100% CS; 0.44 w/c; 150 days curing **Method**: Not known; samples were immersed in leachants of different pH[a] for 150 days **Tested element**: Cu	**Effect of pH**: Leaching of Cu does not seem to be affected by pH of leachant

CS, copper slag; *TCLP*, toxicity characteristic leaching procedure; *w/c*, water/cement ratio.
[a] Acid rainwater (pH 2.4); tap water (pH 7.2); seawater (pH 8.68).

The main points to emerge from Table 4.14 are briefly described in the following paragraphs:

1. Some of the elements tested, Ba, Cu, Mn and Pb, were found to leach from CS used as sand, with leached concentration increasing when the CS sand content in the concrete test specimens was increased (Brindha and Nagan, 2010b; Cheong et al., 2007).
2. Whilst some leached concentration values of CS in concrete were affected by the age of the concrete, this was observed only for Ba and Pb, which were found to decrease with increasing concrete curing age from 28 to 91 days; however, the opposite was observed for Cu (Cheong et al., 2007).
3. The leaching of CS as sand in concrete was not influenced by the water/cement ratio of the concrete (Cheong et al., 2007).
4. Saraswathy et al. (2014) tested the leaching behaviour of only elemental Cu and the results did not show any consistent leaching behaviour as the pH of the leachant was varied, using acid rainwater (pH 2.4), tap water (pH 7.2) and seawater (pH 8.68), even though CS is known to be more prone to leaching in a highly acidic environment.

4.12 Case Studies

The use of CS as a sand component in concrete blocks and in structural and non-structural concrete applications is summarised in Tables 4.15(a) and (b), respectively. These case studies are largely from Singapore and a few from the United Kingdom and Portugal. Moreover, the information provided in the literature for each case is very brief and the field assessment data for CS concrete are not available.

Although not much relevant field experience can be learnt, the limited available information does provide a good summary of the development of using CS in the construction industry. Although a great deal of work has been undertaken to study the properties of concrete made with CS since 1989 in Taiwan (Hwang and Laiw, 1989), and probably its first concrete application was initiated in 1996 for the construction of a five-storey office building in Singapore (Wee et al., 1996), the material started to become relatively more commonly discussed and used in the construction industry only at the end of the first decade of the 21st century (Table 4.15).

One interesting point to note in Table 4.15 is that the quantity of CS used as replacement for natural sand in Singapore has increased over the years, from 15% WCS used in the construction of an office building in 1996 to 30% and 50% WCS used in non-structural elements in 2009 and 2011, respectively. Additionally, its use in conjunction with coarse recycled concrete aggregate in concrete seems to be a recent phenomenon, and as such, concrete has been used in the construction of two commercial offices in 2009 and 2011 (BCA, 2012). This suggests that the confidence level of using WCS in the construction industry has improved with time, which is mainly due to the drive from the local authority, the Building and Construction Authority, in promoting resource efficiency in an endeavour to achieve zero landfill policies (BCA, 2008, 2012).

4.13 Conclusions

Owing to its low porosity, high hardness and hydrophobic nature, as a granular material CS could be an ideal material for use as sand in concrete to comply with specified requirements for consistence, strength and durability. Its low water demand offers several benefits and potential for new innovative developments, for example, improving consistence, reducing cement content of mixes, developing HPC in terms of its fresh and hardened concrete properties, as well as durability.

In the fresh state, the improvement of the consistence of concrete has been found to be related to the proportion of CS used as a sand component. This should be weighed against the risk of concrete bleeding and segregating, especially at a high level of CS replacement of natural sand, where particle size and distribution of the materials can assume importance to protect the concrete from becoming unstable, and its initial and final setting times prolonged. The published literature showed a great deal of indifference in this respect. This offers considerable scope for improvement in the current practice and for exploiting the effective use of CS as a sand component in producing concrete with the desired properties in the fresh state.

Table 4.15 Case studies involving the use of copper slag in concrete applications

	Application Details			
References	**Location**	**Year**	**Use in**	**Description**
(a) Concrete Blocks				
Cachim et al. (2009)	Portugal	2009	Concrete paving blocks	The use of 25% CS as sand does not affect the compressive and tensile strength of blocks
BCA (2011)	Singapore	Not given	Concrete blocks	WCS was used in conjunction with RCA up to 30% for the construction of concrete blocks for a non-residential building
Charcon (2012)	United Kingdom	Not given	Concrete paving blocks	CS and other wastes were used for over 50% content in the production of concrete blocks
G&W Ready-Mix (2012)	Singapore	2012	Concrete paving blocks	The strength of various types of concrete paving blocks containing WCS was found to be satisfactory
(b) Structural and Non-structural Applications				
Wee et al. (1996)	Singapore	1996	Office building	Concrete made with 15% CS was to be used in the construction of a five-storey office building
BCA (2011)	Singapore	Not given	Non-residential building	Concrete made with WCS sand and GGBS cement was used for the construction of a non-residential building
BCA (2012)	Singapore	2009	Structural and non-structural elements	Some of the structural elements of a three-storey commercial office were made with 10% WCS and 20% RCA, whilst the non-structural elements contained 30% WCS and 20% RCA
BCA (2012)	Singapore	2011	Superstructural and non-structural elements	The superstructural and non-structural elements of a four-storey commercial office contained 30% RCA and 30% WCS and 50% RCA and 50% WCS, respectively.

CS, copper slag; *GGBS*, ground granulated blast furnace slag; *RCA*, recycled concrete aggregate; *WCS*, washed copper slag.

In the hardened state, a great deal of the published data are related to concrete mixes designed on the basis of equal water/cement ratio. Whilst it can be argued that this provides a sound basis for understanding how CS may affect the performance of concrete in the hardened state, the relatively lower water demand of CS makes comparing the mixes difficult and the conclusions drawn somewhat uncertain. Notwithstanding this, concrete using CS as sand can be designed for any strength, and where necessary its early age retardation effect can be compensated for by its ability to reduce the water demand of the mix. Concrete designed using CS sand should have the corresponding estimated tensile and flexural strengths. Such a concrete for a given compressive strength should also comply easily with the estimated modulus of elasticity values, as well as creep and shrinkage strains. Although no information is available in the literature, the use of CS as sand in concrete is unlikely to adversely affect its thermal properties including under fire conditions.

In terms of durability, given the physical and chemical characteristics of CS, and provided that other important aspects are attended to, its use as sand should not in principle adversely affect the longevity of the concrete. The main aspect that will require consideration in this respect, as per normal practice, is the particle packing of the mix including CS sand that can be attained to ensure acceptable permeation behaviour, as this generally dominates the response of concrete to both physical and chemical attacks. The information available in the literature covers resistance to carbonation, chloride ingress, corrosion of reinforcement, acid attack, sulphate attack, freeze–thaw and abrasion. This can be taken to conclude that the use of CS as sand in concrete does not significantly change its durability, except for its resistance to acid attack.

Given that the incorporation of CS as sand in concrete lowers its water demand, it follows that its use will be beneficial in developing HPC in the fresh state, such as SCC, and in the hardened state, such as high-strength and high-durability concrete, though this has not been demonstrated conclusively in the literature. This offers scope for further research.

The elements leached from CS have been judged to be within the safe limits set out by the US EPA. Similar observations have been made for leaching tests on concrete containing CS as sand. CS is used in real concrete practice, though at present, this is limited to small proportions of the total sand content of the concrete mixes. The use of copper tailings as sand in concrete requires further investigations, though its use as a filler may prove to be more appropriate.

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Copper Slag in Cement Manufacture and as Cementitious Material

5

Main Headings

- Copper slag used in cement clinker manufacture
- Chemical and mineralogical composition
- Copper slag as cementitious material
- Characteristics of copper slag cement
- Performance of copper slag cement concrete

Synopsis

In this chapter, the use of copper slag (CS) as part of the raw feed in Portland cement clinker calcination or in the ground form as supplementary cementitious material is discussed. Cement produced with CS, as an iron source replacement, has shown few differences in both mechanical and durability-related performance when compared to cement manufactured with conventional raw materials. Ground CS as supplementary cementitious material exhibits mild pozzolanic activity in comparison to other conventional pozzolanas. This leads to the production of cementitious mixes with lower initial strength, yet with higher development over time and with enhanced durability. Furthermore, mixes containing CS and conventional mixes without it showed equivalent environmental impacts, in terms of leachability of heavy metals.

Keywords: Copper slag, Grindability, Clinker, Calcination, Supplementary cementitious material, Concrete, Mortar.

5.1 Introduction

Traditionally, Portland cement (PC) is manufactured using natural materials (calcareous rocks such as chalk or limestone and argillaceous rocks such as clay or shale). An increasing number of materials with the same characteristics are now being procured from more sustainable sources in response to the increasing worldwide demand for cement. In a report produced by the International Energy Agency (IEA, 2009), the projected worldwide production of cement showed that, for a low and a high demand scenario, the estimated production of cement by 2015 could be between 3.6 and 3.8 billion tonnes, and by 2050 it is likely to

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be 3.9 to 4.7 billion tonnes. However, in 2014, the European Cement Association (CEMBUREAU, 2014) estimated that the global production of cement, in that year, was of 4.3 billion tonnes, well above the initial projections.

Notwithstanding the preceding, owing to the cement industry's high CO_2 emissions and increasing concerns regarding climate change mitigation, new alternatives are being sought to reduce its carbon footprint. Consequently, in addition to cements with lower energy demands and CO_2 emissions, other approaches are being developed to improve the energy efficiency of clinker calcination (Yin et al., 2016), use alternative fuels and/or raw materials (Deolalkar, 2016), promote grinding efficiency (Sverak et al., 2013), and develop cement-based technology systems in carbon capture and storage (Siriwardena and Peethamparan, 2015).

Copper slag (CS) has been progressively looked upon as a technically viable alternative to the production of cementitious materials, either as a raw feed constituent in PC clinker production or being used separately as ground powder as a cement constituent. Given the economic, environmental and social vectors of the cement industry, the aim of this chapter is to examine the potential use of CS either as part of the raw feed for the production of PC clinker or as a constituent of cement similar to those specified in the European Standard EN-197 (2011).

5.2 Copper Slag Used in Cement Clinker Manufacture

PC is normally manufactured by heating a mixture of limestone or chalk and shale or clay to temperatures in the region of 1350–1450°C. Other materials of similar composition and sufficient reactivity are also gaining the attention of cement producers as more sustainable alternatives to those that are conventionally used. The amount of each of these raw feed materials must be carefully calculated, taking into consideration their chemical composition (i.e., silica, alumina, calcium oxide and iron oxide contents) to produce a hydraulic binder with very specific requirements. With the aim of evaluating the potential use of CS as a raw feed material in the production of clinker, it is first necessary to study its mineralogical and chemical composition, since the performance of the final product mainly depends on the particles' chemical reaction with water and how they will interact in the production of a single solid material.

5.2.1 Chemical and Mineralogical Composition of Copper Slag

The chemical composition of CS is well documented in the literature and has been dealt with in some detail in Chapter 3; it consists predominantly of iron oxides (Fe_2O_3) and silica (SiO_2) [making it a feasible substitute for ignimbrite and hematite in PC manufacture (Medina et al., 2006)], with small amounts of alumina (Al_2O_3), calcium oxide (CaO) and magnesium oxide (MgO), among other components (Gorai et al., 2003; Alp et al., 2008).

The CaO-Al_2O_3-SiO_2 ternary system is the most frequently used, and it provides a basis for a preliminary understanding of the chemistry underlying the formation of PC clinker, since it is used to predict which solid phases will be present for various bulk chemical compositions (Taylor, 1997; Kurdowski, 2014).

Figure 5.1 presents a comparison of the chemical composition of CS based on the CaO-Al_2O_3-SiO_2 ternary system with those normally observed in PC, ground granulated blast furnace slag (GGBS), fly ash (FA), silica fume (SF) and natural pozzolanas (Lothenbach et al., 2011). The diagram suggests that the chemical composition of CS resembles the one normally observed in some FA and SF because of its high silica content; however, merely comparing these components based on the CaO-Al_2O_3-SiO_2 ternary system can be misleading, considering the high amounts of iron oxide encountered in CS. Therefore it is necessary to analyse it based on the (CaO + MgO + Al_2O_3)–Fe_2O_3–SiO_2 system (Figure 5.2), so that a suitable comparison to that normally exhibited by steel slags (Douglas and Malhotra, 1987) becomes possible.

A statistical analysis of the chemical composition of 94 distinct CS samples from 67 publications can be seen in Figure 5.3 and Table 5.1 (Ali et al., 2013; Ambily et al., 2015; Gorai et al., 2003; Shi et al., 2008; Siva et al., 2014; Afshoon and Sharifi, 2014; Alp et al., 2008; Brindha and Sureshkumar, 2010; Douglas and Malhotra, 1987; Medina et al., 2006; Murari et al., 2015; Sharifi and Kaafi, 2013; Tan et al., 2000; Al-Jabri and Shoukry, 2014; Al-Jabri et al., 2002, 2011, 2009a,b, 2006; Baragano and Rey, 1980; De Schepper et al., 2015, 2013, 2014; Douglas et al., 1986; Moura et al., 2007; Nazer et al., 2013; Pavez et al., 2004; Snellings et al., 2012; Taha et al., 2004; Tixier, 2000; Wu et al., 2010; de Rojas et al., 2008; Lee et al., 2007, 2003; Lorenzo et al., 1991; Mavroulidou and Liya, 2015; Moosberg et al., 2003; Najimi and

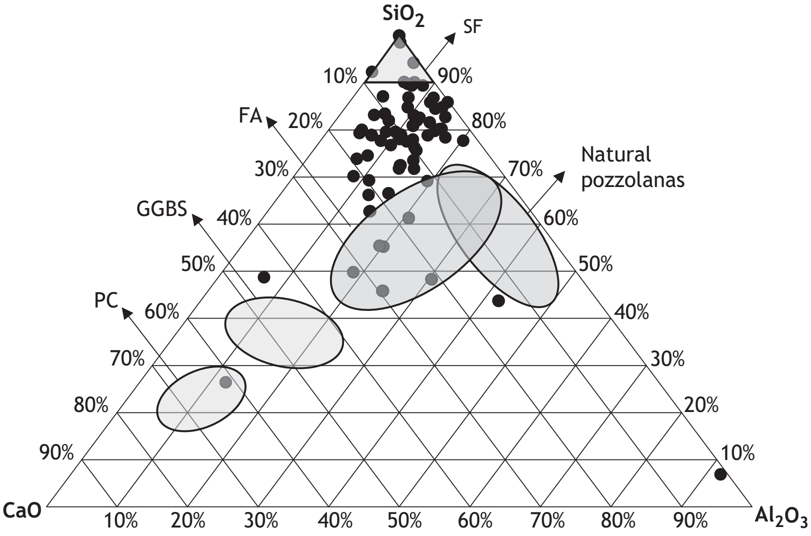

Figure 5.1 CaO–Al_2O_3–SiO_2 ternary diagrams of copper slags in comparison with those of other cement constituents. *FA*, fly ash; *GGBS*, ground granulated blast furnace slag; *SF*, silica fume.

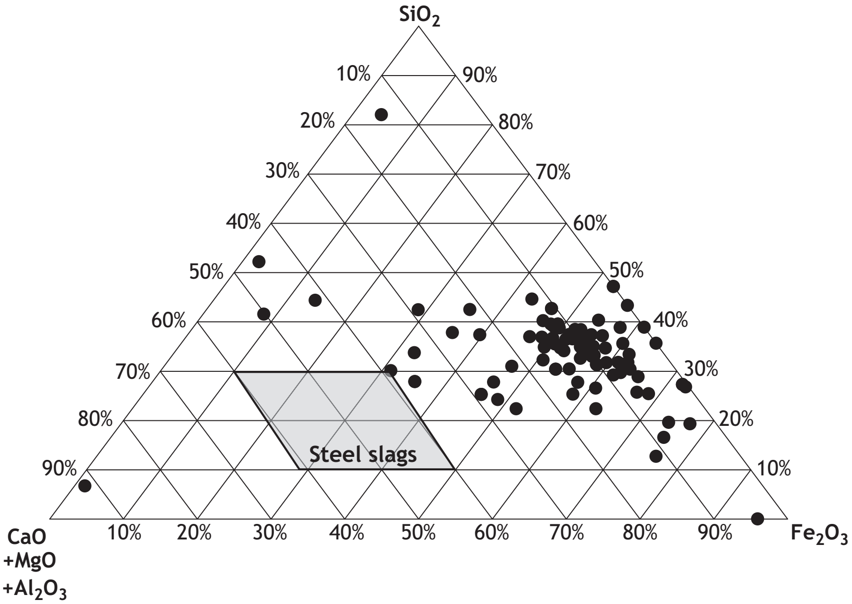

Figure 5.2 (CaO + MgO + Al_2O_3)–Fe_2O_3–SiO_2 ternary diagram of copper slags in comparison with steel slags.

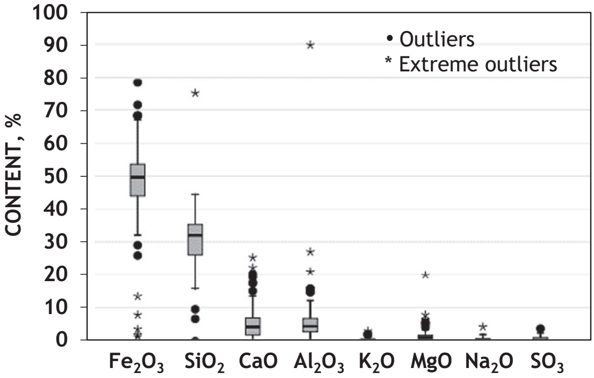

Figure 5.3 *Box* and *whisker plots* of the distribution of collected chemical data.

Pourkhorshidi, 2011; Resende, 2009; Sahu et al., 2011; Yang et al., 2010; Arino and Mobasher, 1999; Boakye and Uzoegbo, 2014; Dai, 1998; Hong, 2003; Huang et al., 2012; Kikuchi, 2001; Mobasher et al., 1996; Taeb and Faghihi, 2002; Vitkova et al., 2011; Zain et al., 2004; Lam et al., 2010; Lowinska-Kluge et al., 2011; Mohsenian and Sohrabi, 2009b; Thomas et al., 2013; Weicai and Tiandi 1993). The results showed that CS comprises 34–60% iron oxide phases, 22–39% silica, 1–11% calcium oxide and 1–16% alumina, the sum of which normally constitutes 90% of the total amount of oxide constituents present in CS.

Table 5.1 Statistical indicators for the chemical composition

Chemical Compound	Fe_2O_3	SiO_2	CaO	Al_2O_3	K_2O	MgO	Na_2O	SO_3
Mean, %	47.23	30.88	5.53	6.39	0.56	1.73	0.55	0.71
Standard deviation, %	13.82	8.59	5.28	9.86	0.65	2.49	0.72	0.78
Median, %	49.64	31.94	4.60	4.43	0.42	1.16	0.28	0.40
Interquartile range, %	9.36	8.99	5.05	3.99	0.70	1.33	0.80	1.04

Additionally, X-ray diffraction analyses of CS, carried out by various authors (Alp et al., 2008; Arino and Mobasher, 1999; Mobasher et al., 1996; Murari et al., 2015; Tixier, 2000) revealed that the majority of mineralogical species are fayalite (Fe_2SiO_4) and magnetite (Fe_3O_4). These phases are usually observed in high peak frequencies, which suggest a basically crystalline structure (Murari et al., 2015), along with the potential presence of a copper-bearing spinel ($Cu_{0.5}Mn_{0.5}Fe_2O_4$) phase in smaller amounts (Ali et al., 2013).

5.2.2 Grindability of Copper Slag

Given the relatively coarse size of CS upon its production, to use it in the manufacturing of PC clinker or as a constituent of cement, CS particles must be ground to equivalent or higher fineness than that of PC, which implies expending energy in the grinding processes, with potentially high costs involved.

Douglas et al. (1985) carried out a comparative study on the energy required to grind CS to a Blaine fineness of around 4000 cm^2/g. Their results showed that to attain this fineness, the air-cooled and quenched CS samples from various sources would have to be ground for 190–240 min. This corresponded to energy consumption of 76–96 kWh/tonne and the resulting samples exhibited 80–90% of material passing the 45-μm sieve. However, one CS sample exhibited remarkably high grinding time and energy consumption (around 600 min and 240 kWh/tonne, respectively) to achieve a Blaine fineness of around 4000 cm^2/g, comparable only to lead blast furnace slag, also evaluated in the same study. A comparison between the amounts of energy required when grinding CS with those of PC and GGBS, with similar Blaine fineness, showed that there could be an average increase in energy consumption of over 100% and 70%, respectively.

Using a different testing method, Baragano and Rey (1980) had previously observed similar trends to those of the aforementioned study. The calculated theoretical grindability of CS was 40 kWh/tonne, whilst those of GGBS and OPC were 23 and 34 kWh/tonne, respectively.

The Bond grindability index of CS, evaluated by Supekar (2007), provides quantitative data on the energy required to grind 1 tonne of CS. The results given in Table 5.2 reveal that, although CS requires similar energy input to that of GGBS, it is considerably

Table 5.2 Bond grindability index

Material	Bond Grindability Index, kWh/tonne
Copper slag (CS)	17.6
Ground granulated blast furnace slag	16.7
Portland cement (PC) clinker with 1.5% CS	10.2
Normal PC clinker	9.5

Data sourced from Supekar (2007).

higher than that required for PC (85% higher), which justifies the slight increase when 1.5% CS was used as raw feed in the manufacture of PC clinker. A similar increase in the grindability index was also observed by Ali et al. (2013), which was 12.8 and 13.3 kWh/tonne for control PC and cement containing 2% CS, respectively.

The results of another study (Sahu et al., 2011) also agree with the previous trends, in which, for the same amount of grinding time, the average particle size of the raw mix increased when introducing 2% CS as replacement of 1% limestone plus 1% iron ore. This means that a greater amount of time and thus energy is required in the grinding procedure to achieve similar particle sizes.

In the study of Al-Jabri and Shoukry (2014), the authors studied the effect of subjecting CS and cement kiln dust to a milling procedure that lasted for 2 or 4 h in a high power planetary ball mill, in which the larger particle structures are reduced in size to the nanoscale, whilst maintaining their original properties. The texture of nanostructured CS particles changed from glassy smooth to irregular and rough surfaces, which is of interest when using this material as partial cement replacement, since the rough particles will achieve good bonding within the cement matrix with consequent enhanced mechanical strength.

5.2.3 Characteristics of Portland Cement Clinkers Containing Copper Slag as Raw Material

CS has been used in the 1–10% range to formulate the raw feed for the manufacture of PC clinker, with clinkerisation temperatures from 1250 to 1400°C. The studies undertaken in this specific area are summarised in Table 5.3. Four studies were conducted in a laboratory and only one reports on factory production trials (Alp et al., 2008).

Mineralogical Characterisation of Cements Containing Copper Slag

In the manufacturing of PC clinker, the raw materials are mixed and heated to temperatures up to 1450°C. To identify the potential phases after heating the raw mix blend, the lime saturation factor (LSF) is often used to verify the ratio of C_3S to C_2S. It also shows whether

Table 5.3 Copper slag used as part of raw material

References	Raw Materials Used	Amount of Copper Slag Used, %	Purpose
Alp et al. (2008)	Iron ore, marl and limestone	2.5 to 6.0	Replacement of iron ore with copper slag (CS)
Medina et al. (2006)	Not specified	1.25 and 1.85	Replacement of hematite with CS
Sahu et al. (2011)	Average grade limestone, iron ore, bauxite, coal ash, petcoke ash	1.0 and 2.0	Partial replacement of limestone, iron ore and bauxite with CS
Supekar (2007)	Ground granulated blast furnace slag, limestone, bauxite, coal ash	1.5, 2.0, 2.5 and 3.0	Partial replacement of iron ore and bauxite with CS
Taeb and Faghihi (2002)	Not specified	2, 4, 6, 8 and 10	Not specified

the clinker is likely to contain an unacceptable proportion of free lime. Values between 0.92 and 0.98 are typical of modern clinkers, and a mix with an LSF greater than 1.0 will yield free CaO, which is liable to persist in the final product, regardless of the degree of mixing and time during which the clinkering temperature is maintained (Taylor, 1997).

The silica ratio and alumina ratio (also respectively called silica modulus and alumina modulus) are empirically used to characterise the potential mineralogical composition of the cement clinker. The silica modulus mainly governs the proportion of silicate phases in the clinker, whilst the alumina modulus governs the ratio of aluminate to ferrite phases in the clinker; for normal PC clinker, the silica and alumina moduli usually vary from 2.0 to 3.0 and from 1.0 to 4.0, respectively (Taylor, 1997).

Ali et al. (2013) studied the effect of incorporating up to 2.5% CS in the raw mix by replacing limestone, bauxite and iron ore. An analysis of the LSF and silica and alumina moduli showed that, although the LSF was not affected by the incorporation of CS, the silica and alumina moduli decreased mainly because of the greater Fe_2O_3 content of CS, when compared to that of the raw ingredients that were replaced. This would suggest that the amount of silicate and aluminate phases would decrease with an increase of the C_4AF phase. This was also shown by Bogue's method, in which the estimations for the amount of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) phases were in the ranges of 54.7–58.9%, 16.3–19.3%, 4.6–6.3% and 12.9–15.3%, respectively, with liquid content varying between 27.4% and 28.9%.

Although the aforementioned methods suggested a decrease of the silicate phases with increasing CS content, the results of the X-ray diffraction analysis indicated that the incorporation of CS resulted in relatively rapid clinker mineral phase formations.

Table 5.4 Clinker composition by phase

Temperature, °C	Sample	Phase, % by Weight			
		C_3S	C_2S	C_3A	C_4AF
1350	Control	62.32	18.12	6.36	10.10
	1.25% CS	61.22	18.70	8.21	9.07
	1.85% CS	62.21	18.75	6.92	9.27
1400	Control	69.18	12.66	5.76	10.55
	1.25% CS	70.90	10.37	8.34	8.86
	1.85% CS	69.05	13.26	6.60	9.43
1450	Control	73.57	9.20	6.30	10.11
	1.25% CS	74.21	7.64	8.44	8.95
	1.85% CS	73.61	9.47	5.88	10.18

CS, copper slag.
Adapted from Medina et al. (2006).

Indeed, C_3S and C_2S contents in samples containing CS, heated at 1400°C, were found to be within the range of 52–58% and 23–28%, respectively, and were comparable to those of the control PC clinker, with C_3S and C_2S contents of 56% and 26%, respectively, calcined at 1450°C.

In the study of Medina et al. (2006), the amount of each phase produced during clinkerisation at 1350 and 1450°C was quantified by means of the Rietveld method (Table 5.4). Although no significant changes were found in the C_3S phase, a slight increase in the C_2S phase was observed when 1.85% CS was used, which would explain the slight decrease in the free CaO content (Table 5.5) in comparison to that of the control PC clinker.

The cement clinker must be correctly burned, to minimise its free lime (CaO) content with the least expenditure of energy (Taylor, 1997). The free lime content of clinker is regarded as a practical measure of the degree of raw mix clinkerisation and is used as a means of controlling the quality of clinker produced. The typical range of free lime content in PC is 0.5–3%. Table 5.5 presents the free lime content in clinker manufactured with and without CS at different temperatures. As expected, the free lime content decreased with increasing clinkerisation temperatures and it decreased even further when increasing CS was incorporated in the raw mix (Figure 5.4). This trend was explained by the enhanced lime combinability at lower temperatures with the incorporation of CS containing copper oxide (CuO) as well as a decrease in the liquid phase's viscosity (Kakali et al., 1996; Kolovos et al., 2005; Ma et al., 2010).

Figure 5.5, which reflects the results presented in Table 5.5, presents the relative free lime of cement clinker samples taken from several studies, in which the CS was ground with the other raw mix components and subjected to normal clinkerisation temperatures (Ali et al., 2013; Medina et al., 2006; Sahu et al., 2011; Supekar, 2007;

Table 5.5 Free lime content of cement with increasing copper slag (CS) content

Publication	CS Content, %	Free CaO Content (%) for Temperatures of				
		1250°C	1300°C	1350°C	1400°C	1450°C
Ali et al. (2013)	0	–	3.18	1.42	0.99	0.40
	1.50	–	3.10	1.34	0.96	0.38
	2.00	–	2.98	1.23	0.78	0.37
	2.25	–	2.76	1.14	0.69	0.35
	2.50	–	2.75	1.12	0.68	0.33
Medina et al. (2006)	0	–	–	3.11	1.85	0.82
	1.25	–	–	2.80	1.53	0.79
	1.85	–	–	2.86	1.66	0.88
Sahu et al. (2011)	0	–	–	4.64	2.56	1.20
	1	–	–	4.25	2.45	1.24
	2	–	–	3.85	2.22	1.01
Supekar (2007)	0	–	0.71	0.51	0.35	0.21
	1.5	–	0.35	0.31	0.19	0.10
	2.0	–	0.45	0.34	0.22	0.10
	2.5	–	0.35	0.30	0.23	0.11
	3.0	–	0.41	0.27	0.13	0.08
Taeb and Faghihi (2002)	0	16.72	10.1	3.83	2.09	0.87
	2	10.60	8.50	1.67	1.01	0.32
	4	9.30	5.07	1.01	0.34	0.27
	6	7.30	2.25	0.55	0.28	0.30
	8	5.30	1.03	0.30	0.20	0.18
	10	2.80	0.41	0.21	0.17	0.09

Taeb and Faghihi, 2002). The results indicate a clear decrease in free CaO content with increasing CS content, revealing greater lime combinability at lower temperatures as observed in other studies (Kakali et al., 1996; Kolovos et al., 2005; Ma et al., 2010). The presence of CuO, which acts both as mineraliser and as flux, decreases the melting temperature by at least 50°C and favours the combination of free lime, resulting in accelerated C_3S formation (Kolovos et al., 2005).

Specific Gravity

In a study undertaken by Alp et al. (2008), a series of cement clinkers was produced incorporating 2.5–6.0% CS, by weight. The specific gravity of the control mixes and those containing CS ranged from 2.99 to 3.07 kg/m^3 and from 3.05 to 3.10 kg/m^3,

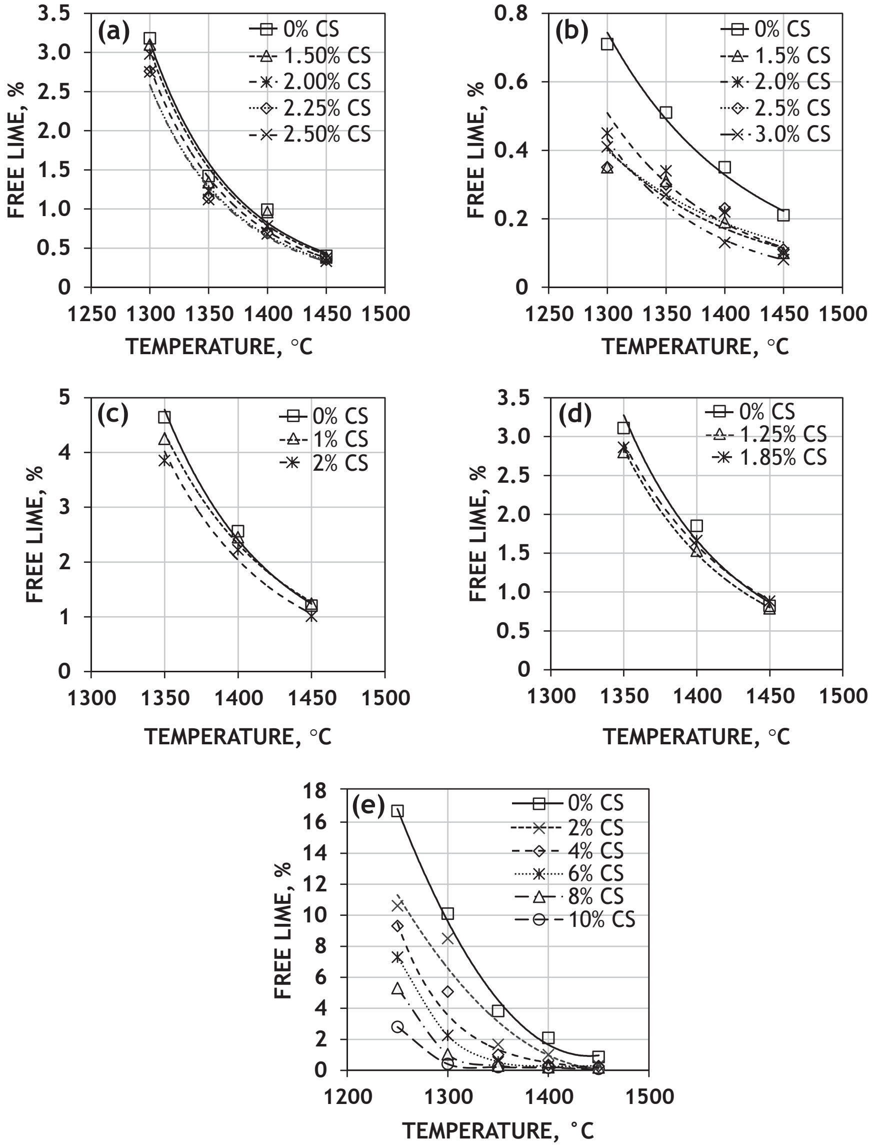

Figure 5.4 Effect of copper slag (CS) incorporation on free lime content of cement clinker subjected to increasing temperatures based on the results of (a) Ali et al. (2013) (b) Supekar (2007) (c) Sahu et al. (2011) (d) Medina et al. (2006) (e) Taeb and Faghihi (2002).

respectively. Though a small increase is clearly visible, for practical purposes, the difference is not significant. Moreover, these values are comparable to those of cements specified in EN-197 (2011). A similar trend was observed for bulk density values, which ranged from 1286 to 1320 kg/m^3 and from 1317 to 1337 kg/m^3 for control mixes and those containing CS, respectively.

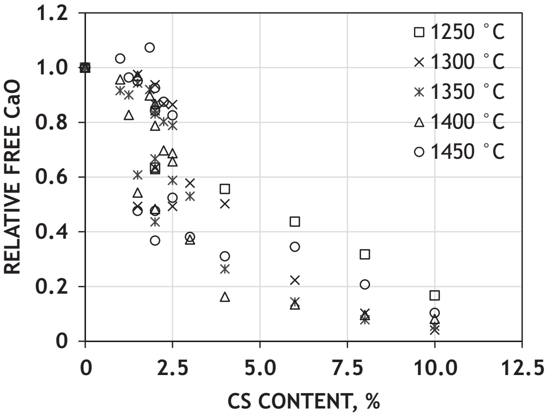

Figure 5.5 Effect of copper slag (CS) content on the relative free CaO of cement clinker.

Water Demand

The results of existing studies (Alp et al., 2008; Ali et al., 2013), on the water required to maintain standard consistence in the production of cement paste samples, suggest that the incorporation of 2.0–6.0% CS does not affect the mixes' water demand, when compared to control PC samples without CS.

Initial and Final Setting Times

Initial and final setting times of cement, which are determined using the Vicat needle test, are used as a quality control measure for cement characterisation (EN-196, 1995) and specified as a requirement in related standards (EN-197, 2011; ASTM C150, 2015). A comparison between the initial and the final setting time of cements manufactured with and without CS (Alp et al., 2008; Supekar, 2007; Ali et al., 2013) is shown in Table 5.6.

The results suggest that the incorporation of small amounts of CS in the raw mix used for cement production may cause some increase in the initial setting time compared to the control cement sample. However, the differences are not significant and the cements produced in this manner are in compliance with the minimum initial setting times, for all types of cement and strength classes, specified in EN-197 (2011) and in ASTM-C150 (2015). Whilst the requirements for the maximum final setting time have been withdrawn from most standards, the figures provided in Table 5.6 for this are all well below the maximum figure of 10 h specified in BS12 (1989).

Strength Development

Early – 2 and 7 days – and standard 28-day strengths are the main criteria for quality control when classifying a cement based on its mechanical requirements (EN-197, 2011). Table 5.7 presents the early and standard compressive strength results of mortar mixes prepared with PC and cement that were manufactured using CS in the raw feed.

Table 5.6 Initial and final setting time of cement samples containing copper slag (CS)

		Setting Time, min	
References	**CS Content, %**	**Initial**	**Final**
Ali et al. (2013)	0	105	155
	2.0	115	165
Alp et al. (2008)	0	139	208
	2.5–6.0	154	231
Supekar (2007)	0	79	160
	2.5	84	152

Table 5.7 Compressive strength of clinker prepared with and without copper slag (CS)

		Compressive Strength, MPa				
		Age, days				
References	**CS Content, %**	**2**	**3**	**7**	**28**	**Strength Class (EN-197, 2011)**
Ali et al. (2013)	0	–	30.0	40.0	50.5	52.5
	2.0	–	30.0	40.0	51.0	52.5
Alp et al. (2008)	0	18.4	–	34.5	45.5	42.5R
	2.5–6.0	17.1	–	33.8	47.5	42.5N
Supekar (2007)	0	–	34.0	52.1	64.2	52.5
	2.5	–	34.9	51.2	65.8	52.5

The results suggest that the incorporation of CS as raw mix material did not affect the strength development of cement. In fact, the 28-day compressive strength of mixes containing CS showed slightly higher values than those of the control PC samples.

According to EN-197 (2011), the strength class of cement samples produced by Ali et al. (2013) and Supekar (2007) was 52.5. It was not possible to ascertain with confidence the cements' classification based on their early strength as the 2-day compressive strength was not disclosed. The strength classes of cement mixes produced by Alp et al. (2008) were 42.5R and 42.5N for control PC and cement mixes containing 2.5–6% CS, respectively. The results appear to suggest that the incorporation of CS as an iron ore replacement causes a decrease in the early strength of mortar. This reduction was also observed when CS was used as a sand replacement in concrete production (Chapter 4). Clearly, further research is required to determine the magnitude of the effect of using CS as a cement constituent on the strength development.

Durability Requirements

In severe environmental conditions, the choice of cement has a great influence on the durability of concrete, mortar and grouts, in terms of frost and chemical resistance as well as the protection of steel reinforcement from corrosion.

Table 5.8 Loss on ignition (LOI), sulphate (SO_3) and insoluble residue of cements containing copper slag (CS)

References	CS Content, %	LOI, %	SO_3, %	Insoluble Residue, %
Ali et al. (2013)	0	0.98	0.17	0.009
	2.0	1.13	0.56	0.039
Alp et al. (2008)	0	0.72	0.27	0.048
	2.5–6.0	0.61	0.12	0.023
Supekar (2007)	0	–	–	–
	2.5	0.08	0.06	–

Table 5.8 presents the loss on ignition, sulphate and insoluble residue of cements produced with CS in the raw feed. The results are well below the limits specified by EN-197 (2011) and ASTM-C150 (2015) for the production of any common type of cement.

Soundness

The soundness test determines whether hardened cement paste is prone to excessive expansion by boiling the test specimens for a fixed period of time. The soundness of cement is mainly tested by two methods: EN-196 (1995), which is based on the Le Châtelier test method, and the autoclave test (ASTM-C151, 2015), in which pressure is also applied to the sample.

The soundness values for hardened cement paste specimens produced with 2.5–6% CS (Alp et al., 2008) showed an average reduction of 13% in expansion when compared to control specimens without CS. Other studies also showed that the incorporation of CS as part of the raw feed may allow the production of cement clinker with equivalent (Ali et al., 2013) or lower expansion (Supekar, 2007) than that of control PC without CS. Expansion of specimens containing 2.5% CS decreased by 20% when compared to the corresponding PC specimens. These results can be correlated with the decrease in the free CaO content (Alp et al., 2008; Supekar, 2007). The reason for this is that, by applying elevated temperatures (or pressure in the autoclave test method), it is possible to measure the extent of expansion caused by the delayed hydration of unburnt CaO.

Leaching of Heavy Metals

Studies on the leachability of mortars made with cement containing CS as part of the raw feed (Alp et al., 2008; Supekar, 2007) subjected mortar samples to the toxicity characteristic leaching procedure (TCLP) or synthetic precipitation leaching procedure (SPLP) tests to evaluate potential contaminants.

Although the TCLP and SPLP tests carried out in one of those studies (Alp et al., 2008) indicated that high amounts of heavy metals could be released from CS, when characterising the leachates of mortars made with cement containing 2.5–6% CS as part of the raw feed, it was found that it posed no real environmental concerns. Similar results were observed in another study (Supekar, 2007), in which the leached elements of mortar specimens made of cement containing 2.5% CS were found to be well within permissible levels after exposure to three aqueous media (i.e., tap water, seawater and acid rainwater) over a period of 150 days.

5.3 Copper Slag as Cementitious Material

In contrast to what was observed in the previous section, where the use of CS was examined as part of the raw feed in cement production, this section discusses the use of CS as a cement constituent. The advantage of this approach is in the saving of significant amounts of energy due to the elimination of the clinkerisation process (Shi et al., 2008).

5.3.1 Early Age Performance

The long-term performance of concrete and mortars in the hardened state can be significantly affected by their characteristics while still in the fresh state, i.e., consistence, compaction, stability, hydration, setting times, among others. Therefore, it is important to consider first how the use of CS as a cement constituent may influence the performance of concrete or mortars in their fresh state.

Heat of Hydration

The heat of hydration is the heat generated during the hydration of cement particles, which exhibit strong exothermic reactions. Other cementitious materials are routinely used to regulate the hydration characteristics of cement, including temperature rise and setting times. The knowledge of such effects allows preventative measures to be taken to reduce thermal cracking thereby improving the durability of the resulting product in the form of mortar or concrete.

Figure 5.6 presents the relative heat of hydration of several specimens with increasing CS content, as partial PC replacement (Baragano and Rey, 1980; de Rojas et al., 2008; Mohsenian and Sohrabi, 2009c). Although the results are based on a few studies, a very good correlation was obtained between CS content and heat of hydration, showing that the heat of hydration reduces at a constant rate with increasing CS content. A single sample of air-cooled CS is considered as a clear outlier and was not considered in the correlation.

Among the results plotted in Figure 5.6, one stands out the most for exhibiting exceptionally low heat of hydration. This specimen was produced using CS that was cooled down at a very slow rate (Mohsenian and Sohrabi, 2009c). This may have caused greater crystallisation of the materials, which in turn caused a slower reaction with the cement and thus less heat of hydration being produced in comparison with mixes containing quenched CS.

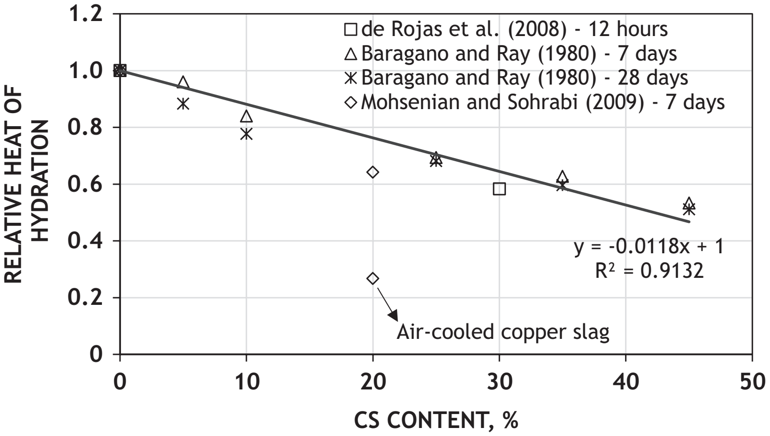

Figure 5.6 Relative heat of hydration of specimens containing increasing copper slag (CS) content as partial cement replacement.

de Rojas et al. (2008) carried out a comparative analysis on the heat of hydration of specimens with 30% SF, FA or CS as partial cement replacement. After 12h, it was observed that the incorporation of SF, FA and CS reduced the heat of hydration by 20%, 30% and 40%, respectively.

Initial and Final Setting Times

Several studies have reported on the effect of incorporating CS on the initial and final setting times of cement when used as partial cement replacement (Baragano and Rey, 1980; CSIR, 2007; Mohsenian and Sohrabi, 2009c; Pavez et al., 2004; Supekar, 2007; Zain et al., 2004; Afshoon and Sharifi, 2014; Suresh et al., 2013; Sahu et al., 2011). From the data plotted in Figures 5.7 and 5.8, it is clear that the increasing incorporation of CS as cement constituent results in a linear increase in initial and final setting times in comparison to that of PC (increases around 70% and 60%, respectively, at a CS content of 50%). The literature has also revealed some eccentricities in setting times:

- disproportionally high setting times at 50% CS content, which do not follow the linear relationship observed for most studies (Baragano and Rey, 1980);
- low setting times at 1–2% CS content, which start to increase there from and are very close to the linear relationship at 5% CS content (Sahu et al., 2011);
- linear decrease of setting times to as low as 50% of those of PC with CS content up to 20% (CSIR, 2007).

The linear increase in setting times with increasing CS content is considered to be due to the presence of Cu, Pb and Zn compounds in the CS, which are set-inhibiting, because of the formation of compounds that cover the silicate phases, thus contributing to increased initial and final setting times (Kolovos et al., 2005; Zain et al., 2004).

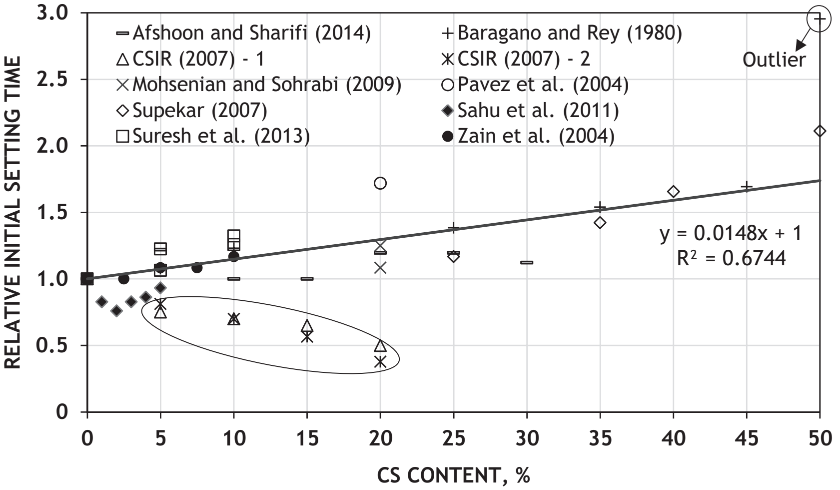

Figure 5.7 Relative initial setting time of cementitious mixes with increasing copper slag (CS) content.

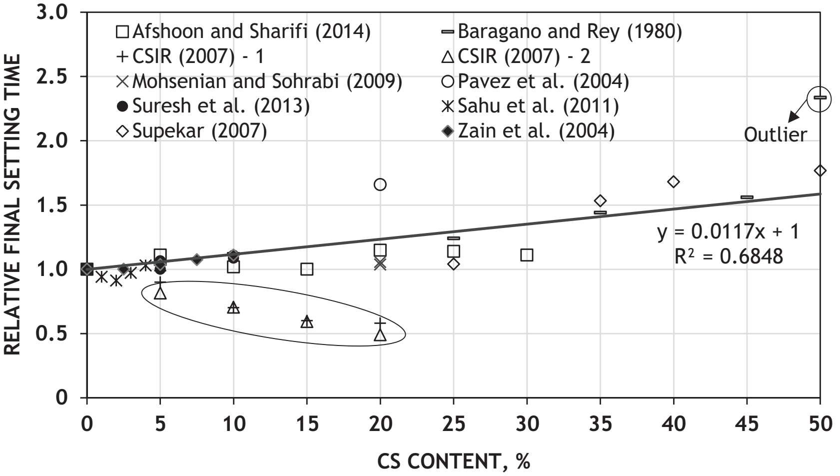

Figure 5.8 Relative final setting time of cementitious mixes with increasing copper slag (CS) content.

In addition to the amounts of Cu and Zn present (Kolovos et al., 2005), which also increase with increasing CS content, there are other factors influencing the initial and final setting times, as suggested by the relatively low coefficients of determination. These are the particle size and specific surface area of CS (Ayano and Sakata, 2000; Suresh et al., 2013; Supekar, 2007) and the production method (Mohsenian and Sohrabi, 2009c). It is important to note, however, that opposite trends have been reported in the literature regarding the effect of cement fineness on the setting times. Ayano and Sakata (2000) and Suresh et al. (2013) observed

Table 5.9 Effect of copper tailing on the initial and final setting times when used as partial replacement of different types of cement

Publication	CT Content, %	Cement Type	Setting Times, min Initial	Setting Times, min Final
Onuaguluchi and Eren (2011)	0	CEM II/A-L 42.5R	–	340
	5		–	384
	10		–	415
	15		–	435
Onuaguluchi et al. (2010)	0	CEM II/A-L 42.5R	600	980
	5		610	1010
	10		620	1200
Onuaguluchi and Eren (2012b)	0	CEM III/A 32.5N	230	330
	5		240	360
	10		260	390

that, when using CS with lower particle sizes and greater surface area, there was a longer delay in the setting times. However, the exact opposite was observed by Supekar (2007), who observed significant decreases in setting times with increasing fineness of CS.

In other studies (Boakye and Uzoegbo, 2014; Mobasher et al., 1996; Murari et al., 2015), although the results for the corresponding control PC specimens were not reported, their results also suggested that the incorporation of ground CS as cement constituent would increase the initial and final setting times.

Additionally, few studies (Onuaguluchi and Eren, 2011; Onuaguluchi et al., 2010; Onuaguluchi and Eren, 2012a,b,c,d) have dealt with the effect of copper tailings (CTs) on the setting times. CTs are waste materials obtained during the cycles of crushing, powdering and froth flotation processes and used to separate copper from its ore, while CS is produced during furnace smelting of copper concentrate to further remove impurities. In Table 5.9, which presents the effect of CT on the initial and final setting times, similar to the trend observed with the use of CS, the results suggest that the increasing incorporation of CT causes an increase in both the initial and the final setting times.

Workability

The water demand is an important performance indicator as it directly affects the consistence of mortar and concrete mixes and can also affect their performance in the hardened state. Baragano and Rey (1980) evaluated the effect of incorporating increasing amounts of ground CS as partial PC replacement in the production of cementitious mortars. A linear increase in flow was observed with increasing CS content. The use of 45% CS, at a constant water/cement (w/c) ratio of 0.5, increased the mortars' flow by 120%. Although a directly proportional relationship was observed in another study (CSIR, 2007), on the effect of using CS as partial PC and Portland slag cement replacement, the increase in consistence (workability) was lower with increasing CS content. In both types of cement, an increase of around 10% was observed when CS replaced 20% of the cement.

To maintain the same flow value in all concrete mixes, Douglas et al. (1986) were able to decrease the amount of water. The use of around 37% CS as partial cement replacement reduced the water requirement by almost 10% when compared with control PC mixes. Similar observations were made in the study of Taeb and Faghihi (2002), in which mixes with increasing CS content required a lower amount of water to maintain the same consistence as that of the control mixes. The results showed that 13% less water was required when 20% CS was used as cement replacement.

Afshoon and Sharifi (2014) evaluated the influence of replacing increasing amounts of cement with CS in self-compacting concrete. The CS content was increased in increments of 5% up to 30% for a total binder content of 400 kg/m^3 with a constant water/binder ratio of 0.51. All mixes were produced with equivalent slump-flow levels and, to do so, the amount of water-reducing admixtures (WRA) had to be reduced with increasing CS content. The use of 30% CS as PC replacement allowed a decrease of 20% in the WRA content to maintain the same workability levels. A similar water-reducing characteristic is observed when CS is used as partial sand replacement in the production of concrete, as discussed in Chapter 4.

Although the findings in the aforementioned studies, in addition to those in Chapter 4, indicate that the use of CS decreases the water requirement of cementitious mixes, the results of some studies are less obvious in terms of the potential water saving with the use of CS (Zain et al., 2004; Moura et al., 2007; Taha et al., 2007; Najimi et al., 2011). In light of this, additional research may be required to achieve consensus on the reduction level of water demand prompted by the use of CS as a cement constituent and as a sand replacement.

Stability

The stability of cementitious mixtures is often judged by the visible bleeding and segregation that can be observed during consistence measurements. The results of bleeding tests carried out by Baragano and Rey (1980) on mortar mixes made with increasing CS content are presented in Table 5.10. Two sets of mixes, with different proportions and CS contents varying from 0% to 45%, were tested. The results suggest an increase in bleeding with increasing CS content for both mixes. Even though the authors attempted to adjust the w/c ratio to the lower water requirement of the mortars with CS, to maintain similar consistence values, the mixes still exhibited increasing bleeding with growing CS content.

Table 5.10 Effect of ground copper slag on bleeding

		Mortar 1:3			Mortar 1:2.5		
Cement, %	**CS, %**	**Water/ Cement Ratio**	**Flow, %**	**Bleeding, %**	**Water/ Cement Ratio**	**Flow, %**	**Bleeding, %**
100	0	0.50	27.3	0.7	0.54	112.8	3.9
95	5		34.5	0.7	0.53	110.3	3.2
90	10		45.7	1.2	0.52	106.8	3.3
75	25		53.4	2.1	0.51	106.5	3.0
65	35		58.0	2.5	0.51	106.8	5.8
55	45		60.5	2.7	0.49	108.3	5.2

CS, copper slag.
Data sourced from Baragano and Rey (1980).

However, more recently, Afshoon and Sharifi (2014), when using ground CS as a cement constituent in the production of self-compacting concrete, observed that all mixes correctly filled the moulds by their own weight and no tendency for segregation or considerable bleeding was observed in any of the mixes during the slump-flow test.

Density

Although few studies (Afshoon and Sharifi, 2014; Moura et al., 2007; Najimi et al., 2011) have reported on the effect of incorporating CS as a cement constituent on the density of concrete, the existing results show a clear consensus, in which there is a linear relationship between CS content and density of concrete (Figure 5.9). This is only natural, considering the relatively greater density of CS in comparison to that of cement. In the aforementioned studies, the density of CS ranged from 3.49 to 3.87 g/cm^3, whereas that of PC is around 3.15 g/cm^3.

5.3.2 Mechanical Performance

The strength-related properties of concrete and mortars, especially compressive strength, are commonly considered to be the most appreciated properties to evaluate cementitious materials. Although other durability-related characteristics may be of importance to evaluate specific features, compressive strength usually offers an overall assessment of the quality of cementitious materials, since it is related to the hydration characteristics of cement and thus its micro- and mesostructure. This section deals with the main features of CS incorporation affecting compressive strength, as well as flexural and splitting tensile strength, modulus of elasticity and shrinkage properties of concrete and mortar.

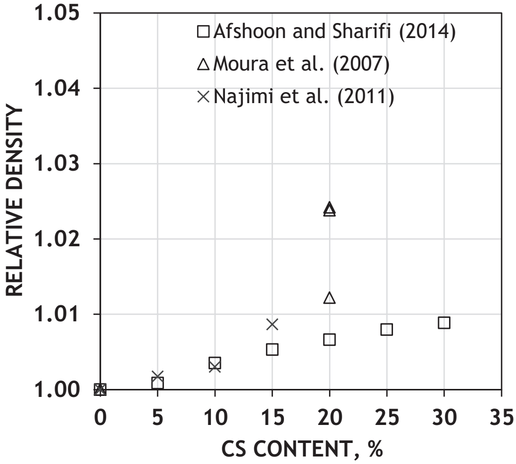

Figure 5.9 Density of concrete with increasing copper slag (CS) content.

Compressive Strength

i) Replacement Level Effect

The most common approach to study the effect of incorporating a material on strength development in a PC-based material is to evaluate the differences in performance with incremental replacement levels. Figure 5.10 presents the results of 75 concrete mixes from 13 publications with increasing CS content, as an addition to or a partial replacement in PC (Al-Jabri et al., 2002, 2006; Douglas et al., 1986; CSIR, 2007; Moura et al., 2007; Zain et al., 2004; Sahu et al., 2011; Al-Jabri and Shoukry, 2014; Arino and Mobasher, 1999; Boakye and Uzoegbo, 2014; Marku and Vaso, 2010; Suresh et al., 2013). From an overall perspective, the results suggest that the incorporation of CS is likely to cause some reduction in the 28-day compressive strength. However, there are some CS-containing mixes with higher compressive strength than the corresponding control PC mixes.

In the study undertaken by Moura et al. (2007), CS was used as an addition to PC, which increased the amount of binder and consequently the compressive strength as well. In another case, where a significantly higher strength was also observed (Al-Jabri and Shoukry, 2014), the authors milled the CS for 4 h until a very fine material with an average particle size of less than 300 nm was obtained and with exceptionally high specific surface area (from an initial specific surface area of around 4000 cm^2/g to around 19,000 cm^2/g). Apart from the filler effect, the use of ultrafine CS particles also allowed a more efficient hydration reaction with the PC.

In terms of the mainstream use of CS as a cement constituent encountered in the literature, the rest of the results in Figure 5.10 suggest that increasing the CS content as partial PC replacement causes a decrease in the 28-day compressive strength. The coefficients of determination and of correlation for the linear regression for the two variables were 0.60 and 0.78, respectively. From a statistical point of view, this means

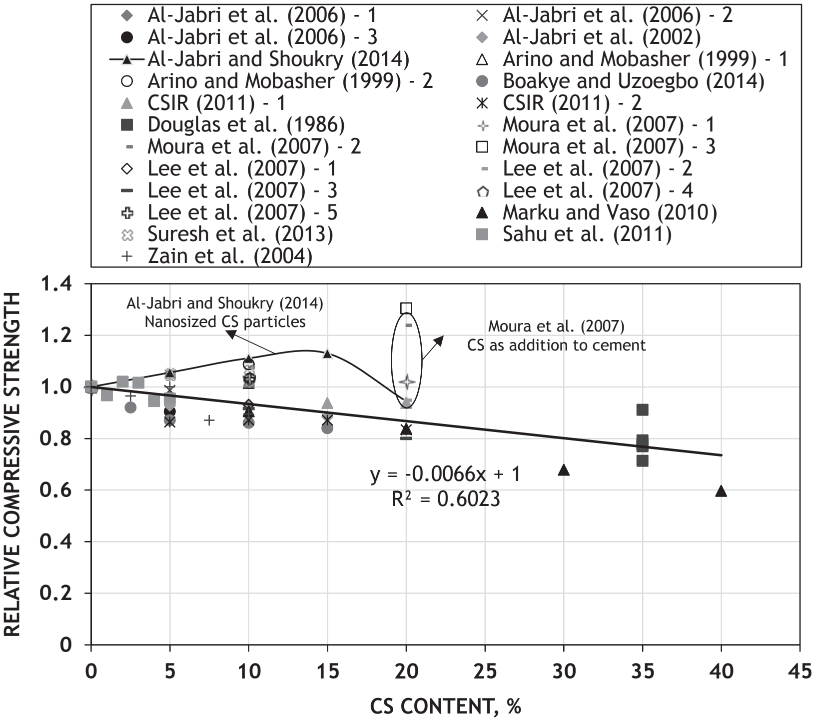

Figure 5.10 Influence of incorporating increasing copper slag (CS) content on the relative compressive strength.

that, although a strong correlation was found between the two explanatory variables (Piaw, 2006), only around 60% of the compressive strength variation can be explained by the CS content. The rest of the variability can be explained by other factors related not only to the characteristics of CS (i.e., chemical and mineralogical composition, production method, grinding procedure) but also to those related to concrete mix design, production and curing.

ii) Thermal History of Copper Slag

Upon CS production, the molten slag may either be air-cooled in an ambient environment or rapidly cooled by quenching it in a granulator. While the former creates a material with more crystalline phases, the rapidly quenched slag allows producing a material with a more amorphous structure, which can then be used as a cement constituent (Walker and Pavía, 2011). The difference between the two methods of production greatly influences its use in PC-based materials, with the quenched granular material having a greater demand than the air-cooled CS.

Quenched CS would be expected to outperform air-cooled CS when used as a cement constituent, based on its mineralogical composition and especially its amorphous material content (Chapter 3). However, the few studies evaluating the influence of using ground CS with different production methods on the properties of mortar (Douglas et al., 1986) and concrete (Mohsenian and Sohrabi, 2009a) have produced inconclusive results as shown in Figures 5.11 and 5.12.

The results of the two studies showed either marginal differences in strength (Figure 5.11) or conflicting results for varying replacement levels (Figure 5.12). This could have been caused by several factors relating to the mix proportioning, as well

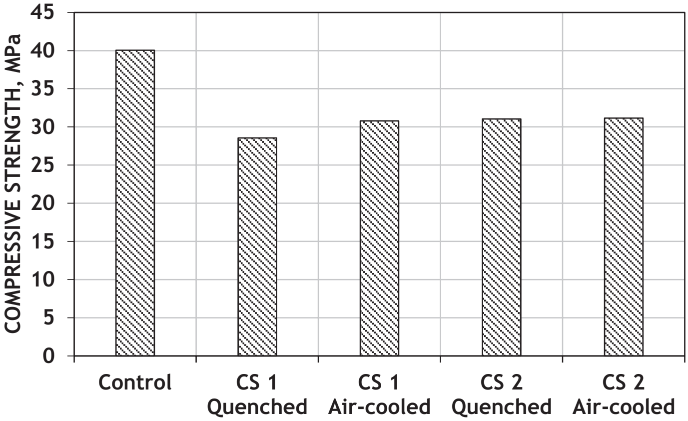

Figure 5.11 Effect of air-cooled and quenched copper slag (CS), sourced from the same batch, on the compressive strength of mortars (CS 1 and CS 2 ground to 300 and 400 m^2/kg, respectively).
Adapted from Douglas et al. (1986).

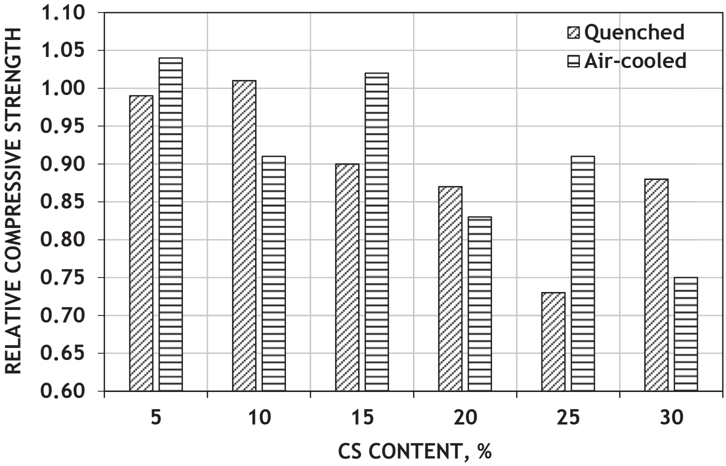

Figure 5.12 Effect of increasing air-cooled and quenched copper slag (CS) content on the compressive strength of concrete.
Adapted from Mohsenian and Sohrabi (2009a).

as the particle packing of aggregates in both sets of mixes, eliminating the advantage that could be accrued by the use of quenched CS as a cement constituent in the form of enhanced pozzolanic activity. Clearly, given the information available in the literature, there is scope for a fundamentally important study to be conducted to investigate the amorphous nature of the quenched glass and its pozzolanic reactivity, the variability attached to it and what benefits, if any, can be derived from it.

iii) Water/Cement Ratio

For a given set of materials and conditions (e.g., concrete mixing, compaction, curing), the relationship between the w/c ratio and the performance of concrete (usually in terms of compressive strength) can realistically be assumed to remain the same. Varying the characteristics of the mix materials, it is possible to observe a change in the strength versus w/c curve. The incorporation of ground CS in PC, for a given w/c ratio, may lead to the following changes:

(i) Increase in strength will move the curve upward.

(ii) Decease in strength will move the curve downward.

(iii) With no variation in strength, the curve will remain unchanged.

Figure 5.13(a) and (b) presents the compressive strength of concrete mixes containing different amounts of quenched CS and with varying w/c ratios. The results clearly show that the use of 5% CS as a cement constituent did not make any significant difference in the performance. On the other hand, owing to its high amount of amorphous material content, the addition of 20% CS improved the strength development of concrete mixes. Still, the results of other authors, who have also assessed the effect of incorporating CS in mixes with varying w/c ratio (Al-Jabri et al., 2006; Arino and Mobasher, 1999;

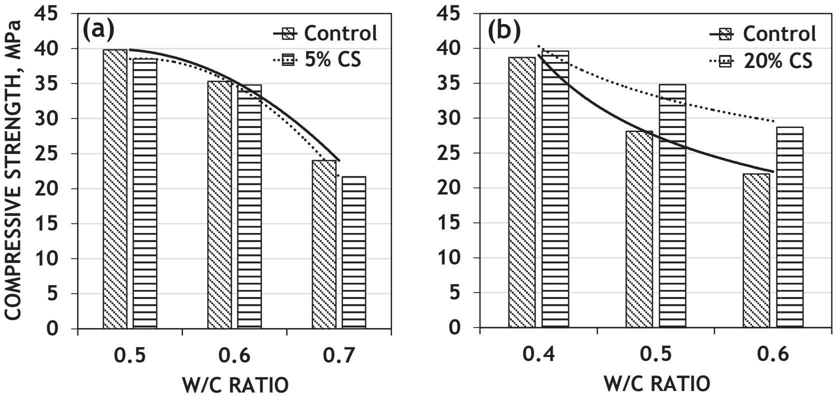

Figure 5.13 Compressive strength of concrete containing (a) 5% (Al-Jabri et al., 2006) and (b) 20% (Moura et al., 2007) copper slag (CS) as cementitious material at different water/cement ratios.

Lee et al., 2007), indicated little variation in strength development when compared with corresponding control mixes. In other words, there is no reason to believe that mixes made with CS will behave differently compared to conventional cementitious mixes when produced at varying w/c ratios.

iv) Strength Development With Time

Another important performance indicator used when designing concrete is the strength development over time. For example, 28-day concrete strength is used by ready-mixed concrete suppliers for quality control of their production, and early age strength is important to precast concrete suppliers to optimise mould rotation and use of space.

Several studies have reported on the strength development of cementitious mixes incorporating CS as a partial PC replacement (Al-Jabari et al., 2002, 2006; Douglas et al., 1986; Lee et al., 2007; Suresh et al., 2013; Zain et al., 2004). The amounts of CS used have usually been small, except in the study of Douglas et al. (1986), where 35% CS was used as a partial PC replacement. In the study of Suresh et al. (2013), CS was used in mixes also containing FA. Figure 5.14 presents the influence of CS presence on the compressive strength development of concrete mixes over time. Despite the scatter of data, owing to the nature and number of variables involved (e.g., scope of the study, type of CS and cement, fineness of CS), the results of some studies (Lee et al., 2007; Suresh et al., 2013) showed that a clear strength increase of CS-containing mixes in relation to control PC mixes can be observed over time. This indicates pozzolanic activity between the CS and the PC's products of hydration, which was also confirmed by the authors when determining the $Ca(OH)_2$ content. There was a general decrease in the $Ca(OH)_2$ levels with increasing age in CS-containing mortars when compared with the control PC mix. The magnitude of the pozzolanic activity also depends on the average particle size of CS, the reduction of which can allow a much faster reaction and thus early age strength increased (Suresh et al., 2013).

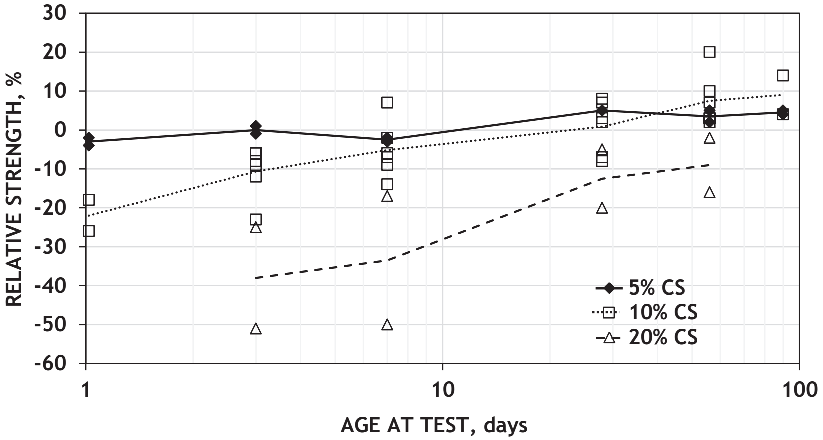

Figure 5.14 Influence of copper slag (CS) on strength development over time. Adapted from Lee et al. (2007) and Suresh et al. (2013).

v) Comparison With Other Cementitious Materials

Comparison of the effect of CS on mechanical performance with other conventionally used additions to PC is also of interest in terms of ranking its reactivity with the PC's products of hydration and, consequently, in determining its appropriate use. Lee et al. (2007) carried out a comparative analysis of the influence of incorporating different cementitious materials (i.e., GGBS, CS and FA) as partial PC replacements (Figure 5.15). For a replacement level of 20%, despite having exhibited a slower strength development when compared to specimens containing GGBS and FA, mixes containing CS showed 28- and 56-day strength values comparable to those of control PC mixes. Owing to the dissimilar fineness of the three materials tested by Lee et al. (2007), it is difficult to comment on the relative reactivity of these materials, as the amount of amorphous material in quenched CS has been reported to be, at least, comparable to those of FA and GGBS (Chapter 3).

The results of a study on the incorporation of CS in the production of mortars (de Rojas et al., 2008) are also encouraging in terms of the pozzolanic reactivity of ground CS when compared to that of FA. For the same replacement level of 30%, the relative strength development over time of CS-containing mixes (Figure 5.16), albeit slightly lower, was quite similar to that of the FA mixes. However, it should also be noted that this difference is well outweighed by the fact that the FA used in the tests showed a Brunauer-Emmett-Teller (BET) specific surface area of 14,000 m^2/g, which is considerably greater than that of the CS of 6800 m^2/g, thereby resulting in enhanced mechanical performance.

One other group of potential sustainable cementitious materials, which have not received the same recognition as FA and GGBS, but have been discussed in the literature, are CTs, cement bypass dust and electric steel dust. Some results have been

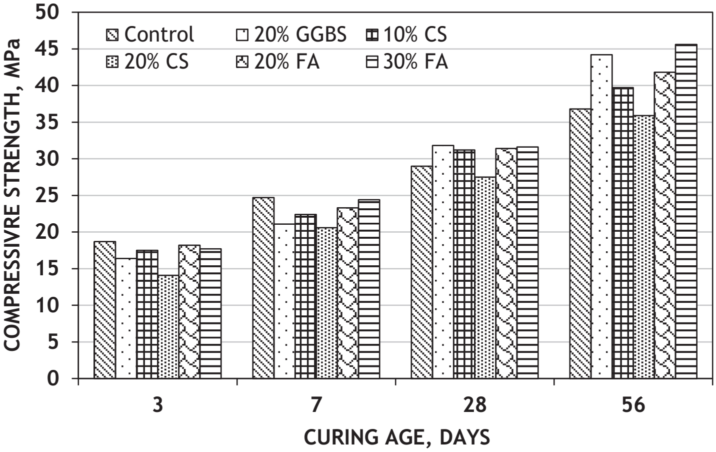

Figure 5.15 Compressive strength of concrete mixes, with a water/cement ratio of 0.45, made with different cementitious materials at different curing ages. *CS*, copper slag; *GGBS*, ground granulated blast furnace slag; *FA*, fly ash.
Adapted from Lee et al. (2007).

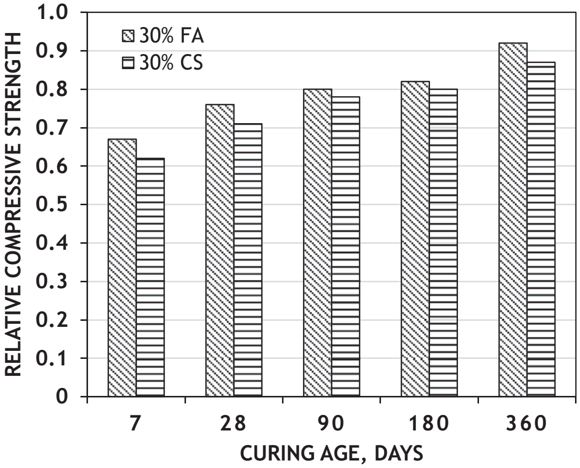

Figure 5.16 Relative compressive strength of mortar mixes made with CS and FA. *CS*, copper slag; *FA*, fly ash.
Adapted from de Rojas et al. (2008).

reported (Onuaguluchi, 2012a; Al-Jabri et al., 2002; Moura et al., 1999). The general view that can be taken at this early stage of development work is that, depending upon how they are handled, these materials and CS can be considered to have a similar strength to concrete mixes.

Flexural and Tensile Strengths

Several studies have examined the effect of incorporating increasing amounts of CS on the flexural strength of cementitious mixes (Al-Jabri et al., 2006; Song, 2014; Mohsenian and Sohrabi, 2009b; Moura et al., 2007; de Rojas et al., 2008). Figure 5.17 presents the relative tensile strength of cementitious mixes with increasing amounts of CS as the cementitious material. Among the studies, one stood out (Moura et al., 2007) for showing much higher tensile strength values than the other cases with the same amount of CS. In this case and as expected, using CS as an addition to PC allowed the production of concrete with higher compressive strength than that of the control mix without CS. The use of 20% CS as the addition to PC allowed an average splitting tensile strength increase of almost 15%.

It is difficult to ascertain a specific trend from the few collated results in terms of the effect of increasing CS content on the tensile strength of cementitious mixes. Some of the plotted values in Figure 5.17 either showed an inconsistent trend (Mohsenian and Sohrabi, 2009b) that exhibited a tensile strength peak for CS contents of 5–10% (Song, 2014) or presented decreasing tensile strength with increasing CS content (Najimi and Pourkhorshidi, 2011).

Figure 5.18 presents the relationship between the mean 28-day tensile strength and characteristic 28-day compressive strength of 20 concrete mixes with a strength class above C12/15, from four publications (Al-Jabri et al., 2006; Moura et al., 2007; Najimi

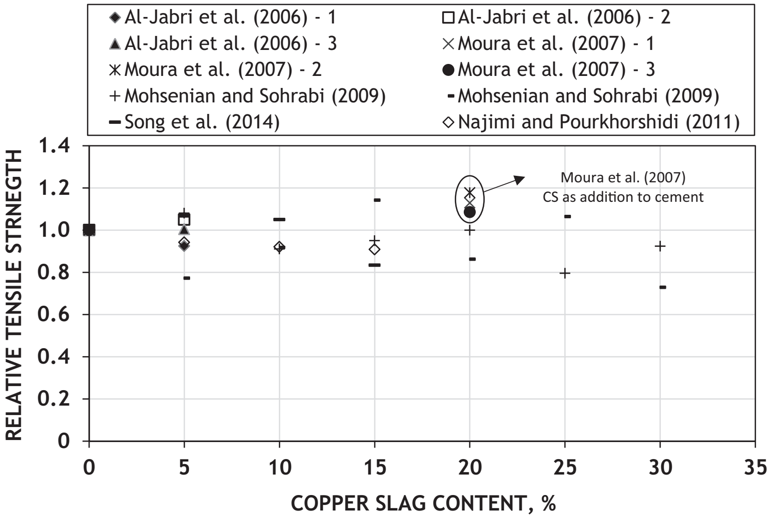

Figure 5.17 Effect of increasing copper slag content on the relative tensile strength.

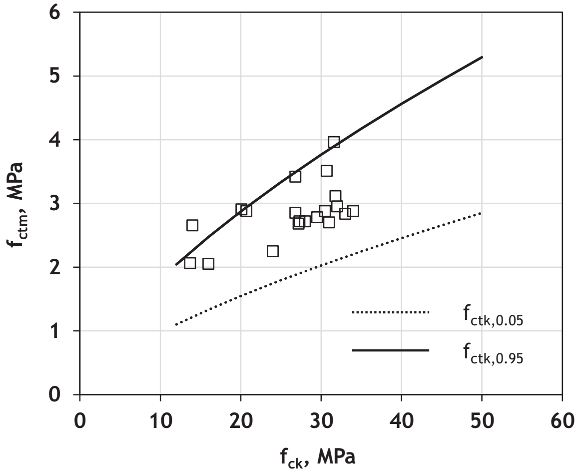

Figure 5.18 Relationship between the tensile strength and characteristic compressive strength of concrete mixes.

and Pourkhorshidi, 2011; Song, 2014). It also contains the 95% confidence interval for the characteristic axial tensile strength of concrete according to Eurocode 2 (EN-1992-1-1, 2008). The results suggest that, despite some of the borderline values, these mixes follow the same relationship as that of conventional concrete mixes without CS.

The results of the effect of increasing CS content, with different thermal histories during production, on the flexural strength of concrete are plotted in Figure 5.19 (Mohsenian and Sohrabi, 2009b). On average, mixes containing quenched CS exhibited slightly higher relative flexural strength over time, when compared to concrete made with air-cooled CS.

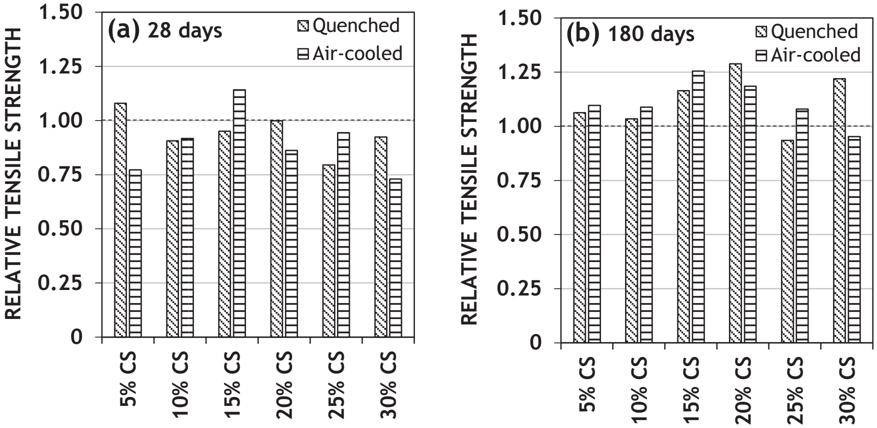

Figure 5.19 Relative flexural strength of concrete with increasing quenched and air-cooled copper slag (CS) content (*dashed line* corresponds to the 28-day flexural strength of the control concrete). (a) 28 days; (b) 180 days.
Adapted from Mohsenian and Sohrabi (2009b).

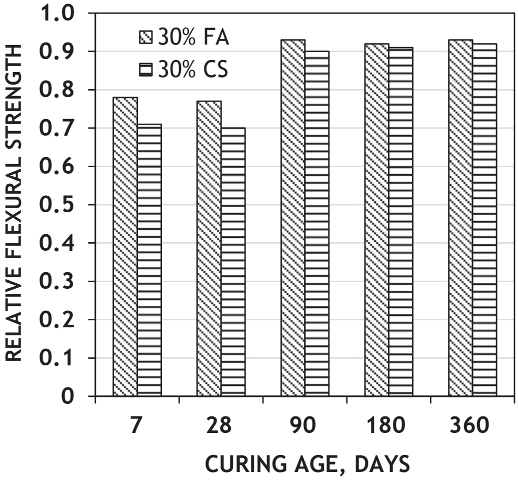

Figure 5.20 Comparison of the relative flexural strength of mortars containing copper slag (CS) and fly ash (FA) as partial (30%) Portland cement replacement.
Adapted from de Rojas et al. (2008).

Still, owing to some of the discrepancies, this difference is not statistically significant, though a much greater strength development in mixes containing quenched CS would be expected because of their higher amorphous material content.

Figure 5.20 presents the results of a study (de Rojas et al., 2008) undertaken to compare the effect of incorporating CS with that of FA on the flexural strength of cementitious mortars. Similarly to what was observed in the corresponding compressive strength

Table 5.11 Effect of copper slag (CS) on the splitting tensile strength

References	Water/ Cement Ratio	CS Content, %	Cement Content, %	Splitting Tensile Strength, MPa	Relative Strength
Al-Jabri et al. (2006)	0.5	0	100	3.46	–
	0.5	5	95	3.20	0.92
	0.6	0	100	3.02	–
	0.6	5	95	3.17	1.05
	0.7	0	100	2.28	–
	0.7	5	95	2.29	1.00
Moura et al. (2007)	0.4	0	100	3.90	–
	0.4	20	100	4.40	1.13
	0.5	0	100	3.23	–
	0.5	20	100	3.80	1.18
	0.6	0	100	2.95	–
	0.6	20	100	3.20	1.08

development of the same mortars in Figure 5.20, mixes containing 30% CS exhibited slightly lower, yet parallel, strength values over time compared to mixes with FA, thus indicating similar pozzolanic activity between the two cementitious materials.

Table 5.11 shows the results of two studies on the effect of using CS as a partial PC replacement (Al-Jabri et al., 2006) and as an addition to it (Moura et al., 2007) in mixes with varying w/c ratio. The results obtained by Al-Jabri et al. (2006) show that the incorporation of 5% CS as PC replacement allowed the production of mixes with splitting tensile strength values essentially similar to those of the control concrete, regardless of the w/c ratio. When using 20% CS as the addition to PC (Moura et al., 2007), even though this caused an expected strength increase, both control mixes and those containing CS exhibited a similar strength decline with increasing w/c ratio. This suggests a similar failure mechanism between mixes with and without CS.

Elastic Deformation

Upon evaluation of the deformation properties of concrete under load, Al-Jabri et al. (2006) studied the stress–strain behaviour of mixes with and without CS. A comparative analysis of the chord and secant moduli between mixes with 5% CS as PC replacement and conventional mixes showed insignificant differences in the elastic moduli of mixes produced with different w/c ratios (Table 5.12).

In the study of Arino and Mobasher (1999), the stress–strain response of concrete mixes containing 10% CS content was evaluated. The results of closed-loop controlled compression tests showed similar moduli of elasticity in mixes with and without CS.

Table 5.12 Modulus of elasticity of concrete containing copper slag (CS) with varying water/cement ratio

Water/Cement	CS Content, %	Cement Content, %	Chord Modulus, GPa	Secant Modulus, GPa
0.50	0	100	17.30	17.62
	5	95	17.72	17.86
0.60	0	100	17.17	17.75
	5	95	18.12	18.15
0.70	0	100	12.86	13.33
	5	95	12.86	13.85

Data sourced from Al-Jabri et al. (2006).

For a w/c ratio of 0.4 and 0.5, the moduli of elasticity of the control mixes were 23.6 and 20.0 GPa, respectively, whilst those of mixes containing 10% CS were 23.9 and 20.0 GPa, respectively.

Shrinkage

Only one publication was found on the effect of incorporating CS on the shrinkage strain of concrete. In the study of Moosberg et al. (2003), the authors carried out a comparative analysis on the effect of using several by-products from the metallurgical and mineral industries as fillers in the production of concrete.

The results, which are presented in Table 5.13, show that the use of CS allowed the production of materials with increased compressive strength, prompted not only by pozzolanic reactivity with the PC's products of hydration but also by a filler effect. Furthermore, it is possible that the higher strength led to greater stiffness thereby allowing a greater ability to restrain shrinkage, when compared to the control mixes containing quartz filler.

5.3.3 Durability-Related Performance

An assessment of the durability-related properties of concrete and mortars is essential to understand their ability to withstand adverse conditions throughout their lives. In this context, this subsection contains a description of the effects of incorporating CS on the main durability-related properties of cementitious materials, such as permeability, carbonation, chloride ion penetration, resistance to sulphate attack, alkali–silica reaction (ASR) and leaching of heavy metals.

Water Absorption

There have been some studies assessing the effect of using CS as cementitious material on the permeability of cementitious mixes by means of the water absorption by capillary action test (Al-Jabri and Shoukry, 2014; Moura et al., 2007; Boakye

Table 5.13 Shrinkage of concrete specimens containing various by-products from the metallurgical and mineral industries

Material	Compressive Strength, MPa	Shrinkage, $\times 10^{-6}$	Relative Shrinkage
Quartz	20.3	690	1.00
Copper slag	24.4	530	0.77
Electric arc furnace slag – 1	25.9	610	0.88
Electric arc furnace slag – 2	24.0	820	1.19
Ladle furnace slag – 1	24.4	820	1.19
Ladle furnace slag – 2	22.9	820	1.19
Ladle furnace slag – 3	21.2	1500	2.17
Slag from steel making – 1	20.3	540	0.78
Slag from steel making – 2	21.8	940	1.36
Waste lime – 1	14.4	1820	2.64
Waste lime – 2	17.4	1080	1.57
Aluminium silicate	29.1	590	0.86
Metal dust recycling slag	20.6	560	0.81

Data sourced from Moosberg et al. (2003).

and Uzoegbo, 2014). Moura et al. (2007) evaluated this property in concrete mixes containing 20% CS as the addition to PC. The results of the capillary absorption coefficient and total absorption values of concrete mixes with and without CS at various w/c ratios are presented in Table 5.14. As expected, the results show that the use of 20% CS decreased the permeability of concrete.

Table 5.15 presents the capillary absorption coefficient of mixes with an increasing amount of CS as a partial PC replacement. The use of 20% CS resulted in a 40% decrease in water absorption by capillary action. The authors of the study (Al-Jabri and Shoukry, 2014) milled the CS for 4 h until a very small-sized material was obtained. Owing to its nanosized particles, which were able to fill the cement grains' interstices, a highly compact material was produced with reduced water mobility in its microstructure. Additionally, the pozzolanic reaction with free $Ca(OH)_2$ resulted in the creation of more C-S-H, which filled the capillary pores and further decreased the material's internal porosity.

The results obtained by Boakye and Uzoegbo (2014) further reinforce the notion that the use of CS as a cementitious material results in a microstructure with reduced porosity. The use of 2.5%, 5%, 10% and 15% CS as partial PC replacement resulted in 4%, 7%, 9% and 11% less water sorptivity when compared with the control concrete.

Table 5.14 Water absorption of concrete with and without copper slag (CS)

Water/Cement Ratio	CS Content, %	Water Absorption by Capillary Action, g/cm^{2}h$^{1/2}$	Water Absorption, %
0.40	0	5.08	3.98
	20	4.62	3.82
0.50	0	8.44	4.43
	20	7.46	4.23
0.60	0	13.30	5.20
	20	10.09	4.50

Data sourced from Moura et al. (2007).

Table 5.15 Capillary absorption coefficient of mixes with increasing copper slag (CS) content

CS Content, %	Water Absorption by Capillary Action, g/cm^{2}h$^{1/2}$	Relative Absorption
0	0.1194	1.00
5	0.0990	0.83
10	0.0804	0.67
15	0.0774	0.65
20	0.0732	0.61

Data sourced from Al-Jabri and Shoukry (2014).

Carbonation

The carbonation of cementitious materials occurs as a direct result of progressive neutralisation of their alkali with the ingress of CO_2. Only one study (Moura et al., 2007) was found on the subject of carbonation of concrete using CS. The authors of that study evaluated the effect of incorporating 20% CS as an addition to PC on the carbonation of concrete specimens subjected to a controlled environmental chamber, with 5% of CO_2 concentration, relative humidity of 68 ± 2% and temperature of 21 ± 2°C. The results, which can be seen in Table 5.16, show that CS-containing specimens exhibited a significant reduction in carbonation depth in comparison with the control mixes at all w/c ratios.

Two overlapping, yet contradictory, effects are in place in this study (Moura et al., 2007). On the one hand, ground CS was used as an addition to PC, which means that a greater amount of binder was used thereby allowing a denser and less porous microstructure. On the other hand, there is enough evidence in the literature to infer that CS is a pozzolanic cementitious material (Douglas et al., 1986; Yang et al., 2010; Al-Jabri and Shoukry, 2014), which means that, as a greater amount of PC is replaced

Table 5.16 Carbonation depth of mixes with 20% copper slag (CS) as Portland cement addition at various water/cement ratios

Water/Cement Ratio	CS Content, %	Carbonation Depth, mm		
		180 days	210 days	240 days
0.40	0	0	0	0
	20	0	0	0
0.50	0	0	1.0	5.0
	20	0	0	1.0
0.60	0	9.0	17.5	21.0
	20	0	7.5	13.5

Data sourced from Moura et al. (2007).

with it, the free $Ca(OH)_2$ is going to react with CS to produce further products of hydration. In other words, there will be less carbonation-prone material in the resulting cementitious material thereby leading to a faster carbonation.

Indeed, several other researchers (Douglas et al., 1986; Yang et al., 2010; Al-Jabri and Shoukry, 2014), though not evaluating the effect of increasing CS content on carbonation, directly assessed its effect on the amount of $Ca(OH)_2$. There is a general consensus that CS-containing binders exhibit an overall decrease in $Ca(OH)_2$ levels when compared to corresponding control mixes at the same age. This clearly indicates a pozzolanic reaction between CS and the PC's hydration products, which would most likely lead to a greater carbonation as also typically observed in binders containing FA or GGBS.

Chloride Ion Penetration

Lee et al. (2007) carried out a comprehensive study on the use of CS as partial PC replacement and compared these mixes with other ones containing pozzolanic additions. Figure 5.21, which presents the chloride migration coefficient of several concrete mixes, shows that there is a general decrease in the chloride ion penetration as PC is increasingly replaced with CS, FA and GGBS. For the same replacement level of 20%, mixes made with CS, FA and GGBS showed a decrease in chloride ion migration coefficient of 5%, 28% and 58% when compared with the control concrete specimens.

Figure 5.21 also shows that, although some of the mixes containing cementitious material as partial PC replacement exhibited higher 28-day chloride ion migration coefficients than that of the control mix, after 56 days the situation reversed. This is due to the slower pozzolanic reactions between the alumina-silicate materials and the PC's products of hydration, thereby resulting in the formation of additional C-S-H, AFt and AFm phases, all of which are known to bind chloride ions (Tishmack et al., 1999).

Using the rapid chloride ion permeability test method according to ASTM-C1202 (2012), Najimi and Pourkhorshidi (2011) also observed a decreasing total charge passed as an increasing amount of PC was replaced with CS (Table 5.17). However,

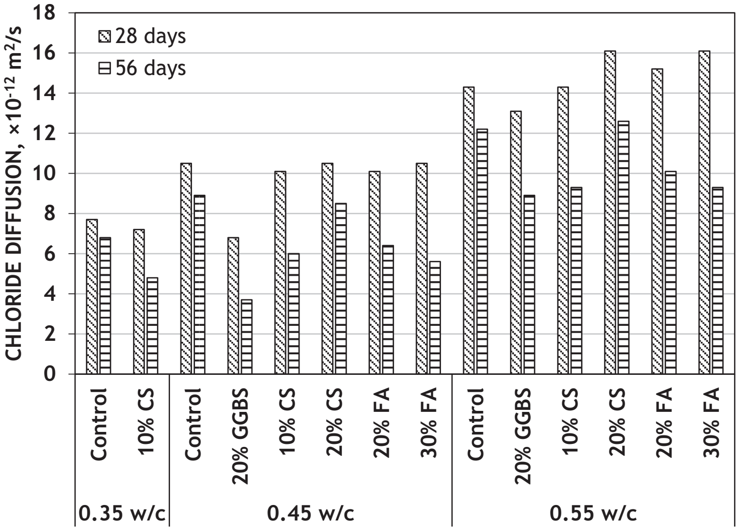

Figure 5.21 Chloride ion migration coefficient of mixes containing copper slag (CS), fly ash (FA) and ground granulated blast furnace slag (GGBS).
Data sourced from Lee et al. (2007).

Table 5.17 Water penetration and total charge passed of mixes with increasing copper slag (CS) content

CS Content, %	Water Penetration Under Pressure, mm		Total Charge Passed, Coulomb	
	28 days	90 days	28 days	90 days
0	14	13	3672	3351
5	12	10	3605	3127
10	9	8	3594	2995
15	13	12	3661	3102

Data sourced from Najimi and Pourkhorshidi (2011).

this improvement was observed only up to a replacement level of 10%, after which the total charge passed began to increase (a trend that can also be observed in Figure 5.21). By analysing the water penetration under pressure of the corresponding mixes, it is clear that there is a correlation between the two properties. It is possible that the increasing amount of CS led to an incongruity in the binder's particle size distribution thereby resulting in a less dense and more porous microstructure.

More recently, Boakye and Uzoegbo (2014) evaluated the conductivity of concrete specimens containing increasing amounts of CS as a partial PC replacement after having been exposed to a concentrated solution of sodium chloride. The authors observed a linear decrease in conductivity with increasing CS content. The use of 2.5%, 5%, 10%

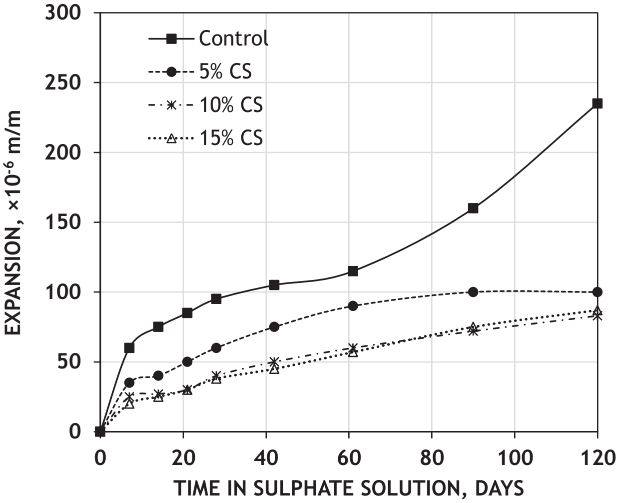

Figure 5.22 Expansion of concrete mixes with increasing copper slag (CS) content subjected to a sodium sulphate solution.
Adapted from Najimi et al. (2011).

and 15% CS led to a decrease of 17%, 25%, 38% and 46%, respectively. This decrease is attributed to the pore-refining effect of CS, as pointed out by the authors, and to the formation of additional products of hydration capable of binding chloride ions by physical adsorption or by anion exchange thereby translating into a lower conductivity.

Resistance to Sulphate Attack

Little research has been carried out on the effect of incorporating CS as a partial PC replacement on the resistance to sulphate attack of cementitious materials. Najimi et al. (2011) evaluated this property in concrete specimens, which were immersed in a sodium sulphate solution for 120 days (Figure 5.22). The results showed that increasing amounts of CS as a partial PC replacement allowed significantly lower expansions when compared with those of the control concrete. Replacement levels between 5% and 15% led to a more than 50% decrease in expansion due to sulphate attack, accompanied by less strength degradation. After an immersion period of 120 days, by means of SEM imaging, the authors were also able to observe needle-shaped formations (i.e., ettringite) in the control specimens, whilst those containing 10% CS exhibited additional C-S-H. Apart from the decreased C_3A content owing to PC replacement, this increased resistance to sulphate attack is explained by the pozzolanic reactions between the CS and the PC's products of hydration. As a result of the calcium hydroxide consumption, a lower amount of calcium sulphate and eventually ettringite will be formed upon long exposure to sulphate.

Though having used a different approach, Baragano and Rey (1980) had previously concluded that the use of CS as a partial PC replacement also leads to enhanced resistance to sulphate attack. By evaluating the ratio between the flexural strength between concrete specimens exposed to a sulphate solution and those cured in normal tap water, the authors observed a lower strength decline in CS-containing mixes than in the control specimens.

Alkali–Silica Reaction

To evaluate the potential ASR expansions in cementitious mortars containing CS, Baragano and Rey (1980) performed an accelerated test method over a period of 75 days, at 43°C. The results in Table 5.18, which presents the expansion of mortars containing different cementitious materials, show that the use of CS as a partial PC replacement can greatly reduce the risk of disruptive expansions due to ASR. The expansion of specimens containing 35% CS, which was very similar to that observed in mixes made with 35% natural pozzolanas, was almost 90% less than that of the control specimens (Baragano and Rey, 1980).

More recently, Najimi et al. (2011) drew similar conclusions after having submitted CS-containing mortars to a sodium hydroxide (NaOH) solution, at 80 ± 2°C, for 30 days. In Figure 5.23, the results show that, after 30 days, mixes containing 15% and 50% CS exhibited around 30% and 80% less expansion, respectively, than that of the control specimen. The expansions observed in specimens made with 5% and 10% CS were similar and approximately 90% of those of the control specimen. These results highlight the effectiveness of CS in controlling expansion due to ASR.

Leaching

According to a 2015 technical report released by the UK government, on the classification and assessment of waste (GOV.UK, 2015), CS is viewed as a non-hazardous material. Nonetheless, some studies have been carried out on the leachability of cementitious mixes containing CS to evaluate the solidification/stabilisation of heavy metals.

Vitkova et al. (2011) directly assessed the leachability of CS in terms of the effect of varying grain size, presence/absence of fine dust particles and the pH on contaminant leaching. The resulting leachates showed a strong dependence on the size distribution and pH level. The leaching of heavy metal, such as Cu, Co and Zn,

Table 5.18 Alkali–silica reaction expansion of binders containing different cementitious materials

	Expansion, %		
Cement Blend	**7 days**	**14 days**	**75 days**
Control	0.12	0.30	0.47
35% Copper slag	0.02	0.05	0.06
35% Pozzolana	0.01	0.02	0.03

Data sourced from Baragano and Rey (1980).

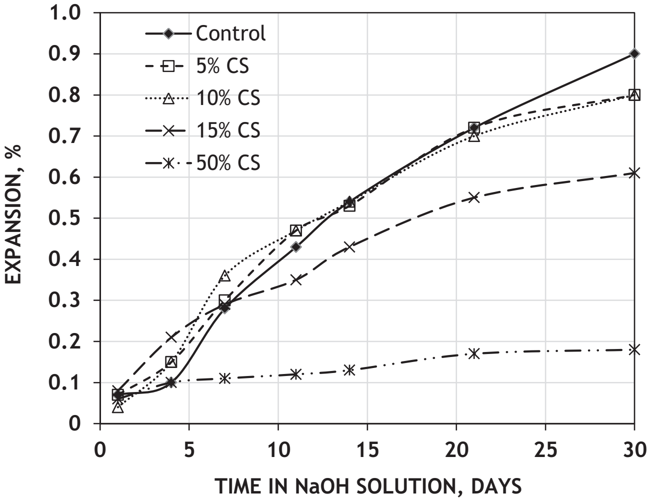

Figure 5.23 Alkali–silica reaction expansion over time. *CS*, copper slag.
Adapted from Najimi et al. (2011).

was generally accelerated by crushing due to the presence of easily soluble dust particles. Furthermore, the highest concentrations were released at pH 4 and 5 with a gradual decrease towards near neutral conditions and a slight increase at pH 11 or 12. Nevertheless, all heavy metal levels in the leachates were below the EU criteria for non-hazardous materials.

In the study of de Rojas et al. (2004), the authors studied the leaching of trace elements (i.e., Cu, Fe and Zn) from CS after having incorporated it into PC mortars. The results showed that the incorporation of CS in cementitious mortars did not cause an increase in the leached elements. When studying the cement-based solidification of CS, Zain et al. (2004) also observed that the amounts of leached Cu, Ni, Pb and Zn ions, from 10% CS-containing mortars, were lower than regulatory limits. These findings suggest that the incorporation of CS as a cementitious material is safe with respect to leachability of the afore mentioned heavy metals.

5.4 Conclusions

A considerable amount of research and development work has been undertaken to determine the performance of CS as a component of raw feed in the manufacture of PC clinker and as a partial replacement of cement. The main points, which have emerged from the systematic analysis and evaluation of the data covering various technical aspects and environmental issues, are summarised as follows.

The chemical analysis of CS indicates that its matrix is compatible with the cement system. It usually contains high levels of iron oxide and can be easily used as a source of iron in the production of cement clinker. However, in comparison to conventional raw materials, the higher grinding energy requirement of CS may not always prove to be economical. On the other hand, the inclusion of CS in the raw feed may allow decreasing the temperature of calcination to achieve the same amount of free lime, C_2S and C_3S contents of the clinker produced and with subsequent reduction of CO_2 emissions. In view of the significant positive outcome of using CS in cement production, a life cycle assessment is required to ascertain both the cost and the environmental impacts.

The use of CS in raw feed may produce PC with somewhat slow setting characteristics. As this effect can be too small to have any significant effect in the use of cement and because the reported data have also been contradictory, this calls for further research. Notwithstanding this, the mechanical performance of specimens produced with 42.5 and 52.5 grade cement, manufactured using 2–6% CS, was similar to the strength development behaviour of corresponding conventional cement, confirming the technical viability of CS use in the manufacture of PC.

Information on both the durability-related and the environmental impact aspects for cement containing CS is encouraging. The resulting cement samples were found to be within the requirements of the soundness test, giving lower expansion than the corresponding normal cement, which correlated well with the lower free lime contents associated with such cements. Based on limited data available, it can be inferred that the use of CS as cement raw feed will not cause any additional concern regarding leaching of heavy metals compared with conventional cement.

Similarly to FA, the incorporation of CS as a cement constituent results in a reduction in the heat of hydration. This effect increases with CS content and can help control the development of high temperatures in concrete structures and reduce evaporation of water and thermal cracking. The retardation of hydration increases the initial and final setting times in an almost linear manner with CS content, such that the incorporation of 30% CS as a cement replacement can extend the initial and final setting times by about 50% and 40%, respectively.

Despite the use of dissimilar test methods producing different types of results, the general trend of the results of several studies undertaken suggests that the addition of CS as a cement constituent reduces its water demand. This is considered to be due to the glassy smooth surface texture of CS particles. Contradictory observations have been reported with regard to the effect of CS addition on the stability characteristics of the cement. Whilst some have not observed any significant effect on segregation, others reported an increase in bleeding with increasing CS content in the cement. Although CS has higher density when compared to PC clinker, the difference between the two should not affect significantly the density of concrete, as the proportion of cement used in concrete is relatively small.

Cements containing CS as a constituent have been shown to conform to Abrams' rule governing the relationship between strength and w/c ratio and therefore existing mix design methods can also be used where CS is incorporated with cement. Notwithstanding this, the studies have shown that the inclusion of CS in cement lowers its 28-day strength and the use of 30% CS is likely to reduce strength by 20%. However, similarly to FA, because of pozzolanic reactivity of CS, the strength development is recovered with time and, in some cases, PC with 10% to 20% CS addition have been known to produce 10% higher strength at 90 days. In general terms, CS is slightly less reactive than FA and GGBS. Given that quenched CS in its amorphous form has a considerably high proportion of glass content (see Table 3.3 in Chapter 3), contrary to what would be expected, the limited data available do not show significant strength difference compared to air-cooled CS. Clearly, further research is needed to resolve this issue.

The tests have shown that, as for compressive strength, the tensile strength of concrete made with cement containing CS develops in a manner similar to that of conventional concrete. The same has been found to be the case with elastic modulus and creep of concrete, even though few data have been found on this subject. This means that concrete made with PC containing CS can be specified in accordance with the specifications of Eurocode 2. The use of cement with CS can be expected to produce concrete with low shrinkage strain, which may be explained by the reduced water demand of the mix, though further research is needed to substantiate this.

Because of its pozzolanic nature and the associated benefits to be accrued, permeation studies indicate that the use of cement incorporating CS produces concrete with relatively lower permeability, absorption, and diffusion properties. This has been shown to have an obvious effect on chloride ingress and carbonation even though, in case of the latter, improvement in the permeation properties has to be offset against some loss of pH through the pozzolanic process. In contrast, owing to pozzolanic reactions the resistance to chloride ingress is also expected to further benefit from additional chloride ions being physically adsorbed and chemically bound. Pozzolanic reactivity of CS has also been shown to improve the resistance of concrete to sulphate attack, prompted by the reduced amount of calcium sulphate and ettringite being produced, and to ASR, as a result of the concrete's reduced alkalinity.

Not only do the existing reports and guidelines show that CS is a non-hazardous material, its incorporation in PC does not result in additional concern in terms of leaching of heavy metals from concrete.

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Use of Copper Slag in Geotechnical Applications

6

Main Headings

- Atterberg limits
- Compaction characteristics
- Permeability
- Consolidation
- Shear strength
- Lateral earth pressure and retaining walls
- Copper tailing
- Environmental impact, case studies
- Standards and specifications

Synopsis

The data published relating to the geotechnical performance of copper slag (CS) since 1964 have been systematically analysed and evaluated. CS is a non-plastic material, which has better compaction characteristics than sand. Its permeability and consolidation rates are similar to those of sand, but it may be more compressible. The material has a friction angle close to that of well-graded sand, and its use as backfill reduces the active lateral pressure on retaining walls. The material does not cause any adverse environmental impact. The views of the construction industry about its use have been mostly positive, and CS has been considered in the development of the new prEN 13242 (2015). The potential for the use of copper tailings in geotechnical applications is also very briefly discussed in this chapter.

Keywords: Copper slag, Atterberg limits, Compaction, Consolidation, Permeability, Shear strength, Geotechnical applications, Environmental impact, Case studies, Standards and specifications.

6.1 Introduction

Under the slag families, two broad classifications can be made—ferrous slags and non-ferrous slags, and copper slag (CS) belongs to the latter category. The former category includes iron and steel slags and has a long service record in geotechnical applications, dating back to the Roman Empire. Indeed, these slags were used in road construction and for railroad ballast during the 19th century across Europe and the United States (Lewis, 1982) and are still used as viable engineering fill materials (National Slag Association,

Sustainable Construction Materials: Copper Slag. http://dx.doi.org/10.1016/B978-0-08-100986-4.00006-7

2005; Nippon Slag Association, 2003) as well as road pavement materials (Australasian Slag Association, 2014). At present, the use of blast-furnace slags and steel slags as an aggregate in civil engineering work is well covered by major national and international standards, such as BS EN 13242:2002+A1 (2007).

In comparison, however, CS has not been widely used in geotechnical applications, even though it has been claimed by the Organization for Economic Cooperation and Development (1977) that CS is suitable for use in road embankments or fill applications.

The increase in population and the surge in urbanisation in both the developed and the emerging economies are resulting in a decrease of suitable land for development of infrastructure. Consequently, it can be expected that the need to quarry slag heaps and landfills containing such materials for use in construction, such as earthworks, pavements and buildings, will increase rapidly. In this respect, for countries such as China and the United States, where CS is readily available, it could be an ideal alternative to natural aggregates, or even ferrous slags, for use in many geotechnical applications.

Although the research in developing the use of CS in geotechnical applications has not been as extensive as that in the area of concrete construction (Chapters 4 and 5), the geotechnical properties of soil mixed with CS and cement- or lime-stabilised CS have been shown to be satisfactory for use as construction fill materials. Whilst some researchers have also expressed interest in the use of CS in ground granulated form as a chemical stabiliser or granular copper tailings as a natural soil replacement, more research still needs to be done to substantiate the current findings.

Perhaps the major concern of using CS in geotechnical applications is not its technical performance, but rather its potential environmental impact arising from toxic metal leaching, which may be generated when CS comes in contact with water (rainwater, groundwater, surface water from flooding or streams and rivers). This issue will be discussed briefly in this chapter and in more detail in Chapter 8.

6.2 General Information

Dealing with non-ferrous slags, including copper, nickel and phosphorus slags, a report of the Federal Highway Administration (FHWA, 2012) states that the use of these high-stability and load-bearing capacity slags would generally exceed the relevant requirements of specifications for construction of embankments and fill, and thereby these materials can provide good load transfer to weaker subgrades. However, their environmental suitability, as well as their corrosion risk to buried utilities, which could have an impact on their service quality and public safety, must be evaluated.

Lavanya et al. (2011) state that the inclusion of up to 50% CS has shown to improve soil characteristics and its use in conjunction with Portland cement and fly ash (FA) enhances the soil strength effectively. In addition, the FHWA (2012) states that CS can also provide good resistance to freeze–thaw attack and frost attack because of its excellent soundness and drainage properties.

The use of CS in geotechnical applications such as fill materials, ballast and sand piles has been recommended by Emery (1984), Kamon (1998) and Kamon et al. (2000).

Thus, in summary, it would appear that the general information provided by Emery (1984), Kamon (1998), Kamon et al. (2000), Lavanya et al. (2011) and FHWA (2012) tends to suggest that CS possibly possesses the desirable engineering properties for use as a replacement for natural sand in many geotechnical applications. However, the concern about its environmental suitability still needs to be addressed to confirm that CS, like iron and steel slags, is a safe and valuable resource.

6.3 Atterberg Limits

Fine-grained soil (silt and clay) can appear in different states of consistency, solid, plastic and liquid, for which the boundaries are defined in terms of Atterberg limits, based on moisture content. The two limits associated with plasticity of soil are liquid limit (LL) and plastic limit (PL). These are used to calculate the plasticity index ($\mathrm{PI} = \mathrm{LL} - \mathrm{PL}$), which is the measure of sensitivity of the soil to changes in its moisture content. These limits were developed over a century ago, in 1911 (Germaine and Germaine, 2009), and since then have been used commonly in practice for determining soil classification, grouping soils in terms of their behaviour, and providing an indication of their potential engineering properties. Thus, soil classifications are typically used to define soils in a range of earthwork specifications.

As confirmed by many researchers, CS is non-plastic in nature (Havanagi et al. 2006, 2009, 2012; IRC Highway Research Board, 2011; Lakshmanan et al. 2014; Lavanya et al. 2012, 2013; Patel et al. 2007, 2011). This implies that CS can be used as a direct natural sand replacement, of similar particle size distribution, as a fill material when non-plastic granular material is needed.

When CS is mixed with silt–clay soil, the LL, PL and PI of the soil have been found to decrease linearly with increasing CS content, as shown in Figures 6.1–6.3, respectively. It has been reported by Havanagi et al. (2006; 2007) that in one case, the soil became non-plastic at 75% CS content ($\mathrm{PL} = 0$). A similar observation showing the Atterberg limits to decrease was also made when CS was mixed with 20–40% FA (Patel et al., 2007).

As typical maxima, LL and PI for soil in engineering applications are about 40% and 10%, respectively. The results in Figures 6.1 and 6.3 indicate that CS may be used with high-plasticity soil to reduce its plasticity. This use of CS may help to change the nature of such soils and thereby possibly reduce the use of stabilisers, such as cement and lime, for controlling stability.

In the ground form, it is important to note that, although there has been only one study undertaken, when CS was used as a stabiliser in a soil, Al-Rawas et al. (2002) showed that the PI of the CS-treated soil increases with increasing ground CS content from

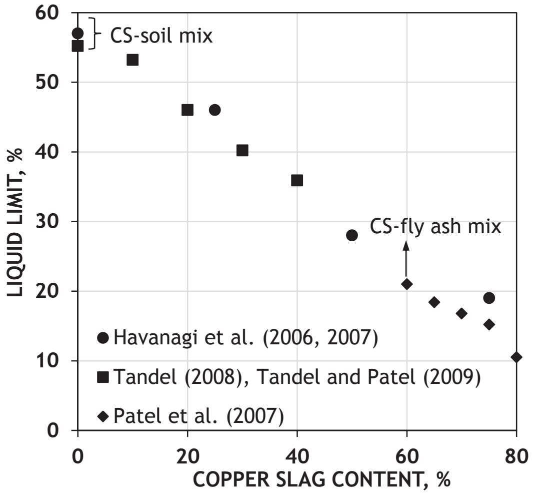


Figure 6.1 Effect of copper slag (CS) on liquid limit of soil and fly ash mixes.

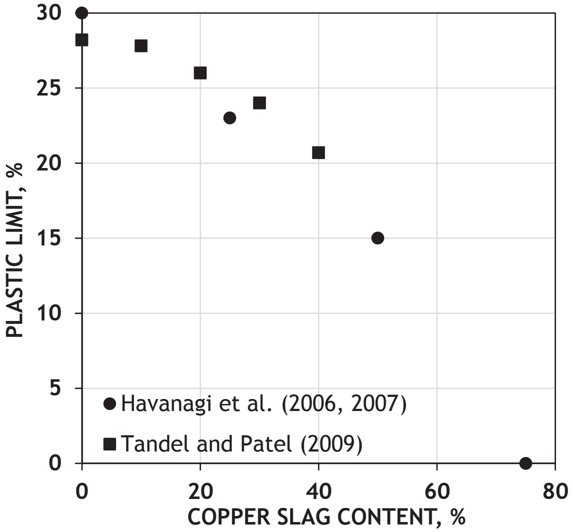


Figure 6.2 Effect of copper slag (CS) on plastic limit of soil mixes.

3% to 9%, whilst soil samples similarly treated with blast-furnace slag cement, ground granulated blast-furnace slag and cement bypass kiln dust showed the opposite results, as illustrated in Figure 6.4.

Furthermore, the LL results of most test samples remain reasonably close, whilst the PI values remain similar to, or higher than, that of the control sample.

This makes the results of this study highly questionable and further work is needed to clarify the effect of ground CS in relation to other cementitious materials.

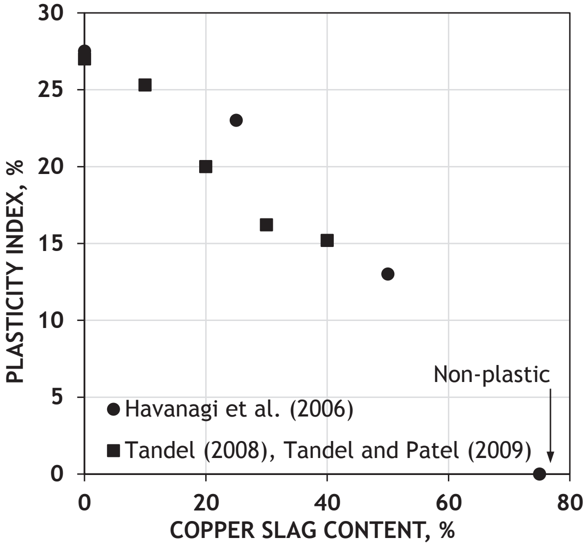


Figure 6.3 Effect of copper slag on plasticity index of soil mixes.

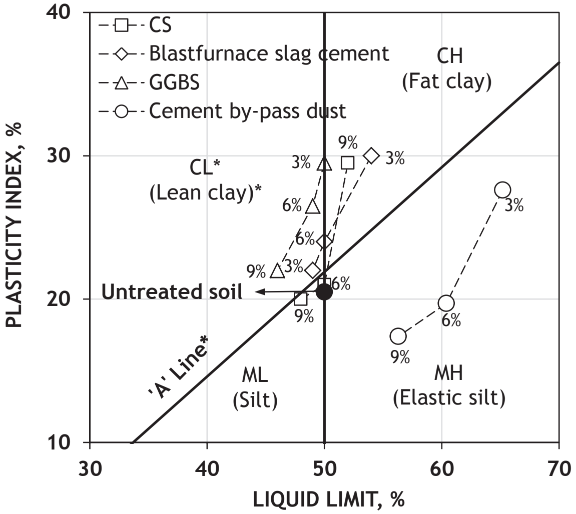


Figure 6.4 Effect of using ground copper slag and other cement as soil stabiliser. *Based on ASTM D2487 (2011). *CS*, copper slag; *GGBS*, ground granulated blast furnace slag; *CL*, lean clay; *ML*, silt; *MH*, elastic silt; *CH*, fat clay.

6.4 Compaction Characteristics

To improve the engineering properties of soils, often they are compacted by applying a load either through a rolling weight or by dropping a weight on the ground. The aim is to achieve improved particle packing, and thereby reduce the void space in the soil. The compacted soil has higher bearing capacity and dimensional stability, as well as reduced permeability and settlement, which are important aspects of earthwork, foundation and retaining structure design.

The two parameters involved in the compaction process are water content and dry density of the soil. The relationship between the amount of water used and the resulting dry density is rather straightforward. Water acts as a lubricant and orients the soil grains into a densely packed state. When water is gradually added to a soil during compaction, the dry density of the soil increases until it has reached a certain point beyond which the dry density decreases, because of an excess of water, which does not allow bonding to be formed between soil grains. The corresponding water content and dry density at that particular point are known as optimum moisture content (OMC) and maximum dry density (MDD). Both of these change with changes in the compactive effort.

A range of standard compaction tests are available for determining the moisture–density relationship of a soil. The choice of test depends on the type of soil and the envisaged end use. One of the earliest tests was developed by Ralph Proctor in California in 1933 (O'Flaherty, 2002). Most of the later tests were developed by modifying the Proctor test, for example, the modified Proctor test, in which the energy consumption level is higher than that with the standard Proctor test.

Table 6.1 compares the mean values of OMC and MDD of CS obtained from the literature, together with the typical values of various natural materials. All these results have been obtained using the standard Proctor and modified Proctor test methods. It

Table 6.1 Comparison of maximum dry density and optimum moisture content of copper slag with other natural materials[a]

	Standard Proctor Test		**Modified Proctor Test**	
Type of Soil	**OMC, %**	**MDD, kg/m^3**	**OMC, %**	**MDD, kg/m^3**
Copper slag[b]	**11.5**	**2185**	**6**	**2510**
Sand	11	1940	9	2085
Gravel–sand–clay	9	2070	8	2200
Sandy clay	14	1845	11	2055
Silty clay	21	1670	12	1945
Heavy clay	28	1555	18	1875

MDD, maximum dry density; *OMC*, optimum moisture content.

[a] Values of natural soils are based on O'Flaherty (2002).

[b] Data taken from Das et al. (1983), Ferguson and Das (1989), Gupta et al. (2012), Havanagi et al. (2006, 2007, 2008, 2009, 2012), IRC Highway Research Board (2011), Lakshmanan et al. (2014), Lavanya et al. (2012, 2013), Navya et al. (2012), Patel et al. (2007), Saravana et al. (2005), Shahu et al. (2012), Tandel (2008), and Tandel and Patel (2009).

can be seen from Table 6.1 that the MDD of CS obtained from the standard Proctor test and modified Proctor test is 2185 and 2510 kg/m^3, respectively, and correspondingly about 12% and 20% higher than that of the sand.

It is also noted that the MDD of CS obtained using the standard Proctor test is higher than that of sand obtained using the modified Proctor test, implying that CS needs less compaction effort to achieve MDD similar to that of sand. Therefore, the use of CS as a replacement of natural sand could potentially reduce the operational cost (less energy consumption) and at the same time increase the productivity (less compaction work). This advantage, even at a marginal level, could strengthen the case for using CS in practice.

It can be seen from Table 6.1 that, under the standard Proctor test, the mean OMC of CS at 11.5% is slightly higher than the typical value for sand at 11% as quoted by O'Flaherty (2002). The corresponding figure with the modified Proctor test for the mean OMC for CS is 6%, which is lower than the typical value for sand at 9% (O'Flaherty, 2012). The marginally higher value of OMC for CS in the standard Proctor test may be attributed to several factors, for example, poor CS particle packing and high CS fineness. However, such information is lacking in some of the studies used to develop Table 6.1. Notwithstanding, it would appear that a well-graded CS, which has low air voids after compaction, should have OMC less than 11.5% as obtained from the standard Proctor test.

Figures 6.5 and 6.6 have been developed using data taken from the literature consisting of 20 sources published over a period of 31 years from 1983 to 2014, to examine the influence on the OMC and MDD, measured with the standard and modified Proctor tests, using CS with the test samples of:

(i) soil only,
(ii) FA only,
(iii) pond ash only,
(iv) mixture of soil and FA and
(v) lime-stabilised soil.

As expected, given the wide source of data used, there is considerable variation in the OMC and MDD values for soil and FA mixes, for which the bulk of the tests have been performed, as plotted in Figures 6.5 and 6.6. However, in general, when CS is mixed with a soil, its OMC value decreases with increasing CS content and possibly at a decreasing rate, whilst MDD increases at a decreasing rate with CS content. Together, these results imply that for a given performance, the use of CS with a soil can result in a reduction of compaction effort required. For example, an MDD of 2000 kg/m^3 as obtained using a modified Proctor test (high energy method), for 100% of certain soils, can be achieved using the standard Proctor test (low energy method) with soils containing 40–60% CS, as shown in Figures 6.6 (b) and (a), respectively.

Although FA and pond ash have somewhat different material characteristics, when CS is mixed with FA and pond ash, both the ashes show similar changes in their compaction characteristics. Their OMC is higher and MDD is lower and they both

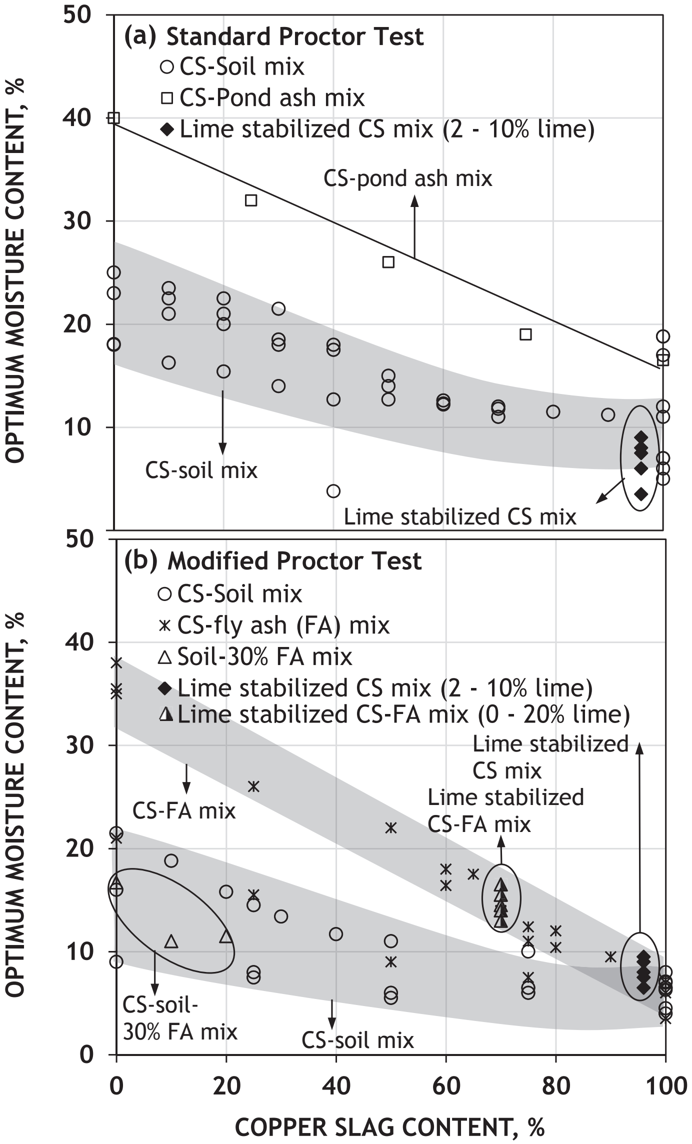


Figure 6.5 The effect of copper slag (CS) on optimum moisture content of soil, fly ash and pond ash mixes obtained using (a) the standard Proctor test and (b) the modified Proctor test. Data taken from Baraskar and Ahirwar (2014), Chandrshekhar et al. (2015), Das et al. (1983), Ferguson and Das (1989), Gupta et al. (2012), Havanagi et al. (2006, 2007, 2008, 2009, 2012), IRC Highway Research Board (2011), Lakshmanan et al. (2014), Lavanya et al. (2012, 2013), Navya et al. (2012), Patel et al. (2007), Saravana et al. (2005), Shahu et al. (2012), Tandel (2008), and Tandel and Patel (2009).

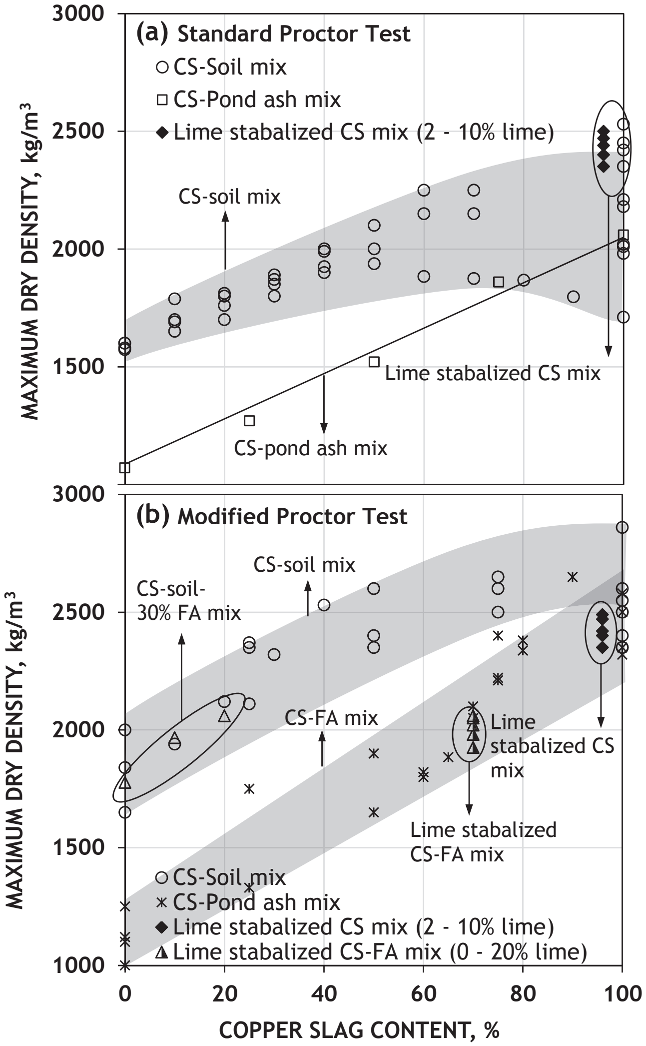


Figure 6.6 The effect of copper slag on maximum dry density of soil, fly ash and pond ash mixes obtained using (a) the standard Proctor test and (b) the modified Proctor test. *CS,* copper slag; *FA,* fly ash.

Data taken from: Baraskar and Ahirwar (2014), Chandrshekhar et al. (2015), Das et al. (1983), Ferguson and Das (1989), Gupta et al. (2012), Havanagi et al. (2006, 2007, 2008, 2009, 2012), IRC Highway Research Board (2011), Lakshmanan et al. (2014), Lavanya et al. (2012, 2013), Navya et al. (2012), Patel et al. (2007), Saravana et al. (2005), Shahu et al. (2012), Tandel (2008), and Tandel and Patel (2009).

vary in a linear manner with CS content, as shown in Figures 6.5 and 6.6. A possible explanation for this difference in behaviour, compared to that of soil alone, in the testing for OMD and MDD could possibly be due to the specific gravity of the two sets of materials, due to the presence of cenospheres in the ashes being lower than in soils, and this in turn is likely to affect their OMD and MDD.

Table 6.2 The effects of copper slag on optimum moisture content and maximum dry density expressed in relative terms with respect to reference samples based on Figures 6.5 and 6.6

		Standard Proctor Test		Modified Proctor Test	
Sample	**CS, %**	**OMC, %**	**MDD, %**	**OMC, %**	**MDD, %**
Soil	0	0	0	0	0
	20	−14	+13	−17	+17
	50	−30	+25	−36	+34
	80	−41	+30	−44	+38
	100	−45	+31	−46	+39
Pond ash/fly ash	0	0	0	0	0
	20	−13	+18	−17	+26
	50	−32	+45	−43	+64
	80	−51	+72	−68	+103
	100	−64	+90	−85	+128

CS, copper slag; *MDD*, maximum dry density; *OMC*, optimum moisture content.

The data presented in Figures 6.5 and 6.6 have been used to develop Table 6.2 in a form that can be used easily by engineers to estimate the likely percentage change in OMC and MDD values for standard and modified Proctor tests for a soil, FA and pond ash, with the inclusion of CS varying from 0% to 100%.

The results of other materials are also shown in Figures 6.5 and 6.6, which show that:

- Under the modified Proctor test, the use of CS in soil–30% FA mixes decreases OMC and increases MDD with increasing CS content, as shown in Figures 6.5(b) and 6.6(b), respectively, whilst it would also appear that, depending on the nature of the soil and FA mixture, the resultant OMC and MDD vary, owing to the addition of CS, within the two respective bands (shaded grey in Figures 6.5 and 6.6). At 30% FA content, the mix shows a trend similar to that of the soil-only sample.
- The use of 2–10% lime as a stabiliser in 100% CS mixes does not significantly change the OMC and MDD values for standard and modified Proctor tests. However, the OMC and MDD values for lime-stabilised 100% CS mixes obtained from these two tests are comparable (Figures 6.5 and 6.6). It must be noted that the ineffectiveness of the addition of lime in modifying the OMC and MDD values in either test is to be expected because lime reacts only with clay minerals and is not effective in sand and gravel soils, as stated in the report by the Building Research Advisory Board (1969).
- For 70% CS and 30% FA mixes, the OMC and MDD values obtained from the modified Proctor test decrease and increase with the addition of lime stabiliser at the 0–20% level, as illustrated in Figures 6.5(b) and 6.6(b), respectively. It should be noted that all these values are within the band of the corresponding values of CS–FA mixes without stabiliser, suggesting that in this case, the stabiliser used need not change the compaction characteristics.

6.5 Permeability

In geotechnical engineering, the movement, retention and profile of water (all related to permeability) in soils have a decisive impact on the properties of soils. A soil mass is made with discrete solid particles with voids between them, and the interconnection of the voids creates pore channels (continuous pores) to allow water to flow from a higher potential zone to a lower potential zone. This property is known as the permeability of soil. In simple terms, permeability describes the ease with which water can flow through a soil.

The permeability of soils is influenced by particle size distribution, void ratio, pore interconnection and orientation and degree of soil saturation. Although all soils are considered to be permeable, their permeability varies in a decreasing order, from gravel, sand, silt to clay, over a wide range. Thus, knowledge of the permeability of soils, as well as the selection of the right construction materials for it, can be the main requirement in some engineering designs, such as in determining the seepage pressure of earth dams and designing highway drainage.

The permeability of mixes containing (i) 100% CS, (ii) 10–40% CS–sand and (iii) 30–40% CS–soil, reported in 16 publications since 1983, is plotted in Figure 6.7, together with the typical permeability values and classifications for natural soils as suggested by Purcell (2003) and Terzaghi and Peck (1967), respectively.

From Figure 6.7, the following main points can be observed:

- The permeability of 100% CS mixes ranges between 1×10^{-3} and 1×10^{-6} m/s with about 75% of the results falling in between 1×10^{-3} and 1×10^{-4} m/s. The average permeability of a 100% CS mix is 3×10^{-4} m/s. It can be seen from the illustration that the permeability characteristics of CS are essentially similar to coarse sand, based on Purcell's work (2003), and considered to be in the medium permeability classification based on Terzaghi and Pecks (1967).
- When CS is used as a natural sand replacement, the only set of results reported by Nawagamuwa et al. (2013) show that the permeability of mixes containing 10–40% CS is essentially similar to that of the corresponding reference natural sand (Figure 6.7). This is to be expected as the gradings of CS and reference sand, as well as the void ratios of the resultant mixes, were reported to be similar. Indeed, this is a good scientific practice that should be adopted, as the discrepancy of the particle packing between CS–sand mixes and reference sand mixes could be eliminated by keeping the gradings of CS and sand the same.
- The preceding two points have shown that CS could be an ideal replacement for natural sand, particularly in some specific geotechnical applications in which the use of sand is required. This includes using CS in (i) sand drains for stratified (layered) soils in reducing the groundwater level, (ii) granular filters for foundations of hydraulic structures in reducing internal erosion or piping of soils and seepage pressure and (iii) coarse materials for ground improvement in preventing frost heaving due to poor drainage.
- The results of another study, Tandel (2008), show that the permeability of soils with 30% and 40% CS is marginally lower than that of the corresponding reference soils (Figure 6.7). However, the permeability values of all the mixes are still on the order of 10^{-9} m/s (very

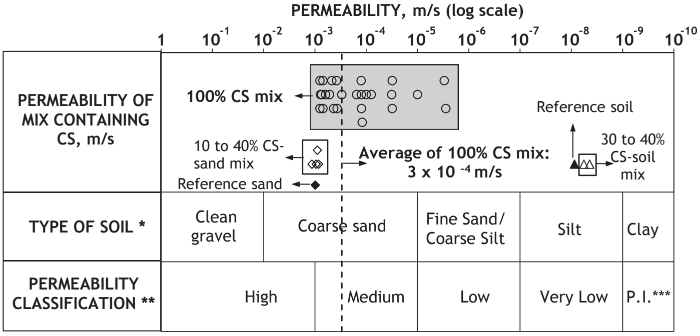


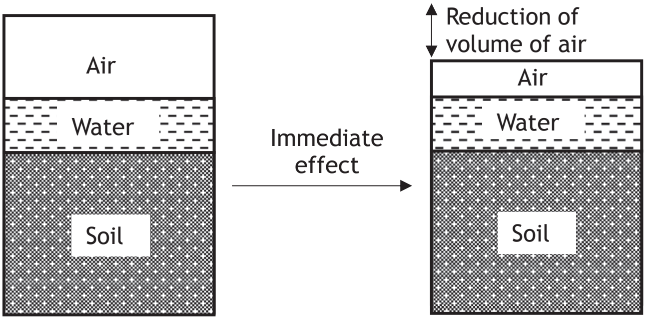
Figure 6.7 Permeability characteristics of mixes containing copper slag (CS) compared to typical natural soils. *Based on Purcell (2003). **Based on Terzaghi and Peck (1967). ***Practically impermeable.
Data taken from Das et al. (1983), Ferguson and Das (1989), Nawagamuwa et al. (2013), Goi et al. (2003), Havanagi et al. (2007, 2008, 2009, 2012), Kitazume et al. (1998a), Lavanya et al. (2012, 2013), Lim and Chu (2006), Patel et al. (2007), Shabber et al. (2012), Tandel (2008), and Tandel and Patel (2009).

low permeability). This small reduction in permeability could be attributed to the reduction of air voids in the mix, as a result of increased MDD and reduced OMC with addition of CS. The aforementioned coverage of performance might suggest the suitability of CS in the construction of impermeable subgrades where the compaction characteristics of soils are improved whilst the permeability characteristics are kept unchanged.

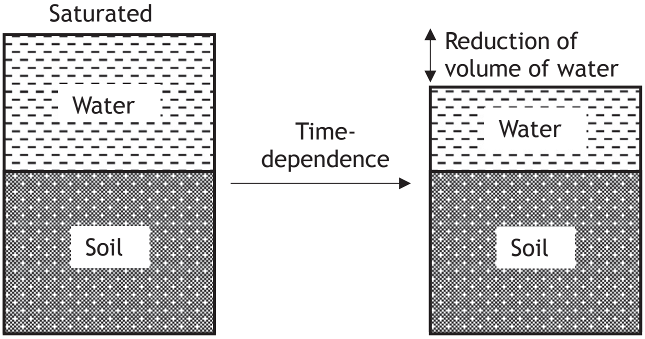
6.6 Consolidation

In general, a soil undergoes deformation when subjected to load in two different forms, namely, compaction and consolidation. In compaction, which was covered in Section 6.4, the volume of soil reduces instantaneously, because of the expulsion of air by the applying load from compaction. On the other hand, in the consolidation process, the volume of the soil reduces gradually with time because of the drainage of some pore water by the acting load on top of the soil, such as the dead load of airfields. A brief comparison between compaction and compressibility is illustrated in Figure 6.8.

The consolidation of soils leads to settlement, also known as consolidation settlement, which is very important in engineering design because its magnitude and rate determine the stability of a structure. As far as the material properties are concerned, consolidation is governed by (i) permeability and (ii) compressibility of a soil, which is mainly responsible for its rate and magnitude, respectively.



(a) Compaction



(b) Consolidation

Figure 6.8 Comparison between (a) compaction and (b) consolidation.

In coarse-grained soils such as gravels and sands, consolidation takes place rapidly after the load is applied because of their high permeability. Thus, their consolidation is rarely an issue. In fine-grained soils such as silts and clays, consolidation occurs at a much slower rate because of their low permeability. Given that CS and sand have similar permeability characteristics (refer to Section 6.5), all other things being equal, the rate of consolidation of CS is considered to be essentially similar to that of the sand.

The compressibility of soils is their volumetric response under compression, in which the soil grains rearrange into a stable orientation as the water is drawn out from the soil mass. For cohesionless materials like sands, the particle shape and grading, as well as the stress level and past stress history of soils, influence the compressibility of soils. For example, sand is more compressible in a loose state than in a dense state. The compressibility of soils can be measured by a one-dimensional compression test using an oedometer in which the vertical strain of a soil sample is determined whilst its lateral strain is restricted when it is subjected to increment loading. The constrained modulus, normally expressed as the secant modulus, the gradient of a straight line of two connecting points in the non-linear stress–strain curve obtained from the test, is used to describe the compressibility of soils.

The behaviour of 100% CS samples and CS–sand samples in a confined compression test has been reported by Das et al. (1983), Ferguson and Das (1989), and Nawagamuwa (2013); however, their findings are not coherent with one another. The properties of CS and sand used, testing parameters, test standard adopted and remarks given by the authors are summarised in Table 6.3.

It can be seen from Table 6.3 that the work of Das et al. (1983) and Ferguson and Das (1989) investigated solely the confined secant modulus of 100% CS at very loose and dense relative density states, whilst Nawagamuwa (2013) studied the effect of 10–40% CS as a natural sand replacement on stiffness (confined modulus, can be tangent or secant). The ranges of particle sizes for CS, sand and CS–sand mixes in both studies are similar, but the CS grading used in the studies undertaken by Das et al. (1983) and Ferguson and Das (1989) is considered well graded, and both the sand and the CS–sand gradings in Nawagamuwa's work are considered poorly graded, according to ASTM D2487 (2011). The one-dimensional

Table 6.3 Comparison of experimental studies on the use of copper slag in one-dimensional compression test

Aspects Considered	Das et al. (1983) and Ferguson and Das (1989)	Nawagamuwa (2013)
Natural sand used as reference	No	Yes
CS content used, %	100	10, 20 and 40
Range of CS particle size, mm	4.75–0.075	4.75–0.075[a]
Classification of CS based on ASTM D2487 (2011)	Well-graded sand	Poorly graded sand[b]
Testing parameter	At 0% relative density (very loose) and 100% relative density (very dense)	As natural sand replacement from 10% to 40%
Standard adopted for one-dimensional compression test	ASTM D2434 (1986)	Not given
Remarks by authors	The confined secant moduli of CS and natural sand are comparable except when the relative density and stress level difference are high, which is due to the crushing of angular CS particles (see Table 6.4).	The stiffness (confined modulus) of CS–sand mix increases at 10% CS content, beyond which there is no change in stiffness with increasing CS up to the 40% level (see Figure 6.9).

CS, copper slag.

[a] The range of particle size for 10–40% CS–sand mixes; that for the 100% CS was not available.

[b] The grading of the reference sand is also classified as poorly graded sand and its grading is close to that of 10–40% CS–sand mixes.

compression test in Das et al. (1983) and Ferguson and Das (1989) was performed in accordance with ASTM D2434 (1986), whilst Nawagamuwa (2013) did not state the standard used.

The results from Das et al. (1983) and Ferguson and Das (1989), as given in Table 6.4, show that the confined secant modulus of very loose CS is always lower than that of the very dense CS. This is to be expected as the air voids in the former CS condition are much higher and thereby make it more compressible (lower confined secant modulus). Indeed, this is why, in practice, very loose sand is always compacted to a greater density before it is loaded. The authors compared the secant modulus of CS with that of the natural sand from Hassib (1951), which was reported by Lambe and Whitman (1969), and suggested that they are of similar orders of magnitude. The low secant modulus of CS at high relative density and stress level difference was associated with the crushing of angular CS particles. However, it should be noted that the particle sizes of CS and sand in the two studies are different, even though both of them are claimed to be well graded (Table 6.4).

The results of Nawagamuwa (2013), expressed as a stress–strain graph illustrated in Figure 6.9, show that the stress–strain behaviours of 10–40% CS–sand mixes are similar, and all these mixes display a smaller strain increase than the reference sand for a given stress. This indicates that CS–sand mixes are less compressible than the sand when their gradings are close. The reason for this observation has not been provided by the author.

As explained earlier in this section, the compressibility of soils is affected by particle size distribution (grading) and the particle shape of soils; these two factors are directly related to overall particle packing and are essentially responsible for air voids in the soils. Given that such information and clarity are lacking in the studies, the data cannot be assessed with confidence. Notwithstanding, it is known that rounded fine sand is less compressible than angular fine sand (Lambe and Whitman, 1969); thus, the angularity of CS is likely to make the soils more compressible if compared to rounded natural sand of similar particle size distribution.

Table 6.4 Confined secant modulus of copper slag and sand as reported by Das et al. (1983) and Ferguson and Das (1989)

		Secant Modulus, MPa	
Relative Density, %	**Stress Level Difference, kPa**	**Well-Graded CS, $4.75 < D^{a} < 0.075$ mm**	**Well-Graded Sand[b], $1 < D < 0.02$ mm**
0 (Very loose)	62.1 to 103.5	12.5	13.8
100 (Very dense)		41.4	51.8
0 (Very loose)	200.1 to 510.6	17.3	25.5
100 (Very dense)		62.1	121.4

CS, copper slag.
[a] D = sand size.
[b] Based on Hassib (1951) and Lambe and Whitman (1969).

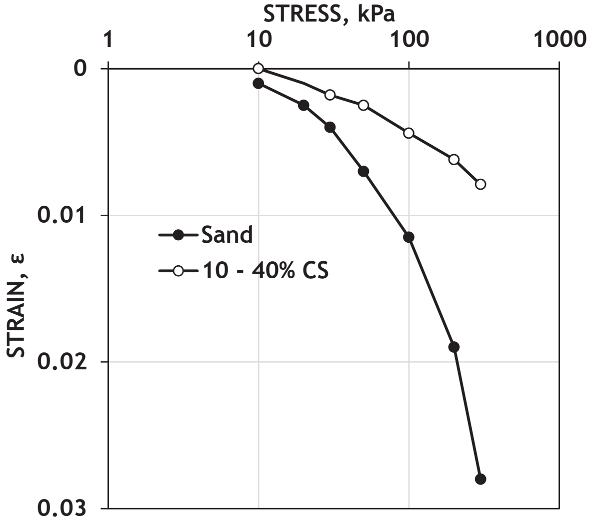


Figure 6.9 Stress–strain relationship of copper slag (CS)–sand and sand mixes. Based on Nawagamuwa et al. (2013).

6.7 Shear Strength

The shear strength of a material is its internal resistance to applied stress before failure. It is perhaps the most important property in soil engineering design and it is required in the analysis of, for example, soil-bearing capacity of embankments, stability of slopes and lateral pressure exerted by soil on retaining walls.

There are two distinct components in the shear strength of soil, namely, (i) friction and (ii) cohesion. For coarse granular soils, like gravels and sands, the shear strength is purely frictional because there is no cohesion. Shear strength can be determined in several different ways, both in the laboratory and in field tests. In the case of the former, a range of parameters such as confining pressures, applied stress and other conditions can be accurately controlled and the direct shear test and triaxial test have been very commonly used. The latter are conducted when satisfactory specimens cannot be recovered for laboratory testing.

Undoubtedly, the shear strength of a soil is greatly influenced by its material properties, which can be narrowed down to two closely related factors:

- **(i)** particle packing, which is governed by particle size distribution, air voids content and density;
- **(ii)** particle interlocking, which is governed by particle shape and its surface roughness.

Thus, it is important to understand the effects of these two factors when selecting the right soil for geotechnical works.

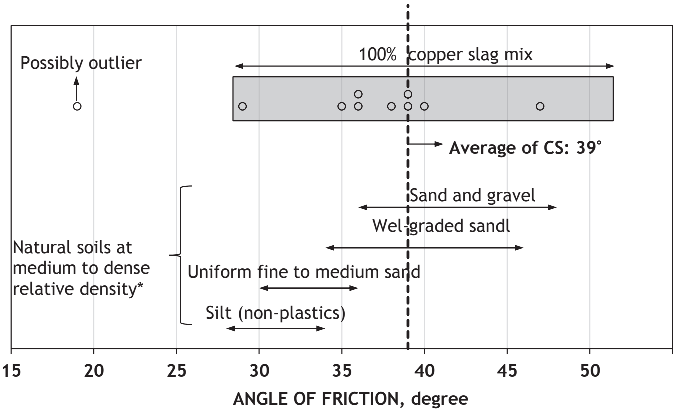


Figure 6.10 Comparison of friction angle of copper slag (CS) with other typical natural soils.
*Based on Lambe and Whitman (1979).
Data taken from Goi et al. (2003), Gupta et al. (2012), Havanagi et al. (2006, 2007, 2008, 2009, 2012); Lavanya et al. (2012, 2013), Patel et al. (2007), Sathya and Shanmugavalli (2014), and Tandel and Patel (2009).

The friction angle measurements of 100% CS mix reported in the published literature since 2003, all obtained from direct shear test, except one from a consolidated drained triaxial test, are shown in Figure 6.10, comparing them to those of typical natural soils at medium to dense relative density (approximately in the range of 40–80% relative density) quoted from Lambe and Whitman (1979).

It is shown that the friction angle of CS ranges from the lowest value of 19 degrees to the highest of 51 degrees. Given that the friction angle of 19 degrees for CS deviates too far from the uniform fine to medium sand, and is even smaller than a weak material like silt (Figure 6.10), it is highly likely that this particular result is an outlier in the overall data population obtained from the literature published during 2003–14. Excluding this potential outlier, it can be seen (Figure 6.10) that the remaining CS data generally fit well in the friction angle ranges for the uniform fine–medium sand and well-graded sand, giving an average friction angle of 39 degrees, which is in the range of well-graded sand and is in fact very close to the midpoint.

Indeed, the higher friction angle of CS is to be expected as CS is more angular than most natural sand, which essentially provides a greater degree of particle interlocking to resist shear motion. Although the grading of CS has not always been reported where such information is available, the CS used has been classified as poorly graded and the CS mix is compacted to its MDD at OMC. This might suggest that a well-graded and dense CS should have a friction angle larger than 39 degrees.

As stated earlier in this section, the packing state of particles in soils, as assessed from its void ratio, as well as relative density values, greatly influences its shear strength. The friction angle of CS at different void ratios and relative densities has been studied by Das et al. (1983), Ferguson and Das (1989), Kitazume et al. (1998a, 1998b), Lima and Chu (2006) and Nawagamuwa et al. (2013), and their results are discussed next.

6.7.1 Effect of Copper Slag at Different Void Ratios

Figure 6.11 shows the relationship between void ratio and friction angle of CS and the corresponding reference Toyoura standard sand, which is commonly used for geotechnical engineering study in Japan. It is evident that the friction angle of both the CS and the reference sand decreases with increasing void ratio. However, the decreasing rates for CS and the reference sand are different, with CS showing a slower decreasing rate than the reference sand. To substantiate the comparison of CS with natural sand, the void ratio and friction angle of two different river sands by Lambe and Whitman (1969) have also been plotted in the same figure. As to be expected, the friction angle of CS is higher than that of the natural sands for a given void ratio (Figure 6.11). Given the limited CS data, perhaps this calls for further investigations into the friction angle of CS across a wide range of void ratios.

Nonetheless, there is a suggestion that the angle of friction of CS is higher than that of the natural sand, suggesting that CS can be used as a natural sand replacement material in fill or other geotechnical applications where frictional properties are important, such as slope stability and embankment.

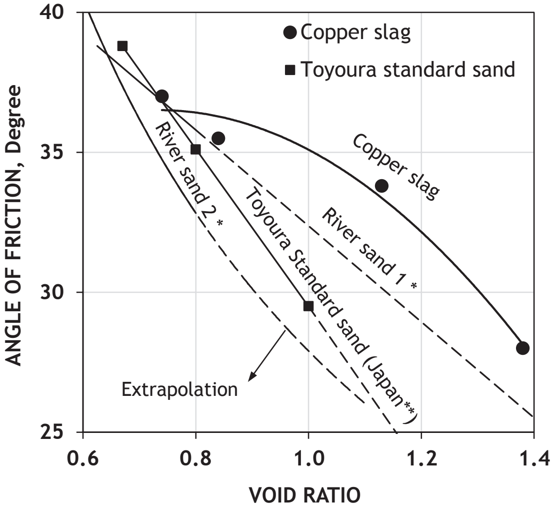


Figure 6.11 Angle of friction of 100% copper slag mixes at different void ratios (for confining stress less than 700 kPa). *Based on Lambe and Whitman (1969). **Based on Kitazume et al. (1998a, 1998b).

6.7.2 Effect of Copper Slag at Different Relative Densities

The friction angles of 10–40% CS–sand mixes (Nawagamuwa et al., 2003) and 100% CS mixes (Chew and Bharati, 2009; Das et al., 1983; Ferguson and Das, 1989; Lim and Chu, 2006) are plotted against their corresponding relative density values in Figure 6.12, together with the typical values for angular sands and rounded sands, as suggested by Das (2001).

It should be noted here that all the results are given as a tangent friction angle measured from a direct shear test apart from the results of Lim and Chu (2006), for which measurements taken from a consolidated drained triaxial test are given as secant friction angle (owing to a curved Mohr–Coulomb envelope).

It can be seen from Figure 6.12 that:

- For 100% CS mixes, the tangent friction angle (Das et al., 1983; Ferguson and Das, 1989) increases with increasing relative density, i.e., increasing from a loose state to a very dense state as classified by Teng (1962).
- Similarly, the secant friction angle (Lim and Chu, 2006) at 70% relative density is higher than that of the 30% relative density.
- At any relative density state, the friction angle of CS, regardless of tangent or secant, is generally higher than that of sands with angular or rounded particles.
- For 10–40% CS–sand mixes at a loose relative density state, their friction angles fall in the range of those of the angular sands at a similar loose state.

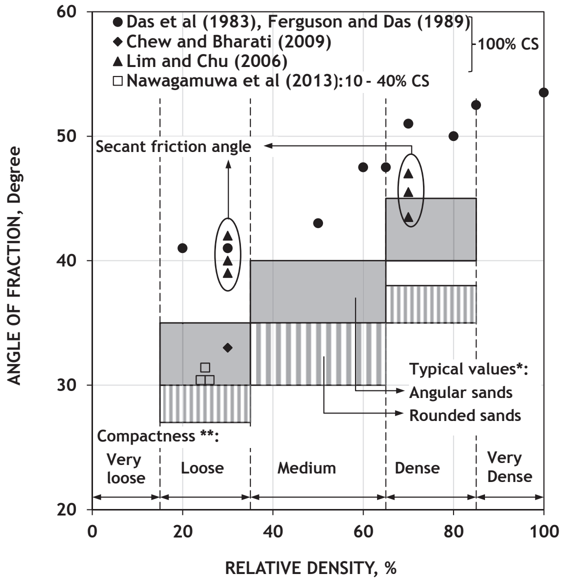


Figure 6.12 Angle of friction of mixes containing copper slag (CS) at different relative densities. *Based on Das (2001). **Based on Teng (1962).

As a summary, and as is apparent from Figures 6.10–6.12, the friction angle of CS is higher than that of the natural sand, even when compared under similar void ratio and relative density conditions. This favourable property of CS may benefit the industry in terms of engineering aspects as well as economic aspects. For example, its high shear strength ensures higher bearing capacity and slope stability. This could be critical for geotechnical applications that require high bearing capacity and slope stability design, such as land reclamation, and its shear resistance can be achieved similar to that of the natural sand, but with a lower compaction effort (higher void ratio/higher relative density).

Undoubtedly, given this observation, the same benefit can also be shared when CS is used in conjunction with other types of soils. The effects of the addition of CS on the friction angle of (i) CS–soil mixes and CS–sand mixes and (ii) CS–FA mixes and CS–pond ash mixes, obtained from direct shear test as reported in the literature published since 1989, are plotted in Figures 6.13(a) and (b), respectively.

From Figure 6.13, the following main observations can be deduced:

- ***CS–soil mixes (Figure 6.13a):*** The initial friction angle of soil (without the addition of CS) varies within a large range and is the lowest compared to other types of materials such as FA, pond ash and sand. The addition of CS increases the friction angle of CS–soil up to about 75% CS content, beyond which no significant change in friction angle is observed.
- ***CS–sand mixes (Figure 6.13a):*** Although there are slight fluctuations in the results, the friction angle of CS–sand generally increases with increasing CS content. It is also noted that the friction angle increment after 70% CS content is considered to be marginal.
- ***CS–FA mixes (Figure 6.13b):*** Although limited data are available, the use of CS in FA mix slightly increases its friction angle with the maximum increase achieved at 75% CS.
- ***CS–pond ash mixes (Figure 6.13b):*** Similar to the observation made with CS–FA mixes, the friction angle of CS–pond mix is improved only marginally with CS content.

Overall, apart from one case in CS–soil mixes, it is surprising that the use of CS has not shown a significant improvement in most of the soils. However, it is noted that the friction angle of most of the reference mixes used in the studies is close to that of the CS, suggesting that the improvement made is due to denser particle packing achieved when they are mixed with CS.

6.8 Lateral Earth Pressure and Retaining Walls

Retaining wall structures are built to provide lateral support to the soil mass of embankments and slopes (vertical or steeply inclined cutting) and prevent them from sliding and eroding. There are several types of retaining wall structures, such as gravity walls, semi-gravity walls, cantilever walls and counterfort walls, which are all made with plain concrete or reinforced concrete.

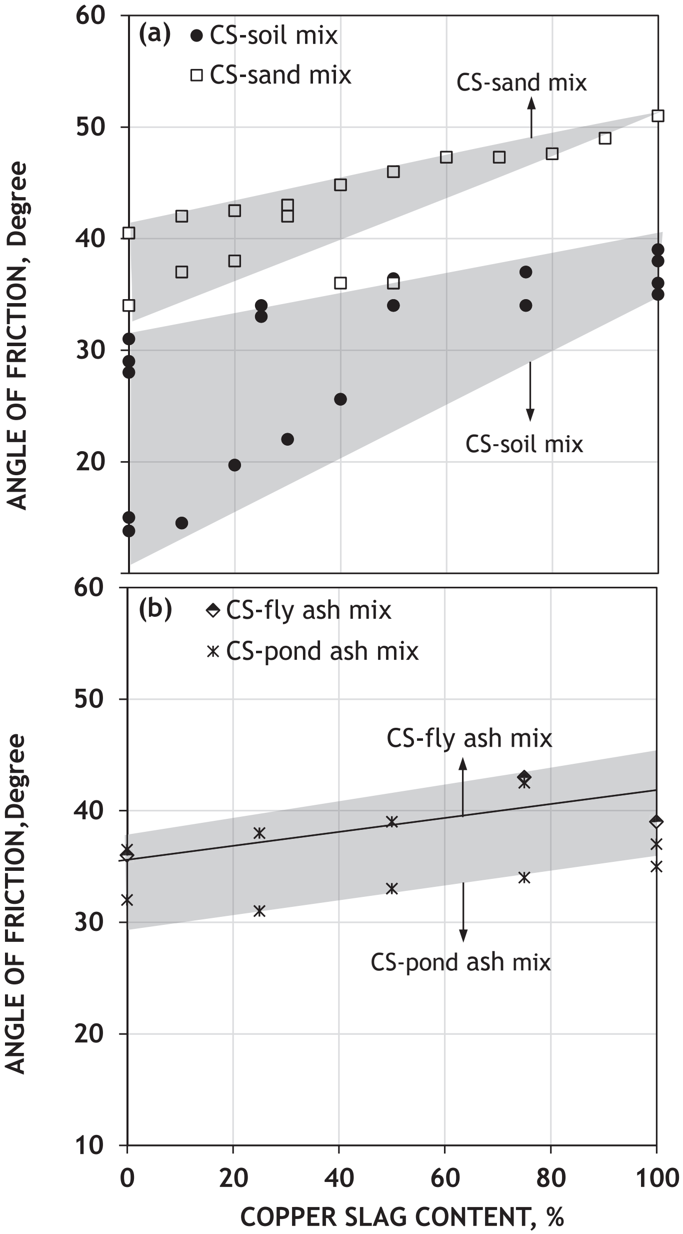


Figure 6.13 Angle of friction of (a) copper slag (CS)–soil and CS–sand mixes and (b) CS–fly ash and CS–pond ash mixes.
Data taken from Goi et al. (2003), Gupta et al. (2012), Havanagi et al. (2006, 2007, 2008, 2009, 2012); Lavanya et al. (2012, 2013), Patel et al. (2007), Sathya and Shanmugavalli (2014), Tandel and Patel (2009), and Viji (2014).

When designing retaining wall structures, engineers are required to determine the unit weight, strength properties and groundwater conditions of the retained soils (backfill), as well as lateral earth pressure, the force exerted by the soils on the structure. In addition, the backfill for retaining wall structures needs to be designed carefully so that the lateral earth pressures supported by the structure are at a minimum. A good backfill material should have high strength and high permeability. Failure in designing proper structures as well as the backfill can affect the stability of structures and lead to sliding, overturning and excessive settlement and bearing capacity.

Investigations on the lateral earth pressure of soils containing CS have been reported by Sathya and Shanmugavalli (2014) and Kitazume et al. (1998b). The former is a laboratory study, which also investigated the seismic behaviour of CS used, whilst the latter is a case study that took place in Japan and will be discussed in the next section.

In the study by Sathya and Shanmuhavalli (2014), CS was used as a sand replacement from 0% to 100% at 10% increments. The coefficient of active earth pressure of the CS–sand mixes, based on Rankine theory, is shown in Figure 6.14.

It can be seen that the coefficient decreases linearly with increasing CS content up to 100%, giving a decreasing rate about 4% for every 10% CS used. The reduction in the coefficient, which also leads to a reduction in lateral earth pressure, indicates that the retaining wall structures can be designed more linearly as the exerted pressure from backfill material made with CS is reduced.

For the seismic study, the displacement of the CS–sand specimens measured by accelerometers in a seismic shake table test shows that the displacement decreases with increasing CS content at a given frequency tested up to 500 Hz, suggesting that

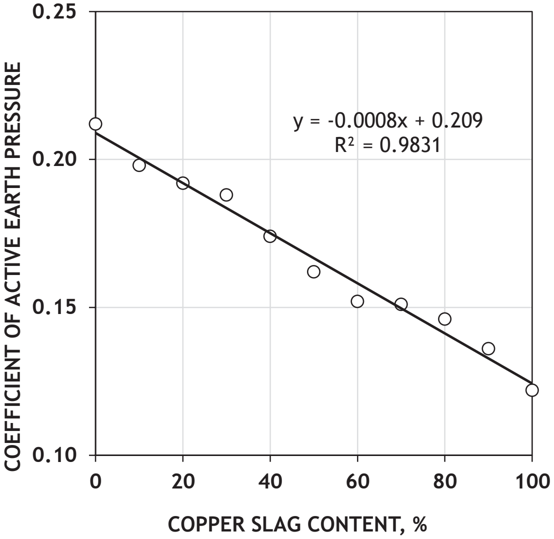


Figure 6.14 The effect of copper slag on coefficient of active earth pressure.

the addition of CS increases the stability of the mix. Given that the earth pressure can increase remarkably during an earthquake, the study of lateral earth pressure of CS–sand mixes under seismic conditions might be useful to engineers for possible application of CS in seismic zones.

6.9 Copper Tailings

Copper tailings are a finely ground waste after copper mineral has been extracted from the ores during beneficiation. Similar to CS, the use of copper tailings as a geotechnical material has also been reported in the literature, but on a relatively smaller scale (Collins and Ciesielski, 1994; Gupta and Thomas, 2013; Nitish et al., 2013; Miller and Collins, 1976). Although copper tailings are not the main focus of this chapter, for completeness, the material properties of copper tailings and their use in geotechnical applications will be discussed here briefly.

The chemical composition of copper tailings, as provided in Gupta and Thomas (2013) and Miller and Collins (1976), shows that copper tailings have low calcium oxide (CaO) at 0.16%, indicating that it has no cementitious property. However, its high total silica, alumina and iron oxides ($SiO_2 + Al_2O_3 + Fe_2O_3$) of more than 85% and low loss on ignition of less than 3% meet the chemical requirements of FA suggested in ASTM C618-12a (2012), which might suggest that copper tailings can be potentially suitable for use as a stabilising agent for soils.

As copper tailings appear in ground form, the grading of copper tailings reported by Gupta and Thomas (2013) and Nitish et al. (2013) has a sizeable silt fraction of 0.06–0.002 mm. Copper tailings are considered to be finer than CS, which usually has a dominant sand fraction. Table 6.5 compares the geotechnical properties of copper tailings to those of CS, which have been reported in this chapter, as well as those of typical sand. In general, the following points have been observed:

- Similar to CS and sand, copper tailings are non-plastic in nature.
- The specific gravity of copper tailings is slightly higher than that of sand but lower than that of CS.
- The compaction characteristics of copper tailings are not clearly understandable from the existing data. In the standard Proctor test, copper tailings have a lower MDD and higher OMC than both CS and sand. However, in the modified Proctor test, the MDD and OMC of copper tailings are higher than those of both CS and sand. Given that copper tailings are generally finer than CS, it can be assumed that CS should have better compaction characteristics than copper tailings; nevertheless, further investigation is needed to establish clarity.
- Because copper tailings have a finer particle size, their permeability is considered to be low, which is similar to fine sand or coarse silt.
- The friction angle of copper tailings is much lower than those of CS and sand, but again, this subject area needs more information to be assessed further.

Table 6.5 Comparison of geotechnical properties between copper tailings, copper slag and natural sand

	Type of Soil		
Property	**Copper Tailings** [a]	**Copper Slag** [b]	**Natural Sand**
Plastic index	Non-plastic	Non-plastic	Non-plastic
Specific gravity	2.9	3.5	2.6
Standard Proctor Test			
Maximum dry density, kg/m^3	1740	2185	1940
Optimum moisture content, %	15.0	11.5	11.0
Modified Proctor test			
Maximum dry density, kg/m^3	2675	2510	2085
Optimum moisture content, %	9.1	6.0	9.0
Permeability, m/s	1.65×10^{-7} (low, similar to fine sand/coarse silt)	3×10^{-4} (medium, similar to coarse sand)	1×10^{-4} (medium)
Angle of friction, degree	21	39	35–40

[a] Data taken from Gupta and Thomas (2013) and Nitish et al. (2013).
[b] Based on the results presented in the previous sections.

Although it might appear that the research in the area of copper tailings characteristics and their potential for use in geotechnical applications has not been as extensive as in the case of CS, in two significant reports of approximately 90 pages each, dealing with waste materials and their recycling as sustainable construction materials in geotechnical applications, prepared under the National Cooperative Highway Research Program (USA), Miller and Collins (1976) and Collins and Ciesielski (1994) have stated that more than 3 million tons of copper tailings were used in embankment construction in Utah, USA, during the 1970s. Although the details of their geotechnical properties as well as service performance are not clear in the reports, this revelation can be encouraging, as it shows that copper tailings may offer a viable use in real geotechnical applications.

6.10 Environmental Impact

As mentioned previously in Section 6.2, a report published by the Federal Highway Administration (FHWA, 2012) in the United States raised a concern over the environmental impacts associated with the use of CS and other non-ferrous slags in geotechnical applications. This might be one of the reasons the use of CS has not been well received by the construction industry there, despite the excellent engineering properties of CS. As the approach adopted by the Federal Highway Agency may become adopted elsewhere, including other countries, it warrants serious considerations to effectively address the environmental impact of using CS in geotechnical applications.

Two groups of researchers, one from Singapore (Chu et al., 2003; Lim and Chu, 2006) and another from the United States (Das et al., 1983; Ferguson and Das, 1989), have studied the leaching of CS, washed copper slag (WCS), a treated spent CS which was previously used in blasting, and a WCS–sludge–Portland cement mix, for their suitability for use in geotechnical applications. The test methods used in the leaching studies were:

- toxic characteristic leaching procedure (TCLP), which is a regulatory test procedure developed by the US Environmental Protection Agency (US EPA, 1992);
- modified TCLP method in which extraction solutions of different pH are used, ranging from pH 3.0 to 8.0, and subjected to 24-h agitation;
- sequential extraction technique (SET), which was originally developed by Tessier et al. (1979) in Canada. In brief, the method extracts elements from test samples under four different conditions in order of increasing reactivity, which are known as exchangeable, carbonate, reducible and organic fractions. The elements left are bound with a crystal matrix and unlikely to release under normal circumstances.

Table 6.6 lists the experimental variables as well as the main observations of the leaching results from these studies.

In general, the leached element concentrations of CS and WCS samples, measured using the standard TCLP method as well as a modified TCLP method at different pH conditions and slightly longer testing duration, were within the regulatory limits set by the US EPA (2012). Additionally, it was also found that the leached element concentrations of WCS decreased with increasing pH of the extraction solution from pH 3.0 (highly acidic) to pH 8.0 (slightly alkaline).

On the other hand, when measured using SET, the elements from the test sample containing a mixture of CS, sludge and Portland cement were reported to be predominantly retained in the residual fraction. This suggests that the elements in this mixture were less likely to leach under normal natural conditions.

6.11 Case Studies

As discussed in the previous sections of this chapter, compared to natural sand, CS can generally have similar or better geotechnical engineering properties. Its application in real situations under field conditions, in addition to the laboratory-based studies, could only help to bolster an engineer's confidence in specifying the material and as such should be welcomed. Indeed, such a use of CS would generally help with sustainability issues.

Table 6.6 Leaching studies of mixes containing copper slag for use in geotechnical applications

References	Experimental Variables	Main Observation
Das et al. (1983) and Ferguson and Das (1989)	**Mix:** 100% CS **Method:** TCLP **Tested elements:** Ag, As, Ba, Cd, Cr, Hg, Pb, Se	The leached element concentrations were well below the regulatory limits.
Lim and Chu (2006)	**Mix:** 100% WCS **Method:** TCLP **Tested elements:** Ag, As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn	The leached element concentrations were well below the regulatory limits.
	Mix: 100% WCS **Method:** Modified TCLP[a] **Tested elements:** Cd, Cr, Cu, Ni, Pb, Zn	The leached element concentrations were well below the regulation limits and they decreased with increasing pH from 3 to 8.
Chu and Lim (2003)	**Mix:** 37.5% WCS–50% sludge–12.5% Portland cement **Method:** Sequential extraction technique **Tested elements:** Cd, Cr, Cu, Ni, Pb, Zn	The elements were predominantly retained in the residual fraction.

CS, copper slag; *TCLP*, toxic characteristic leaching procedure; *WCS*, washed copper slag.
[a] Test was conducted at constant pH 3.0–8.0 with 24-h continuous agitation.

Table 6.7 summarises the geotechnical applications of using CS in revetments, sand compaction piles and embankments and as an unbound aggregate, together with the main observations made in terms of the industrial experience gained, as reported in the literature. The case studies reported cover four countries, namely Holland, India, Japan and the United States. The actual time period when the project construction work took place is not clear in all the cases, but based on the publication year, it could be from the mid-20th century to the early 21st century. The details of the project provided in each case as covered in the relevant literature also tend to vary, from a very brief account of typically one paragraph to as long as a few pages.

In general, although there are mixed views about the use of CS as a geotechnical material in practice, it can be argued that the overall experience is mostly positive.

The main points arising from the reported case studies are discussed in the following sections.

Use of Copper Slag in Revetment, Holland, Year Unknown (Gerritsen and Bruun, 1964)

It is reported that an open filter-type of revetment in the northern part of Holland was constructed using CS-based bound material in conjunction with conventional concrete blocks. The revetment was built to protect the land from hydraulic loadings such as wave

Table 6.7 Case studies involving the use of copper slag in geotechnical applications

	Application Details			
References	**Location**	**Year**	**Used in**	**Main Observations**
Gerritsen and Bruun (1964)	Holland	Unknown	Revetment	The abrasion resistance of CS blocks was high.
Kitazume et al. (1998b)	Japan	Unknown	Sand compaction piles	The field operation of 70% CS–30% clay piles was similar to marine sand piles.
Patel et al. (2007)	India	2005	Embankment	The embankment of a 100-m road section was constructed with 70% CS and 30% fly ash mix. The road condition was satisfactory after 2 years of service.
IRC Highway Research Board (2009)	India	2008	Embankment	Some working difficulties were encountered when 100% CS was used but no such difficulties were experienced for 50% CS–50% pond ash mixes and 50% CS–50% soil mixes.
Transportation Research Board (2013)	Illinois, USA	Unknown	Unbound aggregate	CS was used as aggregate in an unbound application but the project was not successful. The reasons for the failure were not known.

CS, copper slag.

attack and wave uprush. Each of the blocks had a dimension of 0.20 × 0.20 × 0.33 m. The CS blocks were claimed to have a high specific gravity of 2.5 and high abrasion resistance due to a special surface treatment. Although details such as the material design and technical performance of the CS blocks were not provided, the use of CS blocks was reported to be successful.

Use of Copper Slag in Sand Compaction Piles, Japan, Year Unknown (Kitazume et al., 1998b)

A sheet pile wall-type revetment was built at the front of an existing revetment for renovation work at Uno Port in Okayama, Japan. A combination of 70% CS and 30% local clay and 100% marine sand (reference material) were used in sand compaction piles to improve the stability of the clay soil at the front and back of the revetment. The machine used and the operational time for the CS–clay piles were reported to be similar to those for the marine sand piles, suggesting that no changes in the work plan or time schedule were needed when CS was used.

Additionally, the field strength of the piles was evaluated using a standard penetration test and the *N* values of CS–clay piles and marine sand piles behaved similarly, i.e., increased with increasing depth of piles, with the *N* values of CS–clay piles tending to be larger, indicating that CS–clay piles showed higher strength than the marine sand piles. The particle size distribution of CS before and after the construction was also examined. It was found that CS became slightly finer after construction and this might be attributed to particle crushing during in situ compaction. However, such change was claimed by the authors not to affect the strength or permeability of the CS–clay piles.

Use of Copper Slag in Embankment, India, 2005 (Patel et al., 2007)

An embankment of a road section of 100 m length was built using 70% CS and 30% FA mix in India in 2005. The mix had an MDD of 2085 kg/m^3 and OMC of 11%, obtained using the modified Proctor test. After almost 2 years of service, the field condition of the road, for roughness and surface irregularity tests, was reported to be satisfactory. Compared to natural soils, the use of 70% CS and 30% FA was estimated to save about 40% of the production costs. The promising outcome of this field experience was reported to result in another 16-km road construction project using the same mix.

Use of Copper Slag in Embankment, India, 2008 (IRC Highway Research Board, 2009)

CS was proposed for use in the construction of embankment and pavement layers of a road section of 1 km length. To decide the construction methodology to be adopted, three design mixes, (i) 100% CS mix, (ii) 50% CS–50% pond ash mix and (iii) 50% CS–50% soil mix, were proposed for use in the construction of a trial road of 150 m length. It was reported that some working difficulties were experienced with the 100% CS mix, such as uneven compaction and shearing of compacted layers. The reasons for this were not explained in the report. However, such difficulties were not encountered when CS–pond ash and CS–soil mixes were used. No other field performance data were provided as the project was in the interim stage at the time of reporting.

Use of Copper Slag as Unbound Aggregate, Illinois, USA, Year Unknown (Transportation Research Board, 2013)

It was reported that a project using CS as an unbound aggregate that commenced in Illinois was not successful, and the reasons for the failure were not clear. No other information regarding the project, including material properties, mix design and application details, was given.

In summary, it can be seen that the industrial experience using CS as a geotechnical material is limited, and lacks clarity in some cases, particularly for the operational issues associated with the use of CS. Therefore, it may be argued that it is not possible to make cast iron decisions in advancing the use of CS. Nonetheless, the limited information available appears to suggest that the construction industry might be comfortable in terms of technical aspects and operational aspects with the use of CS at up to 70% content.

6.12 Standards and Specifications

For it to penetrate into the construction industry, CS would need to pass the technical performance tests and comply with the regulatory environmental obligations. However, whilst some efforts have been made to judge the environmental credentials of the use of CS, researchers, in the main, have tended to report on the technical results obtained, but have stopped short of assessing compliance with standard specifications

According to BS EN 13242:2002+A1 (2007), *Aggregates for Unbound and Hydraulically Bound Materials for Use in Civil Engineering Work and Road Construction*, the only alternative materials specified therein are the recycled aggregates derived from construction demolition and excavation, steel slags and air-cooled blast-furnace slags. However, the latest draft for Standard prEN 13242 (2015) has been encouraging, as CS, together with other recycled materials such as municipal incinerator bottom ash, has been considered in the development of the standard, and in its present form, prEN 13242 (2015) recognises the history of CS use and does make provision for special requirements and additional requirements, implying that CS and natural sand for use in most geotechnical applications need to comply with the requirements of prEN 13242 (2015). The requirements are explained in the following sections.

6.12.1 Geometric Requirements: Aggregate Grading and Fines Content

Many engineering properties of a material, such as shear resistance, are associated with its particle grading. Thus, it is important to make sure that the particle size distribution of CS always complies with the fine aggregate grading requirement specified in the standard, particularly when crushing air-cooled CS to sand fraction. Unless the CS is contaminated, the maximum fines content of CS (particles passing 0.063 mm) is commonly less than 3% (categorised as f_3); as shown in Chapter 3, a low fines content of CS ensures good drainage properties.

6.12.2 Physical Requirements: Particle Density and Water Absorption

Particle density is used to derive soil properties such as void ratio, saturation degree and bulk density. Depending on the cooling process, the particle density (specific gravity) of CS generally varies from 2.8 to 3.9, as shown in Chapter 3. Water absorption of CS is very low, close to 0%.

6.12.3 Chemical Requirements: Acid-Soluble Sulphate, Water-Soluble and Total Sulphur Content

Sulphur compounds in aggregate can come into contact with either concrete (foundations and retaining walls) or reinforcing steel and thereby result in the failure of the structures. Thus, it is necessary to ensure that CS does not exceed the maximum values specified in the standard. If CS is used in hydraulically bound applications, the organic or other substances of CS should be determined, as these might affect the hydration rate of the materials. This test is particularly important for WCS as it might be contaminated during blasting.

6.12.4 Durability Requirements

The deterioration of aggregate due to freeze–thaw attack can affect the overall integrity of the structure. The fairly low water absorption of CS may suggest satisfactory freeze–thaw resistance, even though this needs to be confirmed by a proper laboratory test.

6.12.5 Leaching of Heavy Metals

As revealed in Section 6.10, CS has been shown to be safe to use in terms of its environmental impact. However, as the regulation limits for leached heavy metal concentrations could be different in different regions, to be sure, a leaching test should be conducted on CS.

A search for recognised specifications documents, such as those from the US Department of Transportation, (MDOT, 2012), that allows the use of CS as a granular material suitable for fill applications and road pavements (and this will be discussed in Chapter 7). The requirements for CS are the same as natural aggregate and no special requirements are mentioned.

Overall, the requirements of BS EN 13242-2002+A1 (2007), as discussed above, are necessary and the properties of CS fit in very well with these. Thus, CS needs to be processed or specified by aggregate manufacturers or engineers to meet the same requirements as natural aggregates and to ensure the environmental suitability of CS, for it to qualify as a viable sustainable source. Given that CS has now been considered in the development of the new standard prEN 13242 (2015), its use in geotechnical applications may soon achieve another historical milestone. Meanwhile, the standards and specifications for ferrous slags, such as blast-furnace slag, can be adopted for using CS in geotechnical applications.

6.13 Conclusions

Although there has been some concern expressed, an overview of the information available is that with its generally sound engineering properties, CS could be an ideal candidate as an alternative to natural sand in geotechnical applications.

CS is a non-plastic material and when mixed with silt, clay soils or FA, the LL, PL and PI of the mixes decrease linearly with increasing CS content. The MDD and OMC of CS obtained using the standard Proctor test are 2185 kg/m^3 and 11.5%, respectively, whilst the corresponding values obtained using the modified Proctor test are 2510 kg/m^3 and 6.0%. Its compaction characteristics are better than those of typical natural sand. The use of CS with soils, FA and pond ash mixes increases and decreases their OMC and MDD, respectively.

The permeability and the rate of consolidation of CS and sand are essentially similar, though its use with sand may marginally reduce the permeability because of improved particle packing of the resulting mixes. Additionally, CS tends to be more compressible because of its angularity compared to rounded natural sand of similar grading.

The friction angle of CS at about 39 degrees falls close to the mid-range of well-graded sand. In general, the friction angle of mixes made with soils, sand, FA and pond ash increases with increasing CS content. When CS is used as backfill material for retaining-wall structures, the coefficient of active earth pressure decreases linearly with CS content, giving an average decreasing rate of 4% with every 10% CS used.

Copper tailings show slightly less favourable geotechnical engineering properties compared to CS. Nonetheless, the material was used in embankment construction in Utah, USA, during the 1970s.

The results of the leaching tests of CS and WCS suggest that these materials should be safe to use in most geotechnical applications, though it should be noted that the corrosivity of CS has not been reported. CS has been used successfully in the construction of revetments, sand compaction piles and embankments, with the results suggesting that the use of CS at up to 70% content may be adopted in practice. The use of CS as an aggregate in geotechnical applications has been allowed by the Michigan Department of Transportation in the United States and also has been considered in the development of a new standard for prEN 13242 (2015).

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Use of Copper Slag in Road Pavement Applications

7

Main Headings

- Unbound applications
- Hydraulically bound applications
- Bituminous bound applications
- Environmental impact
- Case studies

Synopsis

The effect of copper slag (CS) on the engineering properties of road pavements is described based on the literature published since 1992. CS has a similar California bearing ratio to natural sand. When used in hydraulically bound applications, it increases workability and compressive and flexural strengths, and decreases drying shrinkage of concrete. It may also improve the abrasion resistance of concrete. The Marshall method can be adopted when designing a CS bituminous mix. The material reduces the modulus, but increases fatigue life of the bituminous mix and has no effect on its water sensitivity. Though little is known about its use in real applications, CS should not present any threat to the environment. The study of copper tailings has also been included.

Keywords: Copper slag, Unbound applications, Hydraulically bound applications, Bituminous bound applications, Environmental impact, Case studies.

7.1 Introduction

A pavement is made up of multiple layers of road construction materials, and depending on the position of each layer, the materials may be either soils or aggregates or a combination of both as a main component, and made with or without binders, such as bitumen and Portland cement (PC). From the bottom up, a pavement generally consists of subgrade, capping layer, subbase, base course, binder course and/or surface course. Based on the material design for the upper layers after the subbase layer, there are three broad pavement classifications, which are known as:

- flexible pavements, where the upper layers are bituminous bound;
- rigid pavements, where the upper layer (note: one layer only) is hydraulically bound;
- composite pavements, where the bituminous bound layers are laid on top of hydraulically bound layers.

Sustainable Construction Materials: Copper Slag. http://dx.doi.org/10.1016/B978-0-08-100986-4.00007-9

Apart from the subgrade, which is usually made up of in situ soils, aggregates are required in the construction of each layer of the pavement. According to a report by the European Aggregates Association in 2015 (UEPG, 2015), about 20% of the total aggregate production in 38 countries in Europe is used in the construction and maintenance of roads, runways, railways and waterways. On a global scale, in 2020, these applications are projected to consume roughly about 7.02 billion tonnes of aggregates. Although the majority of the specifications in road construction have allowed the use of recycled materials, such as recycled aggregate derived from construction and demolition waste, natural aggregates can still be assumed as the predominant part of the constituent materials for road pavements.

Indeed, for a road pavement structure, the technical performance of the aggregate used in each of the pavement layers generally increases in ascending order, from the bottom layer (subgrade) to the top layer (surface course), suggesting that a wide range of construction materials of different qualities can be used. As such, the origins of these materials can be either natural sources or alternative sources, and the quality of the latter, in terms engineering properties and durability, is not always inferior to the former. When designed properly, the use of alternative sources can make the natural nonrenewable sources last longer.

Although it is a localised material, copper slag (CS) can be a viable replacement material for natural aggregates. Indeed, for use in road pavements, it can be expected that the material will have a similar performance to the more commonly used ferrous slags (steel and blast furnace slags). Depending on the cooling process adopted, CS can be processed into coarse and fine aggregates which possess favourable engineering properties for pavement constructions such as (i) high stability, attributed to its angularity and suitable as a granular base, and (ii) high wear resistance, attributed to its hardness and suitable for bituminous bound applications. However, as highlighted by the Federal Highway Administration (FHWA, 1998), there are perhaps two issues associated with the use of CS as a road pavement material that remain to be addressed, namely:

(i) stripping resistance due to its glassy nature and

(ii) environmental suitability due to its heavy metal content.

This chapter presents a systematic analysis and evaluation of the published data on the performance, environmental impacts, case studies and standards and specifications relating to the use of CS in road pavement applications. The information used in developing this chapter was sourced from studies published worldwide, with significant contributions from the Asian countries, especially India, and the United States, since 1992. As CS can potentially be used in different pavement layers, its use has been considered under three main sections, namely, unbound, hydraulically bound and bituminous bound applications.

7.2 General Information

Technical reports originating from the United States (Baker et al., 2011; Collins and Ciesielski, 1994; FHWA, 1998; Scullion et al., 2010; Transportation Research Board, 2013b) and Canada (LVM-JEGEL, 2009) have reviewed the technical and environmental aspects of using CS in unbound, bituminous and hydraulically bound applications. The main observations of these reports are briefly outlined in Table 7.1 and discussed later. In general, it has been suggested that CS is suitable for use as a natural aggregate in road pavement applications. At the same time, the reports have frequently expressed environmental concerns associated with the use of CS.

Table 7.1 Main observations in terms of technical and environmental aspects for using copper slag (CS) in unbound, bituminous and hydraulically bound applications

	Main Observations	
References	**Technical**	**Environmental**
(i) Unbound Application		
Baker et al. (2011) and Scullion et al. (2010)	–	CS may present risk to the environment and human health.
(ii) Base Aggregate (May Be Unbound or Bituminous/Hydraulically Bound)		
FHWA (1998)	Copper slag is suitable to use as base aggregate and it can be designed using conventional methods.	Environmental assessments should be conducted.
LVM-JEGEL (2009)	Copper slag presents no technical issues as base aggregate.	There could be some environmental concerns.
(iii) Bituminous and Hydraulically Bound Applications		
Collins and Ciesielski (1994) and FHWA (1998)	Copper blasting slag has been used in small scale in California.	–
FHWA (1998)	CS is adequate for making bituminous mix but glassy CS should be avoided owing to poor friction resistance. The mix can be designed using conventional methods.	Environmental assessments should be conducted.
Baker et al. (2011) and Scullion et al. (2010)	CS made the mixes more durable.	There could be some environmental concerns.
Transportation Research Board (2013b)	Copper blasting slag and CS have been used in California and Georgia, respectively.	Illinois discontinued the use of CS because of environmental issues.

7.2.1 Unbound Applications

Technical reports published by Baker et al. (2011) and Scullion et al. (2010) of the Texas Department of Transport, relating to the proposed cleanup of smelting and refining plants in El Paso, Texas, on grounds of total concentration of heavy metals and their leachate concentrations, have expressed concern about the environmental and human health implications of CS, and therefore its suitability for use in unbound applications. Notwithstanding, the use of CS in bituminous and hydraulically bound applications, owing to the much reduced associated risk, was considered to be viable.

7.2.2 Base Aggregates

As suggested by FHWA (1998), CS can be considered to possess desirable engineering properties for granular base construction, offering high stability, high permeability and good resistance to freeze-thaw attack and mechanical degradation. Conventional design methods could be used for granular bases made with CS. However, attention must be given when:

- stockpiling CS, to prevent segregation and leachate contamination;
- compacting CS, to achieve adequate compaction.

Additionally, there is a need to assess CS for its heavy metal contents and leachability.

Although the information provided was brief, LVM-JEGEL (2009) also held the view that whilst the use of CS as a base material in road pavement was technically sufficiently sound, there were some leaching concerns, mainly concerning the colour and odour of the leachate.

7.2.3 Bituminous and Hydraulically Bound Applications

Because of its good stability characteristics, wear resistance and soundness, processed air-cooled and granulated CS has been considered suitable for use as a coarse and/or fine aggregate in hot mix asphalt (HMA) pavements (FHWA, 1998). These mechanical properties of CS were claimed to increase the durability of HMA containing CS (Baker et al., 2011; Scullion et al., 2010).

It has been stated (FHWA, 1998) that conventional bituminous mix design methods such as the Marshall and Hveem methods can be adopted for the design of HMA made with CS, and no special provisions are required, provided the physical properties of the CS comply with standards such as ASTM D692 (1994). However, as CS may be susceptible to stripping because of its glassy nature, the stripping resistance of CS mixes needs to be taken into consideration in the mix design. During the construction of pavements using HMA made with CS, the mixing, placing and compaction procedures and equipment used could be similar to when the conventional HMA is used (FHWA, 1998). Notwithstanding, it is considered that leaching tests of CS and environmental assessments associated with the use of CS in bituminous bound applications would be required (FHWA, 1998; Baker et al., 2011; Scullion et al., 2010).

In the United States, whilst the Michigan State Department of Transportation has considered the use of CS as coarse and fine aggregates for bituminous mixes, the states of California and Georgia have reported using spent CS (which has previously been used in blasting) and granulated CS in bituminous mixes, respectively, (Collins and Ciesielski, 1994; FHWA, 1998; Transportation Research Board, 2013b). However, the Illinois State Department of Transportation discontinued the use of CS for HMA because of heavy metal issues (Transportations Research Board, 2013b).

Overall, it would appear that the use of CS in unbound, bituminous and hydraulic applications generally improves the performance of the mixes, and no modification is needed for the mix design methods and construction procedures for the CS mixes. However, additional care would be needed when designing HMA for the stripping resistance of the mixes containing CS because of its glassy nature. More importantly, the environmental credentials of CS mixes need to improve to inspire confidence in engineers to specify CS for use in these applications.

7.3 Unbound Applications

The unbound applications refer to the pavement layers including subgrade, capping layer, subbase and base course, in which binders such as bitumen and PC are not used. Strictly speaking, subgrade is not normally considered as a pavement layer; however, it plays a decisive role in the pavement design, as its bearing capacity affects the thickness of the pavement layers above it. Subgrade is usually made by in situ virgin soil or imported materials to provide a stable platform for pavements. Capping layer, subbase and base course are made with sand and gravel as granular materials, and they are designed to distribute the load transmitted from above, so that it does not exceed the strength of the pavement layers underneath.

As far as the engineering properties of the unbound applications are concerned, the effect of CS on the strength of subgrade will be discussed in the following section and its effect on the properties of capping layer, subbase and base, such as shear strength and permeability, can be found in Chapter 6. The studies of other important characteristics of unbound aggregates made with CS for pavement applications such as resilient modulus have not been undertaken, suggesting scope for further research to fully appreciate the potential of this material for road pavement applications.

7.3.1 California Bearing Ratio

The strength of a subgrade is commonly expressed in terms of California bearing ratio (CBR), using an empirical test that was originally developed by the California State Highway Department in the 1930s (O’Flaherty, 2002). The test is straightforward. It determines the relative load required for a plunger to cause a certain penetration into a soil sample with respect to a standard well-graded crushed-rock sample. As a guide, the larger the CBR value, the higher the strength of a soil. The test samples

Table 7.2 California bearing ratio (CBR) values of copper slag[a] and typical sand and gravel aggregate[b]

Material	CBR, %
Superfine copper slag	**14**
Copper slag	**45**
Fine or slightly compacted sand	3
Sandy clay	4–5
Well-compacted sand	10–25
Very well-compacted sand	25–50
Well-graded sandy gravel	60
Coarse crushed gravel	80–100

[a] Data taken from Havanagi et al. (2006, 2007, 2008, 2009, 2012), IRC Highway Research Board (2011), Lakshmanan et al. (2014), Tandel (2008), Tandel and Patel (2009).
[b] Based on O'Flaherty (2002).

can be in the soaked or unsoaked condition. The former condition, which corresponds to the worst possible case field condition that soil may experience due to high water table and poor drainage system, is commonly adopted in the standards such as ASTM D1883 (2014) and AASHTO T 193 (2013).

Table 7.2 compares the CBR of normal sand size CS and superfine CS with that of the typical sand and gravel aggregates suggested by O'Flaherty (2002). It can be seen that the CBR of superfine CS at 14% is comparable to that of the well-compacted sand, whilst the CBR of normal sand size at 45% is comparable to that of very well compacted sand. This suggests that CS can be used in place of natural sand as a viable material in unbound applications.

The effects of CS on the CBR of (i) soil–CS and cement-stabilised soil–CS mixes and (ii) fly ash–CS and pond ash–CS mixes, using the data taken from the studies undertaken in India since 2006, are plotted in Figure 7.1(a) and (b), respectively. All the specimens used were reported to be in the soaked condition, except for Patel et al. (2007) and the Indian Research Council Highway Research Board (2011), from which such information was unavailable. Additionally, the thickness requirement of the capping layer for subgrade at different CBRs recommended by the Highway Agency in the United Kingdom is also shown in the figures as an example.

Figure 7.1 shows that:

- For soil–CS mixes (Figure 7.1(a)), the change of CBR value due to the addition of CS can fluctuate; however, it shows an overall increasing trend. Depending on the improvement of CBR with CS and its content level, the thickness of the capping layer is generally reduced and in some cases the capping layer may not even be needed. It should be noted that the soil mix with 75% CS at 80% CBR in Figure 7.1(a) is unlikely to be true as it is significantly higher than that of 100% CS at 45% CBR (Table 7.2).

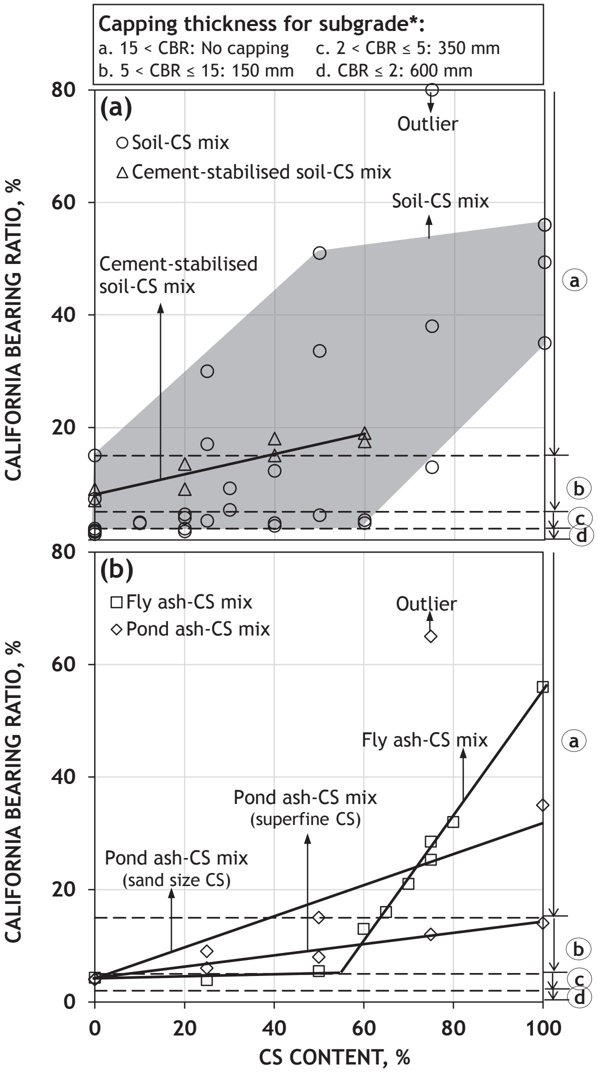

Figure 7.1 Effect of copper slag (CS) on California bearing ratio of (a) soil–CS and cement-stabilised soil–CS mixes and (b) fly ash–CS and pond ash–CS mixes. *Based on Highway Agency (1995).
Data taken from Baraskar and Ahirwar (2014), Havanagi et al. (2006, 2007, 2008, 2009, 2012), IRC Highway Research Board (2011), Lakshmanan et al. (2014), Patel et al. (2007, 2011), Saravana et al. (2005), Tande (2008), and Tandel and Patel (2009).

- For cement-stabilised soil–CS mixes (Figure 7.1(a)), the CBR of the mixes increases as the CS content increases. Although cement stabilisation improves the CBR of soil, the addition of CS further increases the CBR of the cement-stabilised soil, and therefore the capping layer may not be needed at CS content of 40% or more.

- For fly ash–CS mixes (Figure 7.1(b)), the CBR of the mixes is almost unchanged up to 50% CS content, beyond which it increases steadily with increasing CS content.
- For pond ash–CS mixes (Figure 7.1(b)), the CBR of the mixes increases with increasing CS content but at two distinct increasing rates because of the difference in the fineness of CS used, as the results in Table 7.2 suggest. Although the CBR magnitude improvement of superfine CS has not been large enough to eliminate the need for the capping layer, the study showed that the addition of superfine CS significantly increases the maximum dry density. It should, however, be noted that the pond ash mix with 75% CS at 65% CBR is considered to be an outlier (Figure 7.1(b)) as it is higher than that of 100% CS at 45% CBR (Table 7.2).

As mentioned at the beginning of this section, in situ soils are normally used for the construction of subgrade; however, imported materials may also be used (i) when the in situ soils are unstable or (ii) as bulk fill to elevate subgrade. If the material used for subgrade soil is weak, its strength can be improved by cement stabilisation or by adding a capping layer. The overall results shown in Figure 7.1 suggest that the addition of CS in soil, cement-stabilised soil and fill materials such as fly ash and pond ash has been very beneficial, as CS improves the CBR of the material and reduces the thickness of the capping layer, or even eliminates the need for it. Additionally, a higher strength of subgrade also leads to a reduction of total thickness of pavement. Thus, it would appear that the use of CS as subgrade materials can potentially reduce the production cost.

7.4 Hydraulically Bound Applications

The construction of rigid pavements and composite pavements involves using hydraulic cement in the form of PC on its own, or as is becoming increasingly accepted, in combination with pozzolanic materials such as fly ash and ground granulated blast furnace slag in their different layers, including subbases, base courses and concrete slabs, which can be plain or reinforced concrete, jointed or continuous and cast in situ or precast.

Although a detailed analysis and evaluation of the effects of the use of CS on the performance of normal concrete applications has been covered in Chapter 5, this particular section deals with the effects of CS on the fresh and hardened concrete used in the road pavement construction, with its special characteristics such as (i) typically low consistence, (ii) leaner concrete mixes for use in subbases and base courses and (iii) strong aggregate particle interlocking for use in 'aggregate interlock joints' of jointed plain concrete to provide load transfer.

7.4.1 Workability and Stability

Although workability specifications may vary with the type of hydraulically bound application, in general, the workability of concrete used in road pavement construction is low, typically 0–50 mm slump or 0.77–0.91 compacting factor.

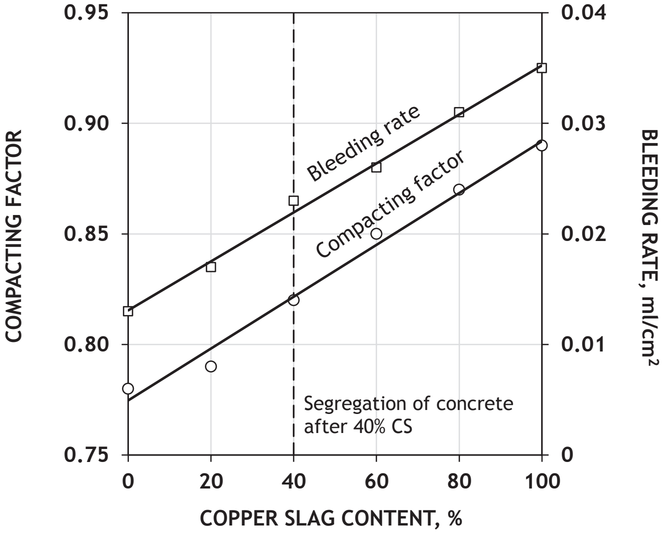

Figure 7.2 Effect of copper slag (CS) on compacting factor and bleeding rate of concrete.

For example, the workability of concrete in slip-form paving operations is lower (zero slump) than in fixed-form paving operations, because concrete in the former operation must hold its initial shape after the extrusion process. In addition to the workability requirement, concrete in the fresh state in all applications must be a stable mix, with its all constituent materials held together as a homogeneous mix throughout the entire concreting process, and it does not suffer from either excessive bleeding or segregation.

Figure 7.2 shows the data of Kumar (2012) plotted for the compacting factor and the bleeding rate of concrete made with CS as a fine stone dust direct replacement from 0% to 100% content level at constant 0.40 water/cement ratio. It is evident in Figure 7.2 that both the compaction factor and the bleeding rate of concrete increase linearly with increasing CS content. This is to be expected as the CS used (3.87 fineness modulus (FM)) is considerably coarser than the fine stone dust (1.62 FM).

Furthermore, the mix with CS content above 40% was also reported to experience segregation, most probably due to particle size and distribution difference between the CS used as a direct replacement of fine stone dust and an increase in workability having an adverse effect on the stability of the mix. This example highlights the importance of adjusting the mix proportions to adopt the use of new materials in hydraulically bound mixes. Notwithstanding this, the conclusion has to be that when properly designed through (i) maintaining the overall particle size distribution and (ii) keeping the workability unchanged by reducing the water content due to the improvement in workability, and all other things being equal, hydraulically bound mixes made with CS with the required workability and good stability can be obtained.

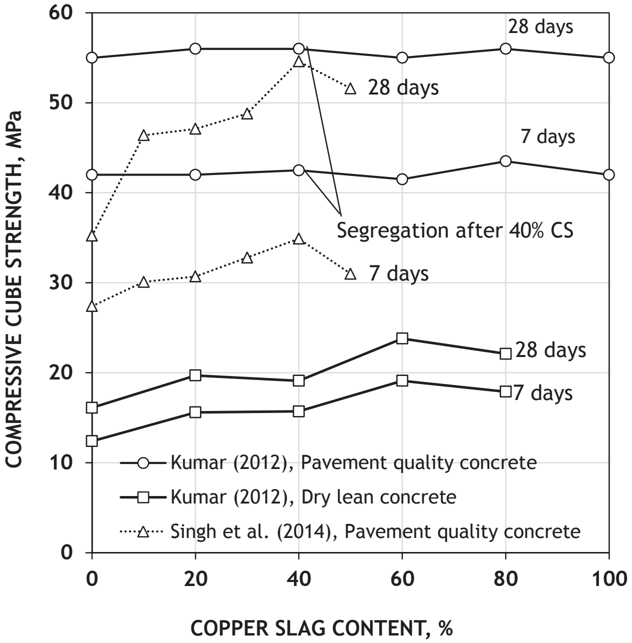

Figure 7.3 Effect of copper slag (CS) on concrete compressive cube strength.

7.4.2 Compressive Strength

Although the flexural strength of concrete pavement is responsible for resisting the bending load of the traffic, compressive strength is still commonly used in specifying the strength requirement of concrete pavements as the test is relatively easier and reliable to perform. Figure 7.3 shows the compressive cube strength of pavement quality concrete and dry lean concrete, made with increasing CS content, at 7 and 28 days. The mixes were designed for constant water content and water/cement ratio allowing workability to increase with the addition of CS.

Given that segregation was observed in the fresh state for concrete containing more than 40% CS, the results were not analysed further because of the nonhomogeneity of concrete. In general, it can be seen from Figure 7.3 that the compressive strength of concrete increases with increasing CS content, except for one case in which the concrete strength remains almost unchanged with CS. As the water content and water/cement ratio were kept constant, the increase of concrete strength could be due to the interlocking of the angular CS particles.

However, both the improvement in workability and the strength of concrete with CS aggregate suggest that concrete mixes can be designed in a more cost-effective yet sustainable manner. This can be achieved by reducing the water content of CS concrete mixes as the water demand of CS to achieve target workability is lower,

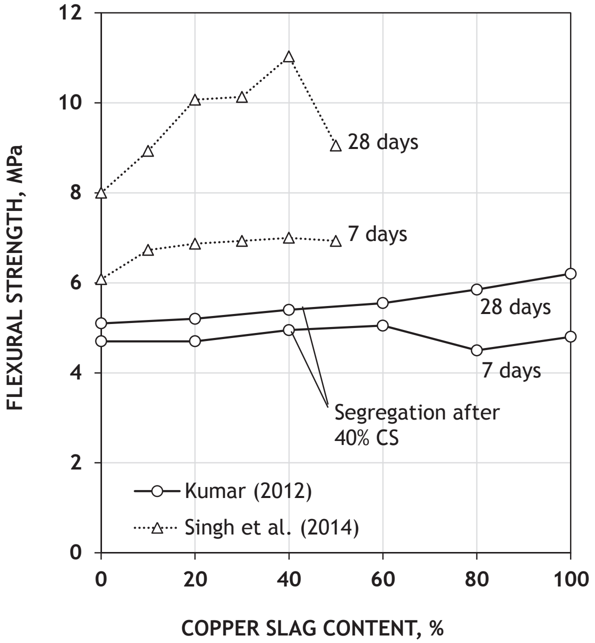

Figure 7.4 Effect of copper slag (CS) on flexural strength of pavement quality concrete.

and at the same time reducing the cement content for a given water/cement ratio. In designing such a mix, the loss of fines content attributed to the cement reduction can be compensated for by using a suitable filler, as suggested by Dhir et al. (2006).

7.4.3 Flexural Strength

As pavements are subjected to bending stresses due to traffic loading, the flexural strength of concrete is commonly specified as a design parameter for rigid pavements. The flexural strength of concrete can be determined using either a third-point loading or a centre-point loading test. Given that the tests are sensitive to specimen handling, curing procedure and testing conditions, both the flexural and the compressive strength of concrete are usually measured during the design stage, but compressive strength is used later for quality control in the pavement construction field.

The 7- and 28-day flexural strength results of pavement quality concrete made with CS from 0% to 100% content measured using the third-point loading test (Kumar, 2012) are plotted in Figure 7.4. These data correspond to those of the compressive strength test results in Figure 7.3, and the effects of mix segregation from 40% onward are reflected in the test results.

In the structural design of rigid pavements, the flexural strength of concrete is one of the primary factors that affect the thickness of a concrete slab. As shown in Pavement Design HD 26/06 of the UK Highway Agency (Highway Agency, 2006), for a given design traffic load and foundation stiffness class, the thickness requirement of a concrete slab decreases with increase in its flexural strength.

Thus, notwithstanding the effect of segregation on the measured flexural strength, which can be overcome by modifying the mix design, the potential improvement in the flexural strength of concrete with the addition of CS should reduce the thickness of the concrete slab and thereby lead to a potential reduction in cost.

7.4.4 Drying Shrinkage

At the end of the curing process, drying shrinkage takes place in concrete as water is withdrawn from the cement paste to the surrounding. During the construction of a concrete slab, the shrinkage movement of the concrete is restrained by the underlying subgrade. If the concrete is not adequately designed for the drying shrinkage, detrimental cracks will occur as a result of the tensile stress exceeding the tensile capacity of the concrete. This degradation affects the vehicle ride quality and service life of the pavement.

The reduction in the drying shrinkage of concrete with the use of CS (Figure 7.5), due to its lower water absorption and higher hardness than natural sand, which concurs with the previously reported trends in Chapter 5, suggests there are potential benefits that can be gained from adopting the use of CS as a replacement for natural sand.

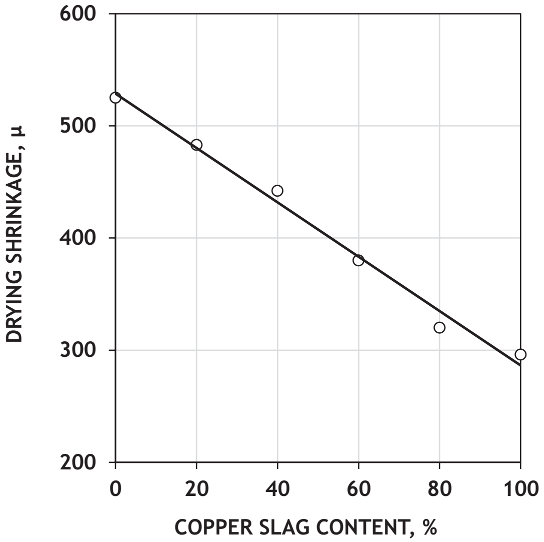

Figure 7.5 Effect of copper slag on drying shrinkage of concrete.

7.4.5 Abrasion Resistance

The concrete surfaces of a rigid pavement are subjected to different types of mechanical abrasion such as tyre sliding and wheel rolling. This deterioration reduces the surface friction of concrete, making the pavement slippery and unsafe to use during wet weather. As cement paste is weak against abrasion, the abrasion resistance of concrete relies on the properties of aggregate used, particularly its hardness and particle size distribution.

This means that with its high hardness property (6–7 Mohs hardness) and low porosity measured as water absorption (close to 0%), the use of CS should generally improve the abrasion resistance of road pavement concrete.

The results of the limited tests undertaken as per Procedure A of ASTM C779 (2000) to measure the abrasion resistance of concrete replacing stone dust with CS as reported by Kumar (2012); however, point to the contrary (Figure 7.6). This calls for further rigorous testing in this respect, as the mixes tested by Kumar (2012) tended to suffer from bleeding (increasing the water/cement ratio of the surface and near-surface concrete, and thereby weakening the test mortar and its interfaces with aggregate particles) and segregation (affecting its compaction and thereby introducing structural weakness in the test mortar).

7.5 Bituminous Bound Applications

7.5.1 Marshall Mix Design

The Marshall mix design method was first developed in the 1930s by Bruce Marshall of the Mississippi State Highway Agency to determine the optimum bitumen content of HMA mixtures (Transportation Research Board, 2011). The method

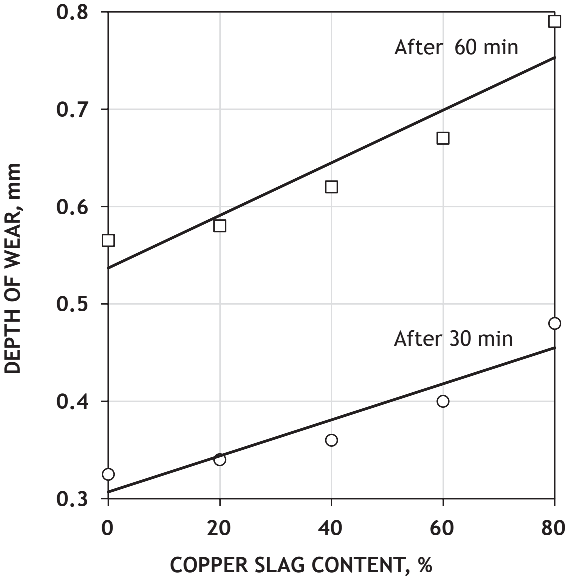

Figure 7.6 Effect of copper slag on depth of wear of concrete.

was later adopted and modified by the US Army Corps of Engineers in the 1940s during World War II and subsequently formalised as standard tests such as ASTM D6927 (2015) and BS EN 12697-34 (2012). In brief, the test procedures involve heating, mixing and compacting the bituminous bound aggregate mix over a range of bitumen contents. The optimum bitumen content of the mix is selected based on a set of design parameter criteria for the mix including stability, flow, air voids, voids filled with bitumen (VFB) and voids in mineral aggregate (VMA).

Bituminous bound mix made with CS designed using the Marshall method has been undertaken in a few countries, but mainly in India, since 1992. The results of Marshall design parameters of all the bituminous bound mixes at their optimum bitumen content (ranging from 3 to 6%) are shown in Figures 7.7(a)–(e). As the majority of the specimens were compacted with 75 blows to simulate heavy traffic conditions, the requirements of the design parameters in heavy traffic conditions specified by the Asphalt Institute (1997) are also shown in the figures.

The main points arising from Figure 7.7 are discussed below:

Marshall Stability (Figure 7.7(a))

Marshall stability measures the resistance to plastic flow of a bituminous bound specimen under a compressive load. The stability of a mix is governed by the viscosity of bitumen as well as the internal friction of aggregate. It can be seen from Figure 7.7(a) that although

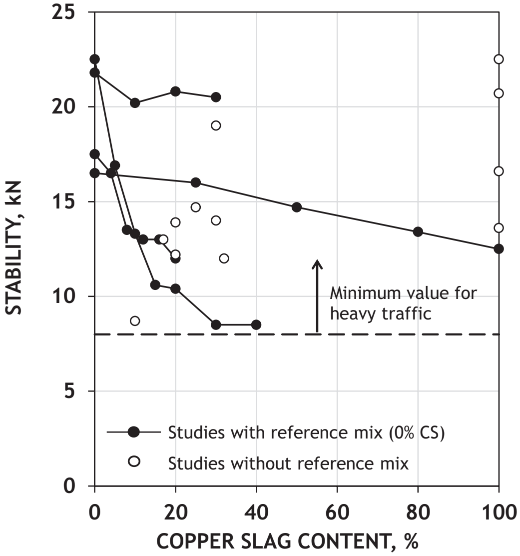

Figure 7.7 (a) Marshall stability of mixes containing copper slag (CS).
Data taken from Al-Sayed and Mandany (1992), Chetan and Sowmya (2015), DON and NASSCO (1999), Hassan and Al-Jabri (2011), Havanagi et al. (2007, 2009, 2012), Pundhir et al. (2005), Selvanambi et al. (2011), Sharma et al. (2013a), and Yildrim et al. (1993).

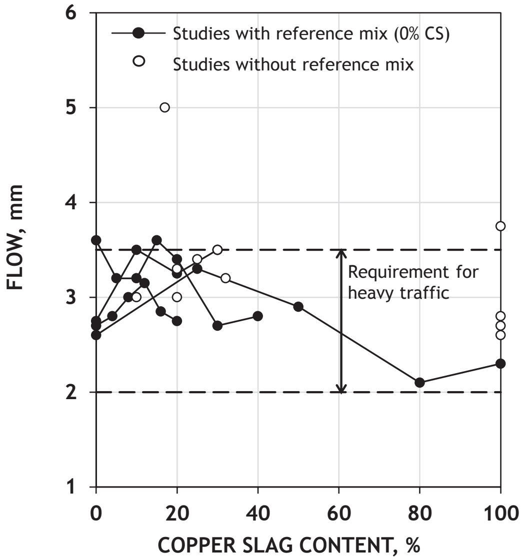

Figure 7.7 (b) Marshall flow of mixes containing CS.
Data taken from Al-Sayed and Mandany (1992), Chetan and Sowmya (2015), DON and NASSCO (1999), Hassan and Al-Jabri (2011), Havanagi et al. (2007, 2009, 2012), Pundhir et al. (2005), Selvanambi et al. (2011), Sharma et al. (2013a), and Yildrim et al. (1993).

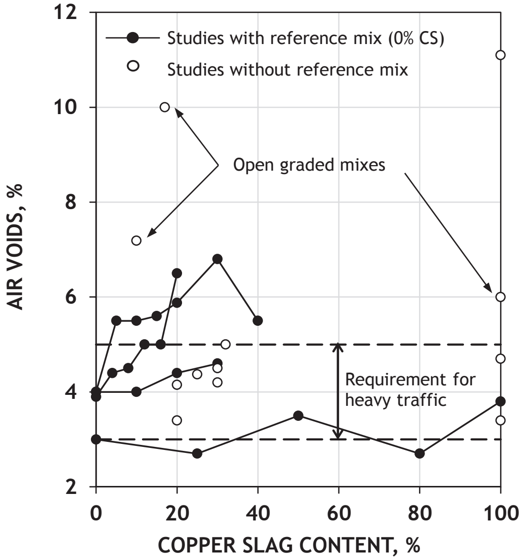

Figure 7.7 (c) Air voids of mixes containing CS.
Data taken from Al-Sayed and Mandany (1992), Chetan and Sowmya (2015), DON and NASSCO (1999), Hassan and Al-Jabri (2011), Havanagi et al. (2007, 2009, 2012), Pundhir et al. (2005), Selvanambi et al. (2011), Sharma et al. (2013a), and Yildrim et al. (1993).

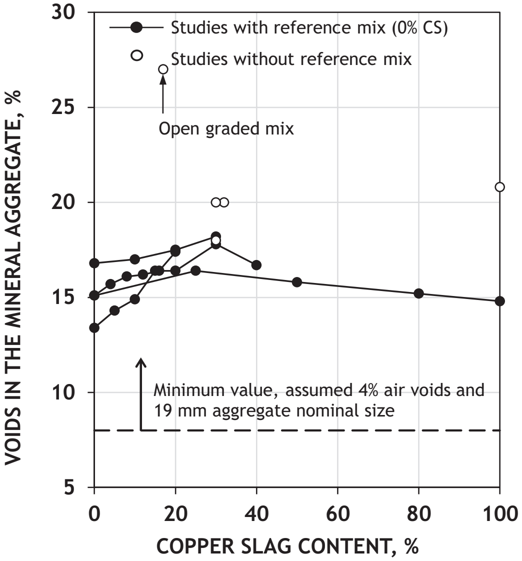

Figure 7.7 (d) Void in the mineral aggregate of mixes containing CS.
Data taken from Al-Sayed and Mandany (1992), Chetan and Sowmya (2015), DON and NASSCO (1999), Hassan and Al-Jabri (2011), Havanagi et al. (2007, 2009), Pundhir et al. (2005), Selvanambi et al. (2011), and Sharma et al. (2013a).

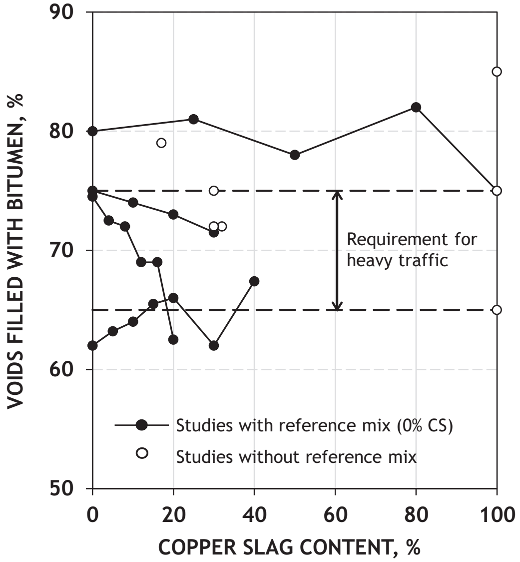

Figure 7.7 (e) Voids filled with bitumen of mixes containing CS.
Data taken from Al-Sayed and Mandany (1992), Chetan and Sowmya (2015), DON and NASSCO (1999), Hassan and Al-Jabri (2011), Havanagi et al. (2007, 2009), Pundhir et al. (2005), Selvanambi et al. (2011), Sharma et al. (2013a), and Yildrim et al. (1993).

all the mixes have a stability higher than the specification limit, the stability of mixes in which CS is used at different replacement levels (denoted as connected solid black dots) decreases with increasing CS. This is surprising, as it is known that an angular aggregate like CS normally will give higher stability due to a better particle interlocking effect. The possible explanation of this observation could be that the CS mixes were not as densely packed as the corresponding reference mixes, because of the difference in particle grading used, which leads to an increase in VMA (see Figures 7.7(c) and (d)).

Marshall Flow (Figure 7.7(b))

Marshall flow is both the elastic and the plastic deformation of a bituminous bound mix during the stability test. The flow value depends on the properties and content of the bitumen used as well as the presence of filler of size less than 75 μm, which has a bitumen stiffening effect. In general, the flow values of the majority of the mixes are within the specification limits (Figure 7.7(b)) and the use of CS is unlikely to cause any changes in the flow of the mix. The high flow values in some of the mixes may be reduced by adjusting the optimum binder content without compromising other design parameters.

Air Voids (Figure 7.7(c))

In a compacted mix, the small air pockets trapped within the bitumen and between the bitumen-coated aggregate particles are known as air voids. The target air void content of a bituminous bound mix is normally between 3% and 5% of the total volume of the mix for all traffic conditions. Figure 7.7(c) shows that whilst the air void content of CS mixes can be designed within the specification limits, the air void content of a mix tends to increase with increasing CS as a sand replacement (see the connected solid black dots). This increase of air voids points to the change of particle packing in the mixes due to the angularity of CS as well as the differences in the aggregate grading between CS and the corresponding natural sand. As high air void content affects the stability and durability of the mix, this perhaps can be prevented by keeping the aggregate grading of CS mixes similar to the reference mix or increasing the bitumen content (but this is not cost effective).

For the open graded mixes made with CS (as labelled in Figure 7.7(c)), it is expected that they have high air void content because of their deliberate open structure with reduced sand and fine fraction contents, which is suitable for use in binder course for free drainage purposes.

Voids in the Mineral Aggregate (Figure 7.7(d))

The void space between aggregate particles of a compacted mix is referred to as VMA and is used to indicate the available space for bitumen to adequately coat each aggregate particle. As the Asphalt Institute (1997) specifies the minimum VMA based on the nominal maximum particle size used and the design air voids of a mix, the requirement for a typical mix containing 19 mm aggregate size and 4% air voids is selected as an example, as shown in Figure 7.7(d).

It can be seen from Figure 7.7(d) that the VMA values of all the mixes made with CS are considerably higher than the specification limit. Similar to the effect of CS observed in the air voids section (Figure 7.7(c)), the general increasing trend of VMA with increasing CS shown in Figure 7.7(d) is due to the difference in the aggregate gradings of the two materials. As high VMA requires more bitumen to reduce the air voids to the design level (which can be uneconomical), the addition of a filler of size less than 75 μm may be needed to offset the increase of VMA using CS.

Voids Filled With Bitumen (Figure 7.7(e))

VFB is the void space in the mineral aggregate that is filled with bitumen. This parameter describes the richness of a bituminous bound mix and it is related to air voids, VMA and effective bitumen content (the portion that is not absorbed by aggregates). Given that these parameters have not been fixed at certain values in all the studies analysed, it is not possible to assess the effect of CS on VFB, although almost half the VFB results fluctuate within the specification limits (Figure 7.7(e)). The high/low VFB values of CS mixes may be adjusted by decreasing/increasing their bitumen content. It should be noted that as the water absorption of CS is much lower than the typical natural aggregate, the effective bitumen content of CS mixes is higher for a given bitumen content and results in an increase in the VFB of a mix, provided other parameters are kept constant.

Overall, the results shown in Figures 7.7(a)–(e) might not truly reflect the effect of CS on Marshall's design parameters because of the discrepancy in grading data; however, in general, it can be seen that it is possible to produce CS mixes that satisfy the specification limits recommended by the Asphalt Institute (1997), particularly the requirement for stability. Modification of the total aggregate particle size distribution, including the fines content, should be considered to meet all the void properties requirements.

7.5.2 Stress–Strain Behaviour

As bituminous mixtures possess both elastic and viscous characteristics, several terms have been used to characterise their stress–strain relationships, including resilient modulus, dynamic modulus and stiffness modulus. The resilient modulus assumes that the material is elastic under repeated loading, the dynamic modulus is the ratio of axial stress to recoverable axial strain under sinusoidal loading and the stiffness modulus is the ratio of maximum stress and maximum strain in a dynamic loading.

The stiffness modulus of a bituminous bound mix determines its ability to support and distribute the applied loads to the layers below. This property can be affected by internal factors such as bitumen, aggregate and voids and external factors (mainly affecting the bitumen) such as temperature, moisture condition, ageing factor and loading rate. Figure 7.8 shows the modulus of bituminous bound mixes made with CS determined using (i) AASHTO TP-62 (2004) for dynamic modulus by Hassan and Al-Jabri (2011), (ii) BS DD 213 (1993) for stiffness modulus by Dawson et al.

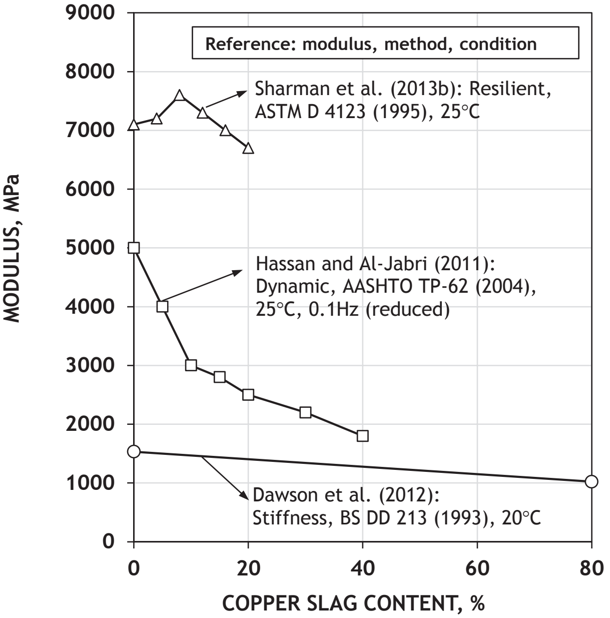

Figure 7.8 Modulus of bituminous mix containing copper slag.

(2012) and (iii) ASTM D4123 (1995) for resilient modulus by Sharman et al. (2013b) at a fixed temperature of 20/25°C. In carrying out these tests, Dawson et al. (2012) kept the bitumen content and aggregate grading constant for all the mixes to eliminate their effect on the results; however, it is not clear whether the same approach was adopted in the other studies.

The main point to emerge from Figure 7.8 is that the modulus of bituminous mixes will decrease with increasing CS content with different studies showing some specific points:

1. The decreasing trend in the results of Hassan and Al-Jabri (2011) is expected to be a result of the higher bitumen and air void contents of CS mixes compared to the corresponding reference mix.
2. The inconsistent results of Sharman et al. (2013b) could not be appreciated as the information on the material properties was not provided.
3. As the influence of internal factors other than aggregate type has been eliminated, the results of Dawson et al. (2012) showed that the use of CS as a limestone replacement for fraction size smaller than 10 mm in bituminous mix can result in lower modulus. The study associated the low value with the surface texture of aggregate, as the surface roughness value of limestone, measured using a surface profilometer, is higher than that of the CS. The rough aggregate surface creates more contact points between particles, thereby forming a more stable aggregate skeleton structure. Additionally, the low absorption property of CS might make the mix appear to be relatively softer because of the excess of bitumen for a fixed bitumen content. This could probably be examined from the VFB in the Marshall design; however, such information is not available.

The low modulus of bituminous bound mix with the use of CS should be taken into consideration during the designing stage. It might be worth looking at modifying the stiffness and content of the bitumen used to enhance the modulus of CS mixes if necessary.

7.5.3 Fatigue Life

Because of the repetitive nature of traffic loading, degradation of the layers of a flexible pavement can occur over time under applied tensile stress that is below the tensile strength of the pavement layers. This progressive fracture is known as fatigue cracking, which is one of the primary load-related distresses in bituminous bound mix. Severe fatigue cracking weakens the durability of a pavement by allowing the permeation of air and water, which can lead to total pavement failure.

The fatigue life of a bituminous mix can easily be assessed by several laboratory tests, such as four-point bending, direct tension–compression and indirect tensile tests for determining the number of load applications required on the specimen before failure. The fatigue tests can be conducted in two modes: (i) controlled stress (more applicable for thick pavement construction) and (ii) controlled strain (more applicable for thin surfacing layers), by keeping stress or strain constant whilst monitoring the resultant strain or applied stress.

The fatigue life of bituminous mixes made with 80% CS and the corresponding reference limestone aggregate was measured using the indirect tensile fatigue test in controlled stress mode, reported in the only study of Dawson et al. (2012), which is shown in Figure 7.9. This shows that for a given strain value, the fatigue life of the CS mix is higher than that of the limestone mix. Given that all the experimental variables, such as bitumen content and aggregate grading, were kept constant in this study, the possible factors causing such an increase may be related to the particle shape and surface texture of CS. Whilst the angularity of CS certainly increases the fatigue life of the mix, its smooth surface might work the opposite; the net effect of these two properties has shown an overall improvement (Figure 7.9). However, further experimental studies are required to substantiate the argument.

7.5.4 Water Sensitivity

The bond that is formed between bitumen and aggregate particles in a bituminous bound mix can be explained by four broad theories: mechanical, chemical reaction, surface energy and molecular orientation (Hicks, 1991). The presence of water can weaken this bond, causing separation of the bitumen adhering to the aggregate, which is known as stripping. This moisture damage reduces the strength and integrity of

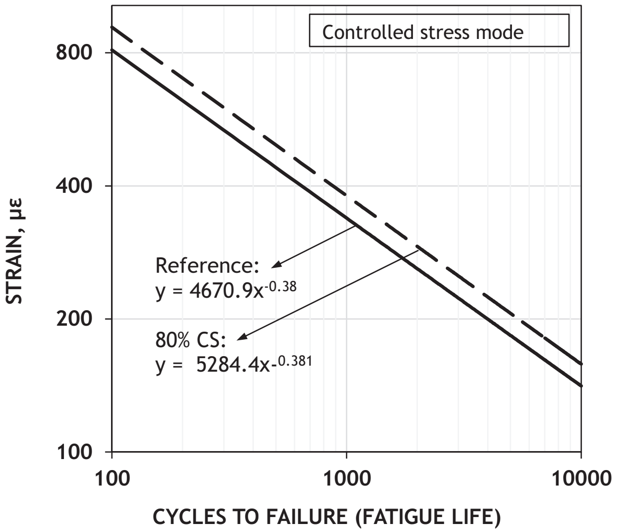

Figure 7.9 Effect of copper slag (CS) on fatigue life of bituminous mix.

the pavement, leading to other problems such as rutting and fatigue cracking and eventually resulting in pavement failure. There are numerous methods that can be used to evaluate the water sensitivity of bituminous mixes. These have been categorised into three main types by Newcomb et al. (2012):

(i) test on loose mixtures, for example, boiling water test (ASTM D3625, 2012)

(ii) comparison of conditioned and unconditioned mixes, for example, tensile test (ASTM D6931, 2012; AASHTO T 283, 2014; BS EN 12697-23, 2003), resilient modulus test (ASTM D4123, 1995)

(iii) repetitive loading under water bath, for example, Hamburg's wheel tracking test (AASHTO T 324, 2014)

Figure 7.10 shows the water sensitivity of mixes made with CS expressed as the ratio of indirect tensile strength measured under wet and dry conditions.

Although the results of Hassan and Al-Jabri (2011) presented considerable variability as the CS content increased from 0% to 40%, on the whole, they show that the use of CS as a natural sand replacement increases the resistance to moisture damage of a bituminous mix. On the other hand, the results of Sharma et al. (2013b) show only a marginal improvement (2%) in the resistance to moisture damage of bitumen mixes when 20% CS is included with sand. As for Havanagi et al. (2007, 2009, 2012) a marginal decline of about 2% in the resistance to moisture is shown for different types

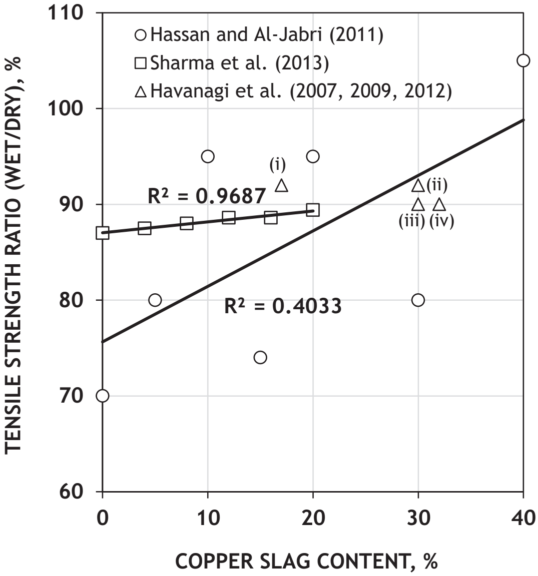

Figure 7.10 Tensile strength ratio of bituminous mix made with copper slag. See text for (i), (ii), (iii) and (iv).

of bitumen mixes, namely, (i) bitumen macadam with CS content at 17%, (ii) semi-dense bitumen macadam with CS content at 30%, (iii) bitumen concrete with CS content at 30% and (iv) dense bitumen macadam with CS content at 32%.

From the evidence of such data where there are many unknowns, and the fact that bitumen bond mechanisms can be affected by a wide range of factors, it is not possible to explain the results obtained. For example, the natural crushed limestone sand used by Hassan and Al-Jabri (2011) and CS are hydrophobic materials, but the two mixes responded differently to moisture damage. On the other hand, the water sensitivity of a bituminous mix is complex and more evidence is needed to understand the response of CS to moisture; overall the data suggest that the use of CS is unlikely to reduce the resistance of bituminous mixes to moisture damage.

7.6 Copper Tailings

The properties of copper tailings, a fine-grained residue waste produced from beneficiation of copper ore, and their effects on the properties of bituminous mix were studied by Oluwasola et al. (2014, 2015). The copper tailings were used at 20% content as a fine granite replacement for fraction size smaller than 1.18 mm. The aggregate grading of the

Table 7.3 Effects of copper tailings on properties of bituminous mix

Property	Standard Used	Effect of Copper Tailings[a]
Marshall stability	ASTM D 5581 (2013)	Increase
Marshall flow		Decrease
Resilient modulus	ASTM D 4123 (2011)	Increase
Water sensitivity (tensile strength ratio)	AASHTO T283 (2007)	Decrease

[a] Comparing the value of mix made with 20% copper tailings with respect to reference mix.

copper tailings mix was kept similar to the reference mix, thus the difference in aggregate packing between the two mixes was kept to a minimum. In the same study, the effects of bitumen characteristics were investigated; however, this is considered to be outside the scope of this section.

Table 7.3 briefly summarises the effects of copper tailings on the properties of bituminous mix and the main observations of the results are highlighted:

- **Marshall properties**: The optimum bitumen content of the copper tailings mix was similar to the corresponding reference mix. As to be expected, the air void content and VMA of the two mixes were very close, because of their similar aggregate gradings. Although all the Marshall properties met the requirements provided by the Asphalt Institute (1997) the copper tailings mix showed slightly higher Marshall stability and lower flow than the corresponding reference mix.
- **Resilient modulus**: The resilient modulus of the copper tailings mixes, measured at 25 and 40°C in both aged and unaged conditions, tended to be higher than the reference mix, which suggests copper tailings may be more angular than the crushed granite.
- **Water sensitivity**: The water sensitivity of both the mixes expressed as the tensile strength ratio (TSR) of the conditioned specimen to unconditioned specimen showed that the TSR of the copper tailings mix at about 92% was slightly lower than that of the corresponding reference mix at about 95%. Nevertheless, the TSR of the copper tailings mix still met the minimum requirement of 80% as specified by AASTHO T283.

Based on the field experience of using copper tailings in HMA applications, the Texas Transportation Agency (Transportation Research Board, 2013a) has suggested that adjustment of construction practice and proper training to field crews would be advisable when dealing with copper tailings.

Overall, although the research on the use of copper tailings is in its preliminary stages, with many aspects still requiring thorough investigation, the limited information available would suggest that copper tailings, like CS, could also be a viable material as a natural sand replacement in road pavement applications.

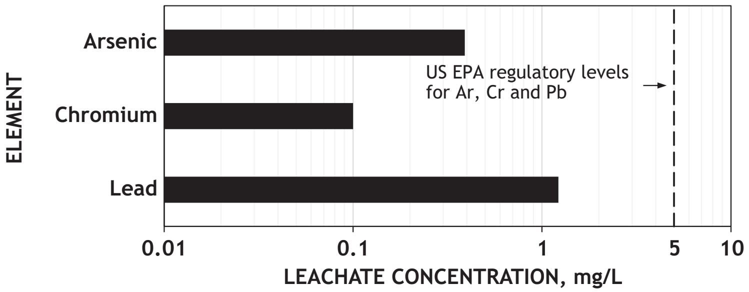

Figure 7.11 Element concentrations of toxic characteristic leaching procedure extracts for copper slag.

7.7 Environmental Impact

Owing to the presence of toxic elements in CS, its associated environmental human health implications have always been a concern. In this respect, CS has been categorised as a special waste and is exempted from the hazardous waste regulations by the US EPA (1991).

The information on leaching tests for hydraulically bound and bituminous bound mixes containing CS has not been widely published. However, Sharma et al. (2013b) have reported limited leaching results of raw CS samples. The work was undertaken in accordance with the toxicity characteristic leaching procedure (TCLP) 1311 method of the US EPA (1992), and the results obtained are provided in Figure 7.11, showing the element concentrations of TCLP extracts for CS together with the US EPA regulatory level given in Document 40 CFR 261.24 (US EPA, 2012) for comparison.

The results suggest that the concentrations of the three tested toxic elements, arsenic, chromium and lead, are well below the US EPA allowable limits. The data are also coherent with the findings from a more comprehensive leaching analysis of CS samples reported previously. Despite the lack of leaching information on hydraulically bound and bituminous bound mixes containing CS, given the leaching studies presented in Chapter 6, it should be safe to conclude that the use of CS as a natural sand replacement in road pavement applications is unlikely to pose a threat to the environment and human health.

7.8 Case Studies

Despite the lack of substantial research on the properties of road pavements where CS has been used, the material has been actually put to use, albeit in a handful of applications in this field, such as (i) unbound, hydraulically bound and bituminous bound mixes at different pavement layers; (ii) paving blocks; (iii) fog seal applications and (iv) roadside walls. These field applications have been initiated by individual organisations and government bodies, mainly from Asia and the United States, and although they can be traced back to the early 18th and 19th centuries, much of the work has been undertaken since 2005 (Figure 7.4).

The details of these applications, together with a brief description of the work undertaken, are given in Table 7.4. The available information is limited and the field assessment of the applications using CS has not generally been provided in all of the relevant literature, thus very few lessons could be learnt from past experiences to enable continuous improvement. Notwithstanding, there are a few points that are worth mentioning and are of some interest, as noted in the following:

- CS has been used in unbound, hydraulically bound and bituminous bound applications in both India and the United States. In one highway widening construction project in India, the pavement layers from subbase to surface course of four trial sections of 500 m length each were made using 10–75% CS (Havanagi et al., 2009; IRC Highway Research Board, 2009).
- In contrast, the use of CS was discontinued in road pavements in one district in Texas on the grounds of environmental concerns; however, the details of this have not been elaborated on (TxDOT, 1999). Given that the leaching studies of CS samples have been proven to be safe in geotechnical (Chapter 6, Section 6.10) and road pavement applications (Section 7.7 of this chapter) such concerns are isolated and are unlikely to carry much weight.
- The experience of using CS in paving blocks for walkways in India (Sterlite Industries, 2012) and residential driveways in Singapore (Building and Construction Authority, 2008) may encourage further development of the products for heavy duty applications, such as use in industrial areas.
- Fog seal is a surface treatment method used to extend the longevity of bitumen pavement. In California (Urbanek et al., 2013) and Selangor, Malaysia (Crown Capital, 2006), CS was used as a sanding material for texture sealing to enhance the friction of the treated pavement surface where the skid resistance normally decreases after fog sealing.

Overall, though it may not be fully assertive, the information emerging from the field trials exploring some aspects of the use of CS in road pavement applications should encourage further assessment of the material's use in place of sand.

Table 7.4 Case studies involving the use of copper slag (CS) in road pavement applications

	Application Details			
References	**Location**	**Year**	**Used in**	**Description**
(a) Unbound, Hydraulically Bound and Bituminous Bound Applications				
Collins and Ciesielski (1994)	California, USA	N.A.	Bituminous mixes	Copper blasting slag has been used in bitumen mixes in California.
TxDOT (1999)	Texas, USA	1993	Hydraulically and bituminous bound mixes	The use of CS was discontinued because of environmental concerns.
Havanagi et al. (2009) and IRC Highway Research Board (2009)	India	2008	Subbase, base, binder and surface courses	CS was used in different pavement layers of four trial sections of length 500 m each in a highway widening project.
IRC Highway Research Board (2011)	India	2011	Dense bituminous macadam, bituminous concrete	Bituminous mixes made with 10–15% superfine CS satisfied the specifications requirements.
(b) Other Applications				
Streetscape Manual (2005)	UK	18th and 19th centuries	Roadside walls	CS was used for moulded coping stones for roadside walls.
BCA (2008)	Singapore	N.A.	Paving blocks	A residential driveway was constructed using concrete pavers containing washed CS.
Sterlite Industries (2012)	India	N.A.	Paving blocks	A walkway covering an area of 2464 m^2 was constructed using paver blocks made with 100% CS.
Crown Capital (2006)	Malaysia	2006	Fog seal applications	CS was used as sanding materials together with fog seal to increase the friction of pavement surface.
Urbanek et al. (2013)	California, USA	2013	Fog seal applications	CS was used as sanding materials together with fog seal to increase the friction of pavement surface.

7.9 Conclusions

It has been shown that CS can be used as a natural sand replacement in unbound, hydraulically bound and bituminous bound applications and as a natural sand replacement in road pavement construction, adding value to the pavement properties, although some precaution would be required to avoid undesirable results.

The CBR of superfine CS and normal sand fraction CS is 14% and 45%, respectively, and is similar to well-compacted sand and very well compacted sand. The addition of CS in soil, fly ash and pond ash for subgrade application could improve the CBR of the material and reduce the thickness of the capping layer.

The use of CS increases the workability of hydraulically bound mixes (concrete) and may have an adverse effect on the stability of the mix if this improvement is not considered in the mix design. For a given water/cement ratio, the addition of CS tends to increase the compressive strength of concrete owing to the interlocking effect of the angular CS particles. The effect of CS on the flexural strength of concrete is essentially similar to that on compressive strength. Because of its lower water absorption and higher hardness than natural sand, the use of CS can result in a reduction in the drying shrinkage of concrete. Although not conclusive, because of a stability problem, all things being equal, the addition of CS should increase the abrasion resistance of concrete owing to its high hardness and low porosity characteristics.

For bituminous bound applications, incorporating CS can be designed using the Marshall method to specification, provided the total aggregate particle size distribution is appropriate. The use of CS reduces the modulus of bituminous mix associated with its smooth surface and low bitumen absorption properties. However, the fatigue life of bituminous mix made with CS can be higher than when natural sand alone is used. The addition of CS is not likely to make the bituminous mixes more susceptible to moisture damage.

Copper tailings are potentially suitable for use as an alternative to natural sand in road pavement applications, but their effects on many engineering aspects have not yet been fully examined.

Although the available information is limited, the leaching test results suggest that CS should be safe for the environment and human health. The use of CS in real road pavement applications as unbound, hydraulically bound and bituminous bound mixes has developed since 2005.

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Environmental Impact, Case Studies and Standards and Specifications

8

Main Headings

- Environmental impact
- Case studies
- Standards and specifications
- Cement manufacture and cementitious material
- Concrete
- Geotechnical applications
- Road pavements

Synopsis

This chapter discusses the leaching of toxic elements of copper slag (CS), the associated environmental impact and case studies in which CS is used in various construction applications. CS is a non-hazardous waste material and its leaching behaviours are not affected by its type, but its particle size and the pH condition can affect the leaching behaviours. The leaching studies on CS used as either raw feed for cement clinker, in ground form as cementitious material, or an aggregate in concrete, geotechnical and road pavement applications, show that the leached element concentrations are generally not to be of concern. Although limited in number and scope, the available information that can be drawn from the case studies of CS suggest that the material is generally suitable for use in construction material. The relevant standards and specifications for CS use in various construction applications are also discussed.

Keywords: Copper slag, Environmental impact, Case studies, Standards and specifications, Cement clinker, Cementitious material, Concrete, Geotechnical applications, Road pavements.

8.1 Introduction

The construction industry is known for its high carbon emissions and negative environmental impact. The industry covers a wide range of activities, starting from the sourcing of natural materials and their use, and ending finally in their disposal in landfills, as has been the case for a very long time. Thus, understandably, governments, at large, expect the construction industry to take major initiatives in reducing its carbon footprint and comply with some increasingly stringent demands in this respect. Whilst it can be

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argued that this challenge can be achieved only through technological development and innovation in construction designs, promoting the use of recycled materials arising from construction demolition and excavation waste such as recycled aggregates and secondary materials arising from industrial operations such as metallurgical slags, waste glass, used rubber tyres and incinerated ashes has an important role to play in achieving sustainable construction. Indeed, recycling of waste as a valuable resource has some classic examples to follow. For example, fly ash (FA) produced at coal-fired electric power stations, which accounts globally for over 2 billion tonnes per annum, is used as a component of cement in the manufacture of concrete. This in turn reduces the amount of Portland cement (PC) used and has the potential for reducing CO_2 emission, arising from the manufacture of PC, by over 0.5 billion tonnes per annum.

The use of recycled and secondary materials is now commonly seen as a potential resource for concrete, geotechnical and road pavement applications. Indeed, standards such as BS EN 12620 (2008), which deals with aggregates for concrete, allows, along with the natural aggregates, for the use of manufactured and recycled aggregates. Encouragingly, other waste materials, including copper slag (CS), crushed glass and municipal incinerator bottom ash, have been considered in the preparation for the latest development of the standard (prEN 12620, 2015). However, the drive to promote the adoption of recycled and secondary materials does not stop at the acceptance of these materials in the standards. Research is continually needed to develop the product to the fit-for-purpose stage, and this also involves the study of the associated environmental impact of the intended applications of the material and their compliance with the regulations controlling the level of harmful species that can be accepted. The balancing of these two sides of the environmental impact can be a difficult task and would require careful scrutiny. It is here that case studies can be most useful in providing real practice experience and guidance on the pitfalls that have been encountered previously.

This chapter provides a comprehensive analysis and evaluation of the information on the studies undertaken to determine leaching of harmful elements and the associated environmental impact when CS is used in concrete, geotechnical and road pavement-related applications. The case studies are presented to provide an indication of how the use of CS has been taken up and what is the possible potential for further development of CS in construction. In addition, the standards and specifications for CS use in various construction applications are also discussed.

8.2 Environmental Impact

Prior to the use of a new material, it is necessary to test it for leaching of heavy metals. Indeed, this becomes an absolute requirement where, in its use in construction, the material is likely to be in contact with drinking water or an aggressive environment that can be conducive to leaching, such as highly acidic soil in geotechnical applications. Thus, leaching studies in the application of CS would be necessary to confirm that the material in use does not have a negative environment impact and remains harmless.

8.2.1 The Material: Copper Slag

As mentioned in Chapter 3, CS is a non-hazardous material in itself and poses no health threat to the environment, as accepted by two independent organisations, the US Environmental Protection Agency (US EPA, 1991) and the Basel Convention of 1996 (Alter, 2005). The decision to exclude CS from the hazardous waste list under Subtitle C of the Resource Conservation and Recovery Act, by the US Environmental Protection Agency in 1991, was based on the investigation of several industrial processing wastes, including CS, copper tailings and calcium sulphate wastewater treatment plant sludge, from 91 plants located in 29 states. Five years later, CS was also characterised as non-hazardous by the United Nations Basel Convention on the Transboundary Movement of Hazardous Wastes and Their Disposal in 1996, based on the studies of slag samples sourced from Canada, Chile and the United States (Alter, 2004).

Figure 8.1 shows the results of leaching concentrations of heavy metals of 43 CS samples. The results were reported over a period of 32 years during 1983–2014 from 10 countries across the world, with India, Singapore and the United States accounting

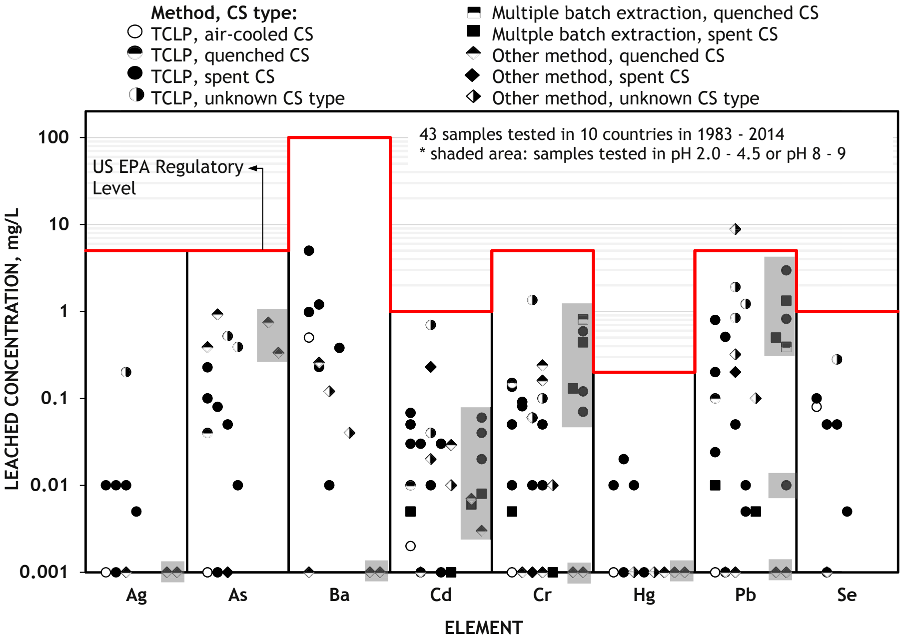

Figure 8.1 Leached element concentrations of copper slag (CS) using the toxicity characteristic leaching procedure (TCLP), multiple batch extraction and other methods. Data taken from Agrawal and Sahu (2010), Alter (2005), Brindha and Nagan (2010, 2011), Brindha et al. (2010), Cheong et al. (2007), Das et al. (1983), Ghosh (2007), JPL Industrial (1997), Lim and Chu (2006), Ling and Thim (1999a,b), Madany and Raveendran (1992), Sanchez de Rojas et al. (2004), Saraswathy et al. (2014), Shanmuganathan et al. (2008), Sharma et al. (2013), Supeakar (2007), Suresh et al. (2013), Dung et al. (2014), and Zain et al. (2004).

for more than half of the results. The test samples were separated based on the type of CS tested, namely, air-cooled (2), quenched (10), spent (16) and not identified (15). As spent CS is usually the quenched CS originally used as an abrasive material, the majority of the results plotted in Figure 8.1 are likely to be those of quenched CS.

Amongst the test methods adopted, the US Environmental Protection Agency (EPA) Method 1311 for toxicity characteristic leaching procedure (TCLP) is most commonly used (US EPA, 1992), which was developed to simulate leaching in a weakly acidic environment at municipal solid waste landfills. Another method worth mentioning is the multiple batch extraction method, which comprises a series of repetitions of single-stage leaching with fresh leachant, which was designed to monitor the leaching behaviour of a material over time. A detailed list of other test methods used can be found in Chapter 3 (Section 3.7.1).

It can be seen from Figure 8.1 that all the leached element concentrations of CS samples measured using TCLP are below the corresponding maximum allowable levels set by the US EPA (2012). Indeed, for several elements, the leached concentrations are well below the maximum allowable limits, as can be seen from Table 8.1. A similar observation is also found for the results obtained from multiple batch extraction and other test methods, except for one Pb leaching value, which exceeds the limit.

When subjected to aggressive conditions such as high acidic and low alkaline solutions, the leached element concentrations of CS do not show an alarming level. The leaching behaviour of CS appears not to be influenced by its type, air-cooled, quenched or spent.

Additionally, the effects of particle size of the test sample and pH condition used for the leaching test of CS were studied by Vitkova et al. (2011), and the results suggest that the leaching of Cu, Co and Zn is the highest for the sample with a high content of particles with size less than 1 mm or tested at low pH of 4 and 5. The latter observation is also confirmed in a case study undertaken in Vietnam by Dung (2012). In a separate

Table 8.1 Maximum leached element concentrations as shown in Figure 8.1

	Leached Concentration, mg/L	
Element	**US EPA Regulatory Level**	**Maximum Value in the Total Data**
Ag	5.0	0.20
As	5.0	0.92
Ba	100.0	5.00
Cd	1.0	0.70
Cr	5.0	1.35
Hg	0.2	0.02
Pb	5.0	8.79
Se	1.0	0.28

study, Harish et al. (2011) carried out an algal growth inhibition test under laboratory conditions to assess the leaching of CS from a copper smelter plant in India. The results show that the leachate of CS is harmless to the growth of the marine microalgae used. However, it has been suggested that further tests on the changes in the growth rate and lipid profile of algae might be needed for a complete understanding of the toxic nature of CS in microalgae.

8.2.2 Copper Slag Use in Cement Manufacture and as Cement Component

Because of its high content of iron(III) oxide and silica, CS is suitable for use as a part of raw feed used for manufacturing PC clinker. Additionally, its amorphous nature makes it potentially suited to use in the ground form as a cementitious material in combination with PC. As discussed previously in Section 8.2.1, fine-grained CS tends to show greater leaching characteristics (Vitkova et al., 2011), thus the leaching studies of cement clinker and cement containing CS become important as the material is finely ground.

Cement Manufacture

The leaching characteristics of cement clinker containing CS have been investigated since the beginning of the 2000s. The cement clinker in these studies contained a small amount of CS, ranging from 0.3% to 2.5%, and possibly in combination with other waste materials such as ashes from sewage sludge, municipal incineration and coal combustion, sewage dry powder and aluminium dross that together amounted to around 8–40% of the total raw feed composition, as provided in Table 8.2.

The leaching results of cement clinker containing CS (1) measured in the ground form or (2) obtained from the cast cement paste and mortar specimens are given in Table 8.2. These results show that the amounts of leached heavy metals of the samples containing CS, with or without other waste materials, are all well within the US EPA (2012) regulatory levels for the TCLP tests. When measured from the cast mortar specimens, the results appear to show that their leaching behaviour is independent of the maturity of mortar, for which the specimens were tested at the ages of 1, 3 and 7 days (Kikuchi, 2001). It should be noted that the US EPA (2012) does not provide regulatory limits for Cl^-, CN, Co, Cu, Ni and Tl.

Apart from the leaching test, the chemical analysis of the exhaust gases emitted during the manufacture of cement clinker can also be important in determining environmental impact. Kikuchi (2001) showed that the values of sulphur oxide, nitrogen oxide, dust and dioxins in the exhaust gases of cement clinker made with CS and other waste materials are well below the permissible levels recommended by the Japanese standards (JIS Z 8808 and JIS K 0107). However, it would have further helped to evaluate the environmental impact if such results were provided together with cement clinker made with natural materials, for comparison purposes.

Table 8.2 Element leaching of cement clinker containing copper slag (CS)

References		**Ali et al. (2013)**	**Kikuchi (2001)**			**Lam et al. (2010)**		
CS Content, %		**1.5 – 2.5**	**0.3**			**1.59**	**0.23**	**0.97**
Other Waste Used		**No**	**SSA, Incineration Municipal Waste Ash, Sewage Dry Powder, Aluminium Dross (Total Content: 31.8–40.6%)**			**PFA, SSA, MIBA, MIFA (Total Content: 12.5–14.6%)**		
Method		**ASTM D5233-92 (2009)**	**JIS K0102 (1996)**			**TCLP (1992)**		
Specimen		**Paste**	**Mortar (0.65 w/c)**			**Ground Powder**		
Test Age, days		**28** [a]	**1**	**3**	**7**	**–**		
Leached Concentration (US EPA Regulatory Level), mg/L	As (5.0)	Neg.	–	–	–	–	–	–
	Ba (100.0)	0.032	–	–	–	2.19	0.6	3.841
	Cd (1.0)	Neg.	<0.005	<0.005	<0.005	–	–	–
	Cl^- (NR)	–	41	38	35	–	–	–
	CN (NR)	–	<0.1	<0.1	<0.1	–	–	–
	Co (NR)	0.008	–	–	–	–	–	–
	Cr (5.0)	0.031	<0.04	<0.04	<0.04	–	–	2.402
	Cu (NR)	0.005	<0.02	<0.02	<0.02	–	–	–
	Hg (0.2)	–	<0.0005	<0.0005	<0.0005	–	–	–
	Ni (NR)	Neg.	–	–	–	–	–	–
	Pb (5.0)	Neg.	<0.01	<0.01	<0.01	–	1.121	3.412
	Se (1.0)	–	<0.002	<0.002	<0.002	–	–	–
	Tl (NR)	–	–	–	–	1.17	0.431	0.872

NR, not regulated; *Neg.*, negligible amount; *TCLP*, toxicity characteristic leaching procedure; *w/c,* water/cement ratio; *PFA,* pulverised fly ash; *SSA,* sewage sludge ash; *MIBA,* municipal incinerated bottom ash; *MIFA,* municipal incinerated fly ash.

[a] Immersed in distilled water for 6 months after 28-day curing.

Copper Slag as Cementitious Material

For the leaching tests carried out using concrete specimens made with ground CS as a cementitious material, the studies undertaken by Van Loo (1995) and Surest et al. (2013) confirm that the presence of ground CS in cement does not pose an environmental threat, as the leached concentration of heavy metals from concrete made with CS are reported to be below the allowable limits recommended respectively in the European Drinking Water Directive of the European Communities (1980) and by the US EPA (2012) determined using the TCLP test. The leaching results of these two studies, measured from 0.40 and 0.45 water/cement (w/c) ratio concretes containing 10% CS at the age of 28 days are provided in Table 8.3.

The data of Van Loo (1995) presented in Table 8.3 were the maximum values reported by eight different laboratories located in seven European countries, namely, France, Germany, Italy, Poland, Spain, Sweden and the United Kingdom. The test specimens used in all these laboratories were from the same source and the leaching test procedure was standardised. The only difference was in the leachants, which were the local drinking water, with pH ranging from 7 to 8.

Additionally, the leaching of zinc and copper elements from concrete made with ground CS as a cement component was measured over a period of 1 year by Zain et al. (2004) for zinc and Supeakar (2007) for copper. For the work of Zain et al. (2004), the leaching tests were performed in accordance with TCLP (US EPA, 1992) on four concrete specimens of 0.50 w/c ratio, made with 2.5%, 5.0%, 7.5% and 10% ground CS, subjected to acetic acid of pH 2.88. In the work of Supeakar (2007), though it is not clear which leaching test method was used, concrete having 0.44 w/c

Table 8.3 Element leaching of concrete made with copper slag (CS) as cementitious material

References		**Van Loo (1995)** [a]	**Surest et al. (2013)**
CS Content, %		**10**	**10**
Method		**NEN 7345**	**TCLP (1992)**
Water/Cement Ratio		**0.45**	**0.40**
Test Age, days		**28**	**28**
Leachant pH		**7–8**	**4.93**
Leached Element (Allowable Limit), mg/L	Ag (5.0) [b]	–	0.01
	Cd (1.0) [b]	–	0.15
	Cr (5.0) [b]	–	1.05
	Cu (3.0) [c]	<0.00019	1.30
	Pb (0.05) [c]	<0.0009	0.04
	Zn (5.0) [c]	<0.0005	0.40

TCLP, toxicity characteristic leaching procedure.
[a] Maximum value recorded from eight laboratories.
[b] Based on US EPA (2012).
[c] Based on European Communities (1980).

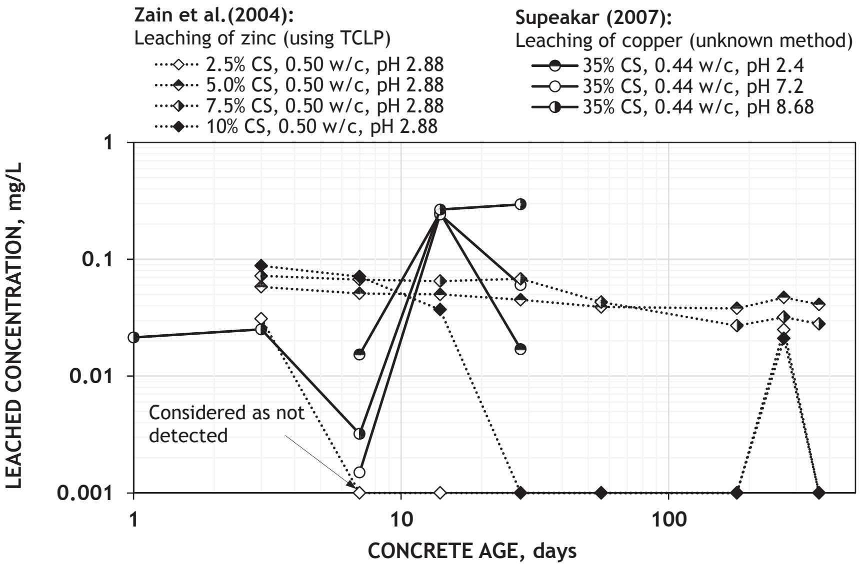

Figure 8.2 Leaching of zinc and copper from concrete made with copper slag (CS) as cementitious material. *TLCP,* toxicity characteristic leaching procedure; *w/c,* water/cement ratio.

ratio and made with 35% ground CS was subjected to three leachants of different pH values, namely acid rainwater (pH 2.4), tap water (pH 7.2) and seawater (pH 8.68). As can be seen in Figure 8.2, there is a degree of ambiguity in the leaching results in terms of CS content effect with the age of the concrete. The results of 5.0% and 7.5% CS concrete are essentially similar, suggesting that the concentration of zinc in the leachate is perhaps not affected by the CS content of concrete, and it decreases with time, but only a little. However, this trend is not supported by the leachate results for 2.5% and 10.0% CS concrete mixtures. The results of Supeakar (2007) are of little help in evaluating the effect of pH on the leaching of copper element at a given age, as well as with increasing age of concrete, as the results are extremely variable.

8.2.3 Copper Slag Use in Concrete

Studies have been undertaken on the leaching of concrete made with a 0.4–0.6 w/c ratio using up to 100% CS as sand and cured for up to 150 days. The results obtained using the TCLP method, a modified extraction procedure, ASTM D5233-92 and atomic absorption spectroscopy are given in Table 8.4, together with the TCLP regulatory limits specified by the US EPA in Document 40 CFR 261.24 (US EPA, 2012).

The TCLP leachate concentrations of concrete containing up to 100% CS content showed traces of heavy elements, but none of them reached the levels of the regulatory limits (Table 8.4). The high concentration of calcium observed in all the samples is likely to be due to the presence of calcium hydroxide released from

Table 8.4 Leaching results of concrete obtained using different methods

		Leached Concentration, mg/L														
		TCLP Method[b]						Modified Extraction Procedure[b]		ASTM D5233-92 (2009)[c]				Test Method Not Known[d]		
	US EPA Regulatory	20%[e]	20%	80%	80%	80%	100%	20%	80%	20%	30%	40%	50%	100%	100%	100%
Element	**Level[a], mg/L**	**0.6 w/c, 28 d[f]**	**0.6 w/c, 91 d**	**0.4 w/c, 28 d**	**0.5 w/c, 28 d**	**0.6 w/c, 28 d**	**0.6 w/c, 28 d**	**0.6 w/c, 91 d**	**0.6 w/c, 91 d**	**0.43 w/c, 28 d**	**0.43 w/c, 28 d**	**0.43 w/c, 28 d**	**0.43 w/c, 28 d**	**0.44 w/c, 150 d [g]**	**0.44 w/c, 150 d [h]**	**0.44 w/c, 150 d [i]**
As	**5**	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	–	–	–	–	–	–	–
Ag	**5**	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Ba	**100**	0.35	<0.001	0.198	0.264	0.183	0.119	1.839	2.335	–	–	–	–	–	–	–
Ca	**NR**	1915.3	2672.2	2030.6	2094	1877.7	1806.9	5429.6	5251.8	200	368	400	480	–	–	–
Cd	**1**	<0.001	–	<0.001	<0.001	<0.001	<0.001	–	–	–	–	–	–	–	–	–
Cr	**5**	0.017	0.016	0.007	0.009	0.008	0.008	0.017	0.016	–	–	–	–	–	–	–
Cu	**NR**	<0.001	0.002	0.020	0.010	0.002	0.001	2.54	10.73	<0.001	<0.001	<0.001	<0.001	0.007	0.131	0.006
Fe	**NR**	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	1.218	1.035	<0.001	<0.001	<0.001	<0.001	–	–	–
Hg	**5**	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Mn	**NR**	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.732	0.855	–	–	–	–	–	–	–
Ni	**NR**	<0.005	–	<0.005	<0.005	<0.005	<0.005	–	–	–	–	–	–	–	–	–
Pb	**5**	0.007	<0.01	0.008	0.008	0.007	0.004	0.008	0.015	–	–	–	–	–	–	–

TCLP, toxicity characteristic leaching procedure.

[a] NR, not regulated.

[b] Based on Cheong et al. (2007).

[c] Based on Brindha and Nagan (2010b).

[d] Based on Saraswathy et al. (2014).

[e] Copper slag content.

[f] Water/cement ratio and curing age of concrete.

[g] Cured in tap water.

[h] Cured in seawater.

[i] Cured in acid rain.

cement hydration, and its level is not regulated by the US EPA. Apart from calcium concentration, the w/c ratio, as well as the curing age of concrete, does not appear to affect the TCLP results, as can be seen from the data for samples made with 20% and 80% CS (Table 8.4).

When tested in a more aggressive environment, using the modified extraction procedure, in which the pH of the leachant was maintained at 5 ± 0.2 for the first 6 h, the leached concentrations of elements, as shown in Table 8.4, are still well below those of the regulatory limits for TCLP test. Although not regulated, the leaching of copper and iron of CS concrete measured using ASTM D5233-92 (2009) and atomic absorption spectroscopy is low and not at a level for concern (Table 8.4).

8.2.4 Copper Slag Use in Geotechnical Applications

The leaching characteristics of mixes containing CS have been studied by two groups of researchers, one from Singapore (Chu et al., 2003; Lim and Chu, 2006) and another from the United States (Das et al, 1983; Ferguson and Das, 1989). This provides an opportunity, which can be interesting, for assessing how the leachability of CS mixes may differ with different geographical locations. The test samples used in these studies were 100% (1) CS, (2) washed copper slag (WCS), a spent CS previously used as blasting agent to remove rust and marine deposits on ships, and (3) WCS–sludge–PC mix. The toxic metals of these samples were assessed using either the well-known TCLP, which is a regulatory test procedure developed by the US EPA or sequential extraction techniques (SETs), which were originally developed by Tessier et al. (1979) in Canada.

Table 8.5 provides the element concentrations extracted from CS and WCS samples using TCLP in standard and modified forms. The values are also compared with the US EPA regulatory levels given in Document 40 CFR 261.24 (US EPA, 2012).

It can be seen from Table 8.5 that toxic metal concentrations in CS and WCS samples measured under standard TCLP conditions (Test 1) are well below the US EPA maximum allowable limits. A similar observation is also found when WCS is tested in more acidic conditions (Tests 2–4) and neutral conditions (Tests 5 and 6) for a slightly longer duration. Although the limits for concentrations of copper and zinc are not regulated by the US EPA (2012), their concentrations are relatively higher than those of other toxic metals.

The concentration of elements extracted from mixes made with 37.5% WCS, 50% sewage sludge and 12.5% PC using SET are presented in Table 8.6. Although the results of these samples are not representative of the leaching characteristics of WCS, because of the presence of sewage sludge and PC, it is worth investigating the combined effect of these three materials on leaching characteristics.

In principle, the elements of the sample have been extracted from four different conditions (in increasing reactivity order): unbuffered salts, weak acids, anoxic condition and oxidising condition, which correspond to exchangeable, carbonate, reducible and organic fractions. The elements left in the residual fraction are in a crystalline

Table 8.5 Leached element concentrations of TCLP extracts for copper slag and washed copper slag

		Leached Concentration, mg/L						
		Copper Slag	Washed Copper Slag					
Element	**US EPA Regulatory Level[a], mg/L**	**Test 1**	**Test 1**	**Test 2**	**Test 3**	**Test 4**	**Test 5**	**Test 6**
Arsenic	5.0	0	0.08	–	–	–	–	–
Barium	100.0	0.5	1.2	–	–	–	–	–
Cadmium	1.0	0.002	0.03	0.06	0.04	0.03	0.03	0.032
Chromium	5.0	0	0.081	0.59	0.12	<0.01	<0.01	0.07
Copper	NR	–	33.6	81.6	52.9	23.3	12.3	2.8
Lead	5.0	0	0.51	2.96	0.82	0.024	<0.01	<0.01
Mercury	0.2	0	< 0.01	–	–	–	–	–
Nickel	NR	–	0.37	7.29	0.58	0.28	0.18	0.18
Selenium	1.0	0.08	0.05	–	–	–	–	–
Silver	5.0	0	< 0.01	–	–	–	–	–
Zinc	NR	–	18.5	54.7	27.6	10.3	5.88	1.86

Copper slag: based on Das et al (1983), Ferguson and Das (1989).
Washed copper slag: based on Lim and Chu (2006).
Test 1: Standard TCLP, pH 5.0, 0.1 mol/L HAc reagent, 18 hours, 1:20 solid:water.
Test 2: Modified TCLP, pH 3.0, 0.1 mol/L NaAc reagent, 24 hours, 1:20 solid:water.
Test 3: Modified TCLP, pH 4.0, 0.1 mol/L NaAc reagent, 24 hours, 1:20 solid:water.
Test 4: Modified TCLP, pH 6.0, 0.1 mol/L NaAc reagent, 24 hours, 1:20 solid:water.
Test 5: Modified TCLP, pH 7.0, 0.1 mol/L NaAc reagent, 24 hours, 1:20 solid:water.
Test 6: Modified TCLP, pH 8.0, 0.1 mol/L NaAc reagent, 24 hours, 1:20 solid:water.
NR: not regulated; *TCLP*, toxicity characteristic leaching procedure.
[a] Based on US EPA (2012).

Table 8.6 Element extraction of washed copper slag–sewage sludge–Portland cement mix[a] measured using sequential extraction techniques

	Heavy Metal Extraction From Different Fractions[b], %				
Element	**Exchangeable**	**Carbonate**	**Reducible**	**Organic**	**Residual**
Zinc	2	6	35	1	56
Copper	0	4	0	22	74
Cadmium	0	2	18	2	78
Chromium	0	2	32	4	62
Lead	0	1	20	0	79
Nickel	0	4	14	0	82

[a] Content: 37.5% washed copper slag, 50% sewage sludge and 12.5% Portland cement.
[b] Data taken from Chu and Lim (2008).

matrix and are not likely to be released under normal conditions. It can be seen from Table 8.6 that the leaching of heavy metals is more apparent in the reducible fraction. As the heavy elements of the test sample are predominantly retained in the residual fraction (56–82%), this suggests that the metals in CS–sludge–PC mix are less likely to leach.

In general, the information on the leaching characteristics of CS or WCS is limited, but the results of the toxicity assessment for CS are encouraging, especially for the TCLP tests, in which the metal concentrations of the leachate are fairly low in different pH conditions, suggesting that the use of CS should be safe for the environment in most cases. However, if CS applications are made in extreme conditions such as acid drainage and sulphate-bearing deposits, the assessment of the leaching characteristics should be performed for greater assurance, even though it is unlikely to be a concern. In addition, it should be noted that the corrosivity of CS (ability to corrode metal pipes and containers), which can raise primary health concerns, has not been reported.

8.2.5 Copper Slag Use in Road Pavements

Four 100-m-length bituminous road sections, of which each subbase was made with quenched CS, air-cooled blast furnace slag (BFS), recycled concrete aggregate (RCA) and crushed rock (biotite gneiss-granite, as reference) were constructed in Northern Sweden in 1997 (Lidelow, 2008). The particle size of the subbase materials varied, as shown in Table 8.7. BFS is the coarsest with maximum particle size of 125 mm, followed by RCA and crushed rock with maximum particle sizes of 100 and 30 mm, respectively; however, the CS used is mainly sand. The design of the road is given as follows, and the groundwater is 1–2 m below the road surface:

- Wearing course, 70 mm asphalt
- Base, 80 mm crushed rock
- Subbase, 500 mm CS, 500 mm BFS, 420 mm RCA, 420 mm crushed rock
- Subgrade, silty clay to clay (thickness not known)

The leachates of the subbases were collected and monitored for up to 10 years after 1998, and their properties are provided in Table 8.7.

It can be seen from Table 8.7 that:

- The leachate of the CS section is essentially neutral, whilst that of the crushed rock and RCA sections and that of the BFS section are alkaline and acidic, respectively.
- The electrical conductivity (EC), which measures the amount of soluble inorganic salt in soil, of the CS leachate is the lowest, whilst that of the BFS leachate is the highest, attributed to its high concentrations of Al, Ca, Fe, K, Mg and sulphur.
- The leached concentrations of Cu, Mo, Ni, Sb and Zn from CS are significantly higher, at least 10-fold higher, than the crushed rock as well as the other two waste materials. This is due to CS having inherently high concentrations of these elements, and also the fact

Table 8.7 The leachate properties of subbase made with different materials

	Aggregate Type Used In Subbase[a]				Swedish EPA[b]	
Variable	**CS**	**BFS**	**RCA**	**Crushed Rock**	**Class 1 or 2**	**Class 5**
Particle size, mm	0 – 5 (95% <2mm)	0 – 125 (10% <8 mm)	0 – 100 (50% <8 mm)	0 – 30 (50% <8mm)		
Subbase thickness, mm	500	500	420	420		
pH	6.9	4.8	8.2	7.6		
Electrical conductivity, mS/cm	0.1	3.0	1.0	0.7		
Element, mg/L						
(a) Monitored from 1998 to 2007						
Al	0.2	4.0	0.3	0.2	–	–
As	3	2	16	5	1 – 5 (Class 1)	> 50
Ba	170	60	26	90	–	–
Ca	15	520	32	110	–	–
Cr	2	21	87	4	–	–
Cu	610	100	50	5	–	–
Fe	0.40	5.0	0.09	0.30	–	–
Mg	2	40	3	18	–	–
Mo	140	16	15	5	–	–
Ni	230	13	7	4	–	–
Pb	1	9	2	2	1 – 3	>10
Sulphur (SO_4^{2-})	26	1600	140	280	–	–
Zn	1300	340	7	5	20 – 300	>1000
(b) Monitored from 1998 to 2002						
Cd	0.50	0.20	0.03	0.03	0.1 –1.0	>5
Hg	0.003	<0.002	0.02	0.002	–	–
K	5	280	87	20	–	–
(c) Monitored from 2006 to 2007						
Sb	60	<5	5	<5	–	–
Se	<7	41	9	8	–	–

[a] *CS*, copper slag; *BFS*, blast furnace slag; *RCA*, recycled concrete aggregate.

[b] Swedish EPA (2000), concentration classification of metals in groundwater; only Classes 1, 2 and 5, which correspond to 'very low concentration', 'low concentration' and 'very high concentration', are shown in this table.

that the particle size of the CS used is relatively smaller than the other materials, making the CS more prone to leaching. According to the concentration classification for metals in groundwater set by the local authority, the Swedish Environmental Protection Agency (SEPA), the As, Cd and Pb measured in the leachate from the CS section are in Class 1 and 2 as 'very low and low concentration' (SEPA, 2000). This suggests no or slight effects on human activities; whilst Zn is in Class 5 as 'very high concentration', which is at a level not safe for consumption. Thus, a more comprehensive environmental impact assessment, also covering the study of groundwater, adjacent soil and vegetation, is needed to characterise the leachate properties of CS.

8.3 Case Studies

8.3.1 Copper Slag Use in Cement Manufacture

A pilot-scale test which produced 50 tonnes of cement a day, using limestone, clay and a spectrum of waste materials such as incineration ashes from municipal solid waste and sewage sludge, CS and aluminium dross sewage dry powder as raw feed, has been reported by Kikuchi (2001). Three different compositions of cement clinkers were designed, as given in Table 8.8, which shows that the composition of municipal waste incineration ash is the highest amongst the waste materials, at 27.5–40.6%, whilst that of CS is the lowest at 0 or 0.3%. Although the reason for the inclusion of CS was not clearly described, it is likely to be its high iron at 48.6%, compared to other natural and waste materials that have an iron content range of between 0.8% and 5.0%.

The manufacturing process for cement made with waste materials was not so dissimilar to that of normal cement. The municipal waste incineration ash was first dried and finely ground in the pretreatment process. The pretreated incineration ash was mixed with other raw feed materials in a mixer, and then the material mixer was heated in a rotary kiln at 1400°C for 30 min to form cement clinker. The resulting clinker was cooled and finally mixed with gypsum and ground into fine powder form.

The production of this 50 tonnes of cement containing waste materials was reported to have consumed 12 kL of heavy oil, 52 m^3 of industrial water and 12,500 kW of electricity, but no comparison was made to that of normal PC production.

Table 8.8 The compositions of Portland cement clinker made with waste materials

	Raw Feed Compositions, %						
	Natural Material		Incineration Ash		Other Waste Material		
Mix	**Limestone**	**Clay**	**Municipal Waste**	**Sewage Sludge**	**Aluminium Dross**	**Copper Slag**	**Sewage Dry Powder**
M1	61.8	6.0	30.4	1.1	0	0.3	0
M2	54.0	6.9	27.5	0	0.9	0.3	10.4
M3	56.6	2.8	40.6	0	0	0	0

Table 8.9 Chemical and physical properties of cement containing copper slag (CS) and other waste material

	Cement			
Property	**M1 (0.3% CS)**	**M2 (0.3% CS)**	**M3 (0% CS)**	**Portland Cement** [a]
(a) Chemical composition, %				
SiO_2	17.7	18.1	19.0	20.0
Al_2O_3	9.4	10.2	10.0	5.0
Fe_2O_3	3.3	3.5	3.0	3.0
CaO	62.4	60.8	61.5	65.0
MgO	1.8	1.8	2.0	1.1
Na_2O	0.1	0.2	0.2	0.2
K_2O	0	0	0	0.9
SO_3	1.4	1.3	1.2	2.4
Cl	0.5	0.4	0.3	–
P_2O_5	1.9	2.1	1.7	–
(b) Setting time, min				
Initial	40	40	30	–
Final	50	60	40	–
(c) Compressive strength, MPa				
7 day	16.0	18.0	22.0	–
28 day	32.5	34.0	37.0	–

[a] Typical value for Portland cement as given by Jackson and Dhir (1996).

The chemical and physical properties of the cement containing waste materials produced in the study are summarised in Table 8.9. It can be seen from Table 8.9 that most of the chemical compositions of the resultant cements are close to that of the typical PC, as given in Jackson and Dhir (1996). However, the cements made with waste materials have a higher content of Al_2O_3, which could be beneficial for its chloride ion binding ability. Another point to note is that these cements can be used as low-alkali cements to prevent deleterious expansions from alkali–aggregate reaction as their alkali content, as expressed in equivalent sodium oxide (Na_2O_{eq}) (which is calculated as $Na_2O + 0.658\ K_2O$), is less than 0.60% (National Ready Mixed Concrete Association, 2014).

However, the SO_3 content of these cements, which is also an indication of the amount of gypsum used during clinker production, is lower than the typical PC (Table 8.9). This probably explains why the initial setting times of the resultant cements are fast, not meeting that of the minimum requirement recommended in BS EN 197-1 (2011) as

75, 60 and 45 min for Class 32.5, 42.5 and 52.5 cement, respectively. On the other hand, the 7- and 28-day strengths of the cements made with CS and other waste materials comply with the strengths requirements of Class 32.5N cement in accordance with BS EN 197-1 (2011).

Additionally, as previously discussed in Section 8.2.2, the exhaust gasses generated during clinker production are reported to satisfy the permissible gas pollutant levels, with the use of cyclone and activated carbon, which was placed in the bag filter.

It should be mentioned here that although the case studies for the use of ground CS as cementitious material in real practice are not available, given that the material is somewhat similar to ground granulated blast furnace slag (GGBS), the concrete design method, mixing procedure and concreting work for concrete made with ground CS can be referred to that of GGBS by analogy.

8.3.2 Copper Slag Use in Concrete

Attributed to its low porosity and high hardness, CS could ideally be used as an alternative source to natural sand in concrete applications. Indeed, a great deal of work has been undertaken to study the properties of concrete made with CS, and it is shown that when designed properly, the use of CS can improve the consistence, strength, deformation, permeability and durability properties of concrete. The material also shows potential for use in self-compacting, high-strength and high-durability concrete mixes.

Table 8.10 lists the concrete applications and events related to the use of CS as sand, which are largely from Singapore, with a few from Japan, Portugal and the United Kingdom, as reported since 1996. Regrettably, the information provided about these applications has been very brief and is in such form that no significant field experience can be learnt from them. Nevertheless, there are some points that are worth mentioning in this regard:

1. Probably the first concrete application made with CS as sand was initiated in 1996 for the construction of a five-storey high office building in Singapore (Wee et al., 1996). The CS used was actually WCS, which was sourced from a CS recycling plant setup in 1990 in Singapore to treat CS that had been previously used as blasting medium (Sembcorp Marine, 2011).
2. In 1997, a Japanese standard, JIS A 5011-3, was established specifying the requirement for the use of CS as a fine aggregate in concrete. This was around 20 years after the first development of standards for BFS use in concrete as a coarse and a fine aggregate in 1977 and 1981, respectively.
3. The percentage of WCS as sand replacement permitted in Singapore has increased over the years, from the initial 15% WCS used in the construction of a five-storey concrete office building in 1996, to its use at 30% and 50% in non-structural applications in 2009 and 2010, respectively. Indeed, one of the concrete manufacturers in Singapore, Holcim, started supplying concrete with up to 100% CS content as sand in 2009 (Holcim, 2009a; 2009b).

Table 8.10 Concrete applications and events related to the use of copper slag (CS) sand

Year	Country	CS/WCS, %	Applications/Events
1996	Singapore	15	Construction of a five-storey office building
1997	Japan	–	Standard for CS as aggregate was established (in Japanese)
2004	Singapore	–	Concrete paving blocks production
2009	Portugal	25	Concrete paving blocks production
	Singapore	10, 30	Use in conjunction with and without 20% GGBS and 20% RCA for the construction of structural and non-structural components of a non-residential building
	Singapore	Up to 100	Supply of concrete containing WCS
	Singapore	–	A non-residential building was awarded for sustainable design and construction, including the use of WCS and RCA
2010	Singapore	30, 50	Use in conjunction with 30% and 50% RCA for superstructures and non-structural elements
2011	Singapore	Up to 30	Two non-residential buildings were awarded for sustainable design and construction, including the use of WCS and RCA
2012	Singapore	–	Concrete paving block production
	UK	>50	Use in conjunction with china clay and RCA in paving block production
2014	Singapore	–	Eleven non-residential buildings were awarded for sustainable design and construction, including the use of WCS and RCA
2015	Singapore	–	Two non-residential buildings were awarded for sustainable design and construction, including the use of WCS and RCA

WCS, washed copper slag; *RCA*, recycled concrete aggregate; *GGBS*, ground granulated blast furnace slag.
Data taken from BCA (2009, 2010, 2011, 2012, 2014, 2015), Cachim et al. (2009), Charcon (2012), G&W Ready-Mix (2012), Holcim (Singapore) (2009a, 2009b), Lawrence et al. (2004), Sembcorp Marine (2011), Otak and Kawano (2002), and Wee et al. (1996).

For the use of WCS in structural applications, the quantity of WCS has also been increased from the allowable maximum of 10% (BCA, 2008; Angagadjaja and Soh, 2009) to 30% in the construction of superstructures of a non-residential building in 2010 (BCA, 2012).

4. Additionally, the use of CS in conjunction with other waste materials such as coarse RCA and ground granulated blast furnace cement has become a common practice since 2009.
5. The construction industry in Singapore has gained sufficient confidence in the use of WCS in concrete over time. To increase resource efficiency aimed at a zero landfill target (BCA, 2012), this use of CS in the form of WCS has been heavily promoted in Singapore by the Building and Construction Authority.

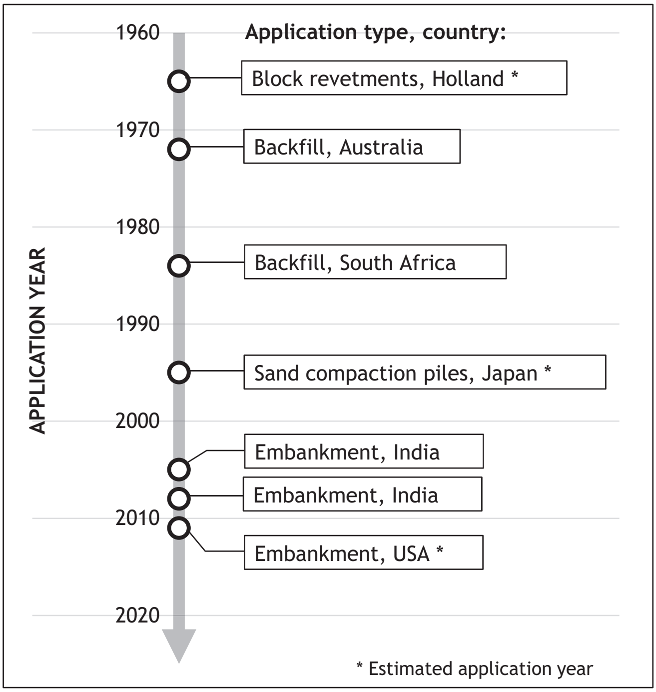

Figure 8.3 Timeline of the use of copper slag in geotechnical applications.
Data taken from Atkinson et al. (1989), Gerritsen and Bruun (1964), Grice (1998), IRC Highway Research Board (2009), Kitazume et al. (1998a,b), Patel et al. (2007), Petrolito et al. (2005), and Transport Research Board (2013).

8.3.3 Copper Slag Use in Geotechnical Applications

The suitability of CS for use in geotechnical applications, due to its similar to or better than natural sand engineering properties, in terms of compaction characteristics, permeability, consolidation and shear strength, has been discussed in Chapter 6. Additionally, in the finely ground form, CS has been shown to exhibit, similar to ground granulated BFS, pozzolanic behaviour (Chapter 5) which could be used as a binder in backfill applications.

Figure 8.3 shows the timeline for the reported case studies of CS field applications as a natural fine aggregate in block revetments, sand compaction piles, embankments and unbound applications, and in the ground form as a binder in mine backfill. The case studies, though global in nature, are unfortunately limited to six countries, namely Australia, Holland, India, Japan, South Africa and the United States. The first case is related to CS's use as sand in block revetments in Holland during the 1960s, and since then no case study about its use as sand in geotechnical applications was reported for almost 30 years. However, in the 1990s, the use of CS was tested in a field application for the construction of sand compacted piles in Japan. The following years saw a slight increase in the development in the use of CS in real geotechnical applications. Ground GC in binder applications was the subject of further field applications in mine backfill in Australia and South Africa during the 1970s and 1980s. The detailed information for each of the case studies is discussed in the following two sections.

Copper Slag as Fine Aggregate in Geotechnical Applications

The geotechnical application of CS as sand was first reported by Gerritsen and Bruun (1964) for the construction of revetments in the northern part of Holland in the early 1960s. The revetment blocks made with CS as sand were reported to have a high specific weight and high abrasion resistance. These CS blocks were used together with normal concrete blocks in the construction of revetments to protect the land from hydraulic loadings such as wave action, and the performance of CS blocks was claimed to be a success.

During the 1990s, a field construction test was conducted to evaluate the suitability of using 70% CS and 30% local clay as marine sand replacement in sand compaction piles for a ground improvement project at Uno Port in Japan (Kitazume et al., 1998a,b). It was reported that the machine used and the operational time for the construction of both the CS–clay and the marine sand were almost the same, indicating that the use of CS does not require a special plan of work and time schedule. The field strengths of CS-clay and marine sand compacted piles were measured using a standard penetration test, and the results showed that the strength of CS-clay sand is similar to or slightly higher than that of the marine sand.

Two embankments of road sections of 100 m and 1 km length were built using CS as sand in India in 2005 (Patel et al., 2007) and 2008 (IRC Highway Research Board, 2009), respectively. In the former case, the material used was a combination of 70% CS and 30% FA, which was estimated to render 40% cost saving in the production. The field condition of the road, assessed using roughness and surface irregularity tests, was satisfactory after almost 2 years of service (Patel et al., 2007). On the other hand, for the latter case, three material design mixes, namely 100% CS mix, 50% CS–50% pond ash mix and 50% CS–50% soil mix, were tested in a trial section. The mix with 100% CS was rejected, as some working difficulties were encountered, such as uneven compaction and shearing of compacted layers by vehicles. However, such difficulties were not experienced for the sections made with CS–pond ash and CS–soil mixes.

A survey conducted by the Transportation Research Board (2013), however, revealed that a highway construction project using CS in unbound application, conducted in Illinois, was claimed to be not successful, but the reasons for this were not clear.

Copper Slag as Binder in Geotechnical Applications

In underground mine activities, backfill is used to provide ground support, as well as for the purpose of mine waste disposal. The materials used for mine backfill generally consist of solid waste from mining activities as bulk fillers, and binder, such as PC, slag cement and FA, to hold the materials together.

A mining company in Mount Isa, Australia, used ground CS as a binder to replace part of the cement used in backfill since the early 1970s (Grice, 1998). This resulted in 25,000 tonnes of cement saving annually.

Another successful case in South Africa has also been reported (Atkinson et al., 1989). A slag milling plant and backfill plant were commissioned in 1984 for a backfill project using ground CS as binder, and the system used for processing ground CS cement was patented in late 1984. The process is briefly discussed here.

The lime-to-silica ratio of CS is increased by adding an increased content of limestone to the furnace. The resultant slag is finely ground with gypsum and sent to a series of flotation cells for copper recovery, followed by a thickener to produce a mixture containing 60% solids. This mixture is blended with tailings, and lime is added for cementation purpose, which is then used as backfill material.

8.3.4 Copper Slag Use in Road Pavements

Compared to concrete (Chapter 4), cement clinker and cementitious materials (Chapter 5) and geotechnical applications (Chapter 6), the research on the effects of CS on the properties of road pavements is relatively less abundant. The analysis and evaluation of the published data (Chapter 7) suggest that CS can be used as a natural sand replacement in road pavement applications. Indeed, the material has been used by the construction industry in various road pavement applications, such as unbound and hydraulically and bituminous bound mixes, paving blocks, roadside walls and fog seal applications, as shown in Figure 8.4.

The first use of CS as a construction material in road pavements can be traced back as far as the early 18th and 19th centuries, when CS was cast in shaped moulds and used as coping stones for roadside walls in the United Kingdom. Since then, there have been only a few case studies regarding the field application of CS. However, the real interest in using CS in road pavement construction became more common from the beginning of the 21st century, mainly in the Asian countries, such as India and Singapore. The following points emerged from these field applications:

1. The use of CS as sand replacement in unbound and hydraulically and bituminous bound mixes for the construction of road pavements has been developed in India, Singapore and the United States. As reported by Havanagi et al. (2009), CS was planned to be used for a content of up to 75% in different pavement layers, from subbase to surface courses, of four trial sections with 500-m length each for highway widening construction in India. No field data were made available at the time of reporting. However, the use of CS as a construction material for hydraulically and bituminous bound applications was discontinued in Texas in 1993 because of environmental concerns. The details of this were not provided in the report by the Texas Department of Transportation (TxDOT, 1999). However, it should be noted that data presented in Sections 8.2.1 and 8.2.3–8.2.5 of Chapter 8, pertaining to leaching studies on CS material, as well as on concrete and soil samples containing CS, have shown them not to have negative environmental impact.
2. It has been reported that a walkway in India (Sterlite Industries, 2012) and a residential driveway in Singapore (BCA, 2008) were built with paving blocks containing up to 100% CS content.

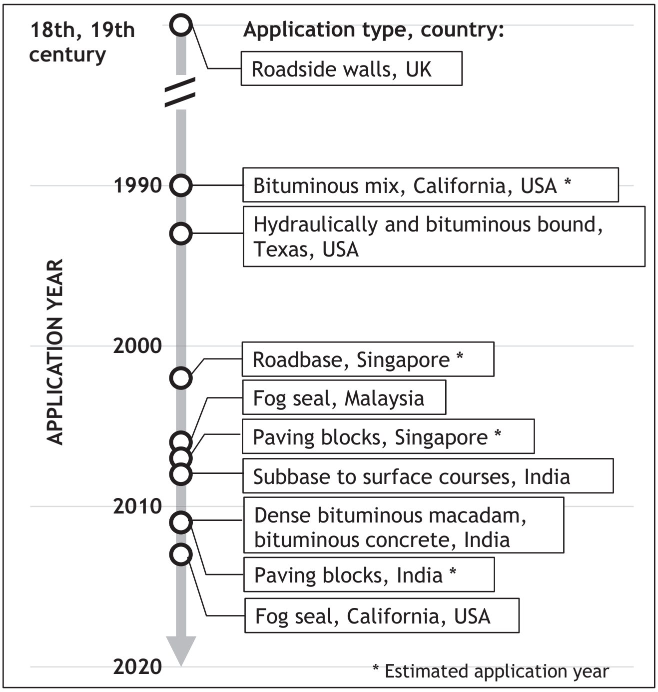

Figure 8.4 Timeline of the use of copper slag in road pavement applications.
Data taken from BCA (2008), Collins and Ciesielski (1994), Crown Capital (2006), Havanagi et al. (2009), IRC Highway Research Board (2009, 2011), JPL Industrial (2003), Sterlite Industries (2012), Streetscape Manual (2005), TxDOT (1999), and Urbanek et al. (2013).

3. Fog seal is a surface treatment method, using a dilute asphalt emulsion, to protect and rejuvenate the surface of bitumen pavement. The application of fine aggregate is normally needed after fog sealing to maintain the skid resistance and friction of pavement. The use of CS as a sanding material for fog sealing application has been documented in California, USA (Urbanek et al., 2013), and Selangor, Malaysia (Crown Capital, 2006), and no adverse effects have been reported.

8.4 Standards and Specifications

As with any other construction material, the use of CS in construction applications must comply with the national standards and specifications, to ensure the reliability and quality of work undertaken. Table 8.11 lists the major standards and specifications that can be referred to when the use of CS is considered for cement, concrete, mortar, geotechnical and road pavement applications. The standards and specifications discussed in this chapter are produced by the American Association of State Highway and Transportation Officials (AASHTO), the American Society for Testing and Materials (ASTM) and the European Committee for Standardisation, implemented in

Table 8.11 Standards and specifications for copper slag use in construction applications

Application	Standards and Specifications
Cement	• ASTM C150/C150M (2012): Standard specification for Portland cement. • ASTM C465 (2016): Standard specification for processing additions for use in the manufacture of hydraulic cements. • ASTM C595/C595M (2013): Standard specification for blended hydraulic cements. • ASTM C989/C989M (2014): Standard specification for slag cement for use in concrete and mortar. • ASTM C1709 (2011): Standard guide for evaluation of alternative supplementary cementitious materials (ASTM) for use in concrete. • BS EN 197-1 (2011): Cement. Composition, specifications and conformity criteria for common cements. • BS EN 15167-1 (2006): Ground granulated blast furnace slag for use in concrete, mortar and grout. Definitions, specifications and conformity criteria.
Concrete and mortar	• ASTM C33/33M (2013): Standard specification for concrete aggregates. • BS EN 206 (2013): Concrete. Specification, performance, production and conformity. • BS EN 12620:2002+A1 (2008): Aggregates for concrete. • BS EN 13139 (2002): Aggregates for mortar.
Geotechnical Applications	• ASTM D2487 (2011): Standard practice for classification of soils for engineering purposes (unified soil classification system). • BS EN 13242:2002+A1 (2007): Aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction.
Road Pavements	• AASHTO M 6 (2013): Fine aggregate for hydraulic cement concrete. • AASHTO M 29 (2012): Fine aggregate for bituminous paving mixtures. • ASTM D1073 (2011): Standard specification for fine aggregate for bituminous paving mixtures. • ASTM D1241 (2015): Standard specification for materials for soil-aggregate subbase, base and surface courses. • ASTM D2940/D2940M (2015): Standard specification for graded aggregate material for bases or subbases for highway or airports. • BS EN 13242:2002+A1 (2007): Aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction. • BS EN 13043 (2002): Aggregates for bituminous mixtures and surface treatments for roads, airfields and other trafficked areas.

the United Kingdom as the British Standard European Norm. Although most of the standards and specifications do not have a provision for CS, the requirements specified therein can be used as a benchmark assessment, for quality monitoring, or as a cross-reference for CS.

8.4.1 Cement Applications

When finely ground to a certain fineness, CS does exhibit pozzolanic behaviour, thus offering potential for use as a cement component. Although the use of CS as a cement component has not been recognised as one of the common cements in BS EN 197-1 (2011), there are two possible ways of introducing CS into cement production, either as a 'minor additional constituent' up to 5% in all the cements or as a 'main constituent', as in CEM II Portland composite cement, for up to 35% content. When used as the main constituent of cement, the characteristics of CS shall comply with all the chemical, physical, durability and other requirements, for example, in the case of ground granulated BFS in BS EN 15167-1 (2006).

Similarly, CS can be used as an 'inorganic processing addition' for an amount not more than 5% in the manufacture of PC and as 'blended cement' in compliance with ASTM C150 (2012) and ASTM C595/C595M (2013), respectively. Its use in the latter cement shall conform to the requirements recommended for slag cement as given in ASTM C989/C989M (2014).

8.4.2 Concrete and Mortar Applications

Both the ASTM C33 (2013) and the BS EN 12620:2002+A1 (2008) standards have a provision for manufactured fine aggregate to be used in concrete, although the definitions of manufactured aggregate therein are different. For the former, the definition is given in a separate standard, ASTM C125 (2013), in which manufactured sand is defined as fine aggregate obtained from 'crushing rock, gravel, iron BFS or hydraulic-cement concrete', whilst for the latter, manufactured aggregate is a material of mineral origin derived 'from an industrial process involving thermal and other modification' (BS EN 12620:2002+A1:2008). Thus, it appears that CS can be considered as manufactured aggregate in the BS EN standard.

Among the compliance requirements, special attention must be paid to the grading of CS, which is governed by the type of CS. As shown in Section 3.4.2 of Chapter 3, quenched CS tends to be a coarse grading material, whilst spent CS is likely to be in the fine to medium zone in accordance with BS EN 12620:2002+A1:2008. On the other hand, air-cooled CS, which appears as rocklike material, needs to be crushed and sieved to a sand grading requirement, though its use as a fine aggregate is unlikely.

8.4.3 Geotechnical Applications

For use in geotechnical applications, particle size and distribution, the liquid limit and plasticity index of CS can be described using the guidelines suggested in the unified soil classification system in accordance with ASTM D2487 (2011).

According to BS EN 13242:2002+A1:2007 for aggregate use in civil engineering work, CS can be considered as manufactured aggregate, which has the same definition as given in BS EN 12620:2002+A1:2008 for aggregate use in concrete. It should be noted that the maximum allowable size for fine aggregate in BS EN 13242:2002+A1:2007 is 6.3 mm.

8.4.4 Road Pavement Applications

In the construction of subbases and bases, CS should be processed or crushed (for air-cooled CS) to the fine aggregate grading requirements like those specified in ASTM 1241 (2007) and ASTM D2940/D2940M (2015). When used as a hydraulically bound and bituminous bound material, the physical requirements, especially the grading, as well as the chemical and durability requirements for CS, should conform to AASTHO M6 (2013), AASHTO M 29 (2012), ASTM D1073 (2011), and BS EN 13043 (2002).

8.5 Conclusions

CS, a by-product produced during smelting and refining of copper, is characterised as a non-hazardous material by the US EPA and the Basel Convention. The leached element concentrations of CS samples, reported since 1983, from 10 countries across the world, measured mostly using TCLP, are well below the maximum allowable limits set by the US EPA (2012), except for one case, in which the concentration of lead exceeded the limit. The leached element concentrations are also safe when the material is subjected to high acidic and low alkaline solutions. The leaching behaviour of CS is not affected by its types, namely air-cooled, quenched and spent; however, CS is more prone to leach when finely ground, or exposed to high acidic environment. The leachate of CS is shown to be harmless to the growth of marine microalgae.

When CS is used as raw feed in cement clinker, the exhaust gases emitted during production have been found to be harmless to the environment. The leached element concentrations of cement clinker containing CS, either measured in the ground form or obtained from cast paste and cement specimens, are not to be of concern. Similarly, finely ground CS used as cementitious material in concrete also poses no risk to the environment. No clear relationships have been observed between the leached element concentrations and the concrete age for the mixes made with ground CS as cementitious material. It has been shown that CS and other waste materials can be used in cement clinker manufacture and the cement produced can meet the requirements recommended in BS EN 197-1 (2011), although some adjustments on the gypsum content may be needed. The chemical compositions of the PCs produced with CS are almost similar to normal PC, with the exception of equivalent sodium oxide being lower and aluminium oxide being higher than the norm.

Concrete made with up to 100% CS as a natural sand replacement is shown to have leached element concentrations below the US EPA regulatory levels by TCLP test, even when tested in an aggressive environment. The w/c ratio and curing age of concrete do not appear to have an influence on the leached element concentration, except for calcium. The construction industry, particularly in Singapore, has been using CS as a natural sand replacement in concrete paving block and structural and non-structural concrete components since 1996. The use of CS in conjunction with RCA has become common in the construction industry in Singapore.

It has also been confirmed that the elements leached from CS in geotechnical applications, exposed to different pH environments from pH 3 to 8, have concentrations well below the US EPA regulatory levels. When measured using SET, the leaching of elements from a mixture of CS, sewage sludge and PC is more apparent in the reducible fraction, but the majority of the elements are retained in the residual fraction, showing that the mixture is less likely to leach. CS has been documented for its use as a natural sand replacement in the construction of revetments, sand compaction piles and embankments, or as a binder (in the ground form) in mine backfill, since the 1960s. No major problems with the use of CS in field applications have been reported.

A 10-year field study of leachate collected from subbase made with CS in Sweden shows that the leachate is essentially neutral and low in EC. However, the concentration of zinc found in the leachate was considered very high, and at a level not safe for consumption for groundwater, based on the SEPA (SEPA, 2000). CS has been used by the construction industry in Asia and the United States in various road pavement applications, including unbound and hydraulically and bituminous bound mixes, paving blocks, roadside walls and fog seal applications.

When CS is used in cement, concrete, mortar, geotechnical and road pavement applications, for its physical, chemical and durability requirements reference should be made to the relevant AASHTO, ASTM and BS EN standards.

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Epilogue

9

The work presented in this book is different to the norm and its uniqueness lies first in undertaking a systematic analysis and evaluation of experimental results taken from the thoroughly sourced literature, published since 1964, on the subject of copper slag and its use in various aspects of construction, and second in packaging this information in a manner that is easy to understand, disseminate and put into practice.

The main purpose of this book is to encourage the added value use of copper slag in construction and to minimise repetitive research, which often confuses the issues, retards progress towards sustainability and wastes valuable resources. The work is based on a data matrix built from 400 sourced publications, originating from 40 countries worldwide, and covers the use of copper slag in cement, concrete, geotechnical and road pavement applications, as well as the associated environmental issues and standards. The relevant case studies have also been evaluated.

Overall, the volume of literature published and the data sourced for different applications of copper slag showed that the highest research activity has been focused in the area of cement, mortar and concrete, where the basic physical and chemical characteristics of the material are the best suited and the environmental impact, in terms of element leaching, is considered to be relatively more of a benign nature.

Amongst the issues that caused concern when dealing with sourced data, and one which happens to be critical, is the reliability of the information provided in some of the studies and the extent of the variability and inconsistencies in the obtained results, though this is to be expected when working with a large database populated by globally sourced literature. This concern is applied to the materials used in different studies and their characteristics, as well as the mix designs, test conditions, test methods and laboratory control. All these made the analysis and evaluation of results difficult, time consuming and at times problematic. Lack of information on the methodologies adopted in some cases did not help. Reference to foreign standards was not possible at times and this led to some uncertainty. Although in most cases, such difficulties were resolved based on authors' experience, there were occasions when specific sets of results could not be comprehended to the extent that the data had to be ignored. One of the main points to emerge from this work is that for the research in the area of construction to be more effective, it needs to go through a process of validation and coordination.

Though not recognised easily from the literature, with its basic physical and chemical properties, copper slag in granular form can be used as a sand, potentially for developing high-performance concrete in the fresh state, for high consistence such as self-compacting concrete, and in the hardened state, for example, high- and

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ultrahigh- strength concrete with excellent elastic modulus, creep and shrinkage properties, as well as high-durability concrete in terms of its resistance to physical and chemical attacks. This potential, which has been recognised and has received preliminary investigations (see Chapter 4, Section 4.9.1), is considered to be achievable and should be further tested. Additionally, the material has also shown some indications that it can improve the use of other waste materials, such as recycled aggregate and sewage sludge ash, in the manufacture of concrete for structural applications (Chapter 4, Section 4.3.1). This potential of copper slag to improve the performance of cementitious mixtures is due to its exceptionally low porosity, high hardness, smooth surface texture and hydrophobic characteristics, which lower the water demand of the concrete mix, offering several benefits, including denser cement paste structure, as well as making the material suitable for further innovative developments.

In terms of its chemical and mineralogical characteristics, copper slag is well placed for developing its use as a component of the raw feed for the manufacture of Portland cement clinker and in the ground form, similar to other pozzolanic materials, as a constituent of cement. The appreciable amount of research undertaken in this area confirms this. The use of the material in this manner is also acceptable in terms of durability and environmentally related aspects. However, copper slag has a considerably high bond grindability index, meaning that grinding to an appropriate fineness can be energy intensive, and therefore, the use of the material for such applications is unlikely in the near future.

For its use in geotechnical applications, copper slag appears to offer satisfactory performance in terms of compaction characteristics, permeability, consolidation, compressibility and shear strength. It has been shown that it is safe to use copper slag in most geotechnical applications. The material has been successfully used in the construction of revetments, sand compaction piles and embankments. As a granular material in geotechnical applications, copper slag is permitted and indeed has been used by the Michigan Department of Transportation in the United States. The material is being considered for adoption in the development of a new European standard, prEN 13242 (2015).

In the area of road pavements, the potential for the use of copper slag as an alternative source of natural sand looks promising in all forms of applications, in unbound, hydraulically bound and bituminous bound mixes, with the material adding value to the performance of pavement properties. Although the available information is limited, the use of copper slag in pavement applications has been developed mainly in Asia and the United States, and the leachate results show that the use of copper slag in such applications should not pose a threat to the environment.

As a by-product material generated during copper processing, copper slag is considered to be safe in terms of its effect on the environment and human health. It enjoys a clean bill of health from the US Environment Protection Agency (US EPA) and the Basel Convention of the United Nations, where copper slag was accepted as a non-hazardous material. The results of leached element tests carried out on copper slag, over a period over 30 years, using the toxicity characteristic leaching procedure, are all below the allowable values set by the US EPA. The leaching behaviour of copper slag is not affected by the type of copper slag, namely air-cooled, quenched and spent. The use of copper slag in the manufacture of Portland cement, in a ground form in concrete as an addition to Portland cement, and in a granular form in concrete, geotechnical and road pavement applications, has been shown to present no environmental or health risks.

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'*Note*: Page numbers followed by "f" indicate figures and "t" indicate tables.'