UNIVERSITY OF
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DURABILITY POTENTIAL OF PORTLAND LIMESTONE CEMENT CONCRETE

by

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ABSTRACT

There is an increasing global concern that has led to efforts to lessen the carbon footprint of the cement industry and make concrete manufacturing more sustainable by using other types of materials as supplements or alternatives, primarily for Portland cement (PC). This research work is concerned with the analytical systemisation, including the analysis, evaluation and structuring of global published experimental results, of ground limestone (GLS) used in concrete as a partial replacement of PC. The work is focussed on the physical and chemical characterisation of GLS and its effects on pore structure (in terms of porosity, water absorption and sorptivity), compressive strength and the durability of the concrete in terms of the carbonation and chloride ingress and the corrosion of steel reinforcement, including a statistical modelling of the carbonation of concrete with Portland limestone cement (PLC). Overall, it is suggested that, though the use of GLS up to 25% with PC should not impair the pore structure, the limit on GLS content for its effect on strength is likely to be about 15%. This should be considered where a higher proportion of GLS content is allowed in the standards. It is also shown that the carbonation rate and chloride ingress into concrete increase with increasing GLS content, within the range permitted by the standard BS EN 197-1:2011. This effect, however, is less marked for concrete designed on an equal strength basis compared to the corresponding PC concrete than for concrete designed on an equal water/cement (w/c) basis. In light of this, the maximum limit on GLS content of CEM II/A may be considered for revision from 20% down to 15%. Furthermore, Eurocode 2 standard specifications for XC3 carbonation exposure and XS1 chloride exposure for the characteristic cube strength of concrete (or its w/c ratio) may need to be reviewed, also for the addition of GLS. The predicted outcomes through the statistical modelling via the SPSS software are in agreement with the analytical systemisation results in suggesting that GLS addition has the potential to accelerate the rate of carbonation of PLC concrete under different exposures.

DEDICATION

This thesis is dedicated to my precious country ***Libya***.

I am also very thankful to my beloved ***family***.

I want to show appreciation for my dear ***parents***, ***wife, children, brothers*** and ***sisters*** whose love and devotion are with me in whatever I pursue.

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DISSEMINATION

PhD STUDY OUTCOMES (PEER-REVIEWED JOURNAL PUBLICATIONS)

Elgalhud A. A., Dhir R. K. and Ghataora G. S., (2016). Limestone addition effects on concrete porosity. *Cement and Concrete Composites (Elsevier Journal), 72*, pp.222-234.

Elgalhud A. A., Dhir R. K. and Ghataora G. S., (2017a). Carbonation resistance of concrete: limestone addition effect. *Magazine of Concrete Research (ICE Journal),* Volume 69, Issue 2, pp. 84-106.

Elgalhud A. A., Dhir R. K. and Ghataora G. S., (2017b). Chloride ingress in concrete: limestone addition effects. *Magazine of Concrete Research (ICE Journal),* http://dx.doi.org/10.1680/jmacr.17.00177

Elgalhud A. A., Dhir R. K. and Ghataora G. S., (2018). Ground Limestone Characteristics and Statistical Modelling of Carbonation of Portland Limestone Cement Concrete. *Construction and Building Materials (Elsevier Journal)*, (UNDER PREPARATION).

PUBLICATIONS PRIOR TO PhD STUDIES

Abdelgader H. S. and **Elgalhud A. A.** (2008). Effect of grout proportions on strength of two-stage concrete. *Structural Concrete* (*fib Journal*), 9(3), pp. 163–170.

Abdelgader H. S., Ben-Zeitun A. E., Saud A. F. and **Elgalhud A. A.** (2008). Effect of admixture type on mechanical behavior of two-stage concrete. The 7th International Congress, Concrete Construction’s Sustainable Option Dundee, Scotland, 8-10 July.

Abdelgader H. S., Ben-Zeitun A. E. and **Elgalhud A. A.** (2007). Influence of different admixtures on the mechanical behavior of pre-placed aggregate concrete. Proceedings of the ACI-KC Second International Conference, March 12-14, Kuwait

Abdelgader H. S., Ben-Zeitun A. E., Saud A. F., and **Elgalhud A. A.** (2006). Mechanical behavior of two-stage concrete. Proceedings of the 10th Arabic Engineering Conference, 13-15 November Kuwait.

Abdelgader H. S., Ben-Zeitun A. E. and **Elgalhud A. A.** (2006). Use of pre-placed aggregate concrete in construction and repair of concrete structures. International Conference on Concrete Repair, Rehabilitation and retrofitting in Cape Town, SA, 21-23 November.

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LIST OF ABBREVIATIONS

CKD: Cement kiln dust
GGBS: Ground granulated blast-furnace slag
GLS: Ground limestone
LD: Liquid displacement
LOI: Loss on ignition
LS: Limestone
MBI: Methylene blue index
MIP: Mercury intrusion porosimetry
MK: Metakaolin
MS: Micro-Silica
NP: Natural pozzolans
PC: Portland Cement
PFA: Pulverised fuel ash or fly ash
pH: Potential hydrogen
PLC: Portland limestone cement
PSD: Particle size distribution
SCMs: Supplementary cementitious materials
SG: Specific gravity
SPSS: Statistical Package for the Social Sciences (software)
TOC: Total organic carbon

CHAPTER 1

INTRODUCTION

1.1 Background

Although concrete was invented thousands of years ago [the origin of the name is the Latin word 'concretus', meaning 'grown together' or 'compounded' (French, 2005)], modern concrete progress started with the development of Portland cement (PC) in 1824 by Joseph Aspdin (Sharp, 2006). By the beginning of the 20th century it was being used in the construction of roads and buildings.

Today, more than 4 billion tonnes of cement are used worldwide per annum, hence concrete has become the second most consumed material after water (Kumar et al., 2016). By the year 2050 the highest and lowest expectations for global cement production are 13.5 and 5.7 billion tonnes, respectively (Figure 1.1). Such great use of concrete has come about through improved understanding of the complex nature of the material.

1.2 Ecological Impact of Concrete and the Need for Sustainability

With every tonne of cement produced, about 1 tonne of carbon dioxide (CO_2) is released into the atmosphere (Benhelal et al., 2013). The production of concrete worldwide leads to 7–10% of global CO_2 emissions (Nixon et al., 2004), and about 90% of this amount is a result of cement production (Kajaste and Hurme, 2016), which is considered to be around 26% of the total industrial CO_2 emissions (Telesca et al., 2017). In addition, the manufacture of 1 tonne of cement requires 1.5 tonnes of natural raw materials and about

3.40 and 5.29 GJ of energy for the dry process and the wet process, respectively (Madlool et al., 2013). Furthermore, the energy cost of 1 tonne of cement represents approximately 40% of the total energy cost of the entire factory (Swamy, 2001). Thus, approximately 3% of the annual global consumed energy is by the cement industry (Juenger et al., 2011). Owing to these high rates, the environmental impact is significant and the movement towards sustainability becomes an inevitable necessity.

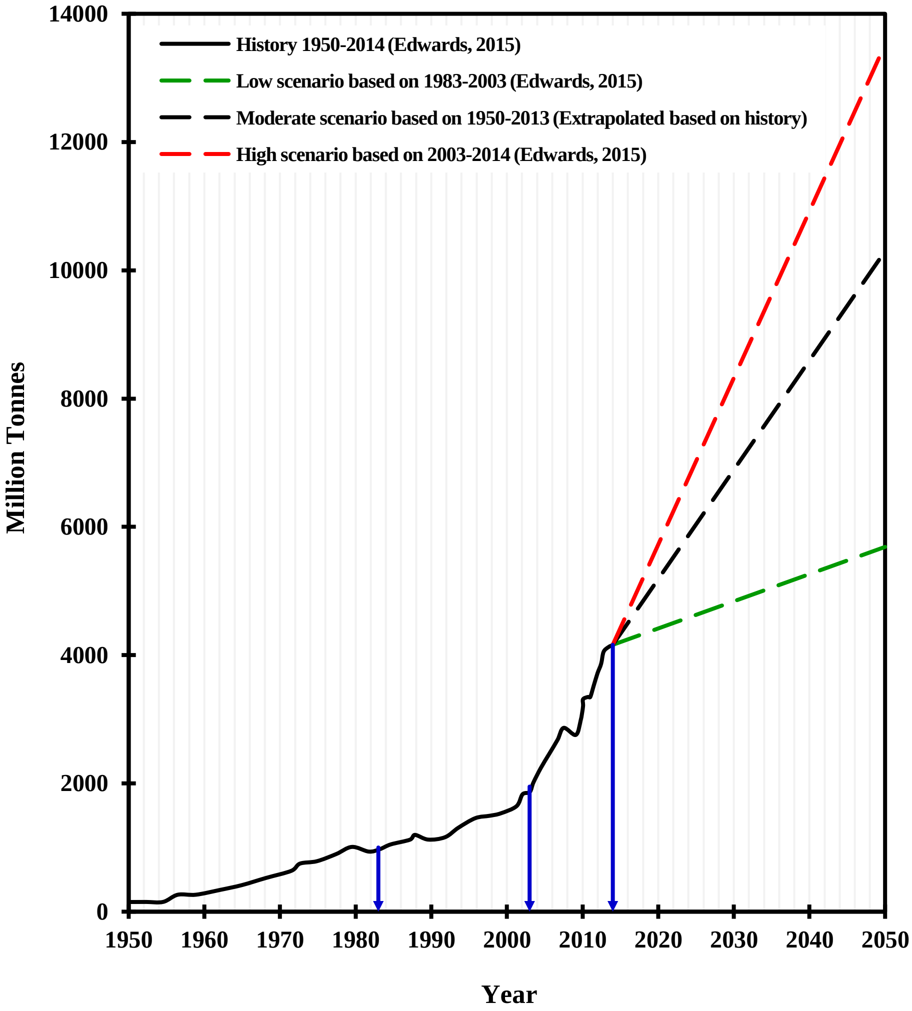


Figure 1.1: Future prospects of global cement production

Sustainability could be achieved through high levels of discipline in several areas. These can mostly be narrowed into three major pillars, environmental, social and economic, as illustrated in Figure 1.2, where the social and economic aspects are hidden in the environment and dependent on it (Henry and Kato, 2012). To obtain sustainability in the cement or concrete sector, in particular, countries worldwide are heading towards various types of approaches. The selection of the approaches to be applied depends primarily on economic factors and the obtainability of facilities and techniques. The prime ideas for these solutions revolve concerning three applications (Figure 1.3; Mehta, 2010). These are briefly described below:

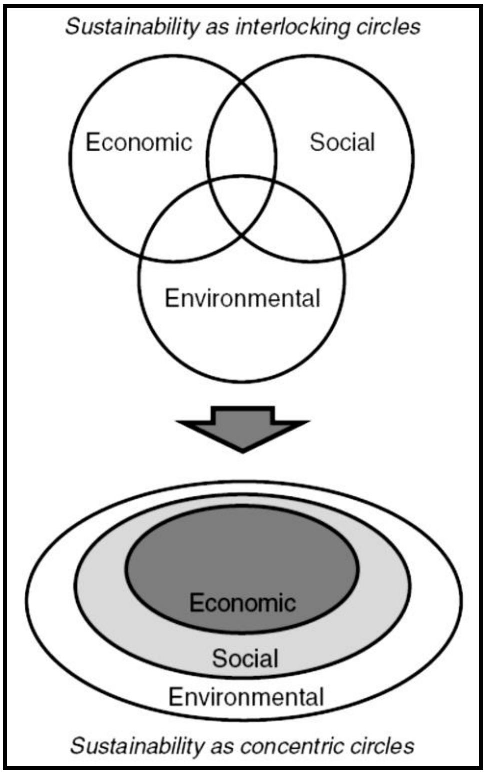


Figure 1.2: Sustainability envisioned as interconnecting against concentric circles (Henry and Kato, 2012)

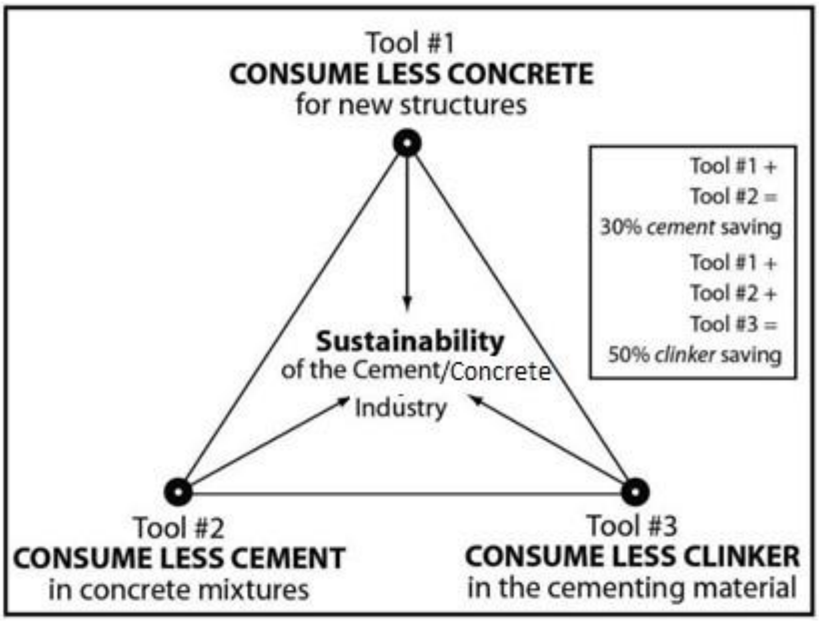


Figure 1.3: Improving the sustainability of cement/concrete sector (Mehta, 2010)

a. Diminishing the amount of concrete by using safe, thinner sections: Structural engineers should think carefully of minimising the dimensions of large structural elements, such as foundations, to the minimum safe level.

b. Consuming less cement in concrete mixtures: Great cement savings can be attained if the specifications specify the target strength of concrete at 56 or 90 days (rather than at 28 days) for footings, piers and abutments that consume massive amounts of concrete. Moreover, to enhance the workability of fresh concrete, effective chemical admixtures and improved aggregate grading should be used rather than greater amounts of water and cement.

c. Reducing the amount of clinker for making cements: In blended or composite cements about 50%–60% of Portland cement can be substituted by one or more of the supplementary cementitious materials, which can be ground with clinker or independently and blended afterward in the cement mills or at concrete mixing plants during batching.

Because cement (binder) is the main reactive component in concrete, it requires a certain amount of attention through the design stage for concrete, when the proportions and types of materials are designated; hence the optimal design could lead considerably to more durable structures. Consequently, the lifetime of concrete has a direct effect on its sustainability, owing to the energy spent and materials consumed through its functional life, in the form of serviceability and remedial works or as demolition works and waste materials when it is decided to destroy and remove the structure (Struble and Godfrey, 2004).

Preventing the corrosion of steel reinforcement is considered one of the major worries for the durability of concrete, as it threatens safety and reduces performance and also distorts the appearance of the concrete. The drive to enhance durability, reduce embodied carbon and increase sustainability has led to the usage of new replacing materials in blended cements. This comprises the use of ground limestone (GLS) as one of the cement component materials.

1.3 Blended Cements

Since the beginning of the 21st century, many cement manufacturers have started to produce blended cements by using supplementary cementitious materials (SCMs), e.g., pulverised fuel ash (PFA), ground granulated blast furnace slag (GGBS), ground limestone, micro-silica (MS), and natural pozzolana (NP). Consequently, this action has reduced the amount of PC, and the reduction in CO_2 emissions and thermal energy savings have been estimated to be 0.30–213.54 kg CO_2/tonne and 0.009–1.400 GJ/tonne, respectively (Madlool, 2013). In addition, these SCMs have managed to provide preferred properties for the newly produced concrete (Swamy, 2001).

The replacement of 15% of cement with GLS can reduce the embodied carbon of concrete by approximately 12% (Schmidt et al., 2010). In addition, about 1.4 tonnes of primary raw materials are required to produce 1 tonne of PC, whereas Portland limestone cement (PLC) needs nearly 10% less of primary raw resources.

Moreover, amongst all the cement addition materials such as GGBS, PFA and MS, GLS is the most widely available natural material, as calcium carbonate occupies 5% of the earth’s crust (Thenepalli et al, 2015) and is also a cheap material and easier to handle for cement manufacturers; it results in a lower grinding effort (Benn et al., 2012) and is usually available in large amounts near the clinker manufacturing plants.

Furthermore, the demand for GLS amongst the other additions has developed rapidly in recent years, particularly in Europe (Figure 1.4; CEMBUREAU, 2013). Consequently, a sound understanding of the behaviour of GLS as a component of PC for manufacturing concrete is essential in terms of its performance in general and its durability in particular. This provided the basis for this study.

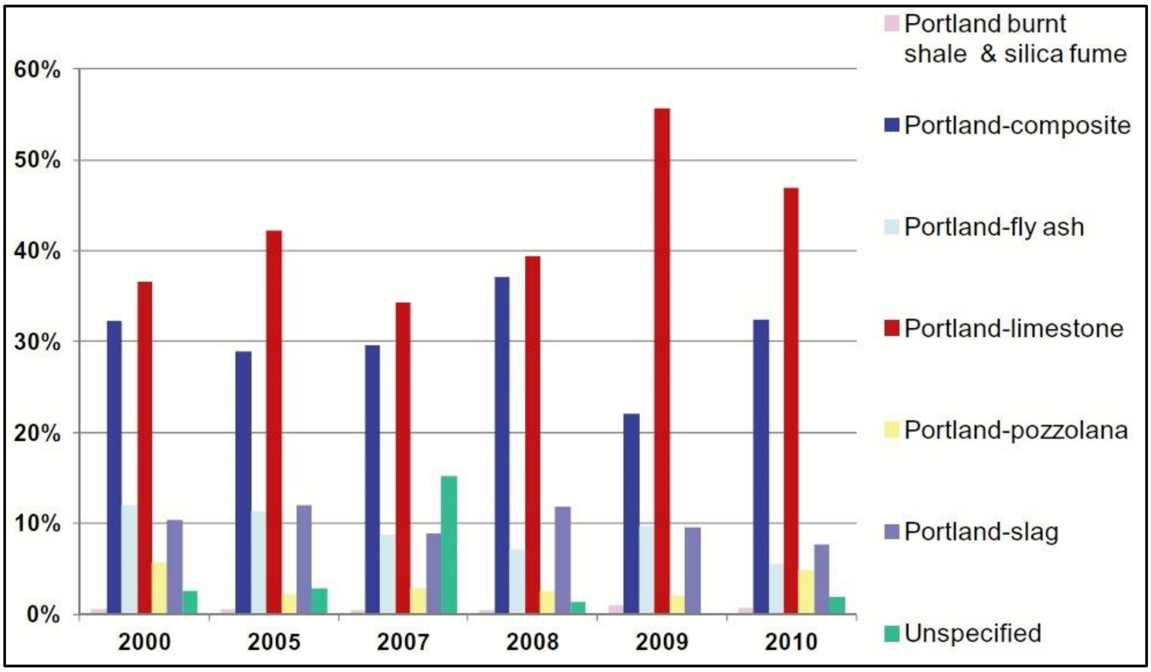


Figure 1.4: Percentage development in European blended cements 2000-2010 (CEMBUREAU, 2013)

1.4 Study Aim and Objectives

The main aim of this study is to evaluate the potential durability of PLC in relation to PC in terms of pore structure and related properties, compressive strength, carbonation resistance and chloride ingress, in a manner that will be able to suggest an optimal level of GLS addition use in concrete, which would be useful and handy for applying in practice. In achieving this goal, the following objectives were adopted:

a. An analytical systemisation approach to global published experimental results would be undertaken, which includes data mining, analysis, evaluation and structuring for the following aspects:

- The chemical and physical characteristics of GLS: This will help in comprehending the nature of the material and also in anticipating its behaviour more successfully.

- The influence of GLS on pore structure and related properties (i.e., porosity, water absorption and sorptivity) and compressive strength: This provides a sound basis for understanding the potential durability of PLC concrete.

- The potential resistance of PLC to carbonation and carbonation-induced corrosion.

- The performance of PLC concrete under chlorides ingress and chloride-induced corrosion.

b. The statistical modelling work of the carbonation of concrete produced with PLC under different carbonation exposures would be addressed.

c. Ways to use PLC more efficiently in practice would be proposed.

1.5 Originality and Significance of Research

The way in which this research has been organised could be considered original in the studied area, whereby a huge amount of published experimental data in the English medium has been synthesised and assessed collectively as in a central global laboratory through the analytical systemisation approach. In addition, performing a statistical modelling of the carbonation depth of PLC based on the previously obtained test results allows one to create an uncomplicated multiple linear model with a plausible degree of reliability.

Moreover, the innovative feature of this work is the role of GLS as a constituent of cement. Results suggest that the presently allowable proportion of GLS in cement may need to be revised to sustain the durable performance of structural concrete.

1.6 Outline of Thesis

This thesis consists of eight chapters. Brief outline of content of each chapter is given below which are as follows:

- **Chapter 1,** which is this chapter, presents a background and general overview of the topic of the study, the importance of the research and the aim and objectives and illustrates the outline of thesis.

- **Chapter 2** describes research approach and methodology adopted: sources of data, methodologies used in assessing available information, tools used in analysis and statistical modelling.

- **Chapter 3** provides an overview of the use of GLS in cement and the production of GLS and PLC. Moreover, it deals with the analysis, evaluation and structuring of the experimental results on GLS characteristics, including the physical properties and the major chemical constituents and properties. In addition, it presents the possible physical and chemical effects resulting from blending GLS with PC.

- **Chapter 4** describes the inspection and assessment of the sourced test results on porosity, water absorption and sorptivity of cement paste and mortar/concrete of PLC compared to PC. Consequently, the relationship between the compressive strengths and pore structures and related properties of PLC mixtures is established.

- **Chapter 5** deals with the analyses, examination and structuring of the experimental data obtained on the carbonation and carbonation-induced corrosion resistance of PLC concrete and how it compares at the end with the use of PFA and GGBS.

- **Chapter 6** describes the investigation, evaluation and synthesis of the chloride ingress and chloride-induced corrosion measurements of concrete made with PLC in relation to those of concrete made with PC.

- **Chapter 7** addresses the statistical modelling of the carbonation of PLC concrete, allowing the prediction of the depth of carbonation and accordingly carbonation as a function of the variables considered through multiple linear regression analysis using SPSS software.

- **Chapter 8** gives the concluding remarks drawn from this study with recommendations for future work.

CHAPTER 2

RESEARCH APPROACH AND METHODOLOGY

2.1 Introduction

This chapter describes the approach and methodology that have been adopted in this research. The work in this thesis is based essentially on the analytical systemisation approach, which consists of the mining, analysis, evaluation and structuring of a huge amount of data obtained from globally published experimental work. The sourced test results have been synthesised and dealt with in a collective manner, whereby the characteristics of ground limestone (GLS), including pore structure and related properties (i.e., porosity, water absorption and sorptivity), compressive strength, carbonation resistance and chloride ingress into Portland limestone cement (PLC) concrete, are discussed. In addition to this, the work includes statistical modelling of the carbonation resistance of PLC concrete.

2.2 Analytical Systemisation Approach

The major advantage of the analytical systemisation approach developed for this research is that it can deal with a very large volume of globally sourced data, as in this case 10,121 test results and a 60,905 data-matrix have been utilised, providing a wide and deep understanding of the various aspects of the research undertaken.

Though there would be an issue of variability in the obtained data, such matters were considered carefully and resolved using several methods depending on the specific batch of data being examined. The first main aim of this study was, in effect, to create what may best be described as a central global laboratory, where the available experimental results from all over the world could be stored and analysed collectively. This would allow a potentially greatly enhanced and in-depth understanding of the subject and the ability to produce a robust set of conclusions, which otherwise generally would not be possible with a limited set of results coming from an individual research study.

2.3 Main Stages of Methodology

A certain strategy was employed to fulfil the objectives of this study, in the main by dividing the study into a number of stages, to maintain a clarity and thoroughness with which the research work could be undertaken. The main stages of this research work were as follows:

- **Stage I:** identifying and sourcing of global test data
- **Stage II:** building the data-matrix
- **Stage III:** analysis, evaluation and structuring of the test results for GLS characteristics, porosity, strength, carbonation and chloride ingress into PLC concrete
- **Stage IV:** statistical modelling of carbonation of PLC concrete
- **Stage V:** publishing of research for peer-review feedback and dissemination of research

2.4 Identification and Sourcing of Global Test Results

The first stage in the study was the sourcing of the globally published results. This was a comprehensive and extensive search to ascertain the nature and extent of related research undertaken and to obtain almost all of the available published material in the

English language. To accomplish this level of catchment, a series of combinations of keywords and search engines as tabulated in Table 2.1 was used.

Table 2.1: Keywords combinations and search engines used

a. KEY WORDS COMBINATIONS USED:
• Concrete; Mortar; Cement Paste.
• Limestone; Calcium Carbonate; $CaCO_3$; Calcareous; Portland Limestone Cement; PLC; CEM II/A-L; CEM II/A-LL; CEM II/B-L; CEM II/B-LL; Blended Cement
• Addition; Additive; Dust; Filler; Fines; Mineral; Powder; Replacement; Substitution; Ground; Supplementary Cementitious Material.
• Porosity; Pore Structure; Pores; Water Absorption; Capillary Suction; Capillarity; Sorptivity; Rate of Absorption; Compressive Strength
• Carbonation; Chloride/s Ingress/Attack/Penetration/Diffusion/Permeability; Durability; Corrosion

b. SEARCH ENGINES AND INTERNET WEBSITES USED:	
• American Concrete Institute	• Rilem
• American Society of Civil Engineers	• Sciencedirect (Elsevier)
• American Society of Testing and Materials	• Scopus
• BASE	• SpringerLink
• British Standards online	• SwetsWise
• Compendex (Engineering Village)	• Taylor & Francis Online
• Find it at bham	• The Construction Information Service
• Google Scholar	• The ICE Virtual Library
• ProQuest	• Web of Science
• ResearchGate	• Wiley Online Library

2.4.1 *Timeline of Sourced Test Data*

The search was not limited to any time span, as the aim was for it to be rigorous and comprehensive in terms of the subject area covered relating to this study. This search produced, as can be seen from Figure 2.1, a total of 504 sources of data published over a period of 32 years, from 1986 to 2017. The sourced literature showed that the real interest in PLC use in concrete-related investigations, more or less, coincided with the introduction of new standards, such as EN 197-1 concerning the new breed of common cements published in the year 2000, with the peak point being reached in 2014.

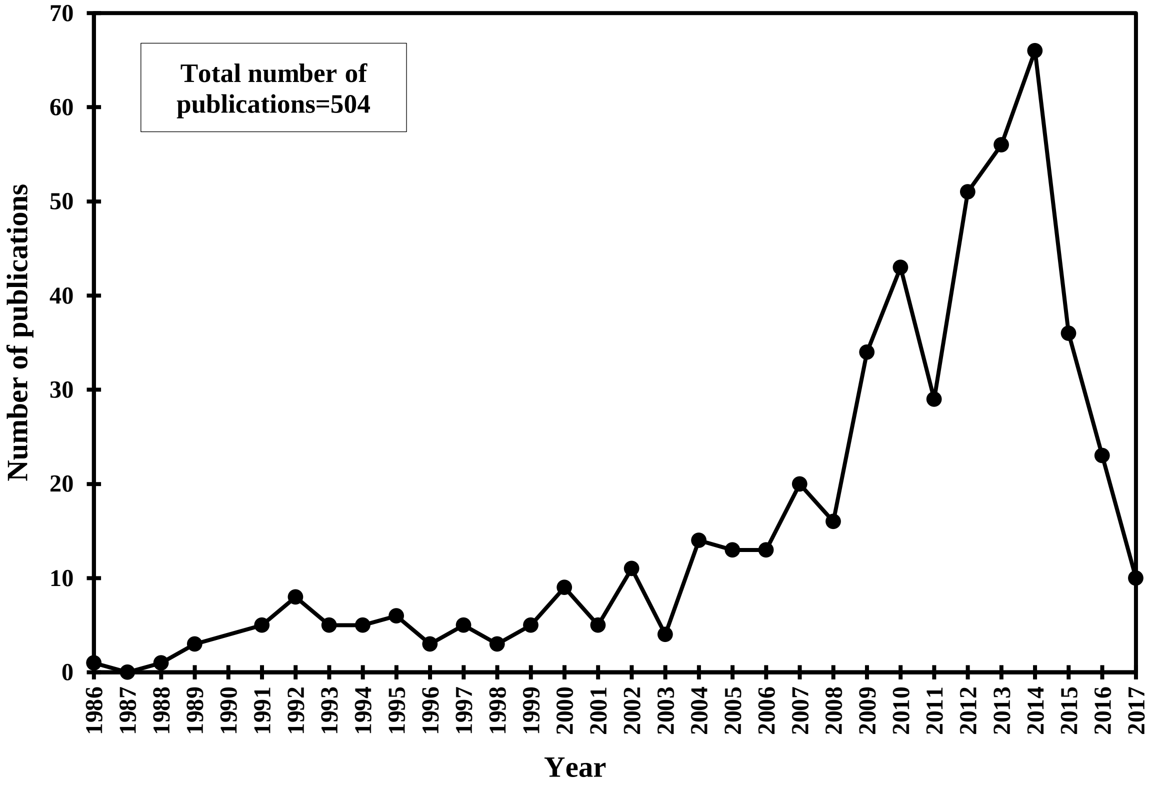


Figure 2.1: Distribution of publications by year

2.4.2 Global Status of Sourced Test Data

The global nature of the data, which is considered another main strength of the study, can be gauged from Figure 2.2. This takes into account all the authors, giving total numbers of 52 source countries and 1380 authors, with the major contributions coming from Europe, North America, Turkey and Argentina. To show the country-wise spread of the obtained test results, all the authors/researchers of the sourced publications have been identified and distributed in terms of their country as seen in Figure 2.2.

The 1380 researchers involved come from 52 countries, with major or significant contributions coming from Greece, France, Italy, the United Kingdom, Spain, Portugal, Switzerland, Germany, Finland and Norway in Europe; the United States and Canada in North America; Argentina and Brazil in South America; Egypt, Iran and Algeria in the Middle East and China and Japan in the Far East.

In addition, the top 10 countries are listed in Table 2.2 with their period of publication, from which it can be seen that the United States and France started a bit early, working in the area of PLC concrete study since 1988 and 1989, respectively, whilst Turkey and Portugal are the most recent countries, starting to undertake research in 2005 and 2007, respectively.

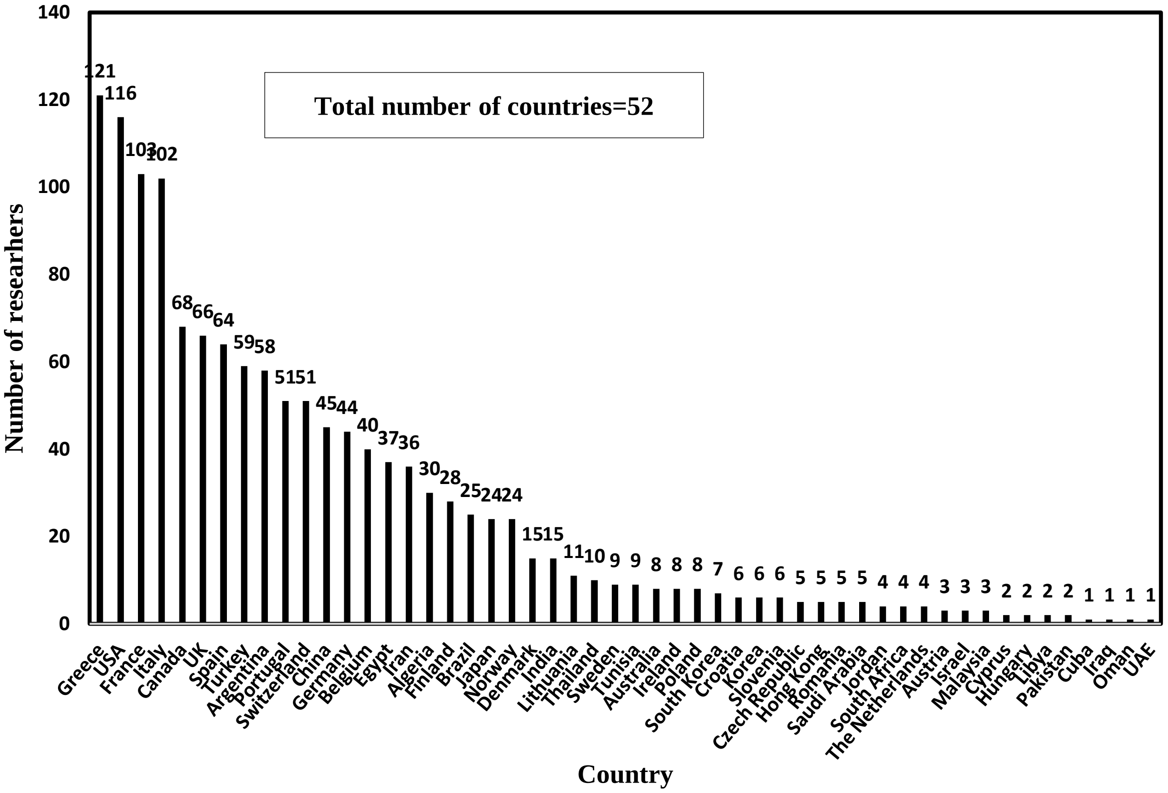


Figure 2.2: Distribution of researchers by country

Table 2.2: Top ten countries for number of researchers

COUNTRY	PERIOD	NUMBER OF RESEARCHERS
Greece	1999-2017	121
USA	1989-2015	116
France	1988-2017	103
Italy	1997-2016	102
Canada	2000-2015	68
UK	1991-2017	66
Spain	2002-2015	64
Turkey	2005-2015	59
Argentina	1998-2013	58
Portugal	2007-2016	51

2.4.3 Sourced Study Types

To gauge the potential quality of the sourced publications, they were sorted into different groups as shown in Figure 2.3, which shows that 77% of the sourced studies were published in peer-reviewed journals. This was seen as an indication of the high quality of the data that were used in the analysis, evaluation and modelling work undertaken in the present study. Of the remainder of the sourced studies, 18% were conference papers and 5% were technical reports.

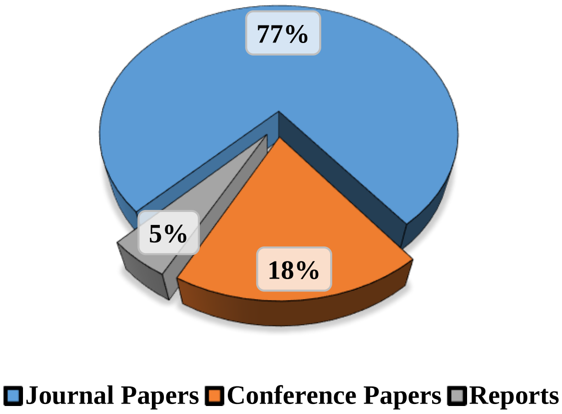


Figure 2.3: Distribution of publications depending on its type

The journals in which the sourced data were published are listed in Table 2.3 in decreasing order of number of publications per journal, up to three, with an additional 16 journals publishing two each and 47 publishing one. The total number of journals providing the base data was 81. The table also shows that half of the studies sourced were published in the top three Elsevier journals.

Table 2.3: Most published journals for the topics pertain of this study

JOURNAL	NUMBER OF PUBLICATIONS	YEARS
Construction and Building Materials	100	1995-2016
Cement and Concrete Research	54	1989-2017
Cement and Concrete Composites	51	1999-2016
Materials and Structures	24	1996-2017
Magazine of Concrete Research	10	1994-2017
ACI MATERIALS JOURNAL	7	2002-2014
Concrete international	7	2009-2014
Ceramics – Silikáty	6	1995-2010
Journal of Materials in Civil Engineering, ASCE	6	2013-2017
Advances in Cement Research	5	2009-2012
Journal of the Transportation Research Board	4	2003-2014
Materials and Corrosion	4	2011-2016
Applied Mechanics and Materials	3	2013-2014
Corrosion Science	3	2002-2010
Journal of Thermal Analysis and Calorimetry	3	2012-2014
Materiales de Construcción	3	2006-2007
Nordic Concrete Research	3	2001-2010
ZKG International	3	1991-1992

2.4.4 Key Researchers and Institutions Involved

To further establish the pedigree of the sourced data, and dealing with the authors and the institutions involved, Tables 2.4 and 2.5 have been developed, and the main points to emerge are:

1) Table 2.4 shows the list of authors with a minimum of five publications in the sourced area of study and additionally there are 26 authors with four publications each, 52 authors with three publications each, 131 authors with two publications each and 608 with one publication each. Table 2.4 shows that L. Bertolini from Italy and S. G. Tsivilis from Greece were the two most consistent researchers working in the subject area covered in the present of PLC concrete study, having the highest number of publications to their names. In addition, E. F. Irassar (Argentina) and G. Escadeillas (France) started their work early in 1997 and 1998, respectively. On the other hand, M. Uysal (Turkey), H. Justnes (Norway), N. Neithalath (USA) and P. Pipilikaki (Greece) had the highest average rate of publications per annum. Additionally, G. Menéndez (Argentina) ceased work in this field in 2007, whilst the most recent key researcher joining in was K. Sotiriadis (Greece), in the past 5 years.

2) The affiliations of all the authors/researchers, from 360 institutions/organisations, are provided in Table 2.5. Whilst the table lists institutions with 10–80 researchers per institution publishing in the area of this research, the numbers of institutions with fewer authors actively publishing are 6, 4, 6, 12, 10, 26, 43, 76 and 148 institutions/organisations with 9, 8, 7, 6, 5, 4, 3, 2 and 1 author, respectively. The dominating countries are Greece, Italy and the United States.

Table 2.4: Key researchers on the relevant topics of this study

AUTHOR	COUNTRY	YEARS	NUMBER OF PUBLICATIONS
Bertolini L.	Italy	2002-2016	18
Tsivilis S. G.	Greece	1999-2017	17
Redaelli E.	Italy	2002-2016	14
Chaniotakis E.	Greece	1999-2016	12
Irassar E. F.	Argentina	1998-2012	12
Lothenbach B.	Switzerland	2007-2016	12
Katsioti M.	Greece	2008-2016	9
Thomas M.D.A.	USA	2007-2014	9
Bonavetti V. L.	Argentina	2000-2012	8
De Schutter G.	Belgium	2007-2016	8
Kakali G.	Greece	1999-2012	8
Lollini F.	Italy	2007-2016	8
Escadeillas G.	France	1997-2017	7
Hooton R.D.	Canada	2007-2014	7
Neithalath N.	USA	2010-2014	7
Pipilikaki P.	Greece	2008-2012	7
Ramezanianpour A. A.	Iran	2009-2016	7
Weiss W. J.	USA	2009-2015	7
Bentz D. P.	USA	2005-2015	6
De Weerdt K.	Norway	2010-2015	6
Gesoglu M.	Turkey	2005-2012	6
Güneyisi E.	Turkey	2005-2012	6
Leemann A.	Switzerland	2007-2016	6
Uysal M.	Turkey	2010-2012	6
Andrade C.	Spain	2002-2014	5
Batis G.	Greece	2000-2017	5
Blair B.	Canada	2009-2014	5
Holt E.E.	Finland	2008-2014	5
Justnes H.	Norway	2010-2012	5
Leivo M.T.	Finland	2008-2014	5
Menéndez G.	Argentina	2001-2007	5
Sotiriadis K.	Greece	2012-2017	5

Table 2.5: Institutions/organisations with a minimum ten publications

Institution/Organisation	Country	Number of researchers
National Technical University of Athens	Greece	80
Department of Chemistry, Materials and Chemical Engineering, "Giulio Natta", Politecnico di Milano	Italy	64
Empa, Swiss Federal Laboratories for Materials Science and Technology	Switzerland	39
National University of the Center of the Province of Buenos Aires	Argentina	39
Laboratory for the Chemistry of Construction Materials (LC2), Department of Civil and Environmental Engineering, University of California, Los Angeles	USA	28
Department of Research and Development, Kamari Plant, TITAN Cement Company S.A.	Greece	22
Amirkabir University of Technology	Iran	19
VTT Technical Research Centre of Finland, Espoo	Finland	19
School of Sustainable Engineering and the Built EnvironmentArizona State University	USA	17
Department of Civil and Structural Engineering, The University of Sheffield	UK	16
National Research Center	Egypt	16
Eduardo Torroja Institute for Construction Science (IETcc-CSIC)	Spain	15
Laboratoire Matriaux et Durabilitdes Constructions, INSA-UPS G&ie Civil	France	15
Lafarge North America	America	15
Magnel Laboratory for Concrete Research, Department of Structural Engineering, Ghent University	Belgium	15
Department of Civil Engineering, Gaziantep University	Turkey	13
University of Toulouse	France	13
Department of Construction Engineering, Public Works and Urban Infrastructure, University of Alicante	Spain	12
LABEST – Laboratory for Concrete Technology and Structural Behaviour, Department of Civil Engineering, Faculty of Engineering, University of Porto	Portugal	12
Civil Engineering Department, Dokuz Eylul University	Turkey	11
Materials and Construction Research Division, National Institute of Standards and Technology	USA	11
SINTEF Building and Infrastructure	Norway	11
Technische Universität Darmstadt	Germany	11
University of Liege, ArGEnCo Department, GeMMe Building Materials	Belgium	11
Civil Engineering Department, Faculty of Engineering, Ege University	Turkey	10
Civil Engineering Department, Purdue University	USA	10
Portland Cement Association	USA	10
Research Institute on Civil Engineering and Mechanics, University of Nantes	France	10
Sakarya University, Civil Engineering Department	Turkey	10

2.4.5 Topic Area Distribution

In general, all the sourced studies were categorised under five main topic areas as shown in Table 2.6. The highest number of publications was on the GLS characteristics discussed in Chapter 3, whilst the next three chapters, 4–6, have similar numbers of publications and Chapter 7 has the lowest number of publications.

Table 2.6: Publications, standards, and references used in chapters 3-7

TYPE OF PUBLICATIONS	CHAPTER 3 GLS Characteristics	CHAPTER 4 Pore Structure and Strength	CHAPTER 5 Carbonation Resistance	CHAPTER 6 Chloride Ingress	CHAPTER 7 Carbonation Modelling
GLS publications	217	155	143	163	121
Standards and specifications	21	11	10	9	2
Other references	19	5	16	6	20
Summation	257	171	169	178	143

Note: Some studies, standards and references were catogrised in more than one topic.

2.5 Building the Data Matrix

The second stage of the analytical systemisation method as used in this study has been further divided into two subdivisions to facilitate the required work to be accomplished, namely, (i) initial appraisal including the sorting of the sourced studies and (ii) the carefully and thoroughly considered data mining and parking of test results.

2.5.1 Initial Appraisal and Sorting of Sourced Test Data

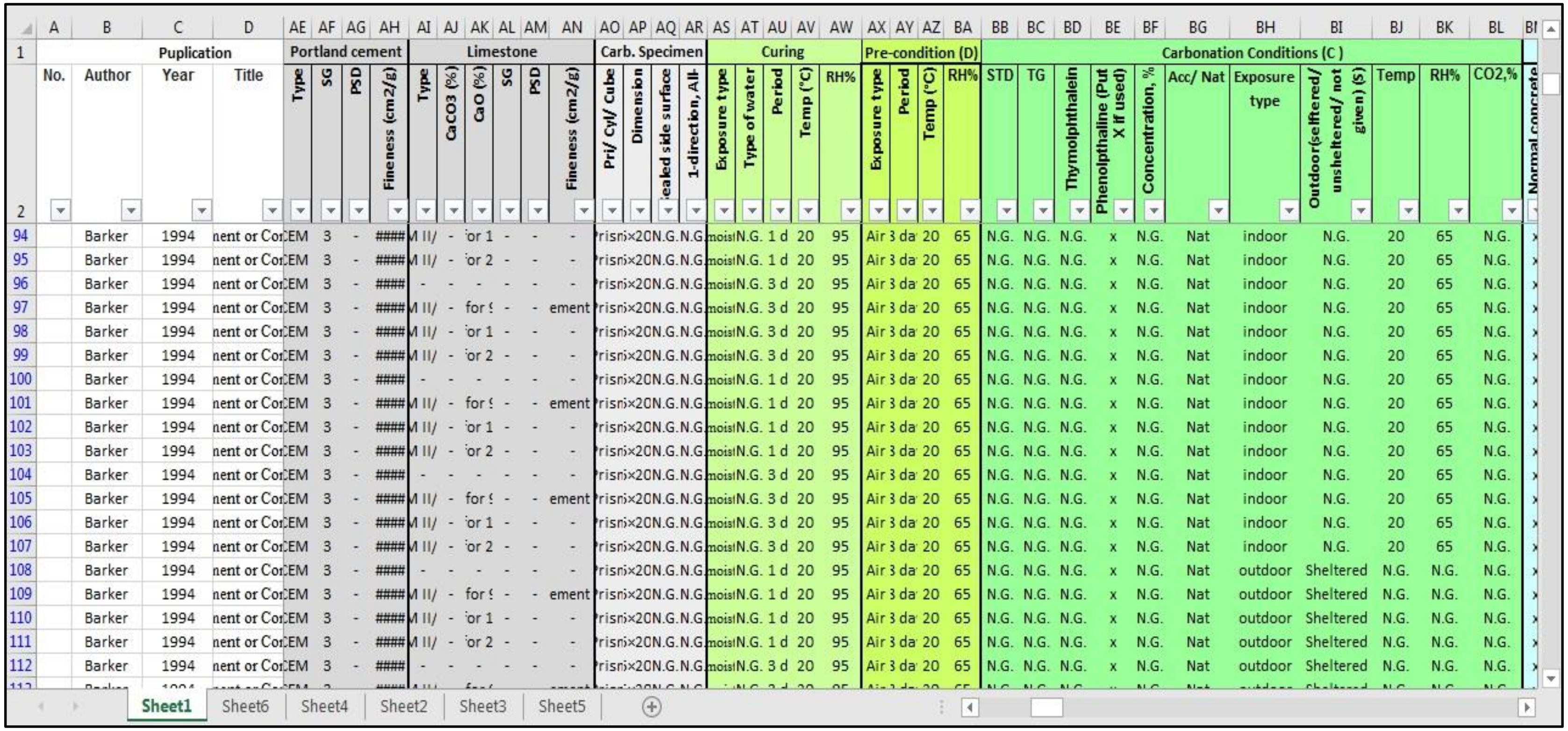
The main aim of this step was to allocate, after careful examination, each sourced study to the relevant topic area, such as porosity or carbonation or chloride ingress. Some studies were allocated to more than one specific topic.

2.5.2 Data Mining and Parking

Once the studies related to each topic were identified, the building of the data matrix (database) could begin, starting with extracting all the required descriptive information and numerical test results (including those pertaining to material characteristics, curing, pre-conditioning, mix design, compressive strength, test methods and procedures) from the text and the figures/tables. The Plot Digitizer software was used where necessary to digitise scanned data plots. A sample of the data matrix in Excel sheet form is shown in Figure 2.4.

This initial foundation work had to be undertaken painstakingly and with utmost care. It is also worth mentioning that the process up to this point was enormously time consuming and required a great deal of attention as the quality of the work that could be produced at the next stage of analytical systemisation depended completely on the way this information was sorted.

By the end of this stage, each of the relevant parts of this study, namely, pore structure and related properties (including compressive strength), carbonation resistance and chloride ingress, consisting of 21,291, 19,091 and 20,523 data-matrix, respectively, was ready for the subsequent stage of analysis and evaluation, which was the most important and difficult part of the study, requiring an enormous amount of intellectual work.



	A	B	C	D	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	AO	AP	AQ	AR	AS	AT	AU	AV	AW	AX	AY	AZ	BA	BB	BC	BD	BE	BF	BG	BH	BI	BJ	BK	BL	BI
1			Puplication		Portland cement				Limestone						Carb. Specimen				Curing					Pre-condition (D)				Carbonation Conditions (C)											
2	No.	Author	Year	Title	Type	SG	PSD	Fineness (cm2/g)	Type	CaCO3 (%)	CaO (%)	SG	PSD	Fineness (cm2/g)	Pri/ Cyl/ Cube	Dimension	ealed side surface	1-direction, All-	Exposure type	Type of water	Period	Temp (°C)	RH%	Exposure type	Period	Temp (°C)	RH%	STD	TG	Thymolphthalein	Phenolpthaline (Put X if used)	Concentration, %	Acc/ Nat	Exposure type	Outdoor(selftered/ unsheltered/ not given) (S)	Temp	RH%	CO2,%	Normal concrete
94		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 1	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
95		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 2	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
96		Barker	1994	nent or Cor	CEM	3	-	####	-	-	-	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	3 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
97		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	for	-	-	ement	Pris	×20	N.G.	N.G.	moist	N.G.	3 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
98		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 1	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	3 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
99		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 2	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	3 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
100		Barker	1994	nent or Cor	CEM	3	-	####	-	-	-	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
101		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	for	-	-	ement	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
102		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 1	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
103		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 2	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
104		Barker	1994	nent or Cor	CEM	3	-	####	-	-	-	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	3 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
105		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	for	-	-	ement	Pris	×20	N.G.	N.G.	moist	N.G.	3 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
106		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 1	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	3 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
107		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 2	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	3 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	indoor	N.G.	20	65	N.G.	x
108		Barker	1994	nent or Cor	CEM	3	-	####	-	-	-	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	outdoor	Sheltered	N.G.	N.G.	N.G.	x
109		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	for	-	-	ement	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	outdoor	Sheltered	N.G.	N.G.	N.G.	x
110		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 1	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	outdoor	Sheltered	N.G.	N.G.	N.G.	x
111		Barker	1994	nent or Cor	CEM	3	-	####	M II/	-	or 2	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	1 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	outdoor	Sheltered	N.G.	N.G.	N.G.	x
112		Barker	1994	nent or Cor	CEM	3	-	####	-	-	-	-	-	-	Pris	×20	N.G.	N.G.	moist	N.G.	3 d	20	95	Air	3 da	20	65	N.G.	N.G.	N.G.	x	N.G.	Nat	outdoor	Sheltered	N.G.	N.G.	N.G.	x

Figure 2.4: Sample of Excel sheet in regard of building the data matrix of the study

2.6 Analysis, Evaluation and Structuring of Test Data

This stage was carried out in four parts. The characteristics of GLS were dealt with first. As the study involved using GLS as a cement component, the chemical and physical properties of GLS were examined and compared with those of Portland cement (PC), and sometimes with other commonly used cementitious materials, such as pulverised fuel ash (PFA) or ground granulated blast furnace slag (GGBS) (BS EN 197-1, 2011).

The next stages of the study involved analysing the pore structure and related properties (including strength), carbonation resistance and chloride ingress of cement paste, mortar and concrete. Each of the aforementioned topics was dealt with by preparing separate data-matrix Excel sheets containing numerical data sourced from the relevant publications.

It was important that the study was undertaken in the sequence as stated above, because the mechanisms of carbonation and chloride ingress in concrete depend primarily on the status of the pore structure and related properties, which assumes greater importance when PLC is involved.

Analytical Tools

During this stage of the work, it was very helpful to use a number of analytical tools as described below to strengthen the evaluation process and make it more efficient:

- Owing to the variability of the parameters involved in the test results obtained (i.e., materials and test methods), it was considered essential to normalise the data of each PLC mix tested relative to the corresponding PC mixture as follows, which allows to improve the data integrity and interpretation of results:

$$\text{Test result w.r.t. PC} = \frac{\text{Test result of PLC} - \text{Test result of PC}}{\text{Test result of PC}} \times 100$$

- The relative data obtained for each topic contained some extreme values, which were generally found to be outliers and were identified by using box-and-whiskers plots. The Tukey box plot is one of the common ways to create the box-and-whiskers plot, which was adopted in this study as shown in Figure 2.5 (Tukey, 1977). The lower end of the whiskers represents the 1.5 interquartile range of the lower quartile (Q1), and the higher end represents the 1.5 interquartile range of the upper quartile (Q3) (Tukey, 1977), where:

Q1 (first/lower quartile) is the median of the *n* smallest entries,
Q3 (third/upper quartile) is the median of the *n* largest entries and
The median (IQR) is the value separating the higher half of a data sample.

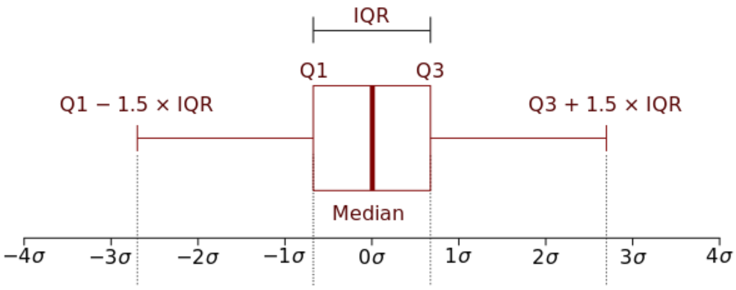


Figure 2.5: Box and whisker plot adopted in this study (Tukey, 1977)

- The mean, standard deviation and coefficient of determination (R^2) were also used in generating and evaluating the fitted curves of the various relationships established.

2.7 Statistical Modelling of Carbonation of PLC concrete

The carbonation resistance of concrete is an important subject related to durability and sustainability. Taking advantage of the large amount of data that were sourced for the analytical systemisation work, a statistical modelling was undertaken to predict the carbonation depth of PLC concrete through multiple linear regression analysis with the use of the SPSS (Statistical Package for the Social Sciences) software.

The depth of carbonation was treated as the dependent variable based on other independent variables such as GLS content, compressive strength and carbon dioxide. The input data used to build the model were based on 2335 carbonation measurements.

In addition, the proposed model was generated using a stepwise method and assessed and verified by using a number of statistical tools: R, R^2, R^2 adjusted, residuals, P values (level of marginal significance), analysis of variance, F value and equality line, in addition to other statistical indicators, which will be detailed further in Chapter 7.

It is worth mentioning that a preference for carbonation exposure effect over chloride ingress effect is given in the work because of the wider threat associated with it compared to chloride exposure, especially with the rapidly growing rates of CO_2 emissions all over the world.

2.8 Important Clarifications

A number of measures have been taken during this study for the ease, reliability and practicality of the work undertaken. These are explained below:

- The process of identifying and sourcing the published global experimental data was undertaken only from work published in the English medium.
- The main source of the data acquisition for the study was limited to works that were in the public domain (i.e., journals, conference proceedings and reports) and theses were not considered.
- Duplicated test results reported in more than one publication were considered only once.
- Mortar and concrete specimens were treated similarly, and their results handled in same manner.
- The use of GLS addition with non-common types of cementitious materials such as alumina cement were not considered in this study
- Wherever the terms water/cement (w/c) ratio or cement content are used in this thesis, ‘cement’ refers to the whole combination (binder) of PC and GLS addition, etc.

2.9 Publishing of Research for Peer-Review Feedback and Dissemination of Research

Because the approach adopted in this study was different to the norm, it was decided at the outset to seek peer review of the work as it progressed. Thus, as each main stage of the study was completed, the work was written up in the form of a technical paper and submitted to a reputable journal for publication. The reviewers' feedback in this respect was very helpful in determining the acceptability of the research and what could be achieved further in this study. The publication of the study on an ongoing basis also facilitated the accomplishment of the second aim of study related to its dissemination. Consequently, a significant part of this study (i.e., the work of Chapters 4, 5 and 6) has been published as research papers as follows:

- Elgalhud A. A., Dhir R. K. and Ghataora G. S. (2016). Limestone addition effects on concrete porosity. Cement and Concrete Composites (Elsevier journal), Volume 72, pp. 222–234.
- Elgalhud A. A., Dhir R. K. and Ghataora G. S. (2017a). Carbonation resistance of concrete: limestone addition effect. Magazine of Concrete Research (ICE journal), Volume 69, Issue 2, pp. 84–106.
- Elgalhud A. A., Dhir R. K. and Ghataora G. S. (2017b). Chloride ingress in concrete: limestone addition effects. Magazine of Concrete Research (ICE journal), http://dx.doi.org/10.1680/jmacr.17.00177.

In addition, the fourth and last paper (which will cover the work of Chapter 3 on the characteristics of GLS and Chapter 7 on modelling) is in preparation as the thesis is submitted. The aim is to complete this paper the soonest possible, and expectantly before the viva is held.

Elgalhud A. A., Dhir R. K. and Ghataora G. S. (2018). Ground limestone characteristics and statistical modelling of carbonation of Portland limestone cement concrete. Construction and Building Materials (in preparation).

CHAPTER 3

GROUND LIMESTONE CHARACTERISTICS

3.1 Introduction

This chapter first provides an overview of the historical developments in the use of ground limestone (GLS) as an addition in cement. This is followed with a description of the procedures utilised in the production of GLS as well as Portland limestone cement (PLC). The physical and chemical characteristics of GLS are analysed, evaluated and discussed in some detail, mainly in accordance with the permissible limits specified in the relevant national/international standards. Additionally, the potential physical and chemical effects resulting from blending GLS with Portland cement (PC) are presented.

3.2 Use of Ground Limestone in Cement

The use of limestone as a building material dates back to ancient times, when calcined limestone or gypsum was used to make mortar mixes (Mayfield, 1990). Limestone has been used since 1824 as a main raw material in the production of Portland cement clinker. Furthermore, over the past few decades it has also been used as a filler aggregate with the main aim of enhancing the rheological properties of concrete such as self-compacting concrete (Cement Concrete and Aggregates Australia, 2011), and as an addition to PC to obtain a blended cement, known as Portland limestone cement, as in BS EN 197-1:2000.

The use of limestone as a part of the blended cements was first attempted at an industrial scale in 1965 in Germany by Heidelberg Cement. The cement produced had a 20%

limestone content and it was used in special applications (Schmidt, 1992a). The use of limestone in cement was later adopted in the French standards in 1979, and in 1983 Canadian Standard CSA A5 allowed limestone to be combined in cement Type 10 at 5% (Hooton et al., 2010). In 1990 the use of limestone in blended cements at 5%–15% was officially permitted in Germany, and in 1992 in the United Kingdom the use of GLS combined with PC at 20% was permitted in the British standards. Ground limestone has been adopted for partial cement replacement in the European specification EN 197-1 since 2000, for two categories of Type II cement, which are CEM II/A-L (6%–20%) and CEM II/B-L (21%–35%).

In 2004 the American Society of Testing and Materials issued a specification, ASTM C 150, which allowed 5% GLS in the main five types of Portland cements (Types I–V). Furthermore, in 2007 the American Association of State and Highway Transportation Officials released its standard AASHTO M85, also permitting the use of 5% GLS as a component of PC. Subsequently, in 2008 Canadian Standard CSA A3001 authorised PLC with up to 15% GLS. Subsequently, in 2010 the Australian standard for cement, AS 3972, allowed for the use of mineral additions, in the form of GLS, ground granulated blast furnace slag (GGBS) and pulverised fuel ash (PFA), up to the level of 7.5% (Benn et al., 2012). Finally, ASTM C595-M 2013 increased the limit on GLS content to 15%. The maximum permissible level for GLS addition currently varies according to national and international standards worldwide, ranging from 10% to 35% as shown in Table 3.1

Table 3.1: GLS contents permitted in PLC in some national and international standards world-wide (Elgalhud et al., 2016).

COUNTRY	GLS CONTENT, %	STANDARD/ REFERENCE
(a) Standards adopt 35% maximum GLS addition level.		
UK and Europe	CEM II/A: 6 to 20 CEM II/B: 21 to 35	BS EN 197-1:2011; EN 197-1:2011
South Africa	CEM II/A: 6 to 20 CEM II/B: 21 to 35	SANS 50197-1:2013 (based on EN 197-1:2011)
Singapore	CEM II/A: 6 to 20 CEM II/B: 21 to 35	SS EN 197-1:2014
Mexico	6 to 35	NMX-C-414-2010
(b) Standards use maximum GLS addition level below 35%.		
USA	>5 to 15	ASTM C 595-M-2015
	>5 to 15	AASHTO M240-2015
Canada	>5 to 15	CSA A3001-2013
Australia	8 to 20	AS 3972-2010
New Zealand	up to 15	NZS 3125:1991 (Amended in 1996)
China	up to 15	Hooton, 2015
Iran	6 to 20	Ramezanianpour et al., 2009
The former USSR	up to 10	Tennis et al., 2011
Argentina	≤ 20	Tennis et al., 2011
Brazil	6 to 10	Tennis et al., 2011
Costa Rica	≤10	Tennis et al., 2011
Peru	≤15	Tennis et al., 2011

3.3 Production of GLS and PLC

Limestone is a natural inorganic mineral substance. It is the most prevalent form of calcium carbonate ($CaCO_3$), which is used largely in the manufacture of PC (Gudissa and Dinku, 2010). $CaCO_3$ is found in nature in three different types, calcite, vaterite and aragonite, of which calcite, in the hexagonal crystal form, is the most common (ACI 211.7R-15). GLS is produced by crushing, grinding and classifying quarried, high-purity, calcite rock in the form of fines with high surface area having an appropriate particle size distribution (Concrete Society, 2011; Kaur et al., 2012).

GLS can either be added separately at the concrete batching plant as an addition, in compliance with BS 7979:2016, or be introduced into PC producing blended cement (Figure 3.1) such as PLC in the form of CEM II/A-L (GLS content, 6%–20%) and CEM II/B-L (GLS content, 21%–35%), in compliance with BS EN 197-1:2011 (Concrete Society, 2011).

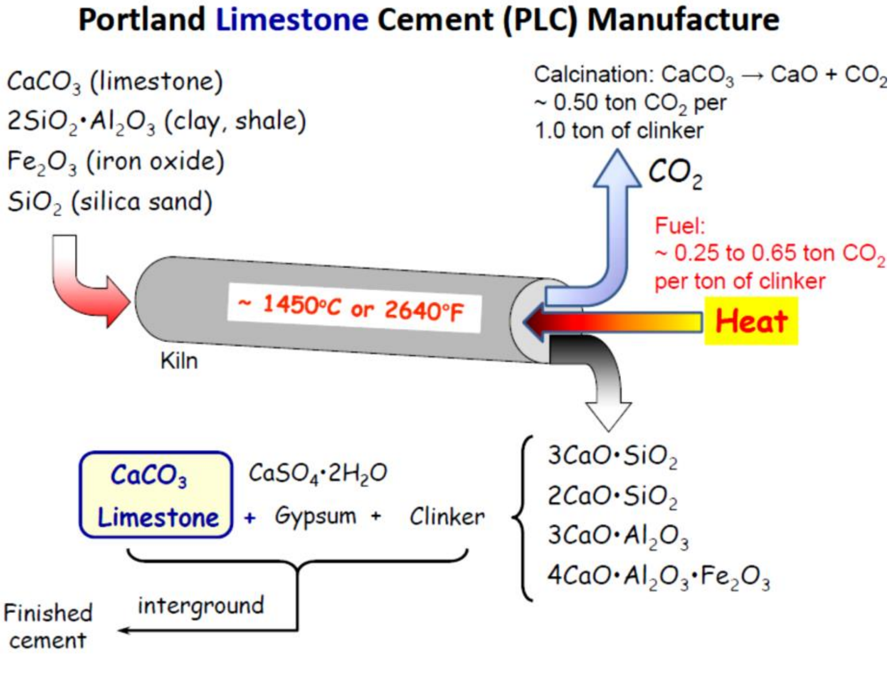


Figure 3.1: Manufacture of PLC (Thomas, 2012)

3.4 Physical Properties

3.4.1 Morphology (Particle Shape, Surface Texture and Colour)

The morphological properties of particles of binder/cement and aggregates in concrete, in the form of shape, angularity and texture, have a notable effect on the rheology of fresh concrete and the bonding between the particles themselves (Neville, 1994).

The results in relation to the particle shape and surface texture of GLS are quite limited. However, Kaewmanee and Tangtermsirikul (2014) reported GLS particles to be irregular, which results in lowering slightly the consistency of PLC concrete mixes in comparison to the corresponding to PC concrete.

The colour of GLS varies from white to buff (a yellowish beige) (Lee et al., 2008; Ryou et al., 2014 and Diab et al., 2016). This variation in colour is attributed to the wide geological spread of limestone. Consequently, PLC concrete tends to be generally slightly lighter in colour than PC concrete (Concrete Society, 2011).

3.4.2 Particle Size Distribution

It is vital to know the particle size distribution (PSD) of the cement and aggregates used in concrete as this can have an important influence on the water demand, stability and volume of voids of a concrete (Dhir, 1996).

Figure 3.2 shows the PSD results of 59 tested GLS specimens, showing a wide range of particle size and distribution at most particle size levels, from fine to coarse. The percentage passing through a 45-μm sieve (the size fraction used for categorising PFA) varies mainly from 75% to 100%, whereas the limits stated in BS EN 450-1:2012 for both fine and coarse PFA are between 60% and 100%. The percentage passing through a 63-µm sieve varies mostly from 78% to 100%, whereas the limits set by BS EN 12620:2002+A1:2008 for filler aggregate are within 70%–100%. The results suggest that the GLS used as a cement component is usually finer than the lower limits for PFA and filler aggregate.

On the other hand, for comparison purposes, Figure 3.3 was generated showing the outcome of the PSD of a total of 71 PC and PLC samples tested for their grading. It shows that both PC and PLC can generally be taken to be of similar grading, though limestone, being the softer component of the two materials and easier to grind, can be expected to comprise more of the fine fraction particles in a PLC blend. Consequently, better particle packing, improved workability and reduced bleeding can be expected in concrete made with PLC. However, the extent of this effect would be the proportion of limestone blended with Portland cement clinker.

3.4.3 Surface Area (Fineness)

Depending on the chemical analysis of a material, the fineness can be considered an indication of its potential reactivity. Fineness can be measured using different test methods, such as Blaine and BET (with Portland cement as per BS EN 197-1), sieve residue (with fly ash as per BS EN 450) or laser diffraction particle size distribution (as in R&D work).

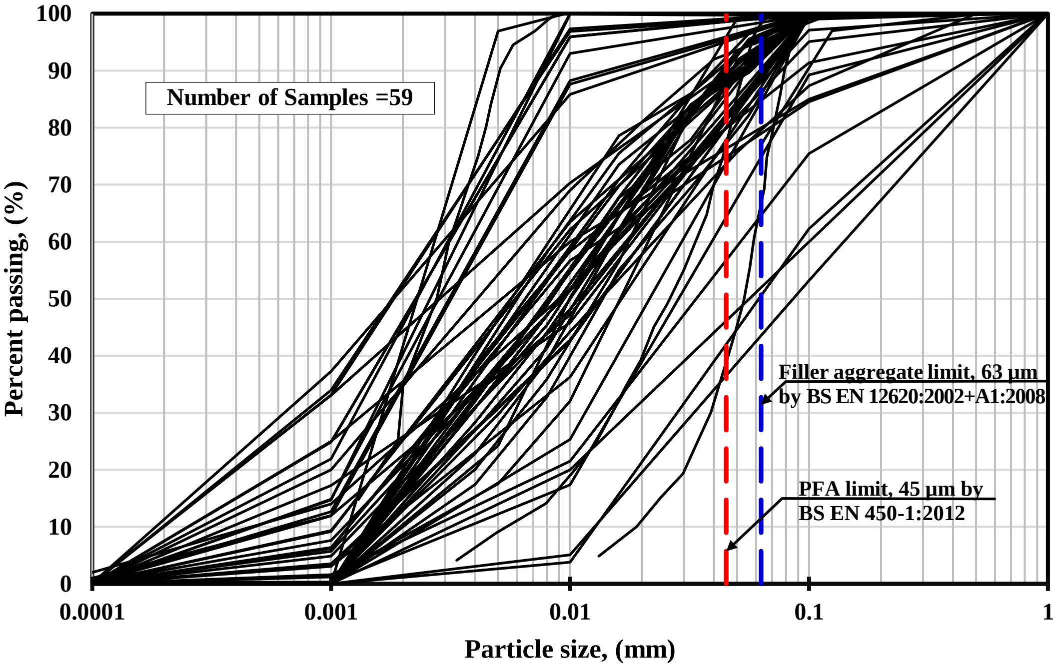


Figure 3.2: Particle size distribution of GLS

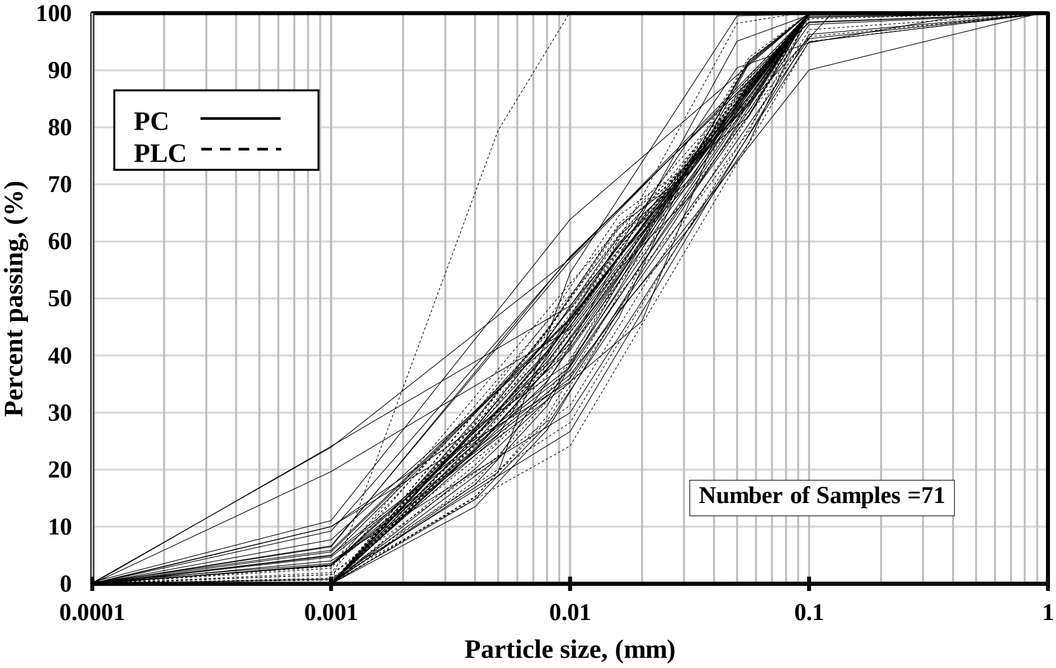


Figure 3.3: Particle size distribution of PC and PLC

Data of Figure 3.2 and Figure 3.3 taken from: Aguayo et al., 2014; Bentz, 2005; Bonneau et al., 2007; Cam and Neithalath, 2010; Celik et al., 2015; Celik et al., 2014a; Courard et al., 2011; Courard et al., 2005; Courard et al., 2014; Das et al., 2014a; Das et al., 2014b; De Weerdt et al., 2011a; Gesoğlu et al., 2012; Ghiasvand et al., 2015; Kaewmanee and Tangtermsirikul, 2014; Knop et al., 2014; Krstulovid et al., 1994; Kumar et al., 2013; Li and Kwan, 2015; Liu et al., 2014; Lollini et al., 2014; Lollini et al., 2016; Luz and Pandolfelli, 2012; Marzouki et al., 2013; Meddah et al., 2014; Michel and Courard, 2014; Pavoine et al., 2014; Phung et al., 2015; Selih et al., 2003; Silva and Brito, 2015; Sun et al., 2013; Thomas et al., 2010d; Tsivilis et al., 2002b; Uysal and Sumer, 2011; Uysal and Tanyildizi, 2012; Uysal, 2012; Wu et al., 2016.

The fineness measurements of GLS, PC and PLC samples are presented in Figure 3.4, in which GLS used as an addition has a broader range of fineness (110–1050 m^2/kg) than PC (250–550 m^2/kg) and PLC (280–670 m^2/kg). The mean values indicate that GLS (507 m^2/kg) has the highest fineness and the PC (367 m^2/kg) has the lowest, whilst the mean value of PLC fineness (443 m^2/kg) is in between.

In addition, Figure 3.5 shows the effect of GLS inclusion on the fineness of PLC. As is to be expected, the trend line obtained indicates that the fineness of the PLC increases as the GLS content increases, mainly owing to the GLS being softer than clinker (the hardness of GLS and Portland clinker on the Mohs scale is 3–4 and 5–6, respectively; Hewlett, 1998). Furthermore, when they are ground together to a certain fineness, GLS will represent mainly the smaller fraction and the resulting PLC will be finer than the corresponding PC. Thus, a better performance from PLC concrete can be expected in the fresh state, and to an extent nearly similar to PC concrete in strength.

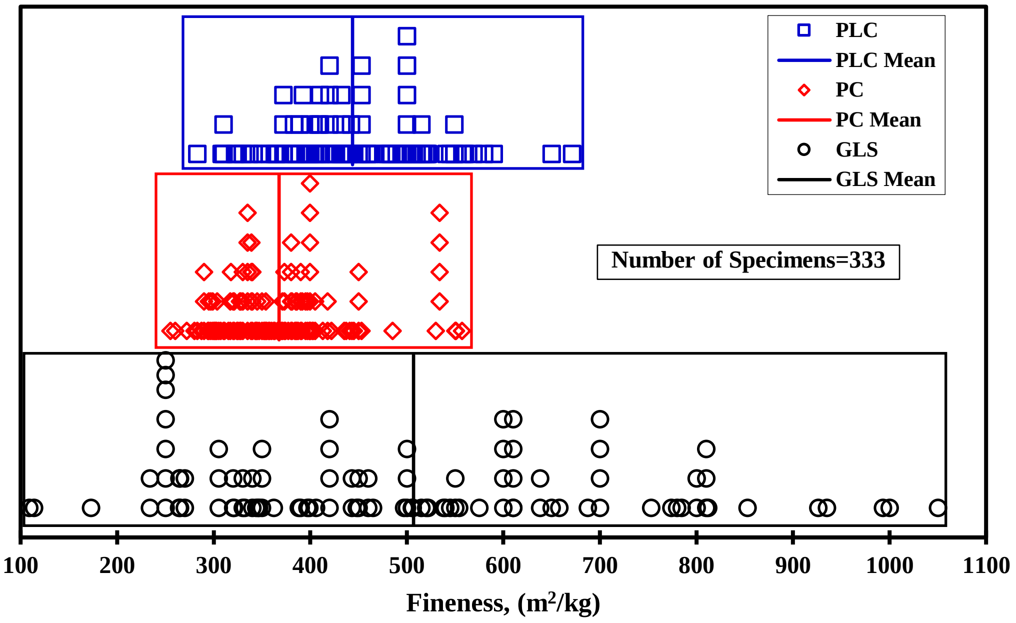


Figure 3.4: Fineness results of GLS, PLC and PC

Data of Figure 3.4 taken from: Allahverdi et al., 2010; Barrett et al., 2014; Bentz et al., 2015; Bertolini et al., 2011; Bonneau et al., 2007; Boubekeur et al., 2014; Boubitsas, 2001; Boubitsas, 2004; Carrasco et al., 2005; Catinaud et al., 2000; Cochet and Jesus, 1991; Collepardi et al., 2004; Corinaldesi et al., 2004; Courard et al., 2005; Courard et al., 2014; Darweesh, 2004; De Weerdt et al., 2011a; De Weerdt et al., 2011b; De Weerdt et al., 2011c; De Weerdt et al., 2012; Deja et al., 1991; Dhir et al., 2004; Dhir et al., 2007; Diab et al., 2016; Ezziane et al., 2010; Felekogˇlu et al., 2009; Figueiras et al., 2009; Frazão et al., 2015; Gesoğlu et al., 2012; Ghiasvand et al., 2015; Guemmadi et al., 2008a; Guemmadi et al., 2008b; Helal, 2002; Hoshino et al., 2006; Hussain et al., 2013; Ipavec et al., 2013; Juel and Herfort, 2002; Kaewmanee and Tangtermsirikul, 2014; Lang, 2005; Lawrence et al., 2005; Lee et al., 2008; Li and Kwan, 2015; Liu et al., 2014; Lollini et al., 2014; Lollini et al., 2016; Lollini et al., 2015; Matthews, 1994; Meddah et al., 2014; Moir and Kelham, 1993; Moir and Kelham, 1997; Müller et al., 2014; Mun et al., 2007; Mwaiuwinga et al., 1997; Owsiak and Grzmil, 2015; Palm et al., 2016; Pavoine et al., 2014; Phung et al., 2015; Pomeroy, 1993; Proske et al., 2014; Proske et al., 2013; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Ramezanianpour et al., 2014; Rozière et al., 2011; Ryou et al., 2014; Saca and Georgescu, 2014; Sakai and Watanabe, 1993; Sakai and Watanabe, 1994; Sezer, 2012; Siad et al., 2013; Sonebi and Nanukuttan, 2009; Sonebi et al., 2009; Tezuka et al., 1992; Tosun-Felekogˇlu, 2012; Turkel et al., 2009; Uysal and Sumer, 2011; Uysal and Tanyildizi, 2012; Uysal and Tanyildizi, 2011; Uysal and Yilmaz, 2011; Uysal et al., 2012; Uysal, 2012; Vyšvařil et al., 2015; Wu et al., 2016; Xiao et al., 2009.

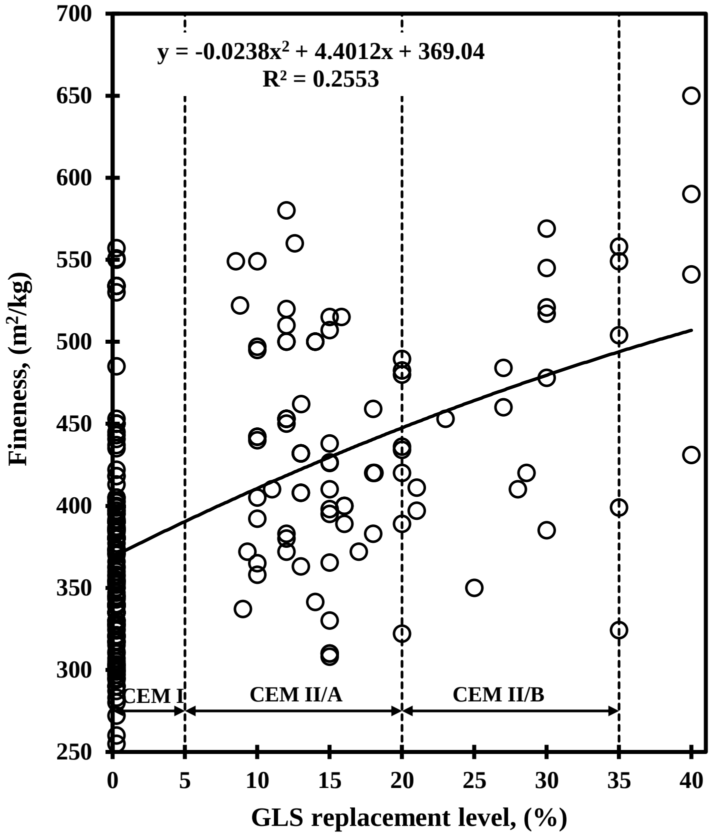


Figure 3.5: Effect of GLS addition on fineness of PLC

Data of Figure 3.5 taken from: Allahverdi et al., 2010; Barrett et al., 2014; Bentz et al., 2015; Bertolini et al., 2011; Bonneau et al., 2007; Boubekeur et al., 2014; Boubitsas, 2001; Boubitsas, 2004; Carrasco et al., 2005; Catinaud et al., 2000; Cochet and Jesus, 1991; Collepardi et al., 2004; Corinaldesi et al., 2004; Courard et al., 2005; Courard et al., 2014; Darweesh, 2004; De Weerdt et al., 2011a; De Weerdt et al., 2011b; De Weerdt et al., 2011c; De Weerdt et al., 2012; Deja et al., 1991; Dhir et al., 2004; Dhir et al., 2007; Diab et al., 2016; Ezziane et al., 2010; Felekogˇlu et al., 2009; Figueiras et al., 2009; Frazão et al., 2015; Gesoğlu et al., 2012; Ghiasvand et al., 2015; Guemmadi et al., 2008a; Guemmadi et al., 2008b; Helal, 2002; Hoshino et al., 2006; Hussain et al., 2013; Ipavec et al., 2013; Juel and Herfort, 2002; Kaewmanee and Tangtermsirikul, 2014; Lang, 2005; Lawrence et al., 2005; Lee et al., 2008; Li and Kwan, 2015; Liu et al., 2014; Lollini et al., 2014; Lollini et al., 2016; Lollini et al., 2015; Matthews, 1994; Meddah et al., 2014; Moir and Kelham, 1993; Moir and Kelham, 1997; Müller et al., 2014; Mun et al., 2007; Mwaiuwinga et al., 1997; Owsiak and Grzmil, 2015; Palm et al., 2016; Pavoine et al., 2014; Phung et al., 2015; Pomeroy, 1993; Proske et al., 2014; Proske et al., 2013; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Ramezanianpour et al., 2014; Rozière et al., 2011; Ryou et al., 2014; Saca and Georgescu, 2014; Sakai and Watanabe, 1993; Sakai and Watanabe, 1994; Sezer, 2012; Siad et al., 2013; Sonebi and Nanukuttan, 2009; Sonebi et al., 2009; Tezuka et al., 1992; Tosun-Felekogˇlu, 2012; Turkel et al., 2009; Uysal and Sumer, 2011; Uysal and Tanyildizi, 2012; Uysal and Tanyildizi, 2011; Uysal and Yilmaz, 2011; Uysal et al., 2012; Uysal, 2012; Vyšvařil et al., 2015; Wu et al., 2016; Xiao et al., 2009.

3.4.4 Relative Density (Specific Gravity)

Specific gravity (SG) is defined as the ratio of the mass of a material to the mass of an equal volume of water (Jackson and Dhir, 1996). The significance of this property for GLS is with respect to its effect on the mass of the final product, i.e., blended cement, and consequently the concrete produced.

The SG measurements obtained from GLS have been analysed and are presented in Figure 3.6. The whole range of the SG results for GLS is from 2.48 up to 2.83, but the effectual majority are within 2.65–2.79. The most frequent result is 2.70 and the mean value is 2.71, clearly establishing that GLS is lighter than PC or CEM I, for which the SG is normally around 3.15. In addition, Figure 3.7 illustrates the effect of GLS inclusion on the SG of PLC through the SG outcomes for PC and PLC. The fitted curve shows that an increase in GLS content would decrease the SG of PLC until it reaches 2.98 with 35% GLS content, at which PLC is lighter than CEM I by approximately 5%.

3.5 Main Chemical Constituents and Properties

To characterise a material, its chemical composition needs to be carefully considered, because the chemical properties have a significant effect on the resultant performance in terms of durability and sustainability. This section assesses the major chemical constituents of GLS.

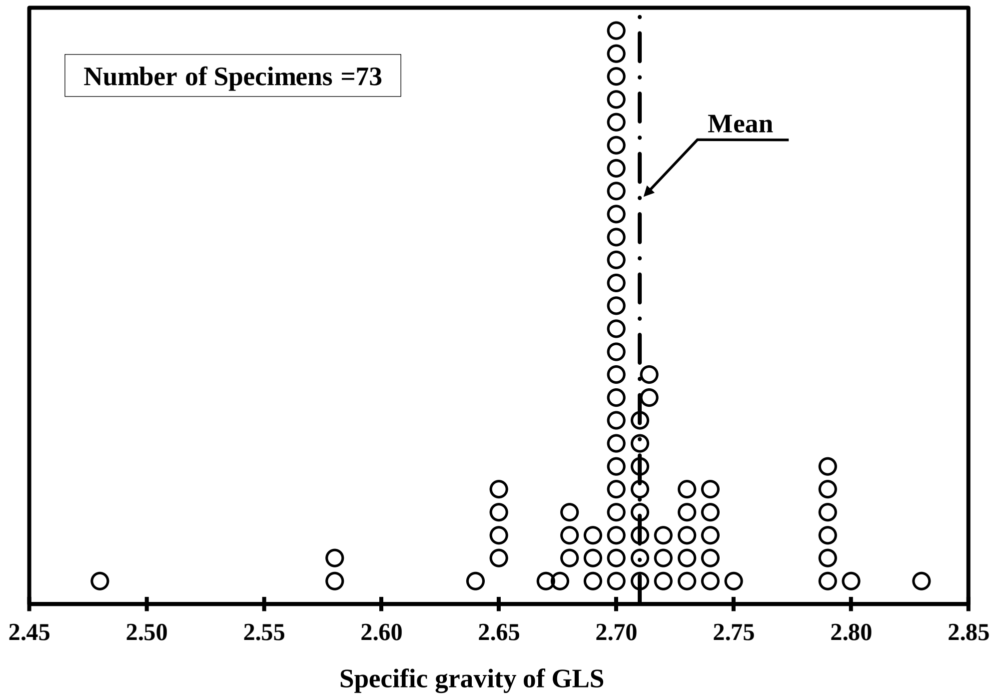


Figure 3.6: Specific gravity results of GLS

Data of Figure 3.6 taken from: Allahverdi et al., 2010; Assie et al., 2006; Assie et al., 2007; Balayssac et al., 1995; Barrett et al., 2014; Bentz et al., 2015; Bonneau et al., 2007; Bouasker et al., 2014; Burgos-Montes et al., 2013; Carrasco et al., 2005; Chiker et al., 2016; Corinaldesi et al., 2004; Cost et al., 2013a; Courard et al., 2014; Courard et al., 2005; De Weerdt et al., 2011a; De Weerdt et al., 2011b; De Weerdt et al., 2011c; De Weerdt et al., 2012; Deja et al., 1991; Dhir et al., 2004; Dhir et al., 2007; Diab et al., 2015; Diab et al., 2016; Felekogˇlu et al., 2009; Figueiras et al., 2009; Gesoğlu et al., 2012; Ghiasvand et al., 2015; Gu¨neyisi and Gesogˇlu, 2011; Guemmadi et al., 2008a; Guemmadi et al., 2008b; Güneyisi et al., 2011; Hussain et al., 2013; Ipavec et al., 2013; Irassar et al., 2006; Kadri et al., 2010; Kaewmanee and Tangtermsirikul, 2014; Kumar et al., 2013; Kwan et al., 2013; Lawrence et al., 2005; Lee et al., 2008; Leemann et al., 2010; Lemieux et al., 2012; Loser and Leemann, 2007; Loser et al., 2010; Marques et al., 2013; Mavropoulou et al., 2016; Meddah et al., 2014; Meira et al., 2014; Mounanga et al., 2011; Müller et al., 2006; Mun et al., 2007; Mwaiuwinga et al., 1997; Nagrockiene et al., 2013a; Nagrockiene et al., 2013b; Palm et al., 2016; Panesar and Francis, 2014; Phung et al., 2015; Rabehi et al., 2013; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Ramezanianpour et al., 2014; Ryou et al., 2014; Sakai and Watanabe, 1993; Sakai and Watanabe, 1994; Saraya, 2014; Schmidt et al., 1993; Segura et al., 2013; Siad et al., 2013; Silva and Brito, 2015; Skaropoulou et al., 2012; Sonebi and Nanukuttan, 2009; Sonebi et al., 2009; Thongsanitgarn et al., 2014; Tosun-Felekogˇlu, 2012; Turkel et al., 2009; Uysal and Sumer, 2011; Uysal and Tanyildizi, 2012; Uysal and Tanyildizi, 2011; Uysal and Yilmaz, 2011; Uysal et al., 2012; Uysal, 2012; Vandanjon et al., 2003; Vyšvařil et al., 2015; Xiao et al., 2009; Yamada et al., 2006; Younsi et al., 2015.

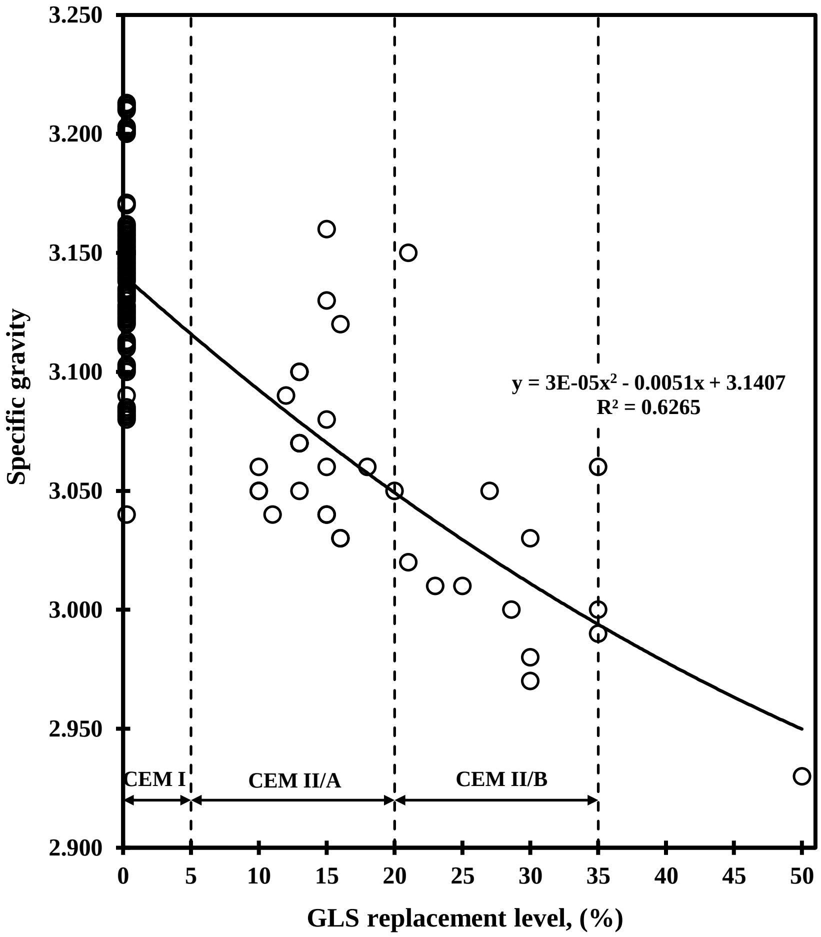


Figure 3.7: Effect of GLS addition on SG of PLC

Data of Figure 3.7 taken from: Allahverdi et al., 2010; Assie et al., 2006; Assie et al., 2007; Balayssac et al., 1995; Barrett et al., 2014; Bentz et al., 2015; Bonneau et al., 2007; Bouasker et al., 2014; Burgos-Montes et al., 2013; Carrasco et al., 2005; Chiker et al., 2016; Corinaldesi et al., 2004; Cost et al., 2013a; Courard et al., 2014; Courard et al., 2005; De Weerdt et al., 2011a; De Weerdt et al., 2011b; De Weerdt et al., 2011c; De Weerdt et al., 2012; Deja et al., 1991; Dhir et al., 2004; Dhir et al., 2007; Diab et al., 2015; Diab et al., 2016; Felekogˇlu et al., 2009; Figueiras et al., 2009; Gesoğlu et al., 2012; Ghiasvand et al., 2015; Gu¨neyisi and Gesogˇlu, 2011; Guemmadi et al., 2008a; Guemmadi et al., 2008b; Güneyisi et al., 2011; Hussain et al., 2013; Ipavec et al., 2013; Irassar et al., 2006; Kadri et al., 2010; Kaewmanee and Tangtermsirikul, 2014; Kumar et al., 2013; Kwan et al., 2013; Lawrence et al., 2005; Lee et al., 2008; Leemann et al., 2010; Lemieux et al., 2012; Loser and Leemann, 2007; Loser et al., 2010; Marques et al., 2013; Mavropoulou et al., 2016; Meddah et al., 2014; Meira et al., 2014; Mounanga et al., 2011; Müller et al., 2006; Mun et al., 2007; Mwaiuwinga et al., 1997; Nagrockiene et al., 2013a; Nagrockiene et al., 2013b; Palm et al., 2016; Panesar and Francis, 2014; Phung et al., 2015; Rabehi et al., 2013; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Ramezanianpour et al., 2014; Ryou et al., 2014; Sakai and Watanabe, 1993; Sakai and Watanabe, 1994; Saraya, 2014; Schmidt et al., 1993; Segura et al., 2013; Siad et al., 2013; Silva and Brito, 2015; Skaropoulou et al., 2012; Sonebi and Nanukuttan, 2009; Sonebi et al., 2009; Thongsanitgarn et al., 2014; Tosun-Felekogˇlu, 2012; Turkel et al., 2009; Uysal and Sumer, 2011; Uysal and Tanyildizi, 2012; Uysal and Tanyildizi, 2011; Uysal and Yilmaz, 2011; Uysal et al., 2012; Uysal, 2012; Vandanjon et al., 2003; Vyšvařil et al., 2015; Xiao et al., 2009; Yamada et al., 2006; Younsi et al., 2015.

3.5.1 Calcium Carbonate Content

Calcium carbonate ($CaCO_3$) represents a major proportion of the chemical composition of GLS addition. For the use of GLS with PC, the minimum allowed content of $CaCO_3$ is 75% by mass, both when ground with the PC clinker (BS EN 197-1:2011) and when blended separately at the batching plant (BS 7979:2016). The corresponding limit for PLC in the American standards, ASTM C595M-16 and AASHTO M 240M-16, is slightly less, at 70%.

The content of $CaCO_3$ is determined using the calcium oxide (CaO) content in GLS (BS EN 197-1:2011), and it is calculated by multiplying the CaO percentage (which is obtained according to BS EN 196-2:2013 or ASTM C114-15/AASHTO T105-16) by a conversion factor of 1.785 (ASTM C595M-16 and AASHTO M 240M-16).

Figure 3.8 shows the results for the $CaCO_3$ content of 120 GLS samples in two groups: (i) those for which the data were provided in terms of $CaCO_3$ (shown in black) and (ii) those for which the data were provided in terms of CaO, and these were used to calculate the corresponding $CaCO_3$ contents (shown in red). The $CaCO_3$ content of the samples tested ranged from 65% to 100%, over the time span of 25 years between 1991 and 2016. In general, the vast majority of the results were above 75%, with a substantial number of them falling within the range of 91%–100%.

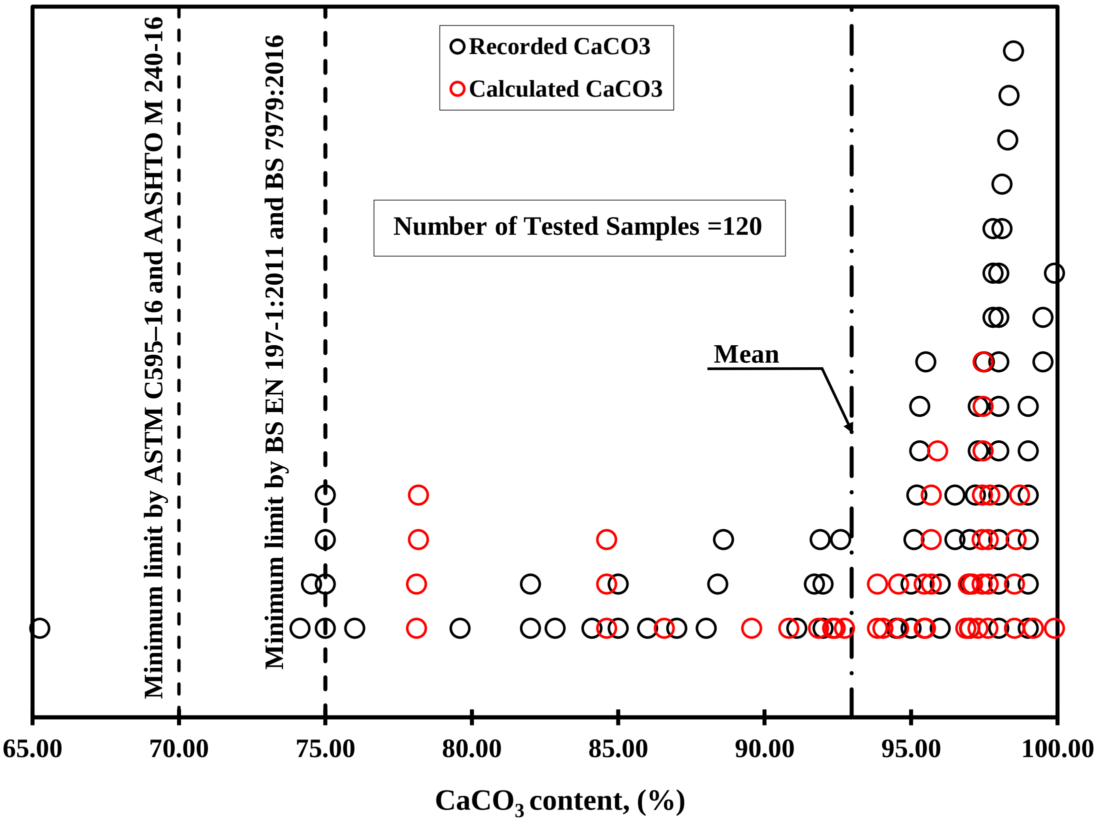


Figure 3.8: CaCO$_3$ content in GLS addition

Data of Figure 3.8 taken from: Abdalkader et al., 2015; Abualgasem et al., 2014; Ali et al., 2013; Allahverdi et al., 2010; Barauskas et al., 2012; Barrett et al., 2014; Bentz et al., 2015; Bertolini et al., 2011; Bonneau et al., 2007; Boubekeur et al., 2014; Boubitsas, 2001; Boubitsas, 2004; Cam and Neithalath, 2010; Cam H. T. et al., 2012; Carrasco et al., 2005; Catinaud et al., 2000; Celik et al., 2014a; Celik et al., 2014b; Celik et al., 2015; Corinaldesi et al., 2004; Courard et al., 2005; Courard et al., 2011; Courard et al., 2014; Darweesh, 2004; Das et al., 2014a; Deja et al., 1991; Dhir et al., 2007; Diab et al., 2015; Diab et al., 2016; El-Alfi et al., 2000; El-Alfi et al., 2004; Felekogˇlu et al., 2009; Ghiasvand et al., 2015; Ghrici et al., 2007; Guemmadi et al., 2008b; Helal, 2002; Hussain et al., 2013; Ipavec et al., 2013; Kadri et al., 2010; Lee et al., 2008; Leemann et al., 2015; Li and Kwan, 2015; Liu et al., 2014; Lollini et al., 2014; Lollini et al., 2015; Lollini et al., 2016; Marzouki et al., 2013; Matthews, 1994; Meddah et al., 2014; Michel and Courard, 2014; Moir and Kelham, 1993; Moir and Kelham, 1997; Mounanga et al., 2011; Müller et al., 2014; Mun et al., 2007; Palm et al., 2016; Pavoine et al., 2014; Phung et al., 2015; Pomeroy, 1993; Proske et al., 2013; Proske et al., 2014; Rahhal et al., 2012; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Ramezanianpour et al., 2014; Revay and Gavel, 2003; Rozière et al., 2011; Ryou et al., 2014; Saca and Georgescu, 2014; Saraya, 2014; Selih et al., 2003; Sezer et al., 2010; Sezer, 2012; Shi et al., 2015; Silva and Brito, 2015; Skaropoulou et al., 2009a; Skaropoulou et al., 2009b; Skaropoulou et al., 2012; Sonebi and Nanukuttan, 2009; Sonebi et al., 2009; Sotiriadis et al., 2012; Sotiriadis et al., 2013; Sun et al., 2013; Tezuka et al., 1992; Thongsanitgarn et al., 2014; Torres et al., 2003; Tosun-Felekogˇlu, 2012; Tsivilis et al., 1999; Tsivilis et al., 2002b; Tsivilis et al., 2003; Voglis et al., 2005; Vyšvařil et al., 2015; Wu et al., 2016; Xiao et al., 2009; Zacharopoulou et al., 2013; Zhang et al., 2016.

Only one result was at 65% (Moir and Kelham, 1993) and was below the two limits set by BS EN 197-1:2011, BS 7979:2016, ASTM C595–16 and AASHTO M 240-16. It should be noted that in the 1990s GLS was still considered a new supplementary cementitious material and therefore most probably under probation. The mean value of all the results was 93%, and the most frequently quoted $CaCO_3$ content was 98%. The data presented in Figure 3.8 show that limestone, which is generally available in most parts of the world, is likely to contain a very high proportion of calcite, with figures well above the minimum limit set in most standards.

3.5.2 Methylene Blue Index (Clay Content)

Based on its chemical composition, and not its size fraction (e.g., smaller than 2 μm) (ACI 211.7R-15), the presence of some deleterious constituents in GLS, such as clay, can have a undesirable effect on some of the properties of the fresh or hardened concrete.

The methylene blue adsorption (clay content) test is conducted on limestone samples ground to a fineness of 500 m^2/kg as required by BS EN197-1:2011 and BS 7979:2016 and tested in accordance with BS EN 933-9 or ASTM C595M-16; the maximum permissible limit set in both cases is at 1.20 g methylene blue per 100 g of GLS.

The clay content of GLS affects its ability to absorb water, which increases with clay content (Hawkins et al., 2003). This high water demand of clay minerals can affect the performance of concrete under a freeze and thaw environment, with absorbed water increasing in volume upon freezing and causing physical damage to the concrete. Thus, it is worth mentioning here that the methylene blue test determines the absorptive capacity of clay in GLS rather than the clay content itself (Hawkins et al., 2003), and that different clays can have different absorption capacities (Tennis et al., 2011).

The results obtained for the methylene blue index (MBI) of 31 GLS samples are plotted in Figure 3.9, with MBI values ranging from 0 to 2.7 g/100 g, and most of them below 1.20 g/100 g. Only one result at 2.70 g/100 g, reported in the study undertaken by Moir and Kelham (1993), exceeded the permissible limit. The average value of 0.35 g/100 g for the MBI signifies that the investigated GLS materials contained clay with low absorptive capacity.

The results of $CaCO_3$ and MBI for limestone samples tested are plotted in Figure 3.10, with permissible limits for both shown. The fitted curve obtained, though having a low determination coefficient of $R^2 = 0.5$, can still serve as a good indicator that an increase in $CaCO_3$ content leads to lower MBI values.

3.5.3 Total Organic Carbon

Another type of deleterious material that can be present in GLS is organic carbon, which occurs naturally within the sediments or soils that can contaminate the limestone layer over time as a result of its geological development (Diab et al., 2016). The determination of total organic carbon (TOC) in limestone can be undertaken in accordance with one of the international standards BS EN 13639, ASTM C595M and CSA A3004-D2.

The importance of measuring the TOC in GLS arises from the potential role of TOC (similar to unburnt carbon in PFA) in disturbing the required dose of air-entraining admixtures to obtain a certain air content in concrete. Thus, the frost resistance of concrete may be affected when PLC is used (ASTM C595M-16 and ACI 211.7R-15). In addition, organic carbon affects the setting time of concrete and also affects its strength development (Tennis et al., 2011).

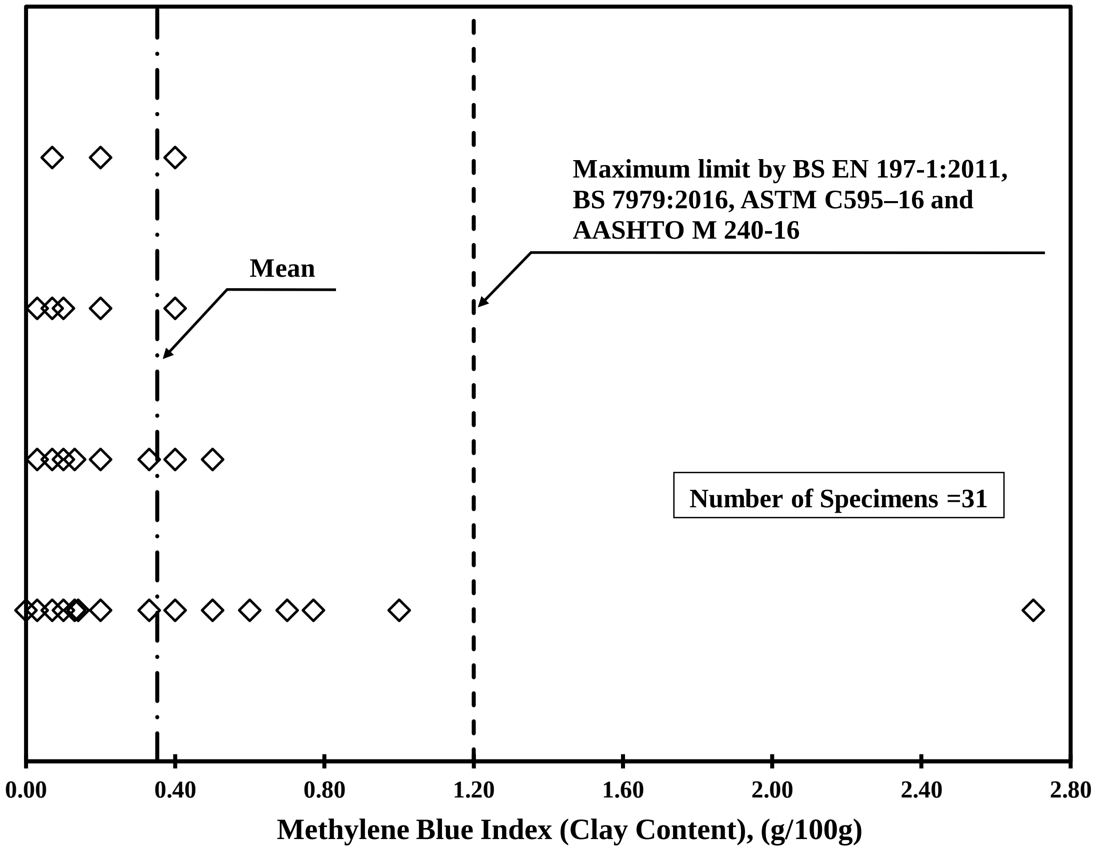


Figure 3.9: Methylene blue index of GLS addition

Data of Figure 3.9 taken from: Ghiasvand et al., 2015; Lang, 2005; Michel and Courard, 2014; Courard et al., 2011; Moir and Kelham, 1993; Matthews, 1994; Moir and Kelham, 1997; Pomeroy, 1993; Müller et al., 2014; Palm et al., 2016; Rahhal et al., 2012; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Tsivilis et al., 1999; Tsivilis et al., 2003

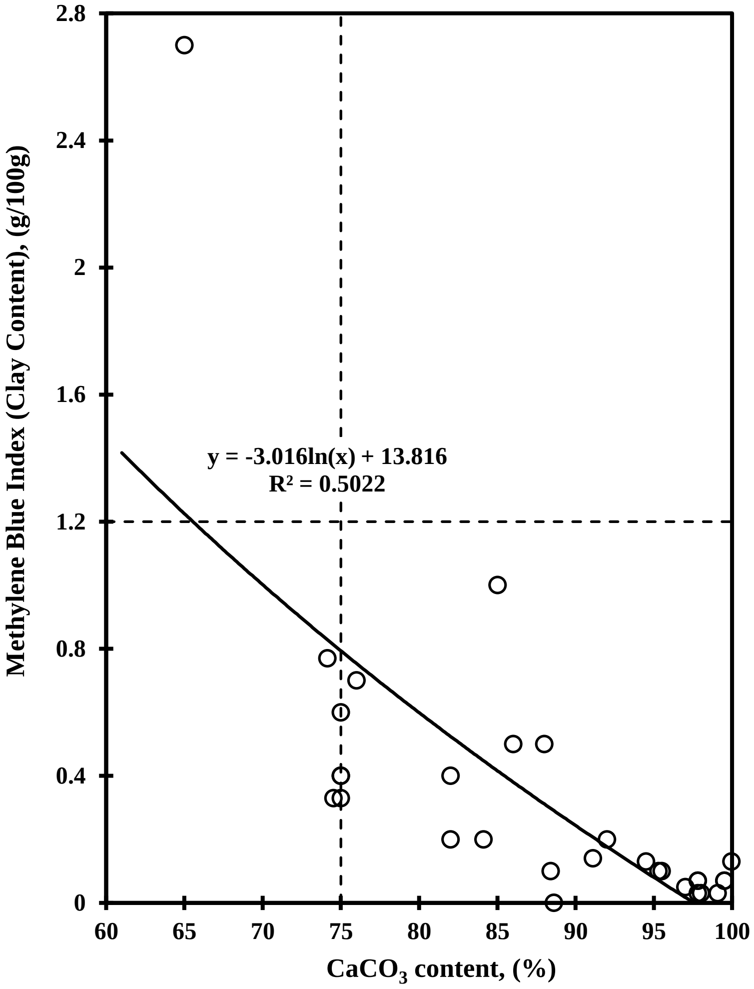


Figure 3.10: Relationship between MBI and $CaCO_3$ of GLS addition

Data of Figure 3.10 taken from: Ghiasvand et al., 2015; Lang, 2005; Michel and Courard, 2014; Courard et al., 2011; Dhir et al, 2007; Moir and Kelham, 1993; Matthews, 1994; Moir and Kelham, 1997; Pomeroy, 1993; Müller et al., 2014; Palm et al., 2016; Rahhal et al., 2012; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Tsivilis et al., 1999; Tsivilis et al., 2003

According to BS EN 197-1:2011, the notations CEM II/A-LL and CEM II/B-LL refer to a maximum content of 0.20% TOC by mass, whereas CEM II/A-L and CEM II/B-L refer to a maximum content of 0.50% TOC. The other standards, BS 7979:2016, ASTM C595M-16 and AASHTO M 240M-16, specify only one maximum limit for TOC content in GLS, which is 0.50%.

The results of TOC measurements (32 specimens of GLS) are shown in Figure 3.11. The TOC values vary from 0% to 0.94%. The large majority of the TOC results are less than 0.50%, with a significant number below 0.15% and a mean of 0.17%. The only high value is 0.94%, outside the permissible limit, from Diab et al. (2016). Based on these results, it could be stated that GLS has a low total carbon content.

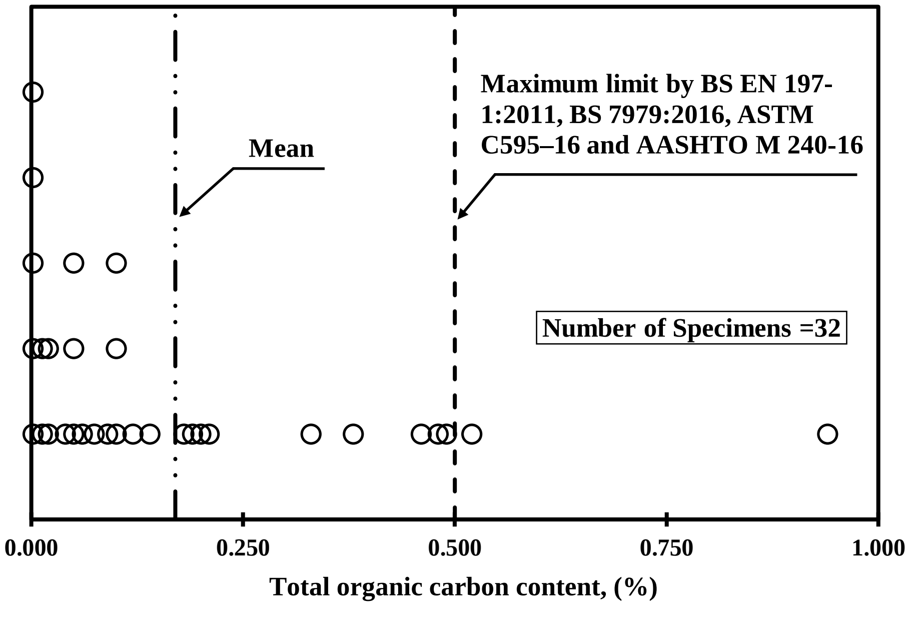


Figure 3.11: Total organic carbon content in GLS addition

Data of Figure 3.11 taken from: Dhir et al., 2007; Diab et al., 2016; Ghiasvand et al., 2015; Lang, 2005; Michel and Courard, 2014; Courard et al., 2011; Moir and Kelham, 1993; Matthews, 1994; Moir and Kelham, 1997; Pomeroy, 1993; Müller et al., 2014; Palm et al., 2016; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Tsivilis et al., 1999; Tsivilis et al., 2003.

In addition, Figure 3.12 illustrates the relationship between the $CaCO_3$ content and the TOC (also their restricting limits as broken lines). Whilst the obtained trend line shows a poor determination coefficient, it is still a good qualitative indicator that a higher content of $CaCO_3$ in GLS usually results in a lower TOC.

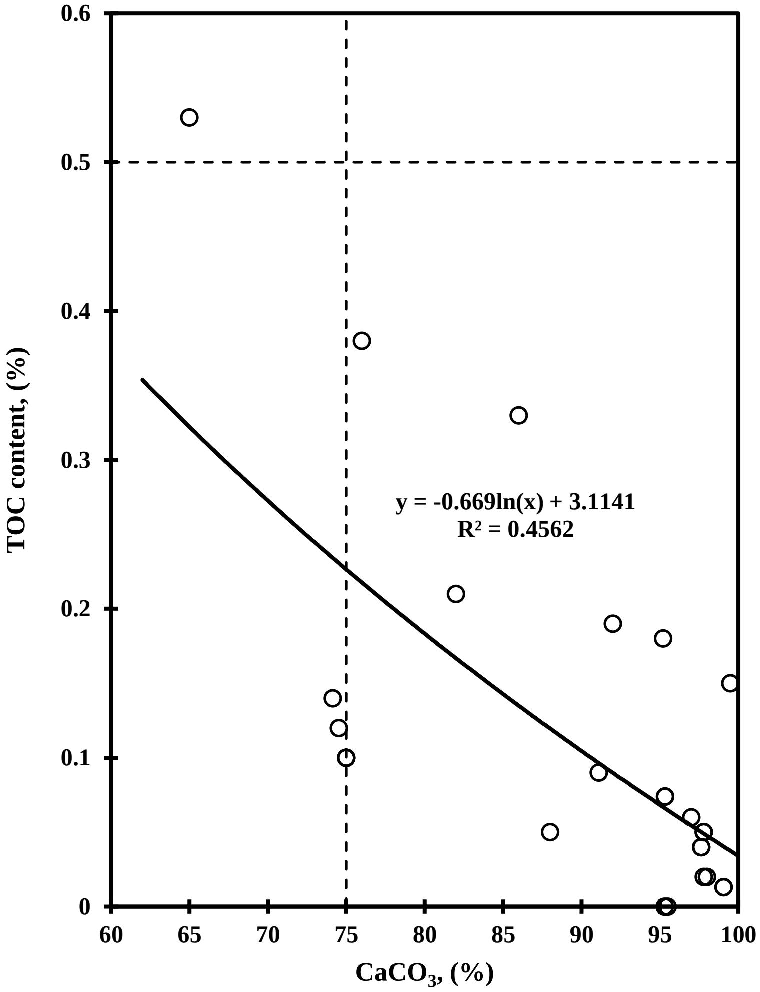


Figure 3.12: Relationship between TOC and $CaCO_3$ in GLS addition

Data of Figure 3.12 taken from: Dhir et al., 2007; Diab et al., 2016; Ghiasvand et al., 2015; Lang, 2005; Michel and Courard, 2014; Courard et al., 2011; Moir and Kelham, 1993; Matthews, 1994; Moir and Kelham, 1997; Pomeroy, 1993; Müller et al., 2014; Palm et al., 2016; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Tsivilis et al., 1999; Tsivilis et al., 2003

3.5.4 Chloride Content

Chlorides are considered to be amongst the major causes of reinforcement corrosion in concrete, in the presence of adequate oxygen and moisture. BS 7979:2016 has set a maximum limit for the chloride content in GLS at 0.1% by mass, whilst BS EN 197-1:2011 has the same limit for the combined PC and GLS content (i.e., the PLC). However, ASTM C595M-16 and AASHTO M 240M-16 do not specify any upper limit for chloride content either for GLS as an addition or for PLC.

The data for the chloride content of GLS and PLC are quite limited, suggesting that it has been found to be of little concern. Indeed, the majority of the results obtained show the chloride content to be very small and within standard limits (Table 3.2). The only considerably high result, by Guemmadi et al. (2008a), could be attributed to the fact that the chloride content was given as an expression of sodium chloride (NaCl), not chloride ions (Cl^-).

Table 3.2: Chloride content results of GLS and PLC

REFERENCE	CHLORIDE CONTENT, %	MEAN, %	UPPER LIMIT	STANDARD
(a) Test results for GLS addition separately from PC				
Guemmadi et al., 2008a	NaCl = 0.560	0.001^a	0.100%	BS 7979:2016
Sonebi and Nanukuttan, 2009	Cl^- = 0.001			
Sonebi et al., 2009	Cl^- = 0.001			
(b) Test results for PLC (with GLS content ranges between 23-28%)				
Chiker et al., 2016	Cl^- = 0.096	0.048	0.100%	BS EN 197-1:2011
Yamada et al., 2006	Cl^- = 0.007			
Younsi et al., 2015	Cl^- = 0.040			

a: The mean value has been calculated considering only chloride ions results.

3.5.5 Total Sulfur (Sulfate Content)

Significant amounts of sulfate, derived from any of the constituents in concrete, can lead to disruption due to the expansion of hardened concrete, which is recognised as a sulfate attack. BS 7979:2016 states that the highest allowable content for total sulfur (determined according to BS EN 1744-1:2009+A1:2012 and expressed as sulfate, SO_4) is 1.0% of GLS addition by mass. However, BS EN 197-1:2011, ASTM C595M-16 and AASHTO M 240M-16 do not designate any upper limits for SO_4 in GLS.

All of the values for SO_4 have been determined from SO_3 results, by multiplying the SO_3 value by a conversion factor of 1.2 (BS EN 1744-1:2009+A1:2012). The calculated SO_4 contents in GLS addition have been examined, as shown in Figure 3.13. The large majority of the SO_4 values are less than 1.0%, with a mean value of 0.25%, and most of the results are within the range of 0% to 0.2%, suggesting that the inspected GLS has a very low sulfur content.

3.5.6 Loss on Ignition

Loss on ignition (LOI) is an expression of the loss in mass (in percentage) due to heating of an inorganic material, such as in this case PC or GLS, at a high temperature of about 1000°C, until all the volatiles have escaped and there is no longer any change in mass (Neville, 1994).

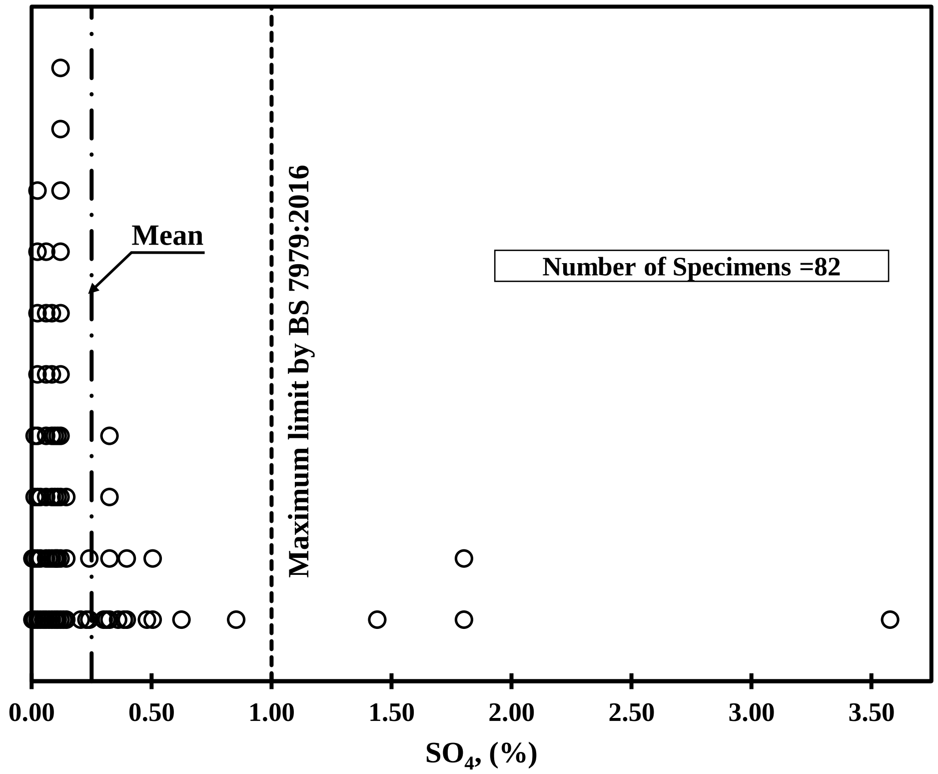


Figure 3.13: Total sulfur in GLS addition

Data of Figure 3.13 taken from: Abualgasem et al., 2014; Abdalkader et al., 2015; Allahverdi et al., 2010; Ali et al., 2013; Barauskas et al., 2012; Boubekeur et al., 2014; Cam and Neithalath, 2010; Cam et al., 2012; Carrasco et al., 2005; Celik et al., 2015; Celik et al., 2014a; Celik et al., 2014b; Corinaldesi et al., 2004; Courard et al., 2005; Courard et al., 2014; Darweesh, 2004; Deja et al., 1991; Diab et al., 2015; Diab et al., 2016; El-Alfi et al., 2004; El-Alfi et al., 2000; Felekog˘lu et al., 2009; Ghiasvand et al., 2015; Ghrici et al., 2007; Guemmadi et al., 2008a; Guemmadi et al., 2008b; Helal, 2002; Hussain et al., 2013; Ipavec et al., 2013; Lang, 2005; Liu et al., 2014; Lollini et al., 2014; Lollini et al., 2016; Lollini et al., 2015; Bertolini et al., 2011; Marzouki et al., 2013; Meddah et al., 2014; Moir and Kelham, 1993; Matthews, 1994; Moir and Kelham, 1997; Pomeroy, 1993; Mun et al., 2007; Palm et al., 2016; Pavoine et al., 2014; Phung et al., 2015; Rahhal et al., 2012; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Ramezanianpour et al., 2014; Revay and Gavel, 2003; Saraya, 2014; Selih et al., 2003; Sezer, 2012; Sezer et al., 2010; Shi et al., 2015; Siad et al., 2013; Skaropoulou et al., 2009a; Skaropoulou et al., 2009b; Skaropoulou et al., 2012; Sonebi and Nanukuttan, 2009; Sonebi et al., 2009; Sotiriadis et al., 2013; Sotiriadis et al., 2012; Thongsanitgarn et al., 2014; Torres et al., 2003; Tosun-Felekog˘lu, 2012; Voglis et al., 2005; Vyšvařil et al., 2015; Zacharopoulou et al., 2013; Zhang and Ye, 2012; Zhang et al., 2016

The European and American standards do not specify any limitation for the LOI value with regard to GLS used as an addition with PC. On the other hand, BS EN 197-1:2011 states the maximum limit of 5% LOI for CEM I and not for CEM II as PLC. Moreover, ASTM C150-2016 and CSA A3001-2013 set an LOI limit of 3% for PC, whilst ASTM C595-16 and CSA A3001-2013 set an LOI limit of 10% for PLC with GLS content >5–15%.

Figure 3.14 shows LOI measurements of 93 samples of GLS used as an addition with PC. The results range from 33.9% to 44.6%, with a mean value of 41.9% and with the majority of results falling within 41.5%–44.5%. This shows that around half of the GLS mass is lost at ignition temperatures of around 1000°C, which is a very high value compared to PC and the other SCMs, such as PFA, GGBS and MS, with typical LOI values of <5%, 3%–20%, <3%, and <4%, respectively (Concrete Society, 2011).

In addition, the LOI measurements for PLC and PC have also been examined and plotted in Figure 3.15, which shows that the LOI value of PLC increases with GLS content, with an LOI of 14% for PLC having 35% GLS content.

3.5.7 Potential Hydrogen

The potential hydrogen (pH) is a number that represents relative alkalinity or acidity on a logarithmic scale, where 7.0 is neutral, above 7.0 is alkaline and below 7.0 is acid. The steel bars in reinforced concrete get the protection from the high-alkalinity environment (pH about 13), which is produced mainly by the PC and makes the steel protected by creating a passive and non-corroding protective oxide layer. This layer is secured in an alkaline environment, nonetheless it can be damaged if the pH level drops below 10, which results in neutralising the concrete cover and potentially initiating the corrosion of the steel reinforcement (BRE Digest 444, 2000).

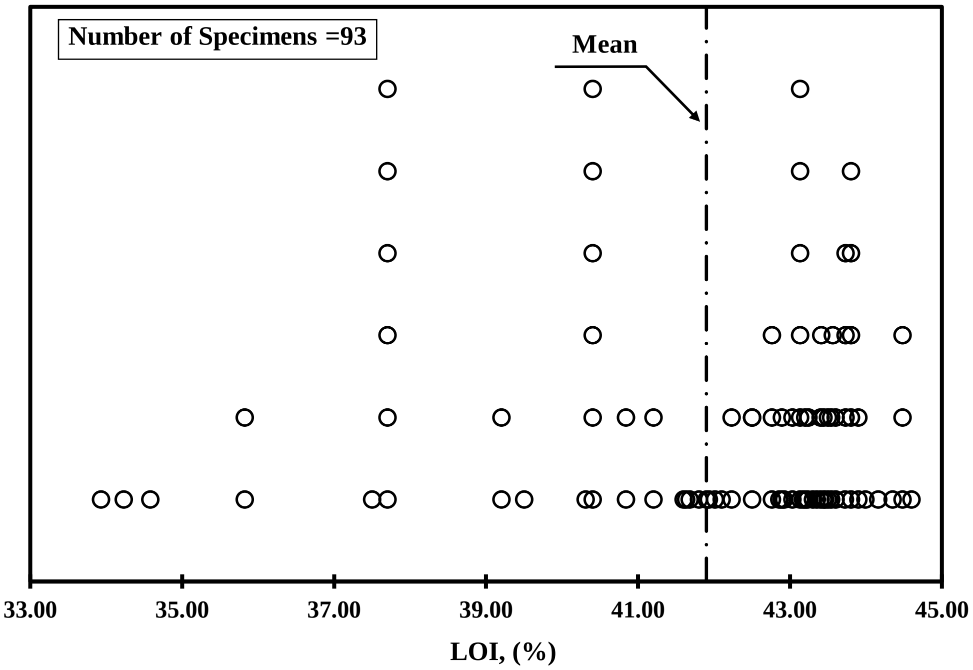


Figure 3.14: LOI in GLS addition

Data of Figure 3.14 taken from: Abualgasem et al., 2014; Abdalkader et al., 2015; Allahverdi et al., 2010; Ali et al., 2013; Barauskas et al., 2012; Boubekeur et al., 2014; Burgos-Montes et al., 2013; Cam and Neithalath, 2010; Cam et al., 2012; Carrasco et al., 2005; Celik et al., 2015; Celik et al., 2014a; Celik et al., 2014b; Collepardi et al., 2004; Corinaldesi et al., 2004; Deja et al., 1991; De Weerdt et al., 2011a; De Weerdt et al., 2011b; De Weerdt et al., 2011c; De Weerdt et al., 2012; Dhir et al., 2004; Dhir et al., 2007; Diab et al., 2015; Diab et al., 2016; El-Alfi et al., 2004; El-Alfi et al., 2000; Ezziane et al., 2010; Felekogˇlu et al., 2009; Gesoğlu et al., 2012; Ghiasvand et al., 2015; Ghrici et al., 2007; Hussain et al., 2013; Kaewmanee and Tangtermsirikul, 2014; Lee et al., 2008; Liu et al., 2014; Lollini et al., 2014; Lollini et al., 2016; Marzouki et al., 2013; Meddah et al., 2014; Moukwa, 1989; Mun et al., 2007; Palm et al., 2016; Pavoine et al., 2014; Rahhal et al., 2012; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Ramezanianpour et al., 2014; Revay and Gavel, 2003; Ryou et al., 2014; Sakai and Watanabe, 1993; Sakai and Watanabe, 1994; Saraya, 2014; Selih et al., 2003; Shi et al., 2015; Skaropoulou et al., 2009a; Skaropoulou et al., 2009b; Skaropoulou et al., 2012; Sotiriadis et al., 2013; Sotiriadis et al., 2012; Thongsanitgarn et al., 2014; Torres et al., 2003; Tosun et al., 2009; Tosun-Felekogˇlu, 2012; Tsivilis et al., 2000; Tsivilis and Asprogerakas, 2010; Tsivilis et al., 2002a; Tsivilis et al., 2002b; Tsivilis et al., 1999; Tsivilis et al., 2003; Turkel et al., 2009; Uysal et al., 2012; Uysal and Yilmaz, 2011; Uysal and Tanyildizi, 2012; Uysal and Sumer, 2011; Uysal and Tanyildizi, 2011; Uysal, 2012; Voglis et al., 2005; Vyšvařil et al., 2015; Wu et al., 2016; Zacharopoulou et al., 2013; Silva and Brito, 2015.

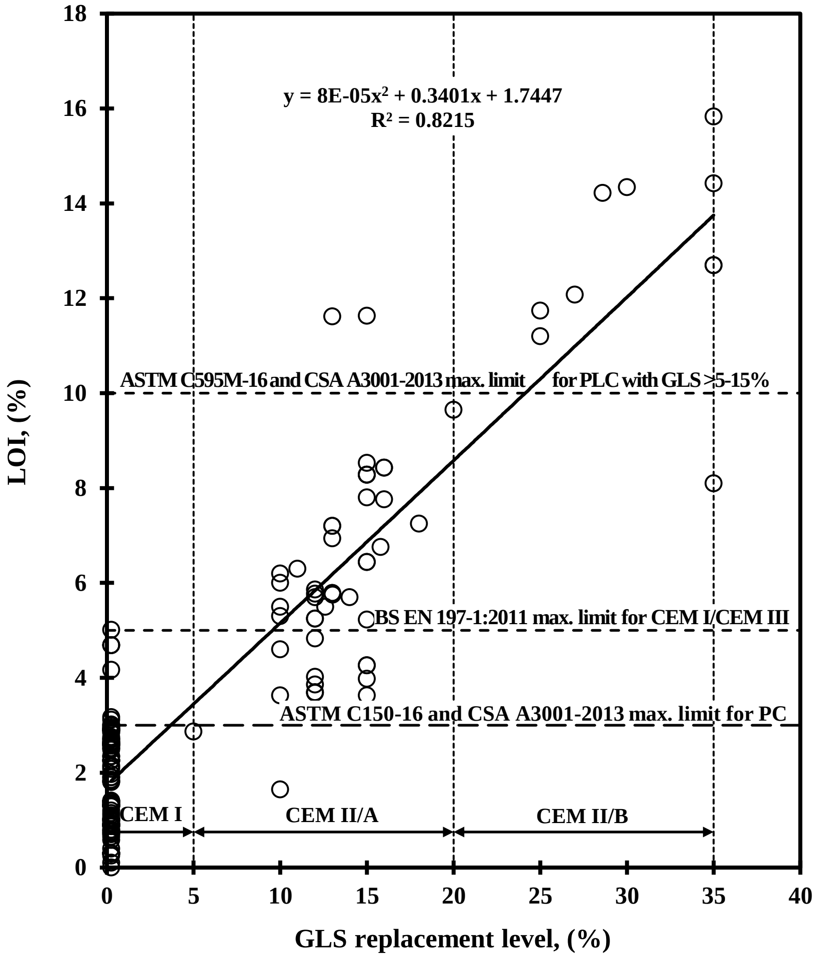


Figure 3.15: Effect of GLS addition on LOI of PLC

Data of Figure 3.15 taken from: Abdalkader et al., 2015; Abualgasem et al., 2014; Ali et al., 2013; Allahverdi et al., 2010; Amin et al., 2010a; Amin et al., 2010b; Arandigoyen and Álvarez, 2006; Assie et al., 2006; Assie et al., 2007; Batic et al., 2013; Bentz et al., 2015; Boubekeur et al., 2014; Burgos-Montes et al., 2013; Cam and Neithalath, 2010; Cam et al., 2012; Carrasco et al., 2005; Catinaud et al., 2000; Celik et al., 2015; Celik et al., 2014a; Celik et al., 2014b; Collepardi et al., 2004; Corinaldesi et al., 2004; Cost et al., 2013a; Cost et al., 2013b; Das et al., 2014a; De Weerdt et al., 2011a; De Weerdt et al., 2011b; De Weerdt et al., 2011c; De Weerdt et al., 2012; Deja et al., 1991; Dhir et al., 2004; Dhir et al., 2007; Diab et al., 2015; Diab et al., 2016; El-Alfi et al., 2004; Ezziane et al., 2010; Felekog˘lu et al., 2009; Gesoğlu et al., 2012; Ghiasvand et al., 2015; Gu¨neyisi and Gesog˘lu, 2011; Guemmadi et al., 2008a; Guemmadi et al., 2008b; Güneyisi et al., 2011; Hooton et al., 2010; Hussain et al., 2013; Hyvert et al., 2010; Ipavec et al., 2013; Irassar et al., 2006; Kaewmanee and Tangtermsirikul, 2014; Kenai et al., 2008; Lee et al., 2008; Leemann et al., 2015; Lemieux et al., 2012; Liu et al., 2014; Lollini et al., 2014; Lollini et al., 2016; Loser and Leemann, 2007; Loser et al., 2010; Marques et al., 2013; Marzouki et al., 2013; Mavropoulou et al., 2016; Meddah et al., 2014; Meira et al., 2014; Menadi and Kenai, 2011; Mounanga et al., 2011; Mun et al., 2007; Mwaiuwinga et al., 1997; Nagrockiene et al., 2013a; Nagrockiene et al., 2013b; Palm et al., 2016; Panesar and Francis, 2014; Phung et al., 2015; Pipilikaki et al., 2008; Pipilikaki and Beazi-Katsioti, 2009; Pipilikaki et al., 2009a; Pipilikaki et al., 2009b; Pourkhorshidi et al., 2010; Rabehi et al., 2013; Rahhal et al., 2012; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Ramezanianpour et al., 2014; Ranc R. et al., 1991; Revay and Gavel, 2003; Ryou et al., 2014; Sakai and Watanabe, 1993; Sakai and Watanabe, 1994; Saraya, 2014; Selih et al., 2003; Shi et al., 2015; Silva and Brito, 2015; Skaropoulou et al., 2009a; Skaropoulou et al., 2012; Skaropoulou et al., 2009b; Sonebi and Nanukuttan, 2009; Sonebi et al., 2009; Sotiriadis et al., 2013; Sotiriadis et al., 2012; Tezuka et al., 1992; Thomas et al., 2010a; Thomas et al., 2010b; Thomas et al., 2010c; Thomas et al., 2010d; Thongsanitgarn et al., 2014; Torres et al., 2003; Tosun-Felekog˘lu, 2012; Turkel et al., 2009; Uysal and Sumer, 2011; Uysal and Tanyildizi, 2012; Uysal and Tanyildizi, 2011; Uysal and Yilmaz, 2011; Uysal et al., 2012; Uysal, 2012; Voglis et al., 2005; Vyšvařil et al., 2015; Wu et al., 2016; Yamada et al., 2006; Zhang et al., 2016

Because GLS is a PC replacement material, it would always be useful to know the pH of GLS in comparison to PC. The results in this regard are very few, and those available indicate a pH of around 9.5 (Phung et al., 2015). It is clearly lower than the pH of PC and therefore it would decrease the pH of PLC in proportion to the GLS content used (especially with high contents of GLS such as in CEM II/B-L, with a maximum allowable GLS content of 35%). Thus, the use of PLC can be expected to potentially accelerate the corrosion activity of steel reinforcement.

3.6 Physical and Chemical Effects Resulting from Blending GLS with PC

GLS addition is different from the majority of the supplementary cementitious materials, in that it is not a silicate-based substance, neither is it a pozzolanic material such as PFA nor a latent hydraulic such as GGBS (Ramezanianpour et al., 2009; Snellings and Scrivener, 2016). The physical and chemical effects of the inclusion of GLS are mainly identified as follows:

- Filler effect: GLS refines and improves the porosity of a concrete mix and in general results in lowering the water demand for a given workability owing its wider PSD (Irassar, 2009).

- Heterogeneous nucleation effect: Because GLS particles work as nucleation sites, they raise the potential for increasing the early hydration of cement (particularly C_3S) and, consequently, creating an additional crystallisation of calcium silicate hydrate, which can potentially improve the early strength of concrete (Sezer, 2012).

- Dilution effect: The dilution effect acts in reverse to the filler and heterogeneous nucleation effects. The dilution effect is an outcome of the reduced cement content and as such gives rise to an increase in the effective w/c of a concrete mix (Irassar, 2009). Moreover, this dilution effect within PLC can be noticed clearly from the reduction in the proportions of the four major oxides (CaO, SiO_2, Fe_2O_3 and Al_2O_3) (Figure 3.16).

In addition, $CaCO_3$ dissolved from GLS reacts with aluminates (C_3A and C_4AF) to form calcium monocarboaluminate, which has a minor or no participation effect in filling the capillary voids (Kaur et al., 2012; Rahhal et al., 2012; Lollini et al., 2014 and Tennis et al., 2011). Furthermore, it has been claimed that the GLS content of PLC could act as an interior source of carbonate ions, which are needed for the thaumasite sulfate attack to take place (Irassar et al., 2005; Ramezanianpour et al., 2009; Shi et al., 2012; Ramezanianpour and Hooton, 2013).

It is worth mentioning that all the aforementioned effects are in essence considered to be reliant on the amount and fineness of GLS used in a particular mix (Sezer, 2012).

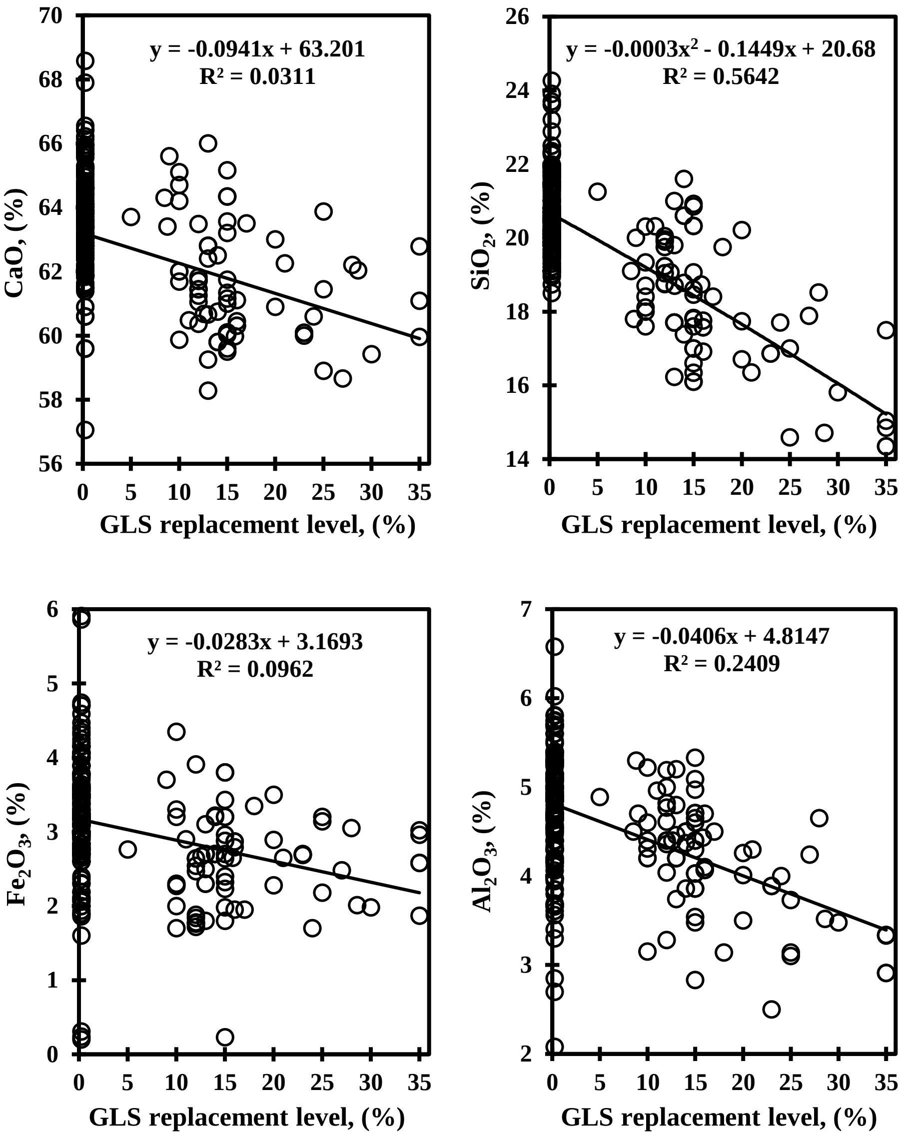


Figure 3.16: Effect of GLS addition on the major oxides of the PLC produced

Data of Figure 3.16 taken from: Amin et al., 2010a; Amin et al., 2010b; Arandigoyen and Álvarez, 2006; Assie et al., 2006; Assie et al., 2007; Balayssac et al., 1995; Barker and Matthews, 1994; Batic et al., 2013; Chiker et al., 2016; Collepardi et al., 2004; Corinaldesi et al., 2004; Cost et al., 2013a; Cost et al., 2013b; El-Hassan and Shao, 2015; Falchi et al., 2015; Fayala et al., 2012; Githachuri and Alexander, 2013; Gu¨neyisi and Gesog˘lu, 2011; Güneyisi et al., 2011; Hocine et al., 2012; Hooton et al., 2010; Howard et al., 2015; Hyvert et al., 2010; Kenai et al., 2008; Leemann et al., 2010; Leemann et al., 2015; Lemieux et al., 2012; Loser and Leemann, 2007; Loser et al., 2010; Lothenbach et al., 2007; Marques et al., 2013; Marzouki et al., 2013; Mavropoulou et al., 2016; McNally et al., 2012; Meira et al., 2014; Menadi and Kenai, 2011; Palm et al., 2016; Panesar and Francis, 2014; Pipilikaki and Beazi-Katsioti, 2009; Pipilikaki et al., 2008; Pipilikaki et al., 2009a; Pipilikaki et al., 2009b; Pourkhorshidi et al., 2010; Rabehi et al., 2013; Ranc et al., 1991; Rostami et al., 2012; Segura et al., 2013; Shao et al., 2013; Sistonen et al., 2008; Thomas et al., 2010a; Thomas et al., 2010b; Thomas et al., 2010c; Thomas et al., 2010d; Yamada et al., 2006; Younsi et al., 2015

3.7 Conclusions

Based on the analysis, evaluation and structuring of the measurements obtained for GLS characteristics in this chapter, the following conclusions can be drawn:

a) The particle shape of GLS is irregular, which leads to PLC concrete losing its consistency slightly earlier than PC concrete. In addition, the colour of GLS varies from white to buff depending on the geological origin of the limestone; thus, PLC concrete has a slightly lighter colour than PC concrete.

b) The obtained PSD results suggest that GLS, when used as a cement component, is mostly finer than the lower limits for PFA and filler aggregate. Also, GLS has finer fraction than PC and PLC. Additionally, PC and PLC can generally be taken to be of similar grading.

c) The typical SG value of GLS addition is 2.71, which is lower than that of PC (about 3.15). This difference leads to the PLC being slightly lighter than PC depending on the content of GLS.

d) The clear majority of the results of $CaCO_3$ content in GLS are above 75% and comply with the BS EN and ASTM standards. In addition, the data for the MBI of GLS are mainly within 0–0.20 g/100 g, suggesting that the studied GLS contained clay with a low absorptive capacity. Furthermore, the majority of TOC values are less than 0.15%, indicating that the studied GLS contained low contents of TOC. Additionally, the higher contents of $CaCO_3$ in GLS result in lower values of TOC and MBI.

e) The measurements for the chloride contents of GLS and PLC are low and conform to the standard limits. Moreover, the large majority of SO_4 values in GLS are less than 1.0% and the most frequent results are in between 0% and 0.2%, signifying that GLS has a very low content of total sulfur.

f) The most frequent results for LOI for GLS are between 41.5% and 44.5%. Thus, the LOI results for PLC are higher than those for PC, as they are between 4% and 14% for the range of 6%–35% of GLS content.

g) Limited results show that the pH of GLS is 9.5, which is lower than the pH of PC, and it might decrease the pH of the PLC (especially with a high content of GLS such as 35%). Thus, it has the potential to accelerate the corrosion activity of steel reinforcements in PLC concrete.

h) The physical and chemical effects resulting from blending GLS with PC are mainly identified in the filler, heterogeneous nucleation and dilution effects. Also, $CaCO_3$ dissolved from GLS has the ability to react with aluminates (C_3A and C_4AF) to form calcium monocarboaluminate. In addition, GLS is considered an internal source of the carbonates required for the thaumasite sulfate attack.

CHAPTER 4

PORE STRUCTURE AND COMPRESSIVE STRENGTH OF PLC MIXTURES

4.1 Introduction

This chapter describes the details of the effects of ground limestone (GLS) use as a cement component on the porosity (including water absorption and sorptivity) of cementitious mixtures (such as cement paste, mortar and concrete) and related to the compressive strength. The effects on pore structure were also examined in terms of type of Portland cement (PC) and limestone, cement fineness and method of producing it, curing conditions, maturity and water/cement ratio, as well as the cement composites using pulverised fuel ash (PFA), ground granulated blast furnace slag (GGBS), micro-silica (MS) and metakaolin (MK).

4.2 Overview of the Literature

An overview of the observed effects on pore structure, in terms of porosity, water absorption and sorptivity, of cementitious mixtures (paste, mortar and concrete) using GLS addition similar to the specifications adopted in standards such as BS EN 197-1:2011, is presented in Table 4.1 and Table 4.2. This is based on the preliminary study of the obtained global experimental outcomes.

Of the nine publications identified as narrative reviews, six were produced by established organisations (in North America and the United Kingdom) (ACI, 2015; Concrete Society, 2011; Detwiler and Tennis, 1996; Hawkins et al., 2003; Hooton et al., 2007; Tennis et al., 2011) and three were produced by individual researchers (Benn et al., 2012; Kaur et al., 2012; Müller, 2012). The opinions stated by these two groups and their main observations are summarised in Table 4.1.

Table 4.1: Summary of the findings of the narrative reviews regarding the GLS effect on cementitious mixtures

REFERENCE	NO. OF CITED REFERENCES	MAIN OBSERVATION
a. Organization		
ACI, 2015, ACI Committee 211, USA	1	Up to 15% of GLS content PLC concrete has a similar porosity to PC concrete.
CSWP, 2011, Concrete Society, UK	3	The literature review shows mixed results for the pore structure and related properties of PLC mixtures when compared to PC.
Tennis et al., 2011; PCA, USA	7	
Detwiler and Tennis 1996; Hawkins et al., 2003; PCA, USA	2	PLC mixtures with GLS content up to 20% has a similar pore structure to PC mixture.
Hooton et al., 2007; Cement Association of Canada.	2	The pore structure and related properties of PLC concrete were unimpaired by the existence of GLS in the cement up to 15% content.
b. Individual		
Benn et al., 2012	2	The porosity and water absorption of PLC concrete with up to 15% of GLS was mainly unaffected.
Kaur et al., 2012	1	The sorptivity values of PLC mixtures containing 30% GLS are found to be higher than the corresponding PC mixtures.
Müller, 2012	1	PLC with GLS content >20% has the potential to increase the porosity and water absorption of concrete.

Though limited in number, and without detailed analysis of the data, both the organisational and the individual reviews suggest that there is agreement among these reviewers that the pore structure of Portland limestone cement (PLC) is not significantly affected by the addition of up to 15%–20% GLS (i.e., cements such as PLC or CEM II/A-L in BS EN 197-1:2011). However, some of the reviews provided by the national cement/concrete organisations in the United Kingdom and the United States concluded that there appear to be some differences in the published data that are related to both the variances in the cementitious mixtures examined and the test methods applied.

Given the large number of parameters involved across the obtained results, the only viable option was to initially examine all the data on GLS use (to obtain a general impression) relative to the corresponding PC mixtures and assign them to one of five categories with respect to porosity and related properties, expressed as follows:

(i) Higher than PC
(ii) Lower than PC
(iii) No change
(iv) Variable, where the relative figures change with GLS replacement level; and
(v) Unclear, where reference/control PC test results have not been provided

The parameters generating the observed data as stated by the researchers in each case have also been summarised, in Table 4.2 (Elgalhud et al., 2016). The overall impression to emerge from the preliminary initial examination as presented in Table 4.2 is one of split opinion regarding the effects on porosity and related properties of cementitious mixtures (cement paste, mortar and concrete) using GLS as a cement component. Further examination revealed that the variability observed in the initial appraisal appears to be caused by the number of parameters involved in the undertaken tests and adding to the assessed variability of the effect of GLS inclusion, such as the:

(a) proportion of GLS used in relation to Portland cement content, ranging from 2% to 50% and about one-third of the obtained results used only one GLS proportion level;

(b) different test methods used and procedures adopted, and the age at test, varying from 1 to 365 days and with it the GLS effect not remaining constant throughout;

(c) water/cement ratio varying from 0.35 to 0.79 and, with a given mix, the PLC effect varying;

(d) fineness of PLC and mineralogical composition of Portland cement.

Notwithstanding the preceding, and the uncertainties thus arising from not being able to establish a clear consensus on the effects of GLS on the porosity and related properties of cementitious mixtures (cement paste, mortar and concrete), the overall assessment of the published data suggests that essentially there are two opposing phenomena at play: (i) particle packing, decreasing porosity, and (ii) a dilution effect, increasing porosity, with the former dominating at the initial introduction of GLS, up to an optimum level of 12%–20%, and the latter taking over thereafter.

Table 4.2: Summary of the published findings concerning the effect of GLS on pore structure[a]

TYPE OF EFFECT		**MAJOR SUGGESTED CAUSES**		
		Porosity	**Water Absorption**	**Sorptivity**
Higher	**Tested Mixes**	**24 %**	**32 %**	**33 %**
		• GLS particles do not expand in the matrix as PC does. • Dilution effect on PC since the GLS is an inert filler. • Higher w/c due to the reduction of PC content. • GLS particles have a greater critical pore diameter than PC. • No clarification.	• Increased permeable pore space. • Formation of coarser pores. • No clarification.	• Higher porosity. • Higher permeability. • Porosity is reduced at the expense of capillarity and sorptivity. • No clarification.
Lower	**Tested Mixes**	**39 %**	**22 %**	**25 %**
		• Enhanced particle packing. • Larger hydration products. • Heterogeneous nucleation. • Lower heat of hydration. • Decrease in the water of consistency of the cement paste. • No clarification.	• Less number of capillary pores. • Finer pores. • Improvement in the distribution and tortuosity of the pores system. • No clarification.	• Less degree of interconnectedness of pores. • Smaller capillarity pores. • No clarification.
Variable	**Tested Mixes**	**15 %**	**30 %**	**38 %**
		• Decreases with improved PSD until optimum level (15-18%) and then increases due to dilution of PC. • Extent of fineness of particles. • No clarification.	• Decreases with improved PSD until optimum level (12-15%) and then increases due to dilution of PC. • No clarification.	• Decreases with improved PSD until optimum level (15-20%) and then increases due to dilution of PC. • Fineness, type of grinding and type of blending with PC. • No clarification.
No Change	**Tested Mixes**	**2 %**	**0 %**	**4 %**
		• No clarification.	-	• No clarification.
Unclear	**Tested Mixes**	**20 %**	**16 %**	**0 %**
		• No reference/control PC mix. • No results and declarations in regard.	• No reference/control PC mix.	-

a: Data of Table 4.2 taken from Ali et al., 2013; Allahverdi eta l., 2010; Alunno-Rosetti and Curcio, 1997; Amin et al., 2010a; Amin et al., 2010b; Antoni et al., 2012; Barrett et al., 2014; Bentz et al., 2009a; Bentz et al., 2009b; Burgos-Montes et al., 2013; Cam, 2010; Cam and Neithalath, 2012; Catinaud et al., 2000; Celik et al., 2014a; Celik et al., 2014b; Chowaniec, 2012; Courard and Michel, 2014; Courard et al.,2005; Courard et al., 2011; Das et al.,2014; De Weerdt et al., 2012; De Weerdt et al., 2011a; De Weerdt et al., 2010; De Weerdt et al., 2011b; Dhir et al., 2007; El-Alfi et al., 2004; EL-Alfi et al., 1999; EL-Didamony et al., 2000; El-Didamony et al., 1995; Felekoglu et al., 2009; Garbacik et al., 2002; Gesoglu et al., 2012; Ghiasvand et al., 2015; Ghrici et al., 2007; Githachuri and Alexander, 2013; Gonzalez and Irassar, 1998; Guemmadi et al., 2008a; Guemmadi et al., 2008b; Güneyisi et al., 2011; Helal, 2002; Hooton et al., 2007; Hornain et al., 1995; Hoshino et al., 2006; Hyvert et al., 2010; Irassar et al., 2006; Irassar et al., 2000; Irassar et al., 2009; Kadri and Duval, 2002; Kargol et al., 2013; Kumar et al., 2013; Leemann et al., 2010a; Leemann et al., 2010b; Lollini et al., 2014; Loser et al., 2010; Lothenbach et al., 2008a; Lothenbach et al., 2007; Lothenbach et al., 2008b; Luz and Pandolfelli, 2012; Marzouki et al., 2013; Matschei et al., 2007; Meddah et al., 2014; Menadi and Kenai, 2011; Men_endez et al., 2007a; Men_endez et al., 2007b; Moir and Kelham, 1993; Mounanga et al., 2011; Müller and Lang, 2006; Nagrockiene, et al., 2013a; Nagrockiene, et al., 2013b; Nielsen et al., 2014; Pandey and Sharma, 2000; Panesar and Francis, 2014; Patsikas et al., 2012; Pavoine et al., 2014; Pipilikaki and Beazi-Katsioti, 2009a; Pipilikaki and Beazi-Katsioti, 2009b; Pourkhorshidi et al., 2010; Rabehi et al., 2013; Ramezanianpour et al., 2010.; Ramezanianpour et al., 2014; Sanish et al., 2013; Saraya, 2014; Schmidt et al., 2009; Senhadji et al., 2014; Sezer, 2012; Tikkanen et al., 2015; Torkaman et al., 2014; Tsivilis et al., 2000; Tsivilis et al., 1999; Tsivilis et al., 2002a; Tsivilis et al., 2003; Tsivilis et al., 2002b; Turkel, and Altuntas, 2009; Vysvaril et al., 2014; Zelic et al., 2000; Zhang and Ye, 2012

4.3 Pore Structure Measurements

4.3.1 Variation in the Testing Procedures Used

Table 4.3 (Elgalhud et al., 2016) shows that widely differing test methods and procedures have been employed in studying the effects of PLC on the pore structure of concrete, and considerably more so in the measurement of porosity than in that of absorption and sorptivity. The porosity test methods have been separated for clarity into four main groups:

(a) environmental scanning electron microscope, backscattered electron imaging, X-ray diffraction and nuclear magnetic resonance;

(b) the model of Powers and Brownyard, hydration kinetics model and computer-based model HYMOSTRUC;

(c) mercury intrusion porosimetry (MIP);

(d) liquid displacement (LD).

This examination also suggested that MIP and LD were the two most used test methods and this is considered to be due mainly to their relative ease of use and, in the case of MIP, the extent of experimental data produced. In regard to the water absorption measurements, absorption by immersion was shown to be the commonly used method, because of its availability and simplicity of use.

Table 4.3: Details of test parameters undertaken to study the effect of GLS on the pore structure[a] (Elgalhud et al., 2016)

PARAMETER	**MEASURMENT**		
	Porosity	**Water Absorption**	**Sorptivity**
Test method	Electron microscopy and microstructural imaging: {Number of tested mixes =17}	Water absorption by immersion: {24}	Capillarity: {42}
	Numerical and computer models: {12}	Capillary rise: {6}	
	Mercury intrusion porosimetry: {38}	Initial surface absorption: {3}	
	Liquid displacement: {29}		
Material	Hydrated cement paste: {47} Mortar/Concrete: {48}	Hydrated cement paste: {2} Mortar/Concrete: {30}	Hydrated cement paste: {2} Mortar/Concrete: {41}
Specimen	Cube: {54}, Cylinder: {11}, Prism and other: {30}	Cube: {20}, Cylinder: {5}, Prism: {9}	Cube: {20}, Cylinder: {20}, Prism: {3}
Curing	Ordinary water: {65}, Air curing {3}	Ordinary water {20}	Ordinary water: {31}, Air curing {3}
	Lime saturated water: {9}, Moist: {18}	Lime saturated water: {3}, Moist: {11}	Lime saturated water: {5}, Moist: {5}
Temperature	5° C {2}, 20°- 25° C {90}, 37°- 40° C {3}	20°- 25° C {33}	20°- 25° C {42}
Relative humidity	≥ 90% {90}, 65 % {2}	≥ 90% {33}	≥ 90% {41}, 65 % {2}
Curing length	1 - 3 days {19}, 7 - 21 days {27}	1 - 3 days {8}, 7 - 21 days {9}	1 - 3 days {4}, 7 - 21 days {9}
	28 - 90 days {50}, 120 - 360 days {17}	28 - 90 days {30}, 120 - 360 days {6}	28 - 90 days {54}, 120 - 360 days {8}
Measuring time	--	10 minutes: {3}, 30 minutes: {6}	Up to 60 minutes: {9}, Up to 6 hours {3}
		24 hours: {9}, 48 hours: {5}	Up to 24 hours: {21}, Up to 48 hours {5}
		72 hours: {2}, Not given: {9}	Up to 72 hours: {5}, Up to 7 days: {3}
Type of outcome	Gel porosity: {2}, Capillary porosity: {45}, Total porosity: {48}	Water absorption: {33}	Initial sorptivity: {42}, Final sorptivity: {3}
Relevant Standard	Specified: {68}, Unspecified: {24}	Specified: {24}, Unspecified: {6}	Specified: {27}, Unspecified: (15)

a: Data of Table 4.3 taken from Alunno-Rosetti and Curcio and 1997; Amin et al., 2010a; Amin et al., 2010b; Antoni et al., 2012; Barrett et al., 2014a; Barrett et al., 2014b; Bentz et al., 2009a; Bentz et al., 2009b; Burgos-Montes et al., 2013; Cam and Neithalath, 2010; Catinaud et al., 2000; Celik et al., 2014a; Celik et al., 2014b; Chowaniec 2012; Courard and Michel, 2014; Courard et al., 2005; Courard et al., 2011; Das et al., 2014a; De Weerdt et al., 2012; De Weerdt et al., 2011a; De Weerdt et al., 2010; De Weerdt et al., 2011b; Dhir et al., 2007; El-Alfi et al., 2004; El-Alfi et al., 1999; El-Didamony and El-Alfi, 2000; El-Didamony et al., 1995; Felekoglu and Tosun, 2009; Garbacik and Chladzynski, 2002; Gesoglu et al., 2012; Ghiasvand et al., 2015; Ghrici et al., 2007; Githachuri and Alexander, 2013; Gonzalez and Irassar, 1998; Güneyisi et al., 2011; Hornain et al., 1995; Hoshino et al., 2006; Hyvert et al., 2010; Irassar et al., 2006; Irassar et al., 2000; Kumar et al., 2013; Leemann et al., 2010a; Leemann et al., 2010b; Lollini et al., 2014; Loser et al., 2010; Lothenbach et al., 2008a; Lothenbach et al., 2007; Lothenbach et al., 2008b; Luz and Pandolfelli, 2012; Marzouki et al., 2013; Matschei et al., 2007; Meddah et al., 2014; Menadi and Kenai, 2011; Menendez, 2007a; Menendez et al., 2007b; Moir and Kelham, 1993; Mounanga, et al., 2011; Müller and Lang, 2006; Nagrockien et al., 2013a; Nagrockien et al., 2013b; Nielsen et al., 2014; Pandey and Sharma, 2000; Panesar and Francis, 2014; Patsikas et al., 2012; Pavoine et al., 2014; Pipilikaki et al.,2009a; Pipilikaki et al., 2009b; Pourkhorshidi et al., 2010; Rabehi et al., 2013; Ramezanianpour et al., 2010; Ramezanianpour and Hooton, 2014; Sanish et al., 2013; Saraya, 2014; Schmidt et al., 2009; Senhadji et al., 2014; Sezer et al., 2012; Torkaman et al., 2014; Tsivilis et al., 2000; Tsivilis et al., 1999; Tsivilis et al., 2002a; Tsivilis et al., 2003; Turkel and Altuntas, 2009; Vysvaril et al., 2014; Zelic et al., 2000; Zhang and Ye, 2012

Although not a preferred choice because of the interference arising from the presence of aggregates, including the formation of interfaces, the vast majority of the studies (76%) relied on the use of mortar and concrete instead of cement paste as the test material, most probably because of the ease of handling of the test specimens. The selection of test specimens in the forms of cubes, cylinders and prisms appeared to be influenced by the relevant standard specifications (Table 4.3).

With few exceptions, and to a certain extent influenced by the local standard specifications, moist curing with relative humidity (RH) ≥90% and temperatures of 20°C–25°C was generally adopted. Interestingly, though, some studies used lime-saturated water for curing to prevent possible leaching and carbonation of the test specimens, and a few adopted RH of 65% and temperatures of 5°C, 37°C and 40°C for curing the test specimens. However, the curing duration varied greatly, in that a period of 28–90 days was used for more than half of the tested specimens, followed by, in decreasing order, periods of 7–21 days, 1–3 days and 120–360 days. Similarly, the time after which measurements were taken for absorption and sorptivity tests varied, with up to 24 h period most frequently adopted (Table 4.3).

Most of the porosity measurements have been provided in the form of capillary porosity and total porosity, with one study reporting the results in the form of gel porosity. The sorptivity results have largely been provided as initial sorptivity that takes up to 72 h to complete, with a few extending the test to measure final sorptivity at the end of a 7-day period. Although a majority of the test specimens were prepared according to standard procedures, a significant minority of 27% of the studies do not cite such information.

Given the large number of variables involved in the test materials, test methods and procedures used, as can be seen from Table 4.3, the results on the effects of GLS on the porosity and porosity-related properties of cementitious mixtures (in the form of cement paste, mortar and concrete) can be best analysed and evaluated in comparison to the corresponding PC (used as reference). However, some of the relative values were considered numerically distant from the rest and therefore have been regarded as outliers and not considered further in the analysis.

4.3.2 Porosity

As the cement paste in concrete is the only chemically active component, and it also contains the majority of the pores (Dyer, 2014), it is reasonable first to study the influence of GLS on the porosity of cement paste before dealing with the results obtained for mortar and concrete mixes. The results obtained using the two most popular methods, MIP and LD, are plotted in Figure 4.1 (a) and (b), respectively. It is clear that the data population is limited, and efforts to model the results using straightforward linear, logarithmic and polynomial trend lines proved to be unsatisfactory, yielding determination coefficient (R^2) values, for example, below 0.40 (solid lines).

Nevertheless, the observation of the results suggests that for practical purposes GLS addition of up to 20%–30% may not significantly affect the porosity of the cement paste, but thereafter the porosity may increase linearly with further increase in the GLS content (broken line). The results obtained for cement paste for all the test methods, as shown in Figure 4.1 (c), tended to confirm the above, possibly with potential for some improvement in the porosity of cement paste with the use of GLS up to 30%. The results plotted from the mortar/concrete mixtures in Figure 4.2 suggest a limit of up to 20%. Thus, on the basis of Figure 4.2, it would appear that:

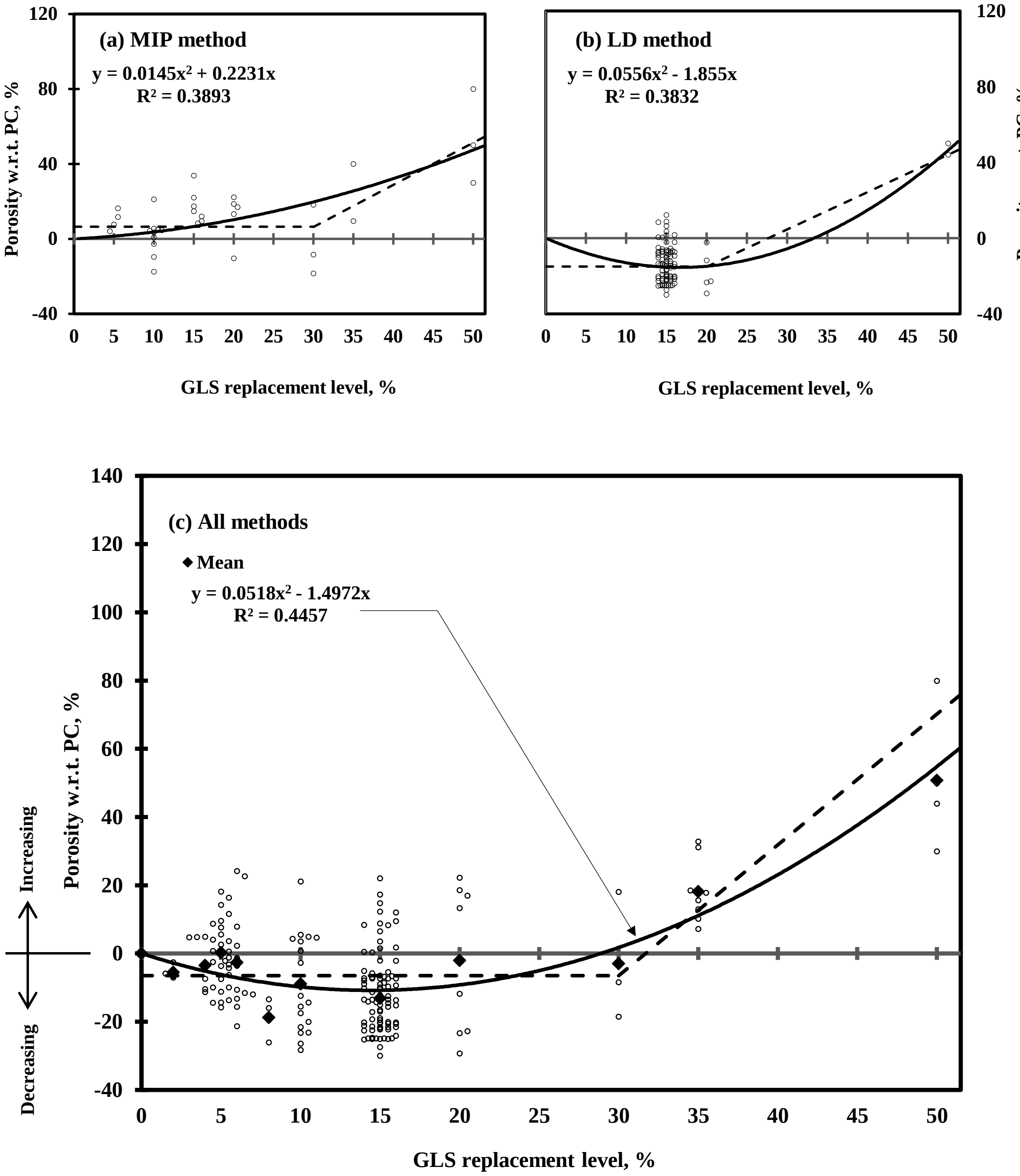


Figure 4.1: GLS addition effect on porosity of cement paste mixtures using: (a): MIP method, (b) LD method and (c) All methods. (Elgalhud et al., 2016)

Data of Figure 4.1 taken from: Amin et al., 2010a; Amin et al., 2010b; Bentz et al., 2009a; Bentz et al., 2009b; Burgos-Montes et al., 2013; Catinaud et al., 2000; Chowaniec, 2012; Das et al., 2014a; De Weerdt et al., 2012; De Weerdt et al., 2011a; De Weerdt et al., 2011b; El-Alfi et al., 2004; EL-Alfi et al., 1999; EL-Didamony and EL-Alfi, 2000; El-Didamony et al., 1995; Hornain et al., 1995; Hoshino et al., 2006; Kumar et al., 2013; Lothenbach et al., 2008; Luz and Pandolfelli, 2012; Panesar and Francis, 2014; Pipilikaki and Beazi-Katsioti, 2009; Pipilikaki et al., 2009; Saraya et al., 2014; Sezer, 2012; Vysvaril et al., 2014; Zhang and Ye, 2012

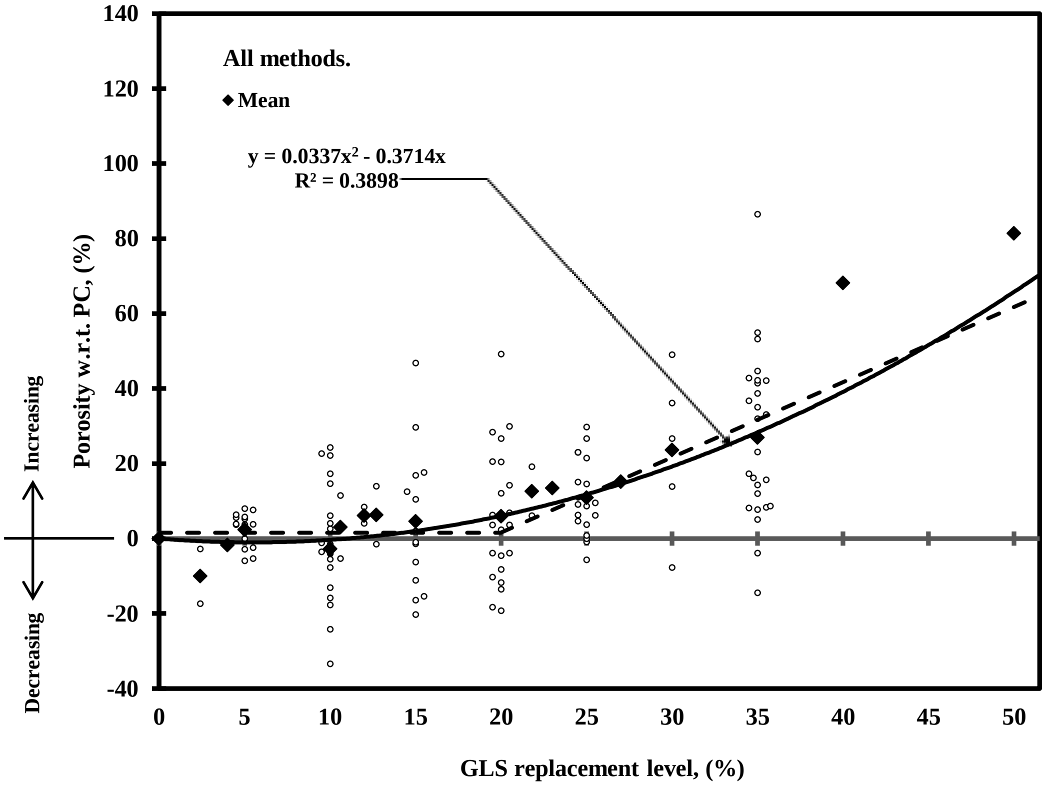


Figure 4.2: GLS addition effect on porosity of mortar and concrete mixtures (Elgalhud et al., 2016)

Data of Figure 4.2 taken from Barrett et al., 2014; Barrett et al., 2014; Cam and Neithalath, 2010; Courard and Michel, 2014; Courard et al., 2005; De Weerdt et al., 2010; Felekoglu and Tosun et al., 2009; Garbacik and Chladzynski, 2002; Gonzalez and Irassar, 1998; Hornain et al., 1995; Hyvert et al., 2010; Irassar et al., 2000; Kadri and Duval, 2002; Leemann et al., 2010a; Leemann et al., 2010b; Loser et al., 2010; Lothenbach et al., 2008; Lothenbach et al., 2007; Marzouki et al., 2013; Matschei et al., 2007; Moir and Kelham, 1993; Müller and Lang, 2006; Nielsen et al., 2014; Pandey and Sharma, 2000; Patsikas et al., 2012; Pavoine et al., 2014; Rabehi et al., 2013; Ramezanianpour and Hooton, 2014; Sanish et al., 2013; Schmidt et al., 2009; Senhadji et al., 2014; Tsivilis et al., 2000; Tsivilis et al., 1999; Tsivilis et al., 2002a; Tsivilis et al., 2003; Tsivilis et al., 2002b; Zelic et al., 2000

(i) Limits on the addition of GLS in cementitious mixtures in the form of cement paste (Figure 4.1) are reduced when aggregates are introduced to form mortar/concrete mixtures (Figure 4.2). As an example, a limit of 30% addition of GLS to cement paste (Figure 4.1c) was found to reduce to 20% GLS addition for mortar/concrete (Figure 4.2).

(ii) The GLS addition of up to 35% as a component of cement, as per specification for CEM II/B in BS EN 197-1:2011 for common cements for use in concrete, may perhaps be too high, and a figure of about 20% (CEM II/A) could be more appropriate and/or safer, depending upon the design strength and durability requirement of the concrete.

4.3.3 Water Absorption and Sorptivity

Limited results have been obtained on the effects of GLS addition on water absorption and sorptivity of cement paste, and the results pertaining to these aspects could not be analysed. Thus, the results obtained for mortar and concrete are analysed as plotted in Figures 4.3 and 4.4. The scatter in the obtained data is understandable given that the procedural differences, particularly the duration of curing and the measuring time, varied greatly in the widely-sourced data.

Figure 4.3 (a) and (b) for absorption and sorptivity, respectively, shows that in essence the two properties are affected similarly; suggesting that GLS addition may be used without adversely affecting these two properties of the concrete. However, the two methods, in a limited manner, give different limiting values for GLS addition: 17.5% for absorption with coefficient of determination (R^2) at 0.755 [Figure 4.3 (a)] and 25% for sorptivity with much reduced R^2 at 0.496 [Figure 4.3 (b)]. Analysing the two sets of results together with the porosity results produced a limiting value of 15% for GLS addition (Figure 4.4).

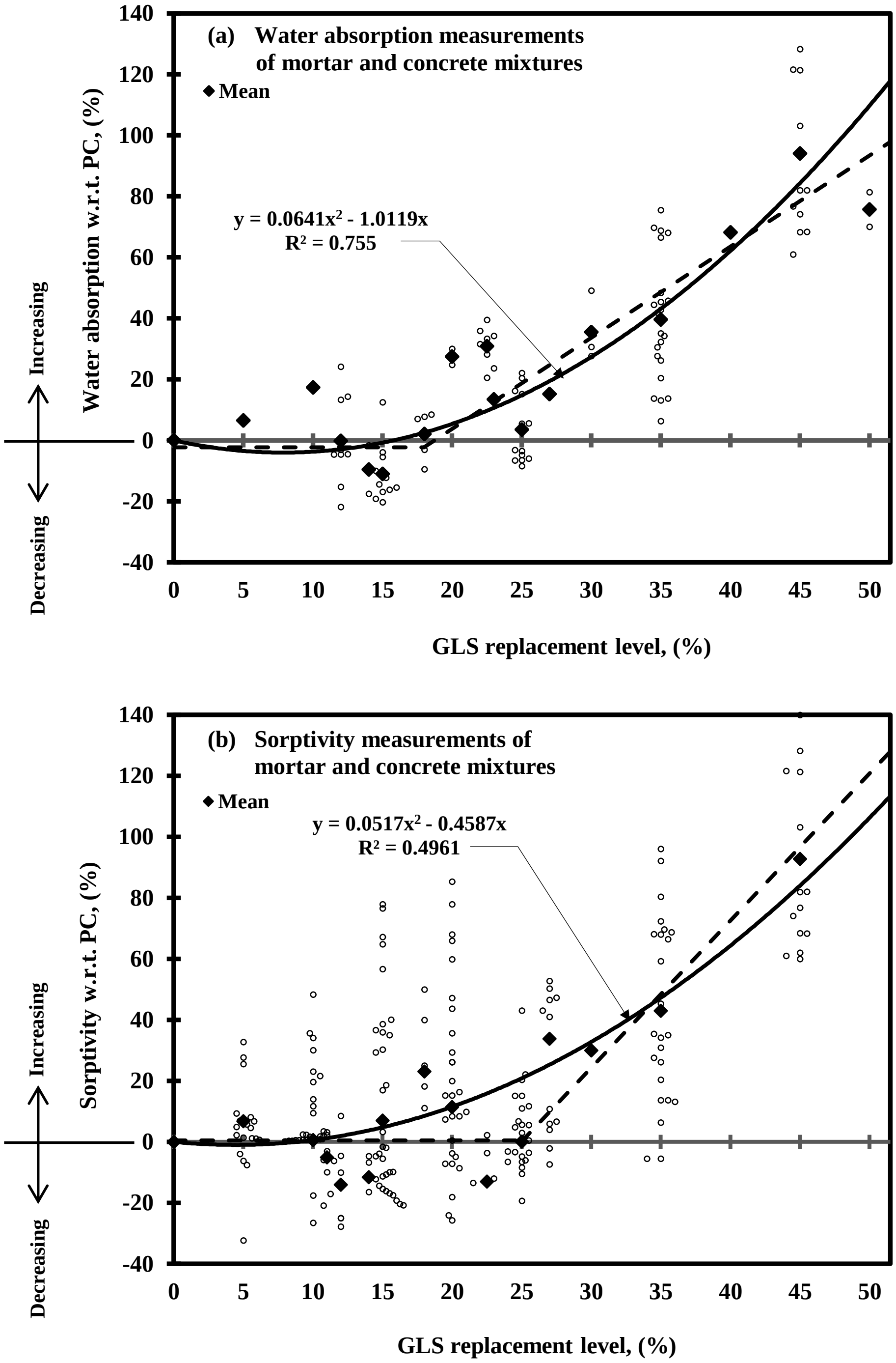


Figure 4.3: GLS addition effect on (a) Water absorption and (b) Sorptivity of mortar and concrete mixtures (Elgalhud et al., 2016)

Data of Figure 4.3 taken from Alunno-Rosetti and Curcio, 1997; Cam and Neithalath, 2010; Chowaniec et al., 2012; Courard and Michel, 2014; Courard et al., 2005; Courard et al., 2011; Dhir et al., 2007; Felekoglu et al., 2009; Gesoglu et al., 2012; Ghiasvand et al., 2015; Ghrici et al., 2007; Githachuri and Alexander, 2013; Güneyisi et al., 2011; Irassar et al., 2006; Lollini et al., 2014; Marzouki et al., 2013; Meddah et al., 2014; Menadi and Kenai, 2011; Menendez et al.,2007a; Menendez et al., 2007b; Moir and Kelham, 1993; Nagrockiene et al., 2013a; Nagrockiene et al., 2013b; Pourkhorshidi et al., 2010; Rabehi et al., 2013; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Torkaman et al., 2014; Tsivilis et al., 2000; Tsivilis et al., 1999; Tsivilis et al., 2003; Turkel and Altuntas, 2009

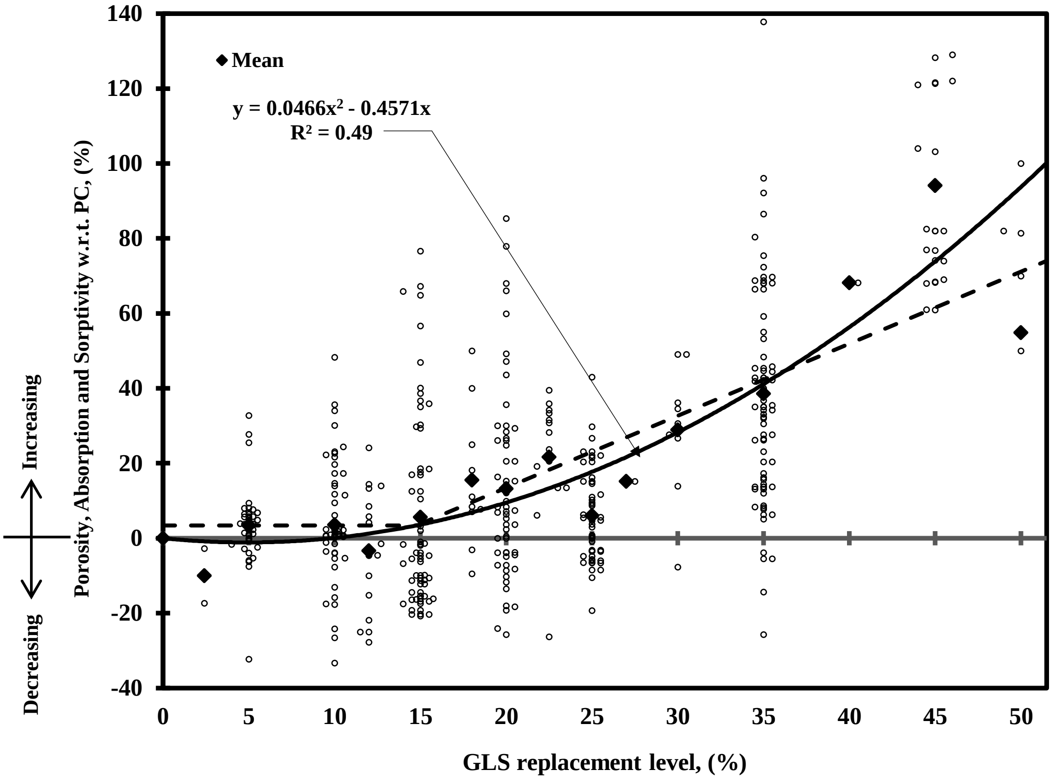


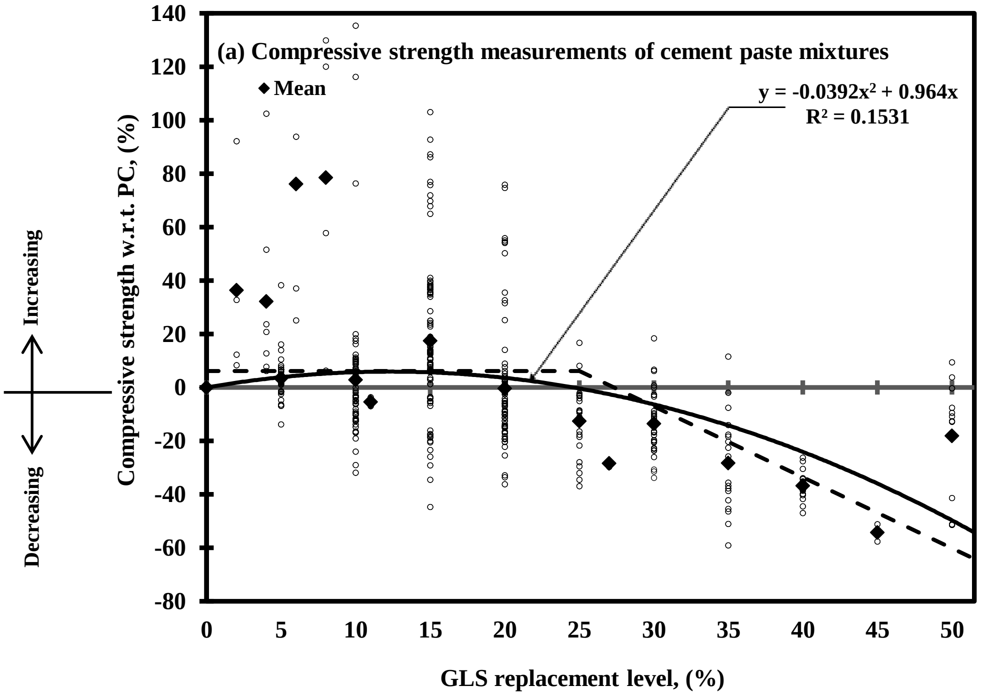
Figure 4.4: GLS addition effect on porosity, water absorption and sorptivity of mortar and concrete mixtures (Elgalhud et al., 2016)

Data of Figure 4.4 taken from Figures 4.2 and 4.3

4.4 Compressive Strength Measurements

Compressive strength, considered as the most important property of concrete, with cement pastes has been shown to relate directly to the volume and distribution of pores (porosity) (Roy and Gouda, 1973). To study the relationship between the strength and the porosity of PLC cement paste and mortar/concrete mixtures, the compressive strength results that have been considered are for the same specimens that were studied for the effect of GLS addition on porosity, absorption or sorptivity, and they have been analysed to evaluate the strength results relative to GLS addition, as shown in Figure 4.5. This shows limits on GLS content of 25% and 17.5% for cement paste and mortar/concrete mixtures, respectively, beyond which strength could be expected to decline with increasing GLS addition. These trends are similar to those observed for the porosity of cement paste and mortar/concrete mixtures [Figures 4.1 (c) and 4.2].

Additionally, and for comparison purposes, strength results from other experiments (in which the pore structure of PLC was not tested), limited to the 10-year period 2005–2014, that have not been included in the main study have been analysed separately to compare and confirm the effects of PLC on strength. These results are plotted in Figure 4.6 and generally suggest a similar trend for the effect of GLS addition on strength, albeit with slightly lower limits on GLS content, and the difference between the cement paste and mortar/concrete limits is less marked.



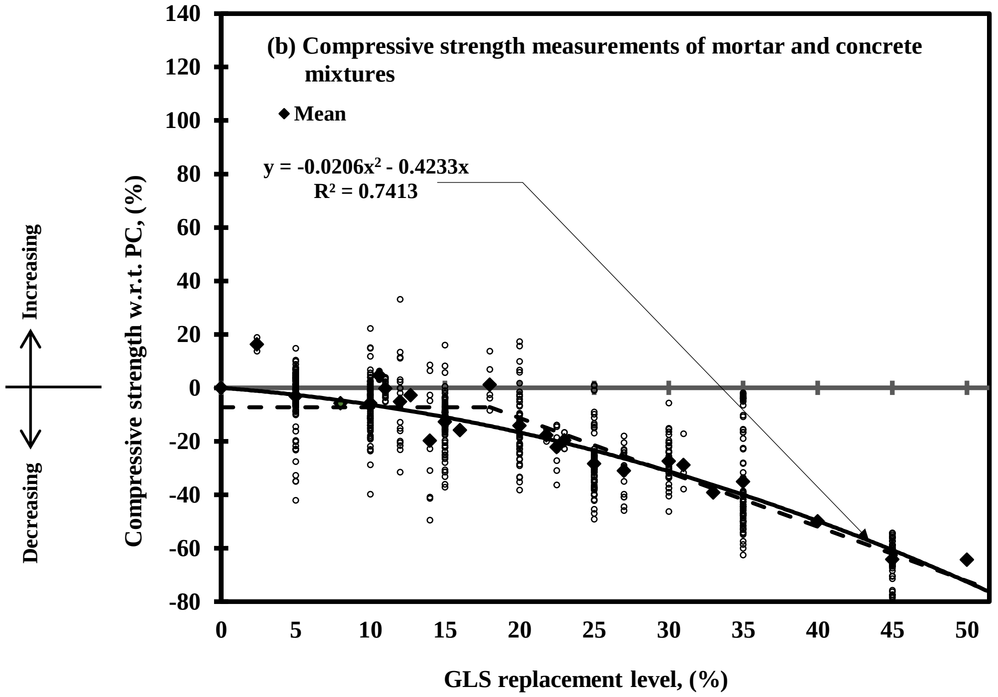


Figure 4.5: GLS addition effect on compressive strength of (a) Cement paste and (b) Mortar and concrete mixtures (Elgalhud et al., 2016)

Data of Figure 4.5 taken from Ali et al., 2013; Amin et al., 2010a; Amin et al., 2010b; Antoni et al., 2012; Barrett et al., 2014a; Barrett et al., 2014b; Bentz et al., 2009a; Bentz et al., 2009b; Burgos-Montes et al., 2013; Cam and Neithalath, 2010; Cam and Neithalath, 2012; Chowaniec, 2012; Courard and Michel, 2014; Courard et al., 2005; Das et al., 2014a; De Weerdt et al., 2012; De Weerdt et al., 2011a; De Weerdt et al., 2011b; De Weerdt et al., 2010; El-Alfi et al., 2004; EL-Alfi et al., 1999; EL-Didamony and EL-Alfi, 2000; Felekoglu and Tosun, 2009; Garbacik and Chladzynski, 2002; Gonzalez and Irassar, 1998; Guemmadi et al., 2008b; Helal, 2002; Hornain et al., 1995; Hoshino et al., 2006; Hyvert et al., 2010; Irassar et al., 2000; Kadri and Duval, 2002; Knop et al., 2014; Kumar et al., 2013; Leemann et al., 2010a; Leemann et al., 2010b; Loser et al., 2010; Lothenbach et al., 2008a Lothenbach et al., 2008b; Lothenbach et al., 2007; Luz and Pandolfelli, 2012; Marzouki et al., 2013; Nielsen et al., 2014; Pandey and Sharma, 2000; Patsikas et al., 2012; Pavoine et al., 2014; Pipilikaki et al., 2009; Rabehi et al., 2013; Ramezanianpour and Hooton, 2014; Sanish et al., 2013; Saraya, 2014; Schmidt et al., 2009; Senhadji et al., 2014; Tsivilis et al., 2000; Tsivilis et al., 1999; Tsivilis et al., 2002a; Tsivilis et al., 2002b; Tsivilis et al., 2003; Zelic et al., 2000

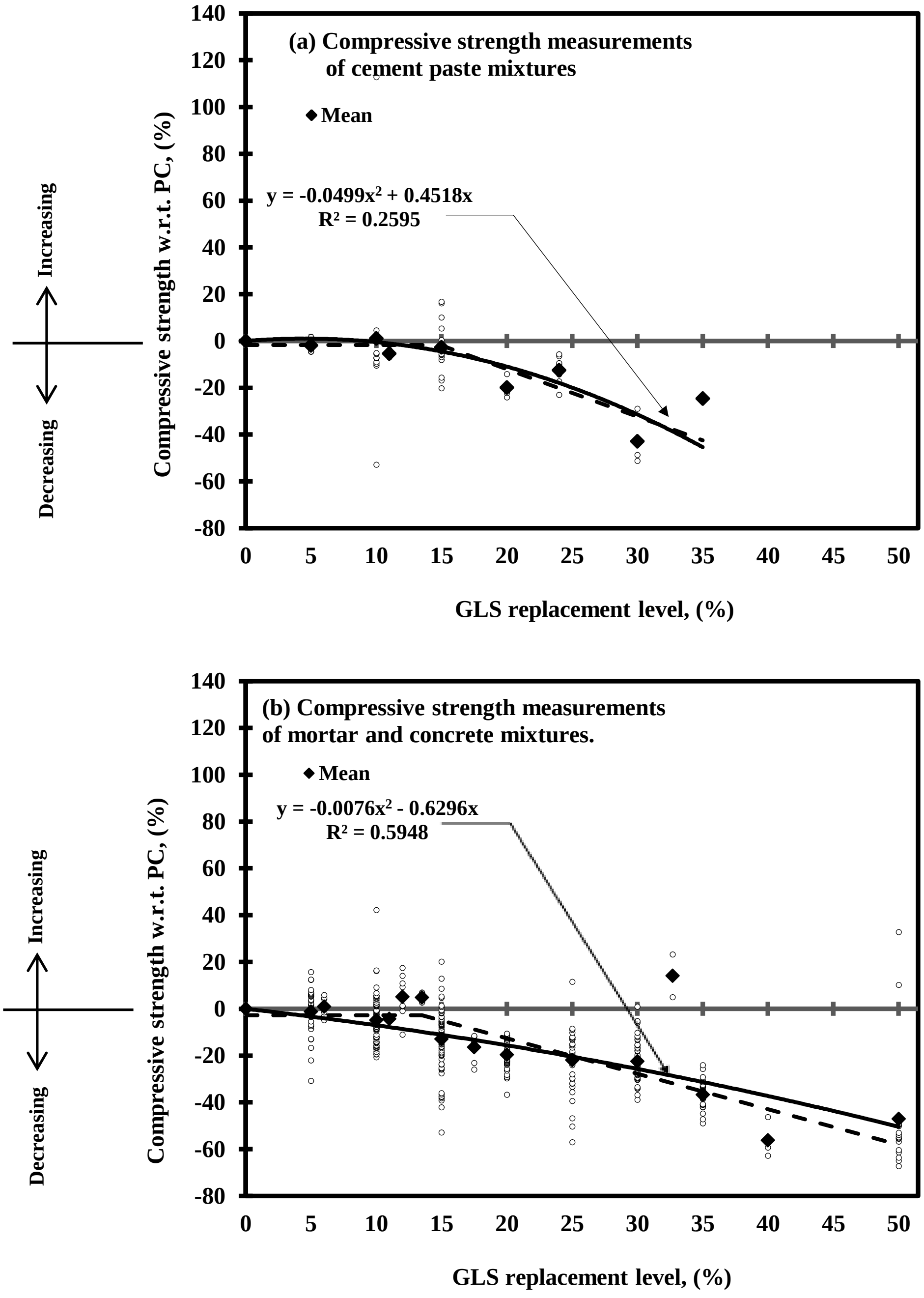


Figure 4.6: GLS addition effect on compressive strength of (a) Cement paste and (b) Mortar and concrete mixtures for additional specimens in the period between 2005-2014 (Elgalhud et al., 2016)

Data of Figure 4.6 taken from Abualgasem et al., 2014; Bentz et al., 2015; Bentz, 2005; Bouasker et al., 2014; Boubekeur et al., 2014; Carrasco et al., 2005; Celik et al., 2014a; Cost et al., 2013a; Cost et al., 2013b; De Weerdt et al., 2011a; Ezziane et al., 2010; Güneyisi and Gesoglu, 2011; Itim et al., 2011; Kadri et al., 2010; Kwan et al., 2013; Lawrence et al., 2005; Lee et al., 2008; Liu and Wang, 2014; Liu et al., 2014; Marques et al., 2013; Mounanga et al., 2011; Pipilikaki et al., 2009; Rahhal et al., 2012; Ryou et al., 2014; Saca and Georgescu, 2014; Sezer et al., 2010; Siad et al., 2013; Skaropoulou et al., 2012; Soriano et al., 2013; Sotiriadis et al., 2012; Sun et al., 2013; Thomas et al., 2010a; Thomas et al., 2010b; Thomas et al., 2010c; Thongsanitgarn et al., 2014; Tosun et al., 2009; Tosun-Felekoglu, 2012; Uysal and Sumer, 2011; Uysal and Tanyildizi, 2012; Uysal and Tanyildizi, 2011; Uysal and Yilmaz, 2011; Uysal, 2012; Uysal et al., 2012; Voglis et al., 2005

4.5 Compressive Strength and Porosity Relationship

The effects of GLS on (i) porosity and porosity-related properties such as absorption and sorptivity and (ii) compressive strength are shown for cement paste mixtures and mortar/concrete mixtures in Figure 4.7 (a) and (b), respectively. This figure is based on global results, and in this respect, whilst the data population shows high variability, it helps to underpin the reported study. Figure 4.7 (a) and (b) is based on total data populations compiled for cement paste and mortar/concrete, and the two messages emerging in a way of confirmation are:

- GLS can be adopted for use as a component of cement up to a limited level, beyond which the quality of cementitious mixtures in the form of cement paste and mortar/concrete in the hardened state will decline.
- The introduction of aggregates into a cementitious mixture reduces the limit on GLS content that can be applied without adversely affecting their quality.

In addition, based on Figure 4.7, the correlation between the porosity-related properties and the compressive strength of PLC can be presented as in Figure 4.8. This shows the inverse relation between the two, in which an increment in pore volume leads directly to a decline in compressive strength. This agrees with what was reported in a previous study (Matschei et al., 2007).

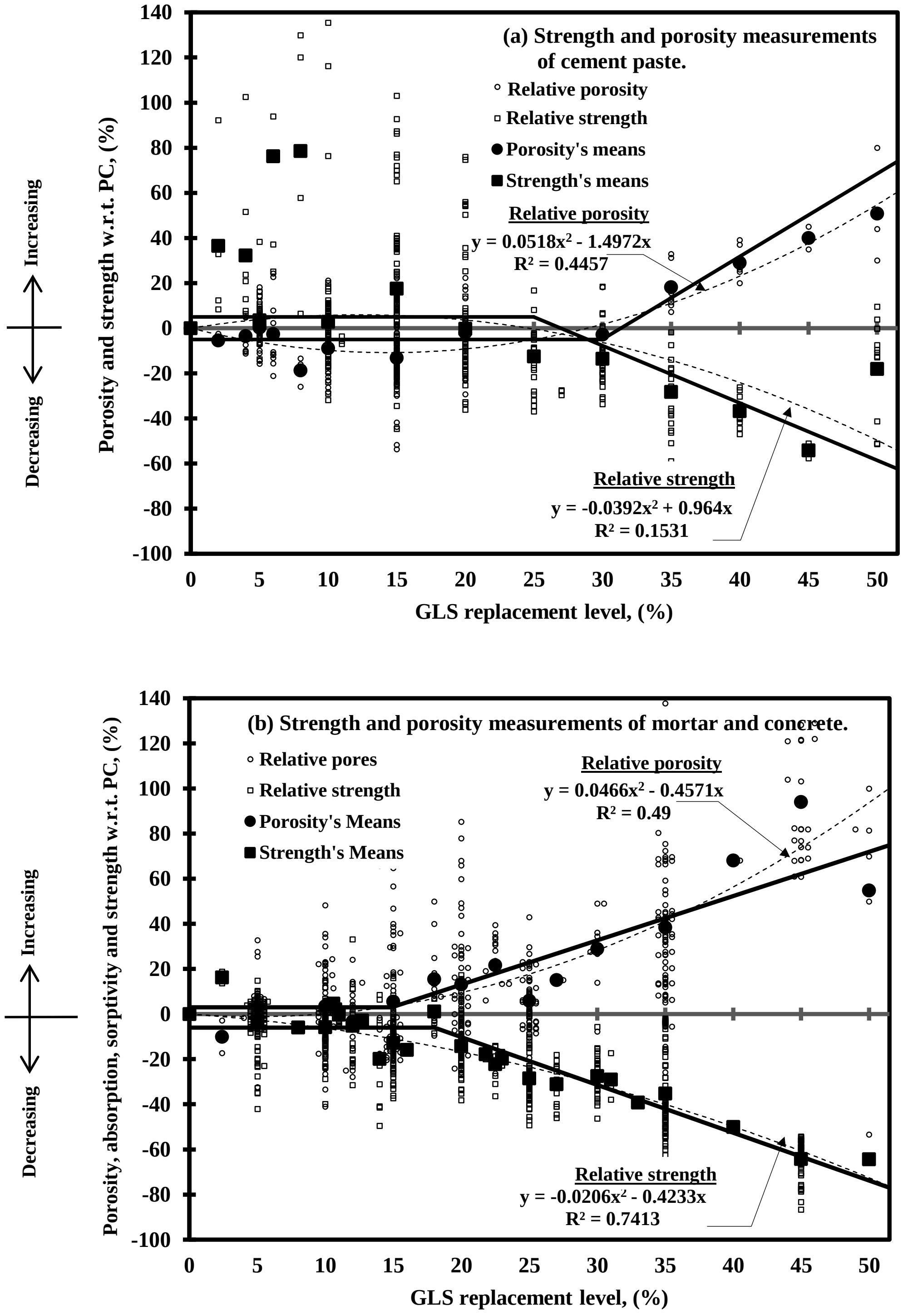


Figure 4.7: Effect of GLS addition as cement component on porosity and porosity related properties and strength development of (a) cement paste and (b) mortar/concrete mixtures. (Elgalhud et al., 2016)

Data of Figure 4.7 taken from Figures 4.1, 4.2, 4.3, 4.4, and 4.5

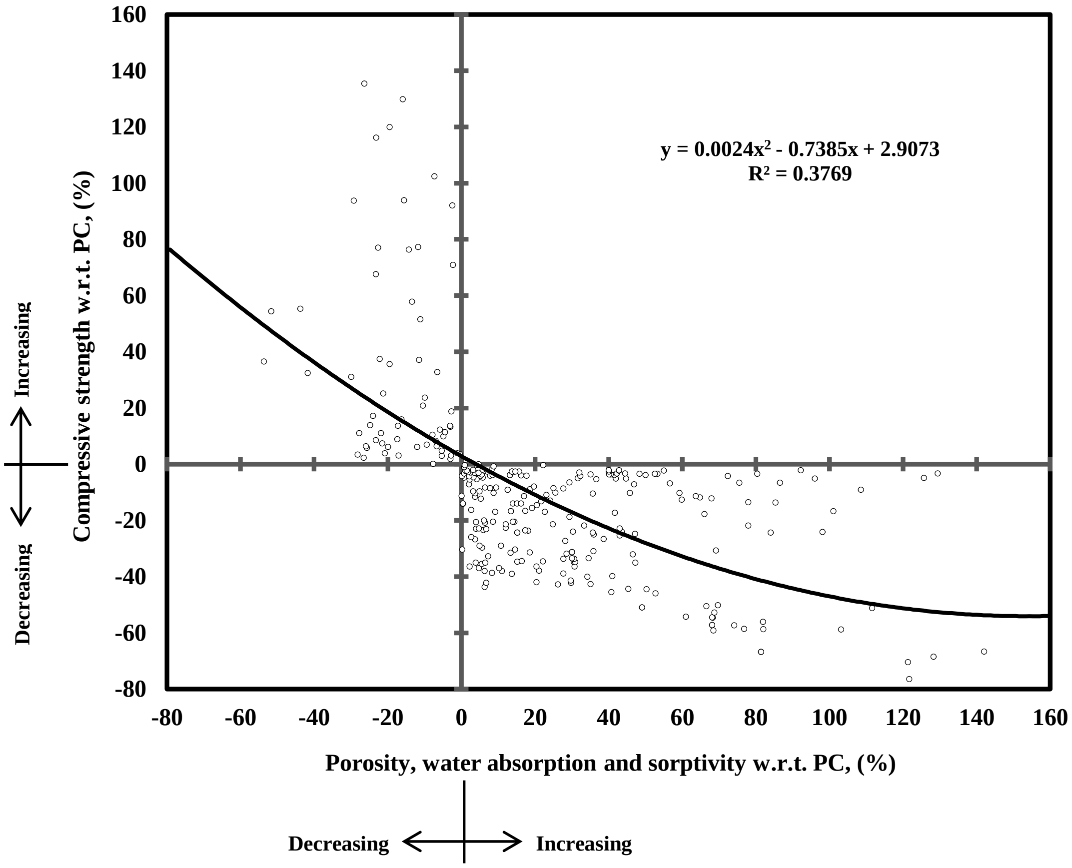


Figure 4.8: Strength verses porosity, absorption and sorptivity of cement paste, mortar and concrete mixtures (Elgalhud et al., 2016)

Data of Figure 4.8 taken from Figures 4.1, 4.2, 4.3, 4.4 and 4.5

4.6 Factors Affecting the Pore Structure of PLC Mixtures

This section considers other parameters that may influence the GLS addition effect on the pore structure of concrete, as follows:

4.6.1 Type of Portland Cement and Ground Limestone

There are a limited number of results on the effects of the chemical composition of Portland cement and GLS on the porosity and sorptivity of cement paste (Chowaniec, 2012) and concrete (Menadi and Kenai, 2011; Moir and Kelham, 1993; Sezer et al., 2010, Tsivilis et al., 1999).

Given the simplified expression used for the complex Portland cement chemistry, for example, in the form of C_3S, C_2S, C_3A and C_4AF, which can easily lead to large variations with small changes in the commonly measured oxide composition and likewise the inability to define finely the compositional make-up of GLS, the PLCs can vary easily with minor changes in the composition of the PC and GLS. Such difficulties in using data arising from different sources make it difficult to establish a definitive correlation between the state of the pore structure of PLC and its chemical composition. Nevertheless, the main findings of each set of results obtained are summarised as follows:

- The results on the porosity and sorptivity of cement paste of two Portland cements having different C_3A contents used with GLS addition showed no clear trend for the effect on the performance of PLC and no conclusion could be drawn between the amount of C_3A in the PLC and its pore structure (Chowaniec, 2012).

- Two types of Portland cement and GLS each were tested, and no considerable difference was observed between the microstructures of the resultant cement pastes. Even so, the cement paste with lower porosity was attributed to its higher C_3S/C_2S ratio giving rise to a higher rate of hydration, so that more hydration products were formed at the studied ages (2 and 28 days) and a denser microstructure was obtained. The change in GLS type (chemical composition), however, was considered not to significantly affect the porosity of the blended cement (Sezer et al., 2010).

- The sorptivity results of PLC concrete with two different clinkers and three types of GLS revealed that, depending on the PC composition and the cement fineness, there is an optimum GLS content at which the sorptivity of concrete is minimum. The analysis of the results obtained showed the optimum GLS content to be about 15% in this case (Tsivilis et al., 1999).

- Two different samples of commercially available PLC (CEM II/A-L 42.5) were tested and no significant effect on the sorptivity of the produced concrete was noticed (Menadi and Kenai, 2011). However, it was observed that the chemical compositions of the two cements were very similar.

- The effects on porosity and sorptivity of concrete with GLS addition, using five different Portland cements and GLS samples at 5% and 25% addition levels, were examined. Although differences in the measured results of up to 10% with GLS type were recorded, no explanation was put forward, probably because the differences were considered to be insignificant (Moir and Kelham, 1993).

4.6.2 Method of Producing and Fineness of PLC

A number of porosity and sorptivity measurements involved two different methods of producing PLC, namely inter-grinding and blending, with GLS content at 10% or 20% (Ghiasvand et al., 2015, Tsivilis et al., 1999). The fineness of the PLC varied from 3640 to 5980 cm^2/g. The concrete mixes were prepared using a constant water/cement ratio of 0.5 or 0.65 and water cured at 20°C for 28, 90 and 150 days. The results showed that, for all intents and purposes:

(i) The pore structure of the concrete, measured in the form of porosity and/or sorptivity for a given fineness of PLC, is not significantly affected, whether it is produced by inter-grinding or blending.

(ii) For a given concrete, in terms of its water/cement ratio, curing and age at test, the fineness of PLC can be expected to lead to some improvement in its pore structure, through the better particle packing achieved.

4.6.3 Curing

The results for the effects of curing on the pore structure of cement paste and concrete incorporating GLS as a component of cement are limited (Weerdt et al., 2012; Moir and Kelham, 1993). Indeed, they are also cursory, as one group of results are for only 5% GLS, which is within the permissible limit for minor additions to Portland cement clinker in BS EN 197-1:2011. As to be expected, PC and PLC that underwent moist storage produced almost similar performance, with respect to curing temperature ranging from 5°C to 40°C and duration of curing up to 180 days. The other group of results, which were for cements with 0%, 5% and 25% GLS content in concrete having a water/cement ratio of 0.6 and curing in water and air for 28 days, showed higher values for porosity and sorptivity at 25% GLS content with water curing, and much higher with air curing.

4.6.4 Maturity and Water/Cement Ratio

Figures 4.9 and 4.10 have been developed based on the results obtained from an examination of the influence of maturity (curing age) and water/cement ratio on the effects of GLS addition on the pore structure of cementitious mixtures in the form of cement paste, mortar and concrete. For these figures, the results of porosity, absorption and sorptivity were considered together to reflect the pore structure of cementitious mixtures and expressed relative to the corresponding mixes without GLS. Furthermore, to eliminate the effects of curing, only the data obtained with water curing, and moist curing with relative humidity greater than 90%, were used. Nevertheless, given that the obtained correlations for the trend lines are poor, the results, though helpful, should be used qualitatively.

Figure 4.9 shows that PLC concrete is noticeably more sensitive to moist curing than PC concrete and makes three useful points for developing the use of GLS as a cement component in concrete:

- PLC concrete would require some initial moist curing to develop a pore structure of denseness similar to that of the corresponding PC concrete. Apart from strength, sound pore structure in concrete is critical in developing its general resistance to deterioration, so curing factor should be considered carefully when deciding on the use of GLS as a component of cement in specifying concrete.

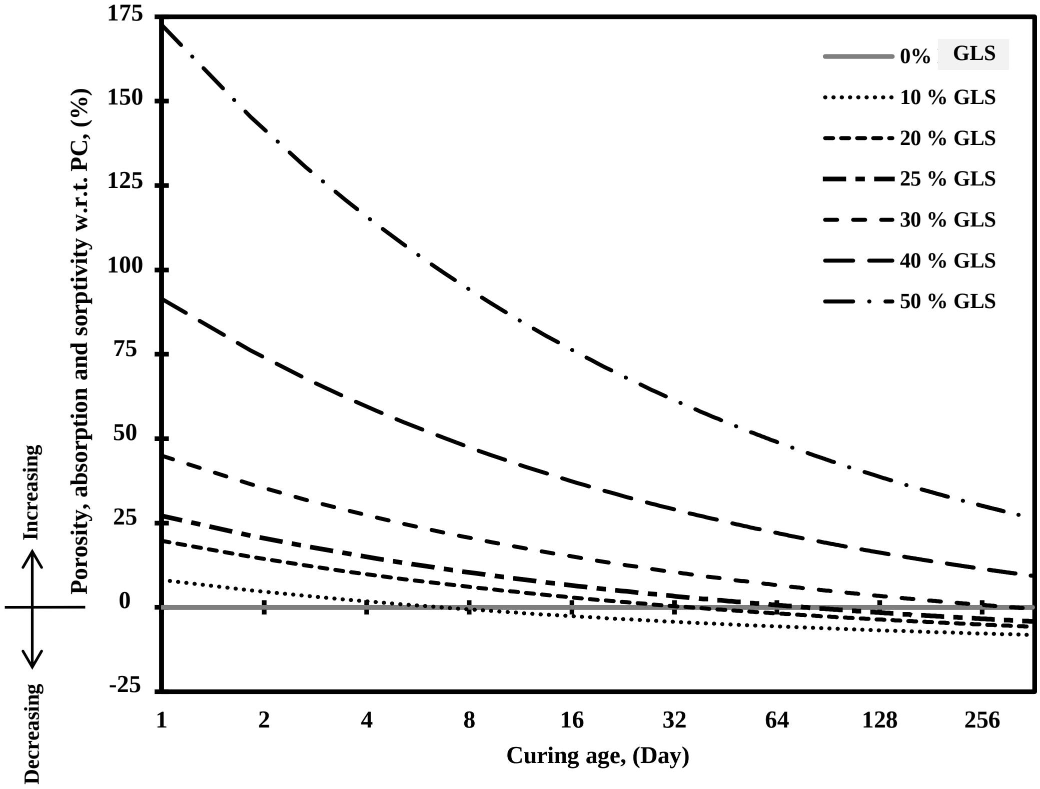


Figure 4.9: Relative porosity, absorption and sorptivity verses the curing age (Elgalhud et al., 2016)

Figure 4.9 has been developed based on the data in Figures 4.1, 4.2, 4.3 and 4.4

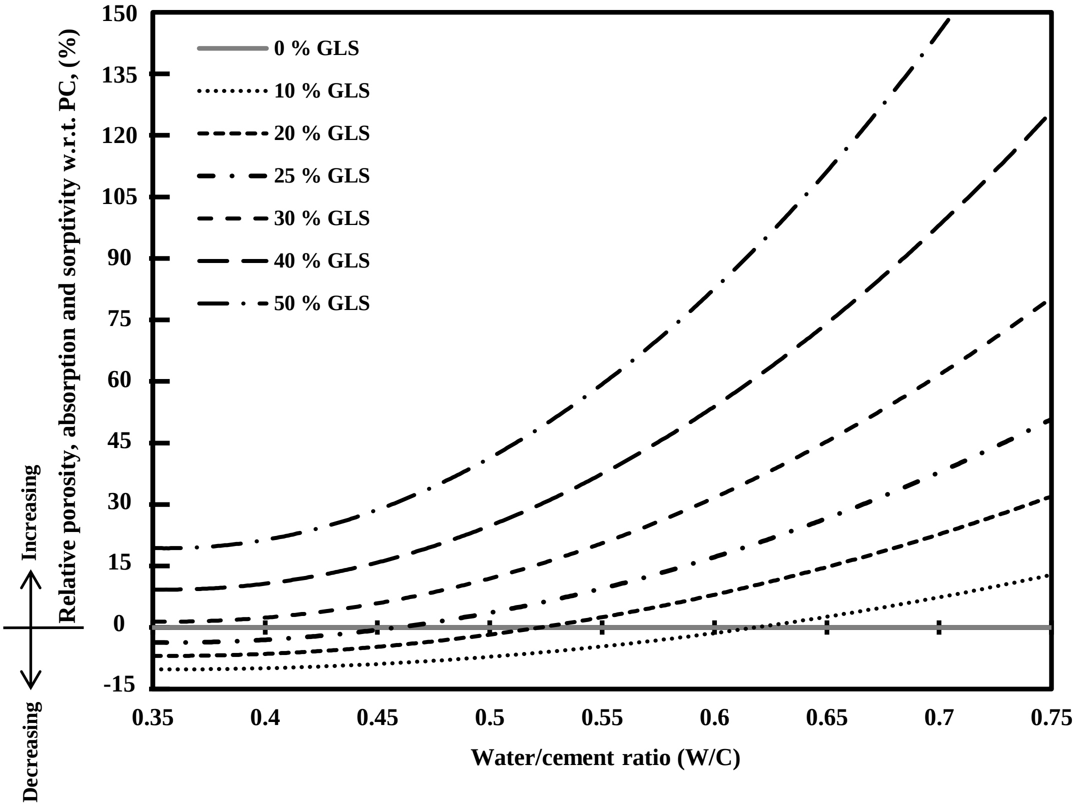


Figure 4.10: Relative porosity, absorption and sorptivity verses water cement ratio (Elgalhud et al., 2016)

Figure 4.10 has been developed based on the data in Figures 4.1, 4.2, 4.3 and 4.4

- Although the required duration of moist curing for PLC concrete to match the pore structure of PC concrete increases with GLS content, it does exceed 1 month with GLS content in the region of 25%.

- The rate of improvement in the pore structure of PLC concrete with moist curing increases with GLS content, but nevertheless it is unlikely that above a certain GLS content, in the region of 25%, the PLC concrete will ever, within a reasonable timescale, develop a pore structure with denseness similar to that of PC concrete.

In developing Figure 4.10, because of the limited data, pore structure and related measurements such as porosity, absorption and sorptivity taken at 28 days with water curing or moist curing with relative humidity greater than 90% were used. This figure shows how the use of GLS as a proportion of cement content may influence the changing pore structure with water/cement ratio and makes the following main points:

- Whilst, as to be expected, the pore structure of concrete improves with decreasing water/cement ratio relative to PC concrete, this effect is also influenced by GLS addition.

- The rate of the above influence may generally be constant with low water/cement ratios, up to about 0.40, and thereafter the pore structure is adversely affected at an increasing rate with increasing water/cement ratio and increasing GLS content.

- The maximum GLS content with moist curing of 28 days is about 25% at a water/cement ratio of between 0.45 and 0.50. Higher water/cement ratios of up to 0.70 may be used if the GLS content is reduced.

4.6.5 Ground Limestone with other Additions

As the new national and international standards such as BS EN 197-1:2011 and BS EN 206:2013 are accepted in practice, the use of composite cements can be expected to grow. The information available on this aspect of GLS addition is summarised in Table 4.4, from which the following main points can be ascertained:

- GLS in combination with PFA: This can improve the pore structure and related properties, such as porosity, absorption and sorptivity, of cement paste, mortar and concrete. However, this improvement is limited up to a certain level of addition, beyond which the opposite happens.

- GLS in combination with GGBS: This performs in the same manner as PFA and, depending upon the addition level, can be beneficial.

- GLS in combination with MS: When properly used, this combination improves the pore structure and related properties of the end product (in the form of cement paste, mortar and concrete).

- GLS in combination with MK: This combination is similar to GLS and MS.

Table 4.4 also suggests that the beneficial effects of these additional materials are generally realised through improvement in the process of hydration, linked with the fineness and chemical composition, in particular the alumina content, leading to additional carboaluminate hydrates and thereby creating a denser cement paste (Ramezanianpour and Hooton, 2014).

Table 4.4: Summary of the published findings concerning the effect of Portland limestone composite cement on the pore structure and related properties[a] (Elgalhud et al., 2016)

TYPE OF EFFECT		MAJOR SUGGESTED CAUSES			
		PFA	GGBS	MS	MK
Higher	**Tested mixes**	**2**	**5**	**2**	**0**
		No clarification.	No clarification.	The increase in volume of pores could be attributed to the absence of a plasticizing agent in the studied ternary mixes, in which MS and GLS cannot act as effective fillers.	--
Lower	**Tested mixes**	**5**	**8**	**5**	**3**
		Finer pore structure due the fineness of PFA and GLS collectively. Hydration products resulting from PFA reaction are able to fill the pores and participate in the formation of gel paste.	Fineness of the GGBS results in denser microstructure produced by lower calcium hydroxide content in which it has the effect of improving the hydration mechanism and the pore filling. Higher content of alumina in the mix (act as nucleation sites), GLS could participate in the hydration process by forming more carboaluminate hydrates, thus denser cement paste.	The pore packing and pozzolanic effects of MS results in a considerable reduction in the pore size and the connectivity of the cement matrix.	The addition of MK increase alumina content in the whole mixture, where it allows more GLS to participate in the hydration reactions, creating additional carboaluminate hydrates.
Variable	**Tested mixes**	**5**	**3**	**0**	**0**
		Decreases until certain level and then increases due to dilution of Portland cement clinker. No clarification.	Decreases until certain level and then increases due to dilution of Portland cement clinker. No clarification.	--	--
Unclear	**Tested mixes**	**11**	**4**	**5**	**3**
		No reference/control PLC mix.	No reference/control PLC mix.	No reference/control PLC mix.	No reference/control PLC mix.

[a] Data of Table 4.4. taken from Abd-El-Aziz and Heikal, 2009; Aguayo et al., 2014; Allahverdi and Salem, 2010; Barluenga et al., 2013; Barrett et al., 2014a; Barrett et al., 2014b; Bouasker et al., 2014; Cam and Neithalath, 2010; Celik et al., 2014b; Celik et al., 2015; Courard and Michel, 2014; Das et al., 2014a; De Weerdt et al., 2010; De Weerdt et al., 2011a; De Weerdt et al., 2011b; De Weerdt et al., 2011c; El-Alfi et al., 2004; Gao et al., 2013; Gesoglu et al., 2012; Githachuri and Alexander, 2013; Heikal et al., 2003; Hoshino et al., 2006; Irassar et al., 2006; Irassar et al., 2001; Liu and Wang, 2014; Liu et al., 2014; Menendez et al., 2007; Panesar and Francis, 2014; Ramezanianpour and Hooton, 2014; Segura et al., 2013; Thongsanitgarn et al., 2014; Turkel and Altuntas, 2009; Zelic et al., 2000; Zhang and Ye, 2012

A variable effect has been observed with the use of PFA and GGBS, whereby an enhancement of the pore structure was present until a certain limit and thereafter the volume of the pores increased owing to the dilution of Portland cement.

Although a few results showed that the use of additions to PLC to form composite cements adversely affected the pore structure of the resulting product, this has been observed to be due to improper use of the additions, such as using MS without a water-reducing admixture (Allahverdi and Salem, 2010).

4.7 Improving PLC Performance in Practice

Although the standards allow up to 35% GLS addition to the cement for making concrete, global results analysed in this study suggest that PLC with GLS content greater than 15%–25% may adversely affect the porosity of concrete, and thereby its overall performance in structures, and in terms of strength the maximum amount of GLS that can be considered safe to use is more likely to be about 15%. However, this situation can be improved by reducing the water demand of the concrete mix, as suggested in a previous study (Dhir and Hewlett, 2008), by:

(i) optimising particle packing by revising the proportions of coarse and fine aggregates and/or introducing the use of fillers;
(ii) adopting the use of water-reducing admixtures, particularly polycarboxylate ether (PCE)-based products;
(iii) developing the use of GLS with other additions such as small proportions of MS and MK, as mentioned previously.

Such applications are being successfully adopted in the use of concrete in practice, and in this case could help to develop a greater and more assured outlet for the use of GLS in concrete and, at the same time, further improve its pore structure and thereby its general performance in terms of engineering properties and durability.

4.8 Conclusions

Based on the analysis, structuring and evaluation of the pore structure and strength results obtained, the following conclusions are made:

a. The pore structure and related properties (porosity, absorption and sorptivity) of cementitious mixtures (paste, mortar and concrete) remain unimpaired up to a maximum 25% addition of GLS to PC, and beyond this threshold the pore structure of the PLC would begin to deteriorate, which for practical purposes can be assumed to take place at a constant rate with increasing GLS content. The GLS addition levels vary in national and international standards, ranging from 10% to 35% (as presented previously in Table 3.1 in chapter 3).

b. Although the addition of GLS to PC does not affect the relationship between the pore structure of the end product and its strength, the limit on GLS content for the strength to remain unchanged is likely to be less than that for the pore structure.

c. Variations in the chemical composition of PC and GLS do not show a clear relationship with porosity, water absorption and sorptivity of cement paste or mortar/concrete.

d. Combinations of PC and GLS after grinding separately or by inter-grinding show no notable change in the pore structure properties, whereas a significant increase in the fineness of PLC can lead to some reduction in the porosity of the end product in the form of cement paste, mortar and concrete.

e. The effects of curing temperature on the pore structure of PLC paste at 5°C–40°C showed that, similar to PC, the PLC paste pore structure is adversely affected by an increase in temperature. However, as very limited results were obtained in this regard, this cannot be considered a definitive conclusion, particularly when the GLS content used was similar to the permissible limit for minor additions in the PC.

f. Similar to Portland cement, water curing of PLC concrete was found to improve its pore structure in comparison to air curing.

g. The condition of the pore structure of cement paste, mortar and concrete made with PLC improves with curing age (maturity), particularly during the first 7 days, after which the improvement progresses steadily up to the age of 28 days and beyond.

h. To achieve pore structure comparable to that of PC with 28-day moist curing at a water/cement ratio of between 0.45 and 0.50, the GLS content in PLC should be limited to a maximum value of 25%.

i. The composite mixture of PLC with other additions may show a complementary effect on the pore structure of cement paste, mortar and concrete. However, this improvement is limited to a certain level of addition, beyond which the opposite happens.

CHAPTER 5

CARBONATION RESISTANCE OF PLC CONCRETE

5.1 Introduction

This chapter defines the details of the effects of ground limestone (GLS) used as a cement component on the carbonation and carbonation-induced corrosion resistance of concrete. The influence of strength and w/c ratio in both natural and accelerated exposures was examined. Other influencing factors, curing, limestone fineness and total cement content, were also studied. In addition, a comparison has been conducted on the carbonation performance of concrete made with Portland limestone cement (PLC) and cement containing pulverised fuel ash (PFA) and ground granulated blast furnace slag (GGBS). Additionally, the conversion factor to convert from accelerated carbonation exposure to natural indoor exposure was determined.

5.2 Overview of the Literature

Although limited in number, and without detailed analysis of the data, both the individual and the organisational reviews (Table 5.1) suggest that there is a consensus amongst these reviewers that the carbonation resistance of concrete is not significantly altered with the addition of up to 15%–20% GLS (i.e., cements such as Portland limestone cement, CEM II/A in BS EN 197-1). However, the reviews provided by the national cement/concrete organisations in Canada, Sweden, the United Kingdom and the United States concluded that at a given water/cement ratio, the use of GLS addition as a cement component (i.e., the use of PLC as per BS EN 197-1) can potentially be expected to increase its carbonation, albeit in some cases, and up to certain level of GLS addition, it may not be significant in the context of overall concrete mix variations. However, the mixes designed on an equal strength basis with PLC can be expected to carbonate at a rate similar to that of Portland cement (PC) concrete.

Table 5.1: Summary of the findings of the narrative reviews regarding the carbonation of the PLC concrete (Elgalhud et al., 2017a)

REFERENCE	NO. OF CITED REFERENCES	MAIN OBSERVATION
a. Organization		
Hooton et al., 2007; Cement Association of Canada.	6	The GLS has the potential to increase the carbonation of concrete.
Lagerblad, 2005; Swedish Cement and Concrete Research Institute CBI, Sweden.	1	The PLC concrete will carbonate somewhat faster as the amount of Portland clinker cement paste and the buffering capacity is less than in the corresponding PC concrete.
Detwiler and Tennis 1996; Hawkins et al., 2003; PCA, USA	9	The literature review shows mixed results of PLC when compared to PC. The variances are of restricted practical significance in the context of over all concrete mix parameters.
Tennis et al., 2011; PCA, USA	6	PLC concrete will carbonate at a comparable rate as PC concrete, providing that concretes are prepared for equal target strength.
CSWP, 2011; Concrete Society, UK	2	PLC increases the rate of carbonation when concretes are produced at a constant w/c. Whereas, PLC has similar carbonation to PC when both concretes are designed to meet an equal strength.
b. Individual		
Ayub et al., 2013	1	The inclusion of GLS addition leads to an increase in the carbonation of concrete, excepting when the level of replacement is 15% or less.
Müller, 2012	1	The use of GLS addition up to 20% could increase slightly the carbonation depth.
Torgal et al., 2012	3	No considerable influence on carbonation resistance with limestone content up to 15%.

On the other hand, an overview of the reported data relating to the effects of GLS addition to PC on the carbonation of concrete (PLC concrete), when subjected to both natural and accelerated exposures, as presented in Table 5.2 (Elgalhud et al., 2017a), revealed that the vast majority of the results of the tested mixes (76%) show that the inclusion of GLS leads to a higher rate of concrete carbonation. In contrast, only 9% of the reported data suggest that the carbonation of PLC concrete can be lower than that of the corresponding PC concrete, 3% indicate no change and 4% show a variable trend; and for 8% of the reported results there were no corresponding PC concrete mixes tested and therefore the PLC data could not be compared with the corresponding PC concrete mixes.

5.3 Variation in the Testing Procedures Used

The test conditions employed to measure the effects of GLS on the resistance of concrete to carbonation using both accelerated and natural exposures are summarised in Table 5.3. Whilst the first impression can be that widely varying conditions have been applied to measure the carbonation resistance of both PC and PLC test concrete mixes, in reality the majority of the test parameters in general have been kept within an acceptable range. The main points emerging from Table 5.3 (Elgalhud et al., 2017a) are as follows:

(i) **Carbonation exposure:** Surprisingly, natural exposure was adopted more than accelerated exposure in the testing of concrete for carbonation, in a ratio of 3 to 2, and within it, indoor exposure was used the most.

(ii) **Specimens:** Whilst the choice of test specimens in the form of cylinders, prisms and cubes appeared to be influenced by the relevant standard specifications adopted in a specific study, a large number of tests were carried out using prisms. Moreover, in most cases information on how the specimens were prepared for testing was not provided.

Table 5.2: Summary of the published findings concerning the effect of GLS on carbonation phenomenon[a]

OBSERVATION* OF CARBONATION DEPTH OF PLC MIXES	MAIN SUGGESTED CAUSES		NUMBER OF TESTED MIXES		
			Accelerated	Natural	Total
Higher (455) Accelerated (155) Natural (300)	**Cement**	Reduction of Portland cement clinker	32	49	81
		Limestone plays as a nucleation site for $CaCO_3$ precipitation	4	0	4
	Design	Low cement content	8	11	19
		Higher water/cement ratio	10	12	22
		Insufficient curing	17	29	46
		High CO_2 concentration	2	0	2
	Hardened properties	Reduction of $Ca(OH)_2$	12	19	31
		Higher porosity/Coarser pore structure	24	35	59
		Higher permeability	0	12	12
		Low strength	6	9	15
		Reduction of alkalinity	6	0	6
		Not given	53	105	158
Lower (51) Accelerated (21) Natural (30)	**Cement**	Higher specific area of limestone	0	5	5
	Design	Lower water/cement ratio	2	2	4
		Sufficient curing	2	3	5
		Higher strength	1	2	3
	Hardened properties	Lower porosity	0	5	5
		Not given	10	19	29
No change (16) Accelerated (8) Natural (8)		Equal strength	0	4	4
		Low w/c	1	0	1
		Not given	7	4	11
Variable (25) Accelerated (1) Natural (24)		Not given	1	24	25
No reference mixture (47) Accelerated (34) Natural (13)		Not applicable	34	13	47

* Higher/lower/no change/variable of carbonation depth of GLS mixture w.r.t corresponding reference PC mixture.

a: Data of Table 5.2 taken from: Abualgasem et al., 2014; Ali and Dunster, 1998; Alunno-Rosetti and Curcio, 1997; Assie et al., 2006; Assie et al., 2007; Balayssac et al., 1995; Balcu et al., 2012; Barker and Matthews, 1994; Baron, 1986; Batic et al., 2013; Bertolini et al., 2007; Bertolini et al., 2008; Bertolini et al., 2009; Bertrandy and Poitevin, 1991; Bolzoni et al., 2006; Bolzoni et al., 2014; Cangiano and Principgallo, 2010; Catinaud et al., 2000; Chowaniec and Karen, 1992; Collepardi et al., 2004a; Courard et al., 2005; Courard et al., 2014; Corinaldesi et al., 2004; Diamanti et al., 2013; Dhir et al., 2004; Dhir et al., 2007; Drouet et al., 2010; El-Hassan and Shao, 2015; Figueiras et al., 2009; Franzoni et al., 2013; Frazão et al., 2015a; Frazão et al., 2015b; Galan et al., 2010a; Galan et al., 2010b; Galan et al., 2012; Holt et al., 2009; Holt et al., 2010; Hussain et al., 2013; Ingram and Daugherty, 1992; Kaewmanee and Tangtermsirikul, 2014; Kargol et al., 2013; Kjellsen et al., 2005; Kuosa et al., 2008; Kuosa et al., 2012; Kuosa et al., 2014; Krell, 1989; Leemann et al., 2015; Livesey, 1991; Lollini et al., 2014; Manns et al., 2001; Marques et al., 2013; Meddah et al., 2014; McNally et al., 2012; Meira et al., 2014; Moir and Kelham, 1993; Matthews, 1994; Moir and Kelham, 1999; Neves et al., 2015; Nieuwoudt et al., 2012; Owsiak and Grzmil, 2015; Perlot et al., 2013; Pomeroy, 1993; Müller et al., 2006; Müller et al., 2014; Mwaluwinga et al., 1997; Nielsen et al., 2014; Parrott, 1994; Parrott, 1996; Phung et al., 2015; Proske et al., 2014; Proske et al., 2013; Rabehi et al., 2013; Redaelli and Bertolini, 2014; Redaelli et al., 2011a; Redaelli et al., 2011b; Ranc et al., 1991; Révay and Gável, 2003; Rio et al., 2015; Rozière et al., 2011; Schmidt, 1992a; Schmidt, 1992b; Schmidt et al., 1993; Segura et al., 2013; Sistonen et al., 2008; Shi et al., 2015; Silva and Brito, 2015; Sprung and Siebel, 1991; Rostami et al., 2012; Shao et al., 2013; Tezuka et al., 1992; Thomas et al., 2010d; Thomas et al., 2013; Thienel and Beuntner, 2012; Tschegg et al., 2011; Tsivilis et al., 2000; Tsivilis et al., 2002a; Vandanjon et al., 2003; Ylmen et al., 2013.

Table 5.3: Compilation of test parameters of the carbonation measurements obtained[a]

	PARAMETER	**VARIABLE**	**NO.**			**PARAMETER**	**VARIABLE**	**NO.**
1. CARBONATION	Accelerated **(219)**	-	219	**2. SPECIMEN**		Specimen **(594)**	Cylinder	143
							Prism	307
	Natural **(375)**	Indoor	200				Cube	128
		Outdoor, sheltered	132				Not given	16
		Outdoor, unsheltered	18			Preparation **(594)**	Sealed	116
		Outdoor, not given	10				Unsealed	22
		Not given	15				Unspecified	456
3. CURING	Exposure **(594)**	Moist	499	**4. PRE-CONDITIONING**		Preparation **(594)**	Omitted	12
		Air	45				Applied	226
		Not given	50				Not given	356
	Duration, days **(594)**	1-14	327			Duration, days **(226)***	1-7	39
		15-28	166				14-28	115
		56-91	40				76-351	45
		>91	7				Not given	27
		Not given	54			Temp, °C **(226)***	20-30	169
	Temp, °C **(594)**	20-30	522				35-80	43
		>30	3				Not given	14
		Not given	69					
	Humidity, % **(594)**	80-100	485			Humidity, % **(226)***	45-85	186
		40-80	37				Not given	40
		Not given	72					
5 (a). ACCELERATED EXPOSURE CONDITIONS	CO_2, % **(219)**	<3	48	**5 (b). NATURAL EXPOSURE CONDITIONS**	**Indoor**	Duration, years **(200)**	<1	92
		3-5	90				1-5	108
		6-10	10			Temp, °C **(200)**	20-25	192
		20-100	68				Not given	8
		Not given	3					
	Duration, days **(219)**	≤30	131			Humidity, % **(200)**	40-65	189
		31-90	53				Not given	11
		91-180	13		**Outdoor**	**Sheltered:** Duration, years **(132)**	<1	48
		>180	21				1-3	47
		Not given	1				4-9	37
	Temp, °C **(219)**	<20	1			**Unsheltered:** Duration, years **(18)**	<1	12
		20-30	203				1-4	6
		>30	10					
		Not given	5			**Unspecified:** Duration, years **(10)**	≤1	10
	Humidity, % **(219)**	<50	6					
		50-60	49					
		61-80	159		**Not given**	Duration, years **(15)**	≤1	15
		Not given	5					
6. MEASUREMENT: Method (594): Phenolphthalein (554#), Not given (40)								

Note: Number in parenthesis is the sum of tested mixes in each individual parameter.

*: Data compiled from tests where pre-conditioning is applied.

#: Phenolphthalein concentration: 1% Phenolphthalein (17) and not given (537).

a: Data of Table 5.3 taken from the same references of Table 5.2

(iii) Curing: With the exception of some, and to a certain extent influenced by the local standard specifications, moist curing with relative humidity 80%–100%, temperature 20°C–30°C and duration of up to 28 days was generally adopted.

(iv) Preconditioning: Although this information was lacking in the majority of studies, where declared the commonly adopted treatment was carried out at a temperature of 20°C–30°C, relative humidity 45%–85% and duration of 14–28 days.

(v) Accelerated and natural exposure conditions: The commonly used accelerated exposure consisted of CO_2 concentration up to 5%, duration $\leq$30 days, temperature 20°C–30°C and humidity 61%–80%, whilst the natural indoor exposure was for a duration of up to 5 years.

(vi) Measurement: The vast majority of the tests utilised the phenolphthalein indicator to measure the depth of carbonation, whilst the rest did not declare the measurement method employed.

5.4 Limestone Effect

Given the large number of test parameters involved, as can be seen from Table 5.3, the effects of GLS addition on the carbonation resistance of PLC concrete have been analysed in terms relative to the corresponding PC concrete (used as reference). The results thus obtained are plotted in Figure 5.1, with the majority of the data being within the 5%–35% GLS replacement band. The scatter in the data is understandably high as their source was global and the variables involved were high. In developing Figure 5.1, some of the results were excluded from further consideration:

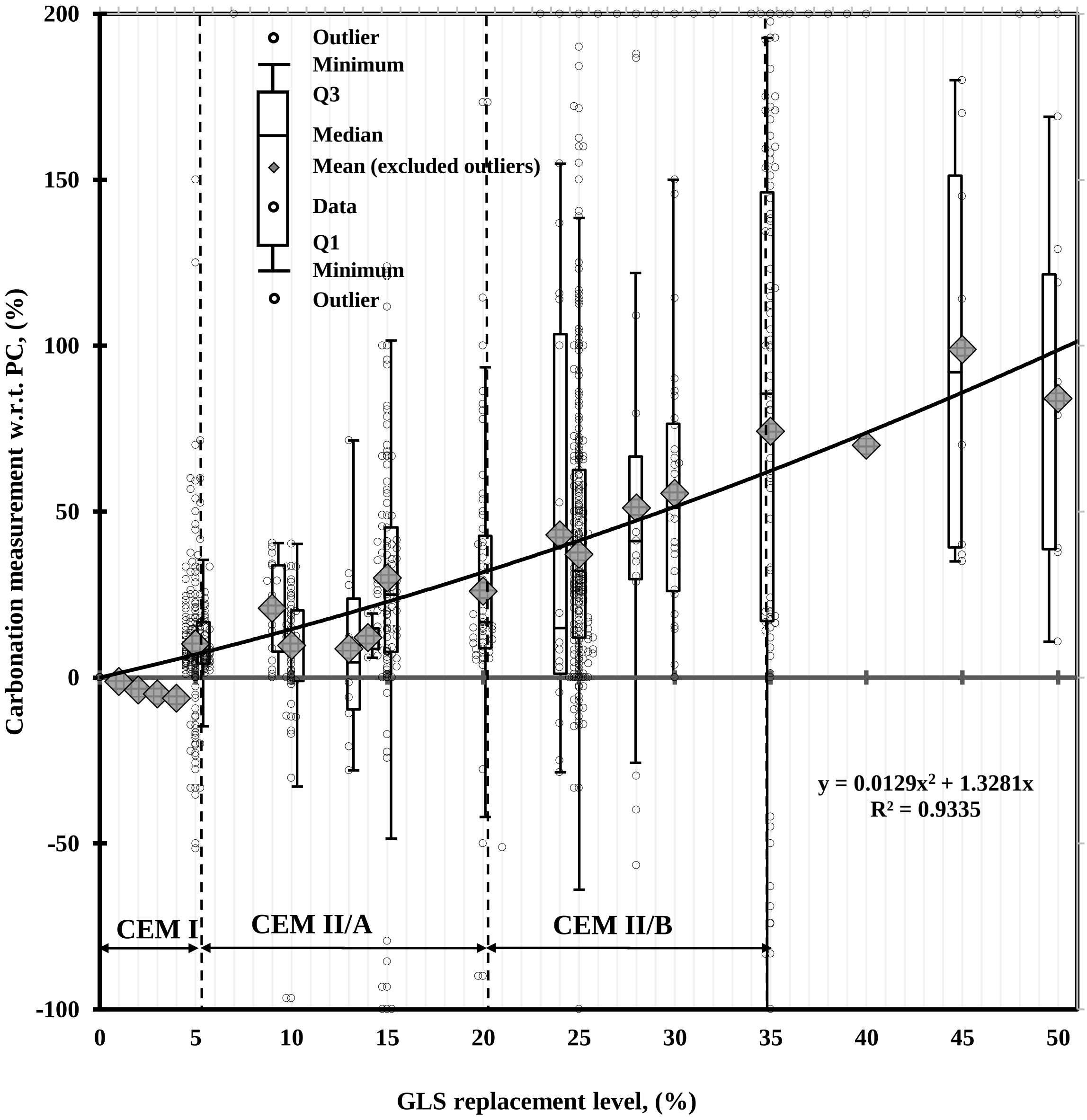


Figure 5.1: Ground limestone addition effect on carbonation resistance of concrete (Elgalhud et al., 2017a)

Data of Figure 5.1 taken from: Abualgasem et al., 2014; Ali and Dunster, 1998; Alunno-Rosetti and Curcio, 1997; Balayssac et al., 1995; Balcu et al., 2012; Barker and Matthews, 1994; Baron, 1986; Batic et al., 2013; Bertolini et al., 2007; Bertolini et al., 2009; Bertrandy and Poitevin, 1991; Cangiano and Principallo, 2010; Catinaud et al., 2000; Chowaniec and Karen, 1992; Collepardi et al., 2004a; Courard et al., 2005; Courard et al., 2014; Dhir et al., 2004; Dhir et al., 2007; Drouet et al., 2010; El-Hassan and Shao, 2015; Galan et al., 2010a; Galan et al., 2010b; Galan et al., 2012; Holt et al., 2009; Holt et al., 2010; Hussain et al., 2013; Ingram and Daugherty, 1992; Kaewmanee and Tangtermsirikul, 2014; Kargol et al., 2013; Kjellsen et al., 2005; Kuosa et al., 2008; Kuosa et al., 2012; Kuosa et al., 2014; Krell, 1989; Leemann et al., 2015; Livesey, 1991; Lollini et al., 2014; Manns et al., 2001; Marques et al., 2013; Meddah et al., 2014; Moir and Kelham, 1993; Matthews, 1994; Moir and Kelham, 1999; Neves et al., 2015; Pomeroy, 1993; Müller et al., 2006; Müller et al., 2014; Mwaluwinga et al., 1997; Nielsen et al., 2014; Parrott, 1994; Parrott, 1996; Phung et al., 2015; Proske et al., 2014; Proske et al., 2013; Rabehi et al., 2013; Ranc et al., 1991; Rozière et al., 2011; Schmidt, 1992a; Schmidt, 1992b; Schmidt et al., 1993; Shi et al., 2015; Silva and Brito, 2015; Sprung and Siebel, 1991; Rostami et al., 2012; Shao et al., 2013; Tezuka et al., 1992; Thomas et al., 2010d; Thomas et al., 2013; Tsivilis et al., 2000; Tsivilis et al., 2002b; Vandanjon et al., 2003.

- outliers at each GLS replacement level using box-and-whiskers plots

- Where the corresponding value for reference PC concrete was not available

- excessively high relative values (greater than 200%) resulting from low carbonation measurement, which were considered to be unrealistic

- results showing full carbonation of test specimens, as in such cases it was not possible to calculate the actual depth of carbonation

The best fit relationship presenting the effect of GLS on the carbonation of concrete for the mean values is also plotted in Figure 5.3, having a coefficient of determination $R^2 = 0.93$. The trend line shows that, as the addition of GLS increases, the relative carbonation of concrete increases at an increasing rate. For simplicity of reference, the range of BS EN 197-1:2011 (BSI, 2011) common cements with GLS addition has also been shown. It can be seen that at 35% GLS addition (the maximum limit permitted in BS EN 197-1:2011) the carbonation of PLC concrete could be about 62% higher than that of the corresponding PC concrete, whilst at 5% GLS inclusion the carbonation of PLC concrete could easily be assumed to be comparable to that of PC concrete.

5.5 Influence of Strength and Water/Cement Ratio

The results shown in Figure 5.1 are separated in terms of 28-day strength and water/cement ratio within natural and accelerated exposures and are plotted on the basis of:

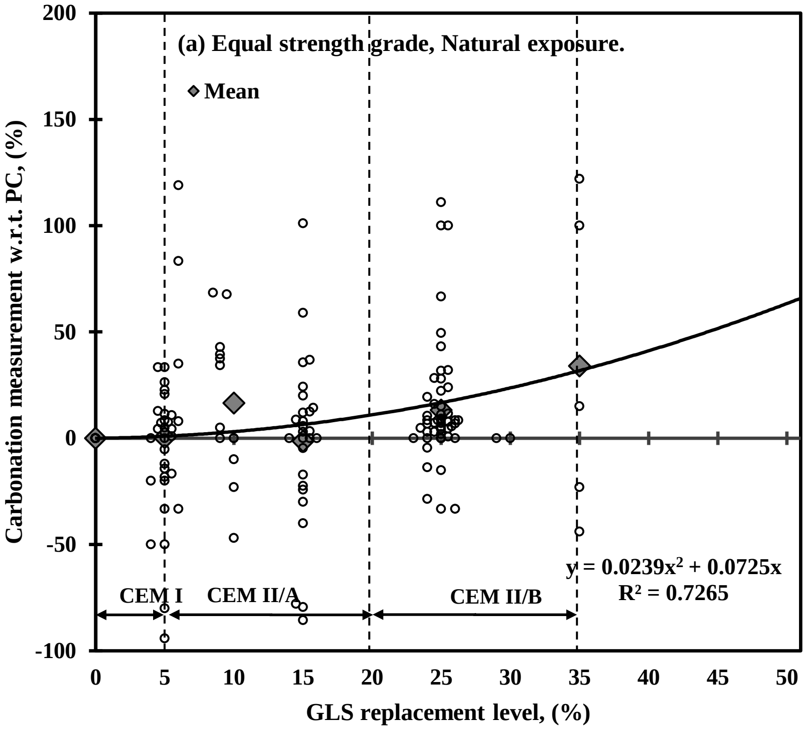
- equal strength, in Figure 5.2 (a) and (b)
- equal water/cement ratio, in Figure 5.3 (a) and (b).

These figures show that:

- The effect of PLC on the carbonation of concrete at equal strength, as to be expected, is less marked than at equal water/cement ratio, showing at 35% GLS content for natural exposure an increase of 32% [Figure 5.2 (a)] and 75% [Figure 5.3 (a)], respectively.

- Accelerated carbonation gives rise to higher carbonation compared with natural exposure, up to 58% on an equal concrete strength basis [Figure 5.2 (a) and (b)] and 85% on the basis of equal concrete water/cement ratio [Figure 5.3 (a) and (b)].

- When concrete mixes are designed on an equal strength basis, an addition of up to 10% GLS can be absorbed without giving rise to an increase in the carbonation of concrete. This facility is not available when the mixes are designed on an equal water/cement ratio basis.



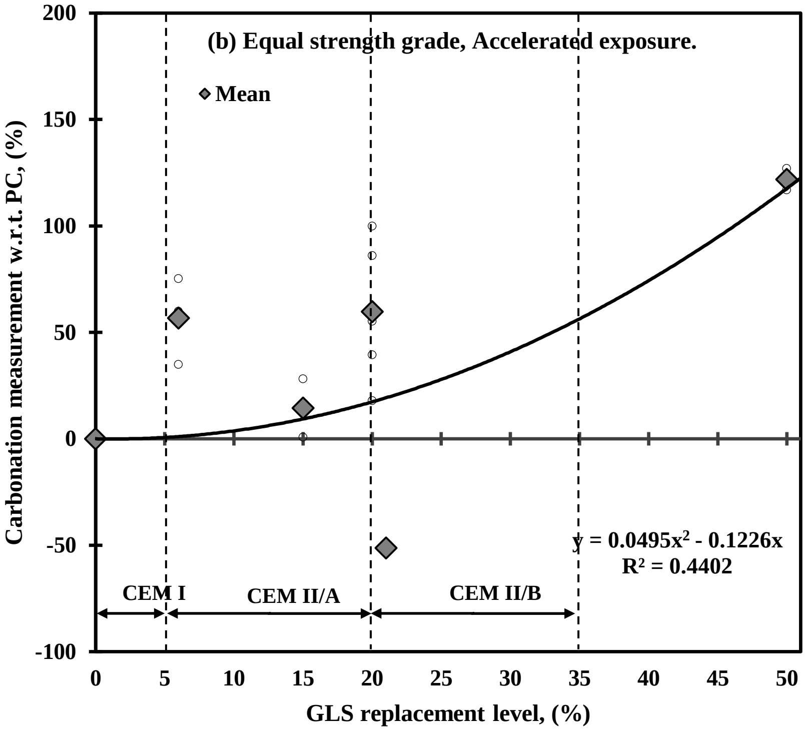
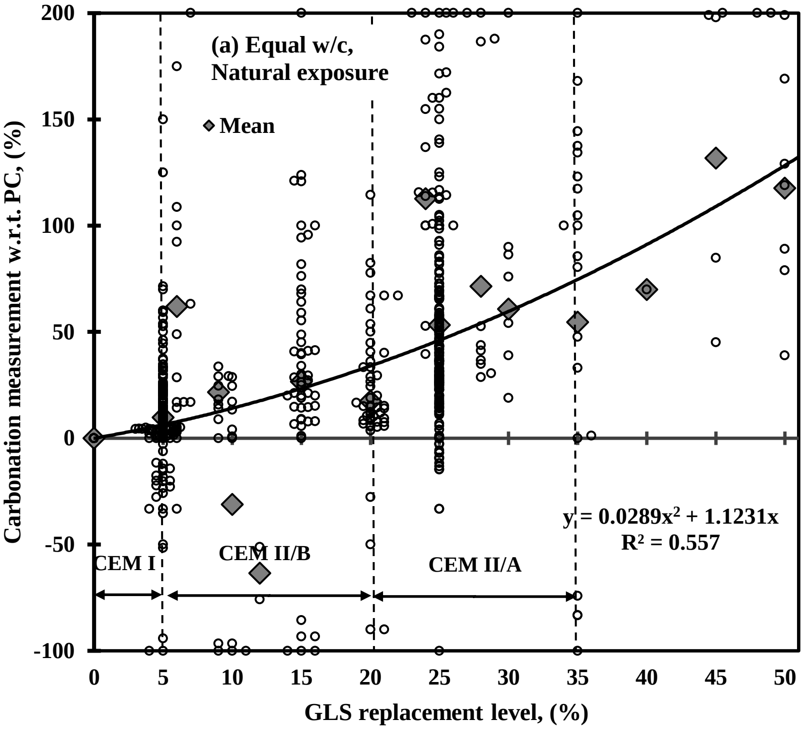


Figure 5.2: Influence of GLS on carbonation resistance of concrete at equal 28 d strength for (a) natural and (b) accelerated carbonation exposure (Elgalhud et al., 2017a)



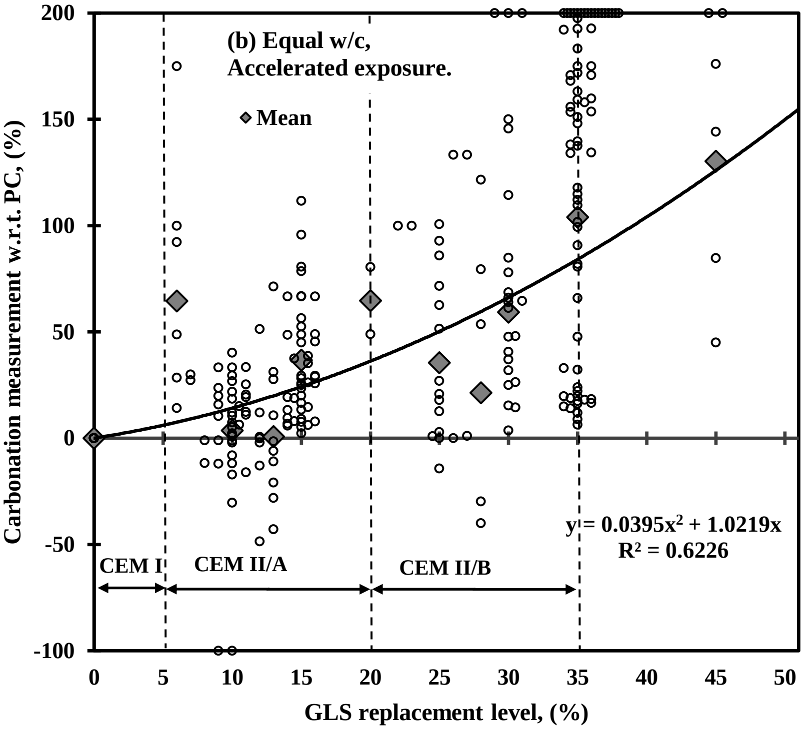


Figure 5.3: Influence of GLS on carbonation resistance of concrete at equal w/c ratio for (a) natural and (b) accelerated carbonation exposures (Elgalhud et al., 2017a)

5.6 Influence of Limestone Fineness

The results on the effects of GLS fineness on the carbonation resistance of PLC concrete were fairly limited. The carbonation measurements obtained using mortar mixes containing only 10% GLS of Blaine fineness essentially similar to that of PC (3320 and 3430 cm^2/g, respectively) showed an increase in carbonation depth of 30%, and increasing the fineness of the GLS from 3320 to 9260 cm^2/g reduced the difference to only 25% (Kaewmanee and Tangtermsirikul, 2014), suggesting that increasing the fineness of GLS to more than that of PC is not a viable solution for controlling the carbonation of PLC concrete.

5.7 Influence of Cement Content

Though not exhaustively, the effects of cement content on the carbonation of concrete have been examined over the cement range of 240–390 kg/m^3, with GLS content of 15%–30% and constant w/c ratios of 0.46–0.65, using accelerated carbonation exposure under the following conditions: moist curing for 28 days, temperature 20°C, relative humidity 55%–65%, CO_2 concentration 2%–5% and exposure duration up to 140 days (Dhir et al., 2004; Lollini et al., 2014 and Marques et al., 2013).

The results obtained are shown in Figure 5.4. Although the data are few, and at times appear to be conflicting, there is sufficient evidence to suggest that the carbonation of both concretes, PC and PLC, decreases at a slow rate with increasing cement content.

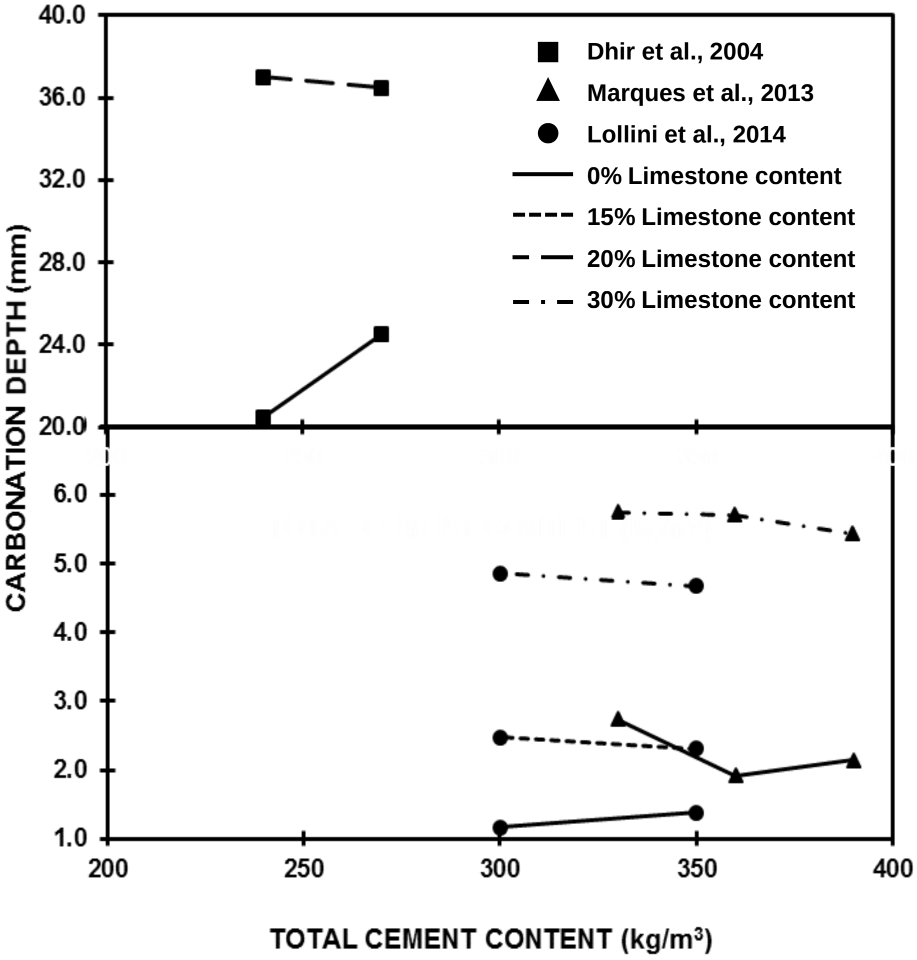


Figure 5.4: Influence of cement content on carbonation depth of PLC concrete exposed to accelerated carbonation (Elgalhud et al., 2017a)

5.8 Influence of Curing

5.8.1 Curing Conditions

The test parameters of the effects of curing on the carbonation of PLC concrete with w/c ratio varying from 0.45 to 0.76 and GLS content up to 35% have been limited to moist and air curing for a period of 28 days. Two types of exposure conditions were employed: accelerated, with temperature 20°C/30°C, relative humidity 60%/65% and CO_2 concentration 50%/4% with a test duration of 28/91 days, respectively, by Rabehi et al. (2013) and Hussain et al. (2013), and natural indoor and outdoor sheltered, for a duration of 1, 4 or 9 years, respectively, by Baron (1986), Ranc et al. (1991) and Ali and Dunster (1998). The results obtained showed, in general terms, that whilst the carbonation of both sets of concrete increased with the air curing of the test specimens, that of the PLC concrete relative to PC concrete did so at an increased rate, which increased with GLS content. The accelerated exposure produced higher carbonation than natural exposure, with the difference between the two widening with GLS content.

5.8.2 Curing Duration

The influence of curing duration on the carbonation resistance of PLC concrete has been investigated with GLS contents of 0%–35%, for a duration of 1–365 days and at temperatures of 20°C and 30°C, under both accelerated (2, 5 and 50% CO_2 concentration) (Lollini et al., 2014; Rabehi et al., 2013; Marques et al., 2013) and natural exposure conditions (indoor and outdoor sheltered) (Balayssac et al., 1995; Barker and Matthews, 1994; Matthews, 1994; Moir and Kelham, 1993; Moir and Kelham, 1999; Parrott, 1996; Thomas et al., 2013). The carbonation resistance of concrete, measured in both accelerated and natural exposures, improves with moist curing duration, particularly with initial moist curing. Whilst PLC concrete mixes give higher carbonation values than PC concrete, the difference between the two decreases with time, and does so more when the GLS content is less than 15% and the mixes are designed on an equal strength basis.

5.9 Carbonation Depth with Strength Grade of Concrete

To envisage the provision of adequate concrete cover to reinforcement of PLC concretes, the obtained results were analysed in terms of carbonation depth and compressive strength. Taking 50 years as the design working life, Category 4 for building structures and other common structures as specified in Eurocode 0 (BS EN 1990:2002+A1:2005), the expected carbonation depth data of concrete are plotted against 28-day characteristic cube strength for different natural exposure conditions, namely (a) indoor, (b) outdoor sheltered and (c) outdoor unsheltered, in Figure 5.5.

Figure 5.5 has been established as an outline as follows:

- The data used are taken from Figure 5.1 and, in addition, the carbonation data of those PLC mixes for which PC control mixes were not adopted (Assie et al., 2006; Assie et al., 2007; Bertolini et al., 2008; Bolzoni et al., 2006; Bolzoni et al., 2014; Corinaldesi et al., 2004; Diamanti et al., 2013; Figueiras et al., 2009; Franzoni et al., 2013; Frazão et al., 2015a; Frazão et al., 2015b; McNally et al., 2012; Meira et al., 2014; Nieuwoudt et al., 2012; Owsiak and Grzmil, 2015; Perlot et al., 2013; Redaelli and Bertolini, 2014; Redaelli et al., 2011a; Redaelli et al., 2011b; Révay and Gável, 2003; Rio et al., 2015; Segura et al., 2013; Sistonen et al., 2008; Thienel and Beuntner, 2012; Tschegg et al., 2011; Ylmen et al., 2013) have also been incorporated for this exercise.

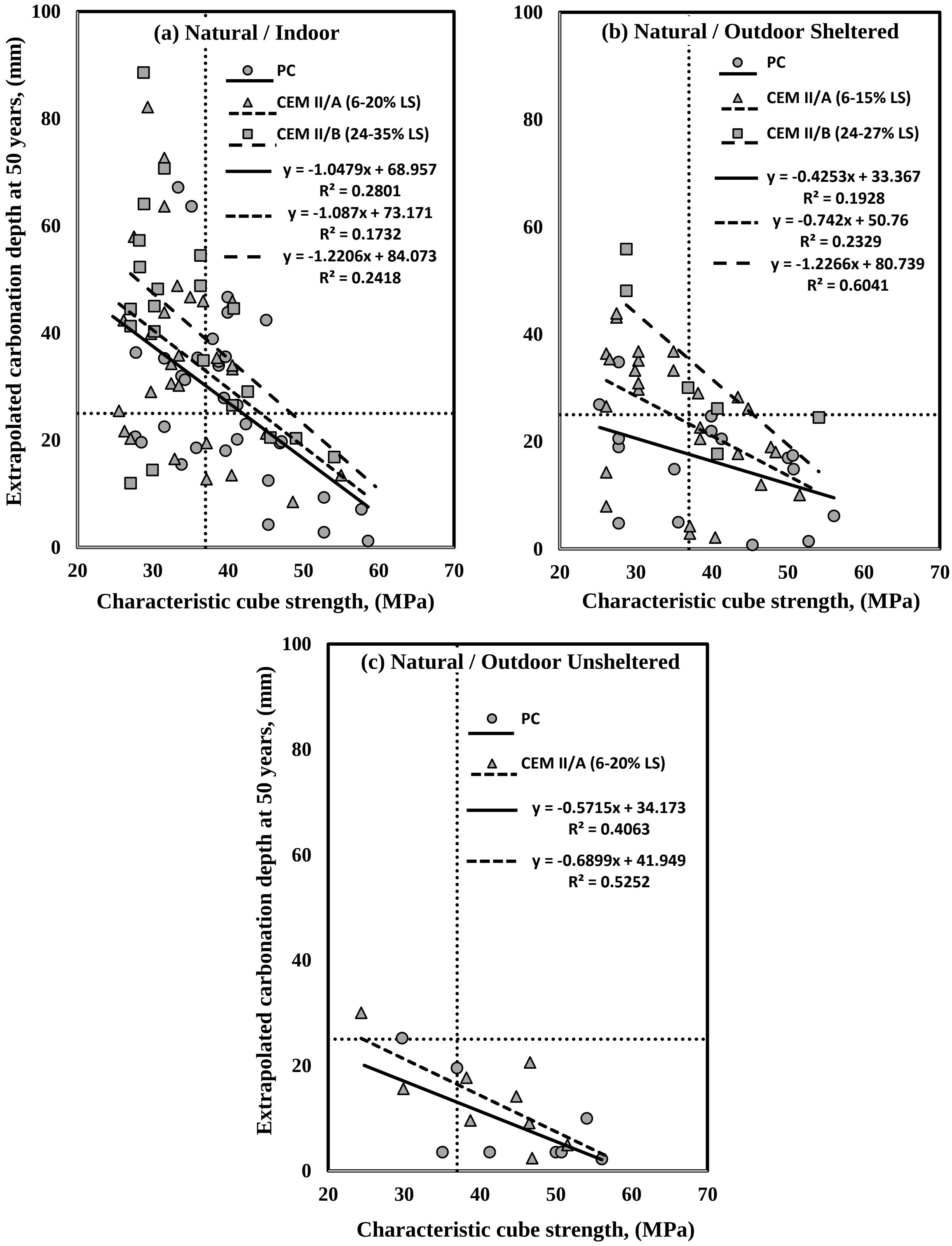


Figure 5.5: Extrapolated carbonation depth at fifty years of PC and PLC concretes subjected to natural carbonation exposures (a) indoor, (b) outdoor sheltered and (c) outdoor unsheltered at different characteristic cube strengths (Elgalhud et al., 2017a)

- Where the ultimate figure for carbonation was recorded as zero, such results have been ruled out from the analysis in this case.

- The predictable carbonation depth data at 50 years (D_{50}) was determined based on Fick's law, $D_{50} = K \times t^{0.5}$, where K is the rate of carbonation (mm/year$^{0.5}$) and t = 50 years. The value of K used was as provided or alternatively calculated by employing the final carbonation depth data recorded.

- Characteristic cube strength was determined using a variation coefficient of 6% given in ACI 301:2005 (ACI, 2005) for fair laboratory control class.

- The results obtained where the test mixes did not comply with the BS EN 206:2013 (BSI, 2013) mix limitations for the carbonation class XC3 were also not considered in this case.

As seen from Figure 5.5, the highest carbonation depths were for the indoor exposure and the lowest for the outdoor unsheltered exposure, with carbonation depth increasing with decreasing compressive strength and increasing GLS content. Additionally, and important to this study, the following observations can be noted:

- For the indoor exposure, the 50-year estimated carbonation depths of both PC and PLC concretes surpass the minimum concrete cover specified in Eurocode 2 (BS EN 1992-1-1:2004+A1:2014) for the minimum cube compressive strength of 37 MPa for exposure class XC3 [Figure 5.5 (a)].

- For the outdoor sheltered exposure, the 50-year expected carbonation depths of PC and PLC (CEM II/A) concretes are below 25 mm, whereas concrete with PLC (CEM II/B) has a carbonation depth greater than the minimum cover requirement [Figure 5.5 (b)].

- In the case of the outdoor unsheltered exposure, though the amount of data is comparatively small, the 50-year carbonation depth of both PC and PLC (CEM II/A) concretes is below 25 mm, with the latter being higher than the former [Figure 5.5 (c)].

Figure 5.5 also proposes an approach to obtain a carbonation of PLC concrete comparable to that of PC concrete. Using a carbonation of PC concrete at 37 MPa, as an example, subjected to indoor and outdoor sheltered conditions, to obtain a carbonation similar to that of the PC concrete, the compressive strength of PLC concrete would have to be increased on average by about 5.5 MPa and 10.5 MPa for CEM II/A (6%–20% GLS) and CEM II/B (21%–35% GLS) cement, respectively (Table 5.4).

In addition, Table 5.4 (a) and (b) summarises, for the indoor and outdoor sheltered exposures:

a. the estimated carbonation depth corresponding to 37 MPa;

b. the characteristic cube strength corresponding to 25 mm cover of concrete made with combinations of PC and different GLS contents, such as those covered by BS EN 197-1:2011 (BSI, 2011).

Table 5.4: Fifty year extrapolated carbonation depth, characteristic cube strength and w/c ratio of PC and PLC concretes for different design parameters (Elgalhud et al., 2017a)

	(a) At 37 MPa		**(b) At 25 mm cover**		**(c) At w/c=0.55**		**(d) At 25 mm cover**	
	Carbonation depth, (mm)		**Characteristic strength, MPa**		**Carbonation depth, (mm)**		**w/c ratio**	
Cement	Indoor	Outdoor sheltered	Indoor	Outdoor sheltered	Indoor	Outdoor sheltered	Indoor	Outdoor sheltered
CEM I	30	18	42	20	27	17	0.54	0.67
CEM II/A (6-20% GLS)	33	23	44	34	32	24	0.49	0.56
CEM II/B (21-35% GLS)	39	35	48	45	44	29	0.42	0.51

The accelerated carbonation results pertaining to 3%–5% CO_2 exposure were analysed similar to the natural indoor exposure conditions shown in Figure 5.5 (a). This showed that 1 week of accelerated carbonation exposure for concrete made with PC, CEM II/A (6%–20% GLS) and CEM II/B (21%–35% GLS) is equivalent to about 0.58, 0.69 and 0.92 year of natural indoor carbonation exposure, respectively. These values are dissimilar to that suggested by Ho and Lewis (1987), who proposed a factor of 1.0 with accelerated carbonation at 4% CO_2 concentration. Figure 5.6 was prepared using these conversion factors and shows trend lines that are similar to the natural indoor carbonation exposure shown in Figure 5.5 (a).

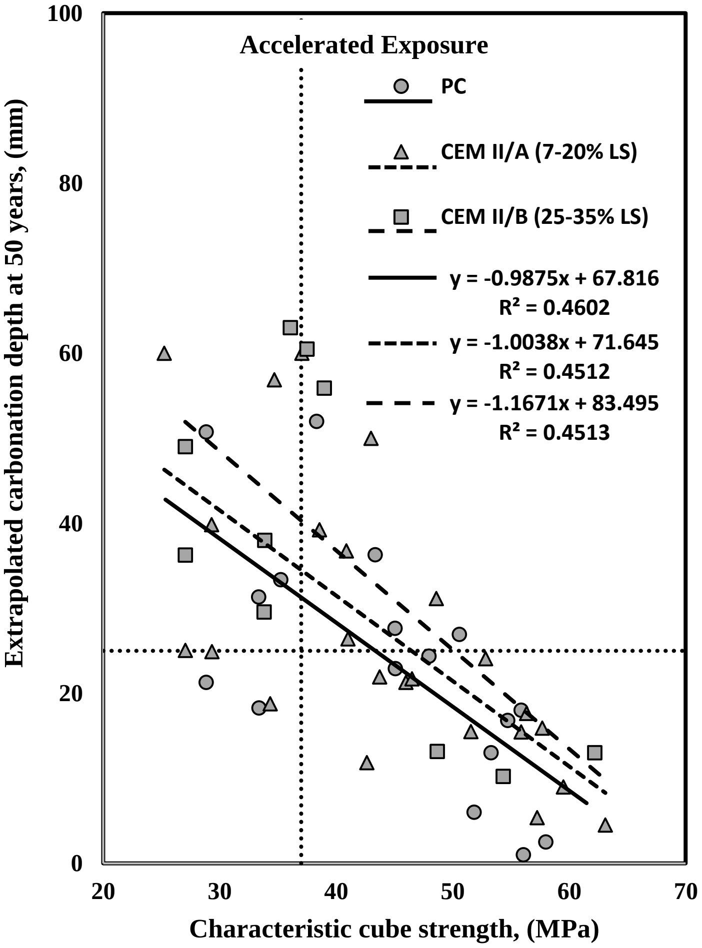


Figure 5.6: Extrapolated carbonation depth at fifty years of PC and PLC concretes based on accelerated carbonation exposure (3–5% carbon dioxide concentration) at different characteristic cube strengths (Elgalhud et al., 2017a)

5.10 Carbonation Depth at Specified Water/Cement Ratio

The 50-year expected carbonation depths of concrete with respect to w/c ratio for natural exposure under indoor, outdoor sheltered and outdoor unsheltered conditions are presented in Figure 5.7 (a), (b) and (c), respectively. The suggested maximum w/c ratio of 0.55 for XC3 exposure provided by BS EN 206:2013 and the conforming minimum concrete cover of 25 mm as specified in Eurocode 2 (BS EN 1992-1-1:2004+A1:2014) are also shown in Figure 5.7.

It is worth mentioning that Figure 5.7 was developed based on the results used in Figure 5.1 and, in addition, the carbonation data of those PLC mixes for which PC control mixes were not adopted, after they were subjected to the selection criterion based on mix limitations for the carbonation exposure.

The relative resistance to carbonation of PC and PLC concretes shown in Figure 5.7 is similar to that in Figure 5.5 (with respect to characteristic strength). For carbonation comparable to that of PC concrete at a 0.55 w/c ratio, as an example, subjected to natural indoor and outdoor sheltered exposures, Figure 5.7 suggests that the w/c ratio of PLC concrete made with CEM II/A (6%–20% GLS) and CEM II/B (24%–35% GLS) require to be reduced by about of 0.06 and 0.13, respectively.

Taking a w/c ratio of 0.55 and a concrete cover of 25 mm, the corresponding carbonation depths and w/c ratios of concrete made with PC and PLC as provided in BS EN 197-1:2011 were obtained and are given in Table 5.4 (c) and (d).

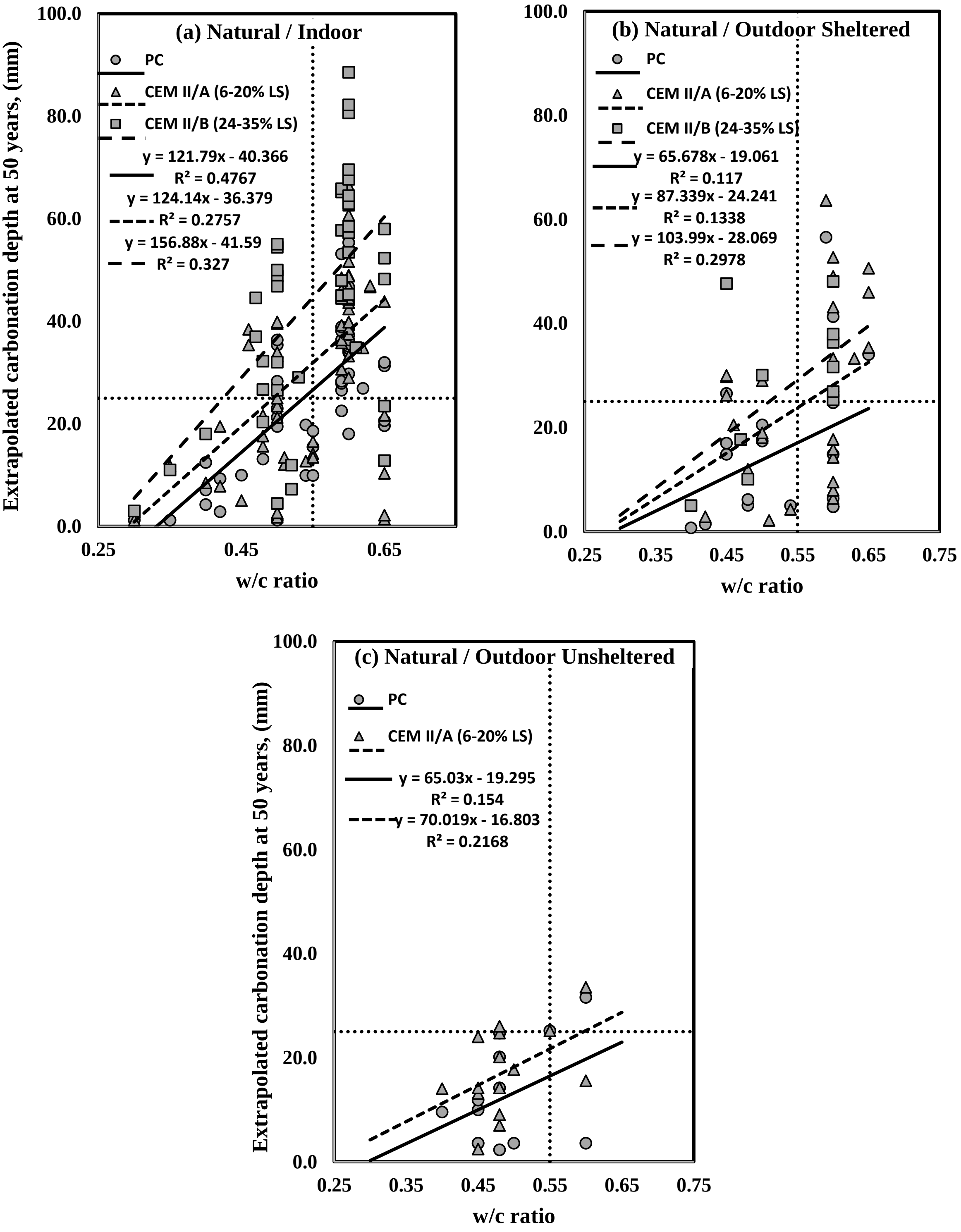


Figure 5.7: Extrapolated carbonation depth at fifty years of PC and PLC concretes subjected to natural carbonation exposures (a) indoor, (b) outdoor sheltered and (c) outdoor unsheltered at different water cement ratios (Elgalhud et al., 2017a)

The 50-year carbonation depths derived for the accelerated exposure measurements at 3%–5% CO_2 concentration, using the established conversion factors of 0.59, 0.79 and 0.90 for PC, CEM II/A (6%–20% GLS) and CEM II/B (21%–35% GLS), respectively, are shown in Figure 5.8. Although, similar to Figure 5.7, there is considerable scatter within the results, an average conversion factor of 1 week accelerated carbonation is equivalent to 0.75 year of natural indoor exposure may be adopted for practical convenience.

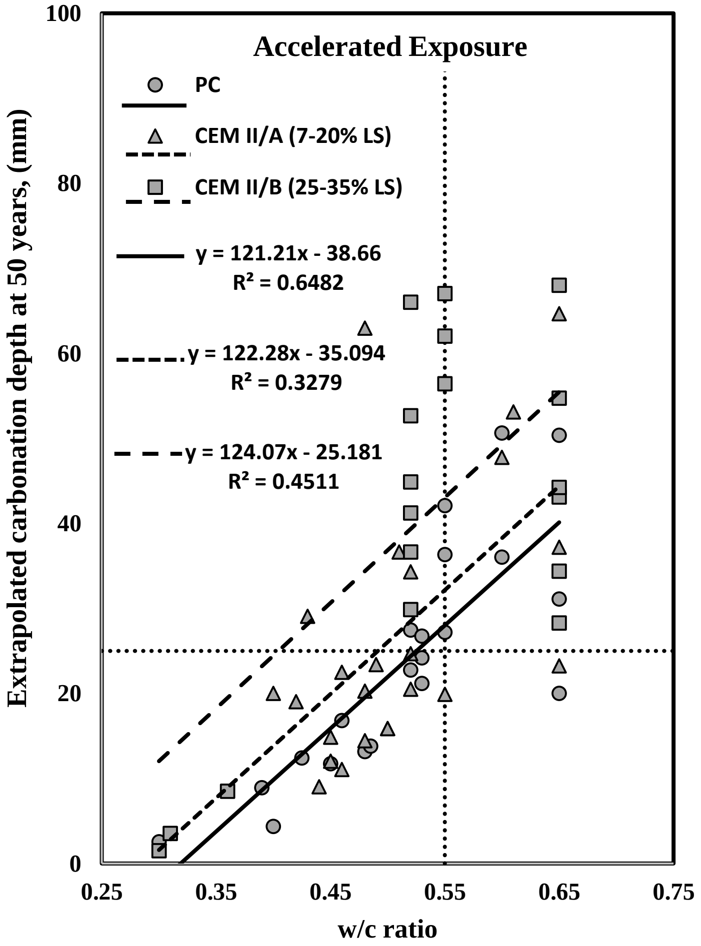


Figure 5.8: Extrapolated carbonation depth at fifty years of PC and PLC concretes based on accelerated carbonation exposure (3–5% carbon dioxide concentration) at different water cement ratios (Elgalhud et al., 2017a)

5.11 In-Situ Carbonation Measurements

The results obtained in this regard are quite limited. The first group of in-situ carbonation measurements were for one of the Italian highway infrastructures (Guiglia and Taliano, 2013). The testing programme covered various structures along 135 km on different members as piers, abutments, tunnels and walls, with the following testing parameters: overall range of age at field measurement 1–5 years; GLS content up to 25%; outdoor sheltered exposure for abutments, piers and tunnels; outdoor unsheltered exposure for walls; range of mean relative humidity 64%–75%; range of mean in-situ core compressive strength 27–45 MPa; mean carbonation depth range for the duration of 1 to 5 years, for sheltered and unsheltered exposures, 3–19mm and 2–13 mm, respectively. Although the exposure duration for which the results are recorded is short, the majority of the results show that PLC concrete had higher carbonation rates than PC concrete for both types of exposure.

In contrast to the Italian project, however, from in-situ carbonation measurements of concrete road pavements constructed in Canada during 2008–2009, taken at the age of 3–4 years, PC concrete was found to carbonate at a faster rate than PLC concrete (Hossack et al., 2014). Some of the information provided covered GLS content, 12%; water/cement ratio, 0.37–0.44; in-situ core strength, 43–59 MPa; outdoor sheltered exposure; measured carbonation within the range 0.5–5.0 mm. Clearly some important information is missing and this, together with the early age for which only carbonation data are available, makes the assessment of PLC concrete difficult, if not impossible.

5.12 Influence of Limestone on Carbonation-Induced Reinforcement Corrosion

For the effects of GLS addition on carbonation-induced corrosion of reinforcement, though an important topic, only a small number of results have been obtained. Moreover, based on the fact that the use of GLS as a component of cement is likely to increase, and the obvious susceptibility of PLC concrete to carbonation as identified in the previous sections, the effects of GLS on the reinforcement corrosion of concrete could give rise to concern. However, given the limited number of test results (Matthews, 1994; Parrott, 1994; Parrott, 1996; Bolzoni et al., 2006; Bolzoni et al., 2014; Redaelli and Bertolini, 2014; Redaelli et al., 2011a; Redaelli et al., 2011b; and Sistonen et al., 2008) reporting on reinforcement corrosion after cover has fully carbonated, and the complexity of the test methodology and measurements used, the information available can at present be examined only in a qualitative manner, as summarised in Table 5.5.

Table 5.5 shows that, in general, the test specimens were made with cement blends of 0%–25% GLS content with w/c ratios of 0.55–0.71 and subjected to natural carbonation exposure for up to 5 years or accelerated carbonation conditions for up to 25 weeks. The corrosion of steel reinforcement was measured in different terms such as weight loss of reinforcement (g/m^2), corrosion current (mA/m^2) and corrosion rate (µm/year). For the tests that have been undertaken, PLC concrete was found to show a higher rate of reinforcement corrosion than the corresponding PC concrete. The rate of corrosion was found not to be significantly affected by w/c ratio or the period of moist curing (Parrott, 1994), though some tests produced conflicting results showing that the corrosion rate of PLC increases with rising w/c ratio (Redaelli et al., 2011a; Redaelli et al., 2011b).

Table 5.5: Summary of influence of limestone addition on carbonation induced corrosion (Elgalhud et al., 2017a)

REFERENCES	MAIN POINTS EMERGING
(a) Test results where PLC concrete assessed alongside with PC reference concrete.	
Matthews, 1994	**Corrosion rate of PLC concrete higher than that of PC concrete.** ***Reinforcement corrosion measurement: percentage rebar weight loss; range of PC results: 0.14-0.19; range of PLC (5%GLS) results: 0.15-0.21; range of PLC (25%GLS) results: 0.32-0.45.*** Prism specimen: 100×100×300 mm; concrete cover: 10 mm; GLS contents: 0, 5 and 25%; w/c ratio: 0.60; moist curing: 28 days; exposure: natural outdoor unsheltered; duration: 5 years; equal w/c mix.
Parrott, 1994	**Corrosion rate of PLC concrete slightly higher than that of PC concrete and was not significantly affected by w/c ratio and curing duration.** ***Reinforcement corrosion measurement: rebar weight loss (g/m^2); range of PC results: 9-17 g/m^2; range of PLC (5%GLS) results: 11-19 g/m^2.*** Cube specimen: 100×100×100 mm; concrete cover: 4 mm; GLS contents: 0 and 5%; w/c ratio: 0.59-0.71; moist curing: 3 and 545 days; exposure: natural indoor, outdoor sheltered and outdoor unsheltered; duration: 4 years; equal w/c mix.
Parrott, 1996	**Corrosion rate of PLC concrete higher than that of PC concrete.** ***Reinforcement corrosion measurement: rebar weight loss (g/m^2); range of PC results: 7-11 g/m^2; range of PLC (15%GLS) results: 8-15 g/m^2; range of PLC (19%GLS) results: 15-26 g/m^2; range of PLC (25%GLS) results: 21-30 g/m^2*** Cube specimen: 100×100×100 mm; concrete cover: 4 mm; GLS contents: 0, 15, 19 and 25%; w/c ratio: 0·60; moist curing: 1–28 days; exposure: natural indoor; duration, 1·5 years; equal w/c mix.
(b) Test results where PLC concrete has been assessed solely.	
Bolzoni et al., 2006 Bolzoni et al., 2014	**The steel rebar of PLC concrete exhibited a high corrosion rate.** ***Reinforcement corrosion measurement: corrosion rate through linear polarization resistance method (μm/year), PLC result: 12 μm/year.*** Prism specimen: 200×250×50 mm; concrete cover: 20 mm; GLS content: 14%; w/c ratio: 0.60; moist curing: 28 days; carbon dioxide: 10%; temperature: 25°C; RH: 65%, duration: 25 weeks.
Redaelli and Bertolini, 2014	**The corrosion rate of PLC concrete considered to be on the moderate level.** ***Reinforcement corrosion measurement: corrosion current (mA/m^2), PLC result: 4 mA/m^2.*** Prism specimen: 40×40×160 mm; concrete cover: 15 mm; GLS content: 13%; w/c ratio: 0.65; moist curing: 7 days; carbon dioxide: 2%; temperature: 21°C; RH: 65%, duration: 6 weeks
Redaelli et al., 2011a Redaelli et al., 2011b	**The corrosion rate results of PLC concrete reflect high activity and increases with increasing w/c ratio.** ***Reinforcement corrosion measurement: corrosion current (mA/m^2), range of PLC results: 15-18 mA/m^2.*** Cylinder specimen: 60×300 mm; concrete cover: 25 mm; GLS content: 15%; w/c ratio: 0.55-0.70; moist curing: 7 days; carbon dioxide: 6%; temperature: 20°C; RH: 60%, duration: 18 weeks.
Sistonen et al., 2008	**The corrosion rate results for PLC concrete indicates an active corrosion.** ***Reinforcement corrosion measurement: corrosion current (mA/m^2), PLC result: 16 mA/m^2.*** Cylinder specimen: 44×200 mm; concrete cover: 15-19 mm; GLS content: 13%; w/c ratio: 0.70; air curing: 21 days; carbon dioxide: 7%; temperature: 22°C; RH: 75%, duration: 10 weeks.

5.13 Measures to Minimise the Carbonation Effect of PLC Concrete

The effects of GLS addition on the carbonation of concrete can be minimised in a number of ways. Though increasing the moist curing will certainly help to enhance the resistance of PLC concrete against carbonation by developing a less porous and less permeable concrete, to achieve this in practice can be difficult owing to present construction practices. Other options for improving the carbonation resistance of PLC concrete could be:

(a) Restricting the GLS addition content to a smaller proportion, i.e., to a maximum of 20%: Such a cement will be in compliance with PLC of type CEM II/A (6%–20% GLS) as in BS EN 197 (BSI, 2011). Whilst this option may be used without greatly reducing the carbonation resistance of concrete, it would be less effective in minimising the embodied carbon of the cement industry.

(b) Increasing the specified characteristic strength of concrete through a significant reduction in its water/cement ratio using a high-range water-reducing admixture: This option should enhance the durability and sustainability characteristics of concrete (Dhir et al., 2000; Dhir et al., 2004; Dhir et al., 2006).

(c) Increasing the thickness of the concrete cover: This could be considered as an additional obvious choice but, nevertheless, will have an impact on the structural design and sustainability aspects, and is unlikely to be preferred by the designer/engineer.

5.14 Comparison of Carbonation Resistance of Concrete Made with PLC, PFA and GGBS

In order to obtain a comprehensive view of the carbonation resistance of concrete under the effects of the three major additions adopted by EN 197-1 (2011) for as a component of cement, i.e., GLS, PFA and GGBS, the results of this chapter have been compared with the results of two other studies that dealt with the effects of PFA (Lye et al., 2015) and GGBS (Lye et al., 2016). Figures 5.9 and 5.10 and Tables 5.6 and 5.7 summarise their relative performance, as discussed next.

5.14.1 Replacement Effect

At the same replacement level, and in a concrete of the same composition, fly ash can be expected to give the highest rate of carbonation, followed by GLS and GGBS (Figure 5.9). This can be explained in terms of the reactivity of each of the three additions and the consumption of $Ca(OH)_2$. However, given that GGBS is usually used at a much higher replacement level, depending upon the actual replacement level, in practice, the carbonation of concrete with GGBS may be higher than that with GLS and PFA.

5.14.2 Fifty Year Extrapolated Carbonation Depth

The estimated 50-year carbonation depth of PLC, PFA and GGBS concretes designed on an equal strength basis [Figure 5.10 (a) and (b)] is lower than that of concretes based on an equal w/c ratio basis [Figure 5.10 (c) and 5.10 (d)]. Taking the minimum concrete cover of 25 mm and w/c ratio of 0.55 or characteristic cube strength of 37 MPa as per BS EN 206 (BSI, 2013), for indoor exposure conditions, all concretes [PC (reference), PLC, PFA and GGBS] are likely to surpass the adopted cover before the period of 50 years [Figure 5.10 (a) and (c)]. Nevertheless, for outdoor sheltered exposure conditions, this minimum concrete cover is:

(i) adequate for concrete made with CEM I, CEM II/A (6%–20% GLS), CEM II/A (6%–20% PFA) and CEM II/B-S (21%–35% GGBS);

(ii) not adequate for concrete made with CEM II/B (21%–35% GLS), CEM II/B (21%–35% PFA), CEM IV/B (36%–55% PFA), CEM III/A (36%–65% GGBS) and CEM III/B (66%–80% GGBS).

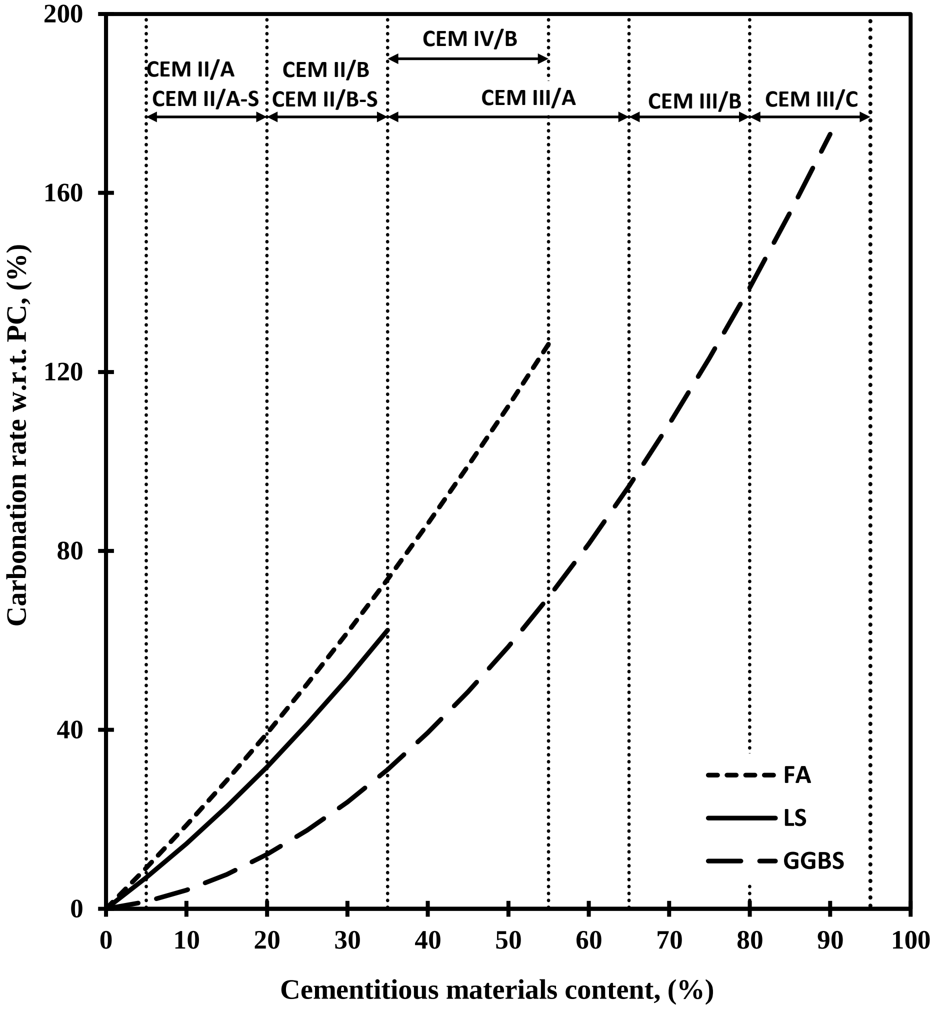


Figure 5.9: Comparison of GLS, PFA and GGBS concretes; effect of replacement (Elgalhud et al., 2017a)

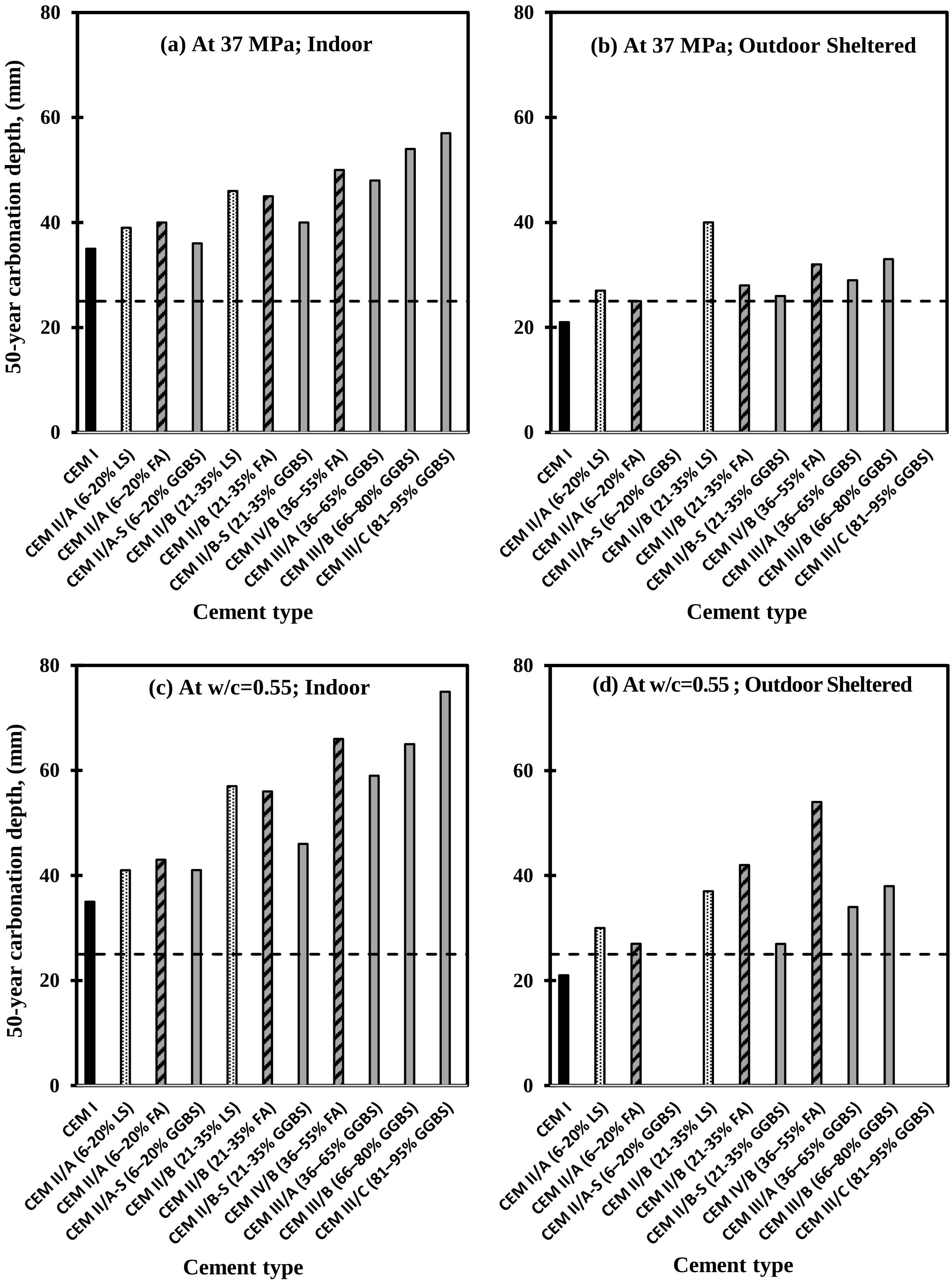


Figure 5.10: Comparison of 50-year estimated carbonation depth for GLS, PFA and GGBS concretes (Elgalhud et al., 2017a)

Note: Data normalized so that the 50-year estimated carbonation of PC reference in PLC, PFA and GGBS results is similar under the same carbonation exposure and data for CEM II/A (6-20% GGBS) and CEM III/C (81-95% GGBS) under outdoor carbonation not available.

5.14.3 Mix Design Adjustment for Similar Carbonation

In order to obtain carbonation comparable to that of PC concrete, the concrete mix design adjustment made in terms of reduction in w/c ratio or increase in compressive strength for PLC and PFA concretes will be more than for GGBS concrete at the same replacement level (Table 5.6).

Table 5.6: Comparison of PLC, PFA and GGBS concretes, mix adjustment for similar carbonation (Elgalhud et al., 2017a)

CEMENT	**MIX ADJUSTMENT FOR SIMILAR CARBONATION**	
	Additional strength, MPa [a]	**w/c reduction** [b]
CEM I	0.0	0.0
CEM II/A (6-20% GLS)	5.5	0.06
CEM II/A (6–20% PFA)	5.0	0.05
CEM II/A-S (6–20% GGBS)	n/a	n/a
CEM II/B (21-35% GLS)	10.5	0.13
CEM II/B (21-35% PFA)	7.5	0.15
CEM II/B-S (21-35% GGBS)	5.5	0.10
CEM IV/B (36–55% PFA)	10.0	0.25
CEM III/A (36–65% GGBS)	9.5	0.20
CEM III/B (66–80% GGBS)	13.0	0.22

a PC at 37 MPa
b PC at 0·55 w/c

5.14.4 Accelerated and Natural Indoor Carbonation Relationship

Though the relationships for natural indoor and accelerated carbonation of concrete developed for PLC in this study and for PFA and GGBS by Lye et al., (2015, 2016) are dissimilar (Table 5.7), for practical purposes, a conversion factor of 1 week of accelerated carbonation (at 3%–5% carbon dioxide concentration) can be assumed to be equivalent to 0.65 year of natural indoor carbonation.

Table 5.7: Relationship between accelerated and indoor carbonation for PLC, PFA and GGBS concretes (Elgalhud et al., 2017a)

CEMENT TYPE	DURATION EQUIVALENT TO ONE WEEK ACCELERATED EXPOSURE, YEAR
PLC	0.58–0.92
PFA	0.38–0.54
GGBS	0.60–0.65

5.15 Conclusions

Based on the analysis, structuring and evaluation of the carbonation measurements obtained, the following conclusions are drawn:

a. In general, combinations of GLS with PC similar to the range in BS EN 197-1 (BSI, 2011) lead to increased carbonation. The degree of this increase depends on the composition of the concrete in terms of its w/c ratio and strength, maturity and pore structure.

b. Carbonation measurements relative to the corresponding PC concrete suggest that the depth of carbonation increases with GLS content, giving an increase on the order of 50% with 35% GLS content, which is similar to PLC type CEM II/B in BS EN 197:2011 (BSI, 2011).

c. The carbonation of PLC concrete designed on the basis of an equal w/c ratio relative to PC is higher than that designed on an equal strength basis, for both natural and accelerated carbonation exposures. This difference in the performance of the two sets of PLC mixes can be narrowed with the use of finer GLS and/or extended moist curing of concrete mixes designed on an equal w/c ratio basis. PLC mixes designed on an equal strength basis and exposed to a prolonged moist curing can attain a carbonation resistance near that of PC concrete.

d. In studying the estimated 50 years of carbonation of concrete with respect to its strength, w/c ratio and cover, in compliance with the mix limits of BS EN 206-1:2013

(BSI, 2013) for the carbonation exposure classes, outdoor unsheltered exposure was found to cause the lowest carbonation and indoor the highest. Additionally, the results showed that, for a certain exposure class and specified strength and w/c ratio, the required thickness of concrete cover increases as the GLS content of the cement increases. On the other hand, for a particular cover, the required strength increases and w/c ratio decreases with the GLS content of the cement.

e. One week of accelerated carbonation of PLC concrete, at 3%–5% carbon dioxide concentration, was found to be about equivalent to 0.75 year of natural indoor exposure.

f. The rate of corrosion in PLC concrete, upon carbonation reaching the reinforcement, was found to be higher than that in PC concrete.

g. In-situ carbonation measurements of 1 to 5 years of concrete structures made with PC and PLC showed that, although the carbonation varied with exposure conditions, PLC concrete is likely to carbonate at a faster rate than the corresponding PC concrete.

h. In order to lower the carbonation influence of PLC on structural concrete, consideration should be given to restricting the addition level of GLS and/or increasing the target strength and/or the thickness of the concrete cover. Nonetheless, these measures require to be assessed alongside the other design requirements of durability and sustainability.

i. Comparing the carbonation performance of concrete made with PLC with that made with cement containing PFA (Lye et al., 2015) and GGBS (Lye et al., 2016), the main points to note are given in the following:

Similarities: Concrete made with cement containing GLS, PFA and GGBS carbonates at a higher rate than concrete made with PC and this increase is higher for concrete designed on an equal w/c ratio basis than on an equal strength basis. The minimum concrete cover suggested for a characteristic cube strength of 37 MPa or w/c ratio of 0.55 as stated in Eurocode 2 for XC3 exposure needs to be reviewed for concrete containing GLS, PFA and GGBS.

Differences: As in practice GGBS is generally used in structural concrete at a considerably higher level than PFA or GLS, this concrete can be expected to be at a higher risk than PLC and PFA concretes. The accelerated-to-indoor carbonation relationship of concrete differs for GLS, PFA and GGBS materials, but even so, for ease of use, it has been proposed that 1 week of accelerated carbonation equals 0.65 year of natural indoor exposure.

CHAPTER 6

CHLORIDE INGRESS IN PLC CONCRETE

6.1 Introduction

This chapter deals with the effects of ground limestone (GLS) use as an addition on the chloride ingress and chloride-induced corrosion resistance of concrete. The influence of strength and w/c ratio on chloride ingress is examined. Other influencing factors, including cement content, GLS fineness, method of producing Portland limestone cement (PLC), aggregate volume content and particle size, combined chloride and sulfate environment, curing and exposure temperature, are also considered. A comparison is made for the performance of PLC concrete in terms of pore structure and related properties, strength, carbonation and chloride ingress. Procedures to improve the resistance of PLC to chloride ingress into concrete are proposed.

6.2 Overview of The Literature

An overview of the literature concerning the performance of PLC concrete under chloride ingress revealed the following: although limited in number, and lacking in detailed analysis of the data, both sets of published works, (a) organisational and (b) individual reviews (Table 6.1), suggest that there is some agreement amongst these studies, in that the chloride ingress into concrete is not significantly affected by the addition of GLS up to 15%–20% (i.e., in PLC such as CEM II/A cement of BS EN 197-1). However, some reviews suggest that there are differences of opinion due to the differences in the concrete mixes tested and the test methods utilised to determine the rate of chloride ingress.

Table 6.1: Summary of the findings of the narrative reviews regarding the performance of the PLC under the chloride ingress (Elgalhud et al., 2017b)

REFERENCE	NO. OF CITED REFERENCES	MAIN OBSERVATION
a. Organization		
ACI Committee 211, USA (ACI, 2015)	2	The rapid chloride permeability of PLC with 10-15% GLS is equivalent to PC, whilst other study showed that PLC with 20% GLS reduced the chloride ion diffusion coefficient of about 20% compared to PC.
Concrete Society, UK (CSWP, 2011)	3	GLS will not produce any significant improvement in resistance to chloride diffusion and may even reduce it slightly.
Hawkins et al., (2003), PCA, USA	7	The literature review shows mixed results of PLC when compared to PC.
Hooton et al., (2007), CSC, Canada	9	PLC (with GLS up to 20%) and PC have similar durability to chloride ingress.
Detwiler and Tennis (1996), PCA, Canada	2	PLC containing 15% of GLS and PC have an equivalent performance with respect to the chloride permeability and chloride diffusion.
b. Individual		
Benn et al., (2012)	7	There appear to be variances of view in the literature that are associated both to the variations in the cementitious mixtures studied and the test methods utilised to obtain the rate of chloride ingress.
Hooton, (2010)	1	PLC (with GLS up to 20%) and PC have similar durability to chloride ingress.
Kaur et al., (2012)	1	Differences in diffusivity coefficient of concrete up to 15% GLS, compared to PC concrete were relatively minor and increased slightly with w/c ratio.
Muller, (2012)	3	PLC has a comparable performance to PC under the chloride ingress.
Van Dam et al., (2010)	1	PLC (with 10% of GLS) and PC have a similar rapid chloride permeability.

The examination of the chloride measurements obtained, summarised in Table 6.2 (Elgalhud et al., 2017b), revealed that most of the results (57%) show that the use of GLS with PC leads to a higher rate of chloride ingress. A variety of causes have been proposed for this increase in chloride ingress into PLC concrete. In contrast, 17% of the obtained results suggest that the chloride ingress into PLC concrete can be lower than in the corresponding PC concrete, 2% indicate no change and 9% show a variable trend; and for 15% of the data there were no corresponding PC concrete mixes tested and therefore the PLC data could not be compared to the corresponding PC concrete mixes.

6.3 Test Methods and Procedures Employed

The test conditions employed to assess the effects of GLS on the chloride ingress into concrete are summarised in Table 6.3 (Elgalhud et al., 2017b) and the main points to be noted are as stated below:

Chloride exposure: The vast majority of the tests measured chloride ingress using a non-natural exposure, whereby the specimens were tested in a laboratory using various accelerated methods.

Material: The majority of the investigations adopted the use of mortar and concrete as test specimens.

Specimens: The choice of test specimens in the form of cylinders, prisms or cubes appeared to be influenced by the relevant standard specifications adopted in a specific study. The largest number of tests were carried out using cylinder/disc specimens.

Table 6.2: Summary of the published findings concerning the effect of GLS on the chloride ingress[a]

OBSERVATION* OF CHLORIDE INGRESS IN PLC MIXES	MAIN SUGGESTED CAUSES		NUMBER OF TESTED MIXES		
			Laboratory	Field	Total
Higher (156) Laboratory (154) Field (2)	**Cement**	Reduction of PC	14	0	14
		Reduced production of calcium silicate hydrate	2	0	2
		Compounds of C_3A in PLC concrete have a lower binding capacity	5	1	6
		Higher level of OH- ions presents in the pore fluid of the concrete made with GLS	8	0	8
	Design	Higher water/cement ratio	18	0	18
	Hardened properties	Higher porosity/Coarser pore structure	42	1	43
		Higher permeability	15	0	15
		Not given	50	0	50
Lower (49) Laboratory (48) Field (1)	**Cement**	Higher specific area of GLS	1	0	1
	Design	Lower water/cement ratio	1	0	1
		Sufficient curing	1	0	1
		Higher strength	6	0	6
	Hardened properties	Lower porosity	6	0	6
		Not given	33	1	34
No change (5) Laboratory (5)		Equal strength	1	0	1
		Not given	4	0	4
Variable (26) Laboratory (23) Field (3)	**Cement**	Decreases with improved particle size distribution until optimum replacement level (10-15% GLS) and then increases due to dilution of PC	11	2	13
		Not given	12	1	13
No reference mixture (44) Laboratory (44)		Not applicable	44	0	44

* Higher/lower/no change/variable of chloride ingress in PLC mixture w.r.t corresponding reference PC mixture.

Data of Table 6.2 taken from: Ahmad et al., 2014; Aguayo et al., 2014; Alunno-Rosetti and Curcio, 1997; Assie et al., 2006; Assie et al., 2007; Audenaert et al., 2010; Audenaert and De Schutter, 2009; Audenaert et al., 2007; Barrett et al., 2014; Batic et al., 2010; Batic et al., 2013; Beigi et al., 2013; Bentz et al., 2015; Bertolini et al., 2002; Bertolini and Gastaldi, 2011; Bertolini et al., 2004a; Bertolini et al., 2004b; Bertolini et al., 2007; Bonavetti et al., 2000; Boubitsas, 2004; Boubitsas, 2001; Bolzoni et al., 2006; Bolzoni et al., 2014; Brenna et al., 2013; Calado et al., 2015; Cam and Neithalath, 2010; Cam and Neithalath, 2012; Carsana et al., 2016; Celik et al., 2015; Celik et al., 2014a; Celik et al., 2014b; Chiker et al., 2016; Climent et al., 2006; Cochet and Jesus, 1991; Cost et al., 2013a; Courard et al., 2005; Courard et al., 2014; Corinaldesi and Moriconi, 2004; Deja et al., 1991; Dhir et al., 2004; Dhir et al., 2007; Figueiras et al., 2009; Franzoni et al., 2013; Frazão et al., 2015; Gesoğlu et al., 2012; Ghiasvand et al., 2015; Ghrici et al., 2007; Githachuri and Alexander, 2013; Güneyisi et al., 2011; Hooton et al., 2010; Hornainl et al., 1995; Hossack et al., 2014; Howard et al., 2015; Irassar et al., 2006; Irassar et al., 2001; Kaewmanee and Tangtermsirikul, 2014; Kenai et al., 2008; Kuosa et al., 2008; Kuosa et al., 2014; Leemann et al., 2010; Lemieux et al., 2012; Li and Kwan, 2015; Lollini et al., 2014; Lollini et al., 2016; Loser and Leemann 2007; Loser et al., 2010; Matos et al., 2016; Meddah et al., 2014; Menadi and Kenai, 2011; Menéndez et al., 2007; Meira et al., 2014; Moir and Kelham, 1999; Moir and Kelham, 1993; Matthews, 1994; Livesey , 1991; Moukwa, 1989; Müller and Lang, 2006; Pavoine et al., 2014; Persson, 2001; Persson, 2004; Pourkhorshidi et al., 2010; Ramezanianpour et al., 2010; Ramezanianpour et al., 2009; Ramezanianpour et al., 2014; Ramezanianpour and Afzali, 2015; Ranc et al., 1991; Romano et al., 2013; Sánchez et al., 2008; Selih et al., 2003; Sfikas et al., 2013; Shaikh and Supit, 2014; Shi et al., 2015; Siad et al., 2014; Silva and de Brito, 2016; Sistonen et al., 2008; Sonebi and Nanukuttan, 2009; Sonebi et al., 2009; Sotiriadis et al., 2014; Tezuka et al., 1992; Thomas et al., 2010a; Thomas et al., 2010b; Thomas et al., 2010c; Thomas et al., 2010d; Tittarelli, 2011; Tsivilis and Asprogerakas, 2010; Tsivilis S. et al., 2000; Uysal et al., 2012; Van Dam T. J. et al., 2010; Xiao et al., 2009; Zhu and Bartos, 2003; Lollini et al., 2015; Bertolini et al., 2011; Wu et al., 2016; Kobayashi et al., 2016; Younsi et al., 2015; Yüksel et al., 2014; Fornasier et al., 2003; Yamada et al., 2006; Juel and Herfort, 2002; Bonneau et al., 2007; Palm et al., 2016, Zhang et al., 2016.

Table 6.3: Compilation of test parameters of PLC chloride ingress measurements obtained

PARAMETER	VARIABLE	NO.	PARAMETER	VARIABLE	NO.
1. CHLORIDE INGRESS	Laboratory Field	275 5	**2. MATERIAL**	Cement paste Mortar/Concrete	3 277
3. (a) SPECIMEN	Cylinder/Disc Prism Cube Column/Slab Not given	161 46 49 4 20	**3.(b) PREPARATION**	Sealed Unsealed Unspecified	68 14 198
4. TEST METHOD	Electrical indication (RCPT)	120	**5. STANDARD/REFERENCE**	ASTM C1202 (ASTM, 2012) ASSHTO T277 (ASSHTO, 2015) Not given	100 14 6
	Steady state migration	25		Dhir et al., 1990 Page et al., 1981 Truc et al., 2000 Not given	4 2 3 16
	Non-steady state migration	106		NT Build 492 (NT Build,1999) Luping and Nilsson, 1993 Nanukutan et al., 2006 SIA 262/1; SS, 2003 Gehlen and Ludwig, 1999 BAW, 2004 Not given	49 1 3 4 2 6 41
	Chloride profile	25		UNI 7928 (UNI,1978) ASTM C1218 (ASTM, 2015) ASTM C1152 (ASTM, 2012) AASHTO T260 (AASHTO, 2009) NT Build 443 (NT Build, 1995) Not given	8 2 3 2 6 4
	Chloride conductivity	4		Streicher and Alexander, 1995	4
	Non-steady state immersion	2		NT Build 443 (NT Build, 1995)	2
	Chronoamperometry	1		Aït-Mokhtar et al., 2004	1
6. CURING			**7. PRE-CONDITIONING**		
6.1 Exposure	Moist Air Not given	210 5 65	7.1 Preparation	Omitted Applied Not given	27 201 52
6.2 Duration, days	1-14 15-28 56-91 >91 Not given	32 112 66 22 48	7.2 Duration*, day	1-7 14-28 Not given	142 25 34
6.3 Temp, °C	20-30 >30 Not given	218 4 58	7.3 Temp*, °C	20-30 35-50 Not given	138 8 55
6.4 Humidity, %	80-100 40-80 Not given	215 5 60	7.4 Humidity*, %	45-85 Not given	68 133
8. LABORATORY CONDITIONS			**9. FIELD CONDITIONS**		
8.1 Chloride solution, %	<3 3-5 10-15	11 152 60	9.1 Exposure	Submerged in the sea Tidal exposure site Marine aerosol	1 4 1
	>15 Not given	8 44	9.2 Chloride solution, %	3-4 Not given	1 5
8.2 Duration, days	≤1 2-30 31-90 91-180 >180 Not given	150 16 11 10 33 55	9.3 Duration, years	2 3 >3	4 1 1
8.3 Temp, °C	<20 20-30	2 194	9.4 Temp, °C	2-20 Not given	1 5
	>30 Not given	1 78	9.5 Humidity, %	>95 Not given	4 2

Note: Number in each individual parameter presents the sum of the tested mixes.

* Data compiled from tests where pre-conditioning is applied.

a: Data of Table 6.3 taken from the same references of Table 6.2

Test Method: Whilst various test methods have been used to measure chloride ingress, the two most commonly used methods were electrical indication-based, as in ASTM C1202/AASHTO T277 (commonly referred to as the rapid chloride permeability test or RCPT method), and the non-steady-state migration, NT Build 492, test method.

Curing: With few exceptions, and the impact of the local standard specifications, most specimens were moist cured at a relative humidity 80%–100% and temperature 20°C–30°C, for duration of up to 28 days.

Preconditioning: Although this information was usually lacking, those that did provide it showed that the commonly adopted treatment was carried out at temperature 20°C–30°C, relative humidity 45%–85% and a duration of 1–7 days.

Laboratory and Field Exposure Conditions: The most commonly used laboratory exposure consisted of chloride solution concentration of up to 5%, for a duration of ≤30 days and at temperature 20°C–30°C, whilst the field exposure (e.g., submerged in the sea or a tidal exposure site) was up to 3 years in duration.

6.4 Limestone Effect

Given that a large number of parameters are involved in the tests undertaken (Table 6.3), the effects of GLS inclusion on chloride ingress can best be analysed and evaluated in relation to the corresponding PC used as reference in the study. The obtained results are plotted collectively in Figure 6.1. To visualise the data distribution and identify the outliers, box-and-whisker plots are used. In Figure 6.1, the data points have been dispersed slightly to prevent overlapping to provide a better view of the results. However, some of the results, as described below, were not considered further:

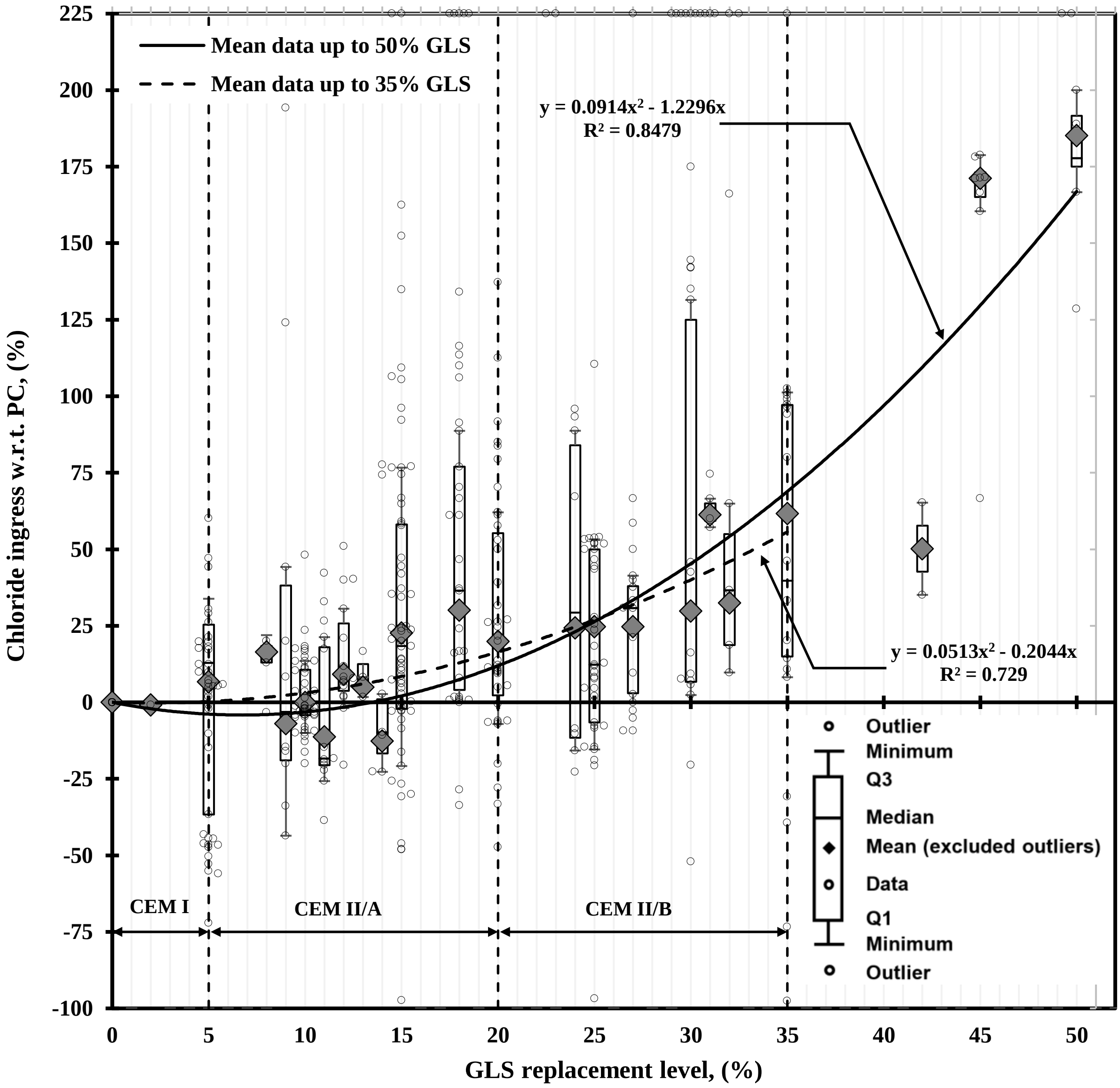


Figure 6.1: GLS addition effect on chloride ingress in concrete (Elgalhud et al., 2017b)

Data of Figure 6.1 taken from: Aguayo et al., 2014; Alunno-Rosetti and Curcio, 1997; Assie et al., 2007; Barrett et al., 2014; Batic et al., 2010; Batic et al., 2013; Bentz et al., 2015; Bertolini et al., 2004b; Bertolini et al., 2007; Bonavetti et al., 2000; Boubitsas, 2004; Boubitsas, 2001; Calado et al., 2015; Cam and Neithalath, 2010; Cam and Neithalath, 2012; Celik et al., 2015; Celik et al., 2014a; Celik et al., 2014b; Cochet and Jesus, 1991; Cost et al., 2013a; Courard et al., 2005; Courard and Michel 2014,; Deja et al., 1991; Dhir et al., 2004; Dhir et al., 2007; Gesoğlu et al., 2012; Ghiasvand et al., 2015; Ghrici et al., 2007; Githachuri and Alexander, 2013; Güneyisi et al., 2011; Hooton et al., 2010; Hornainl et al., 1995; Hossack et al., 2014; Howard et al., 2015; Irassar et al., 2006; Irassar et al., 2001; Kaewmanee and Tangtermsirikul, 2014; Kuosa et al., 2008; Kuosa et al., 2014; Leemann et al., 2010; Lemieux et al., 2012; Li and Kwan, 2015; Lollini et al., 2014; Lollini et al., 2016; Loser and Leemann 2007; Loser et al., 2010; Meddah et al., 2014; Menadi and Kenai, 2011; Menéndez et al., 2007; Moir and Kelham, 1999; Moir and Kelham, 1993; Matthews, 1994; Livesey , 1991; Moukwa, 1989; Müller and Lang, 2006; Pavoine et al., 2014; Persson, 2001; Persson, 2004; Pourkhorshidi et al., 2010; Ramezanianpour et al., 2010; Ramezanianpour et al., 2009; Ramezanianpour et al., 2014; Ranc et al., 1991; Selih et al., 2003; Shaikh and Supit, 2014; Shi et al., 2015; Siad et al., 2014; Silva and de Brito, 2016; Sonebi and Nanukuttan, 2009; Sonebi et al., 2009; Sotiriadis et al., 2014; Tezuka et al., 1992; Thomas et al., 2010a; Thomas et al., 2010b; Thomas et al., 2010c; Thomas and Hooton, 2010; Tsivilis and Asprogerakas, 2010; Tsivilis S. et al., 2000; Uysal et al., 2012; Van Dam T. J. et al., 2010; Xiao et al., 2009; Zhu and Bartos, 2003; Lollini et al., 2015; Bertolini et al., 2011; Wu et al., 2016; Kobayashi et al., 2016; Younsi et al., 2015; Fornasier et al., 2003; Yamada et al., 2006; Juel and Herfort, 2002; Bonneau et al., 2007; Palm et al., 2016.

- outliers at each GLS replacement level using box and whiskers plots;
- when the corresponding value for reference PC concrete was not available to calculate the relative chloride ingress results required for the plot;
- excessively high relative values (greater than 200%), resulting from low chloride ingress measurements, which were considered to be unrealistic;
- the chloride ingress results for cement paste specimens;
- duplicated results were considered once only.

The best fit relationship showing the effects of GLS on the chloride ingress into concrete, using the mean values, was plotted as a solid line in Figure 6.1, up to 50% GLS content, having a coefficient of determination $R^2 = 0.84$. Another best fit curve was plotted as a broken line covering the results up to 35% GLS content (the maximum limit permitted in BS EN 197-1:2011 for structural concrete), having a coefficient of correlation $R^2 = 0.72$. Though the latter curve has a lower coefficient of correlation, it is considered to present a more realistic performance of PLC up to the upper limit permitted for structural concrete.

For convenience of reference, the range of BS EN 197-1:2011 (BSI, 2011) common cements with GLS addition is also shown in Figure 6.1. It can be seen that at 35% GLS addition the chloride ingress into PLC concrete could be about 60% higher than that of the corresponding PC concrete, with performance comparable to that of PC at 5% GLS content.

6.5 Influence of Strength and Water/Cement Ratio

The results plotted in Figure 6.1 were separated in terms of strength and water/cement ratio and are shown in Figure 6.2 (a) and (b). The effect of GLS addition for the equal strength mixes [Figure 6.2 (a)], though the available results are limited [compared to equal w/c, Figure 6.2 (b)], they suggest that 10% GLS addition may be used without adversely affecting the chloride ingress resistance of concrete; thereafter the ingress starts to increase slowly with increase in GLS content. At 35% GLS content an increase of 12% is shown. The equal w/c mixes [Figure 6.2 (b)] show a trend (two trend lines; solid line is for results up to 50% GLS content and broken line for results up to 35% GLS content) similar to that for the overall results plotted in Figure 6.1, suggesting that at 35% GLS content, chloride ingress can be expected to increase by about 65%.

6.6 Curing Effects

The influence of the duration of moist curing was studied for GLS contents of 0%–35%, for the duration of 1–360 days. The results are shown in Figure 6.3 (a) and (b) for the equal strength and equal w/c ratio mixes. Recognising that the coefficients of correlation are generally low, the trend lines observed can be considered only as qualitative. The following points of practical relevance can be noted, however:

- On an equal strength basis, the results are limited and show that PLC concrete with up to 15% GLS (CEM II/A cement) can be expected to develop resistance to chloride ingress similar to that of the corresponding PC concrete.
- On an equal w/c ratio basis, the measurements show that the resistance to chloride ingress of PLC concrete, in comparison to PC concrete, can be expected to improve with moist curing duration, particularly with initial moist curing, and whilst it gives higher chloride ingress values, the difference between the two concretes decreases with time.

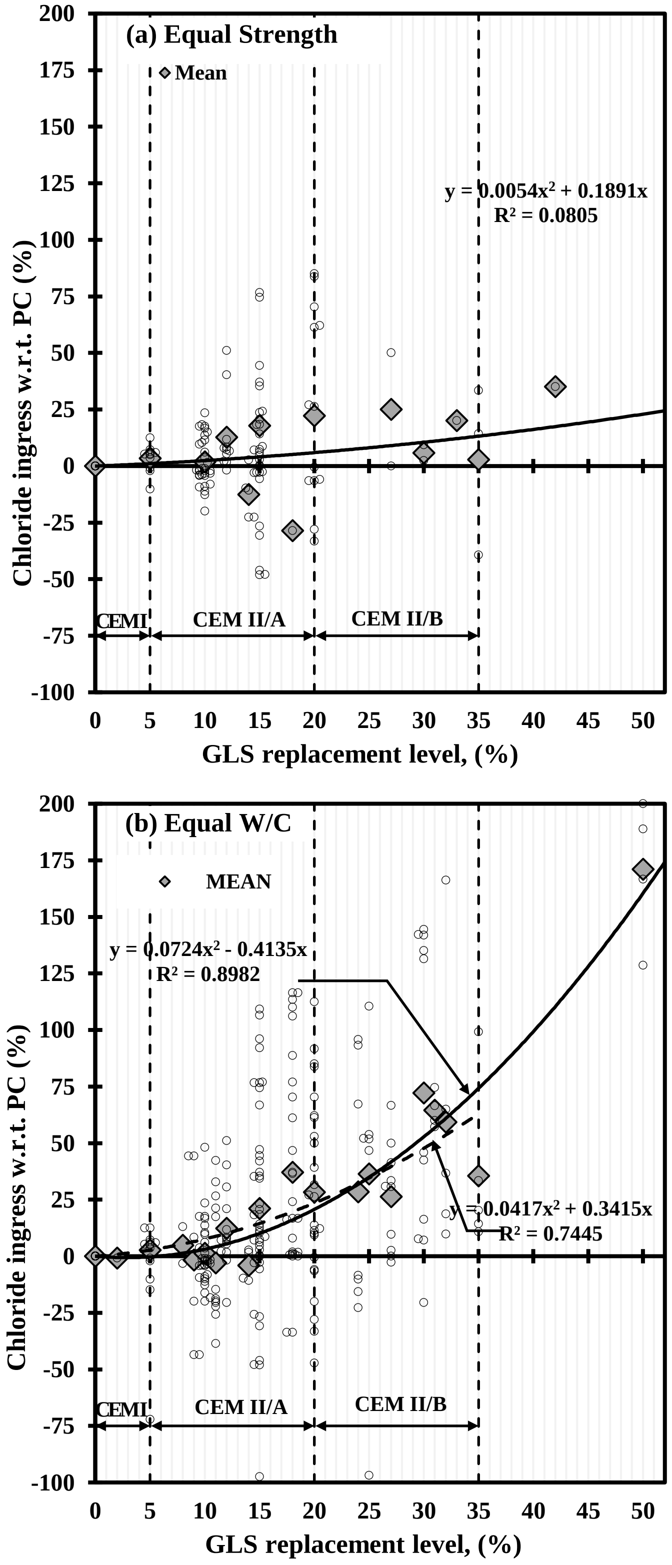


Figure 6.2: Influence of GLS on chloride ingress in concrete at (a) equal 28 d strength (b) equal w/c ratio (Elgalhud et al., 2017b)

Data of Figure 6.2 taken from Figure 6.1

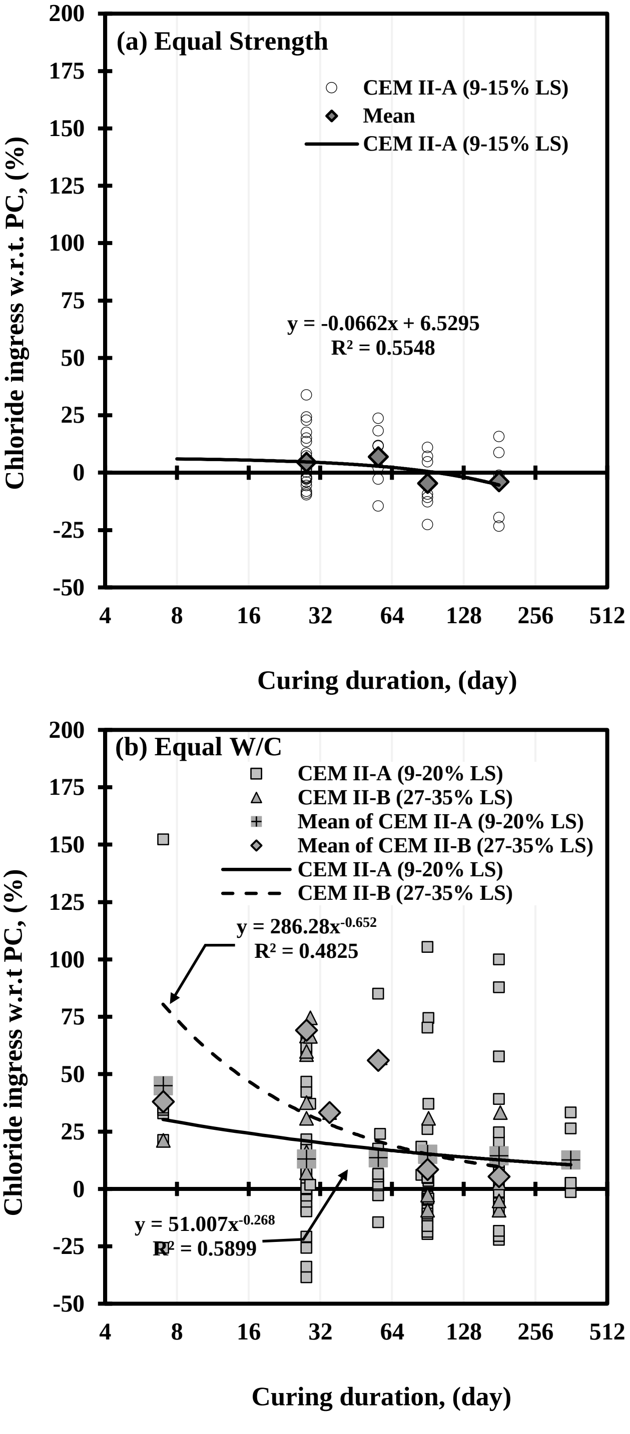


Figure 6.3: Influence of moist curing duration on chloride ingress in PLC concrete of equal strength design and w/c ratio with respect to PC concrete (Elgalhud et al., 2017b)

Data of Figure 6.3 taken from: Aguayo et al., 2014; Bertolini et al., 2011; Cam and Neithalath, 2010; Cam and Neithalath, 2012; Ghiasvand et al., 2015; Ghrici et al., 2007; Githachuri and Alexander, 2013; Güneyisi et al., 2011; Hooton et al., 2010; Hossack et al., 2014; Howard et al., 2015; Irassar et al., 2006; Lollini et al., 2015; Palm et al., 2016; Pavoine et al., 2014; Persson, 2001; Pourkhorshidi et al., 2010; Ramezanianpour et al., 2009; Ramezanianpour et al., 2010; Silva and de Brito, 2016; Thomas et al., 2010a; Thomas et al., 2010b; Xiao et al., 2009

In addition, test results for the effects of curing on chloride ingress into PLC concrete with w/c ratio 0.5, cement content 350 kg/m^3, GLS contents 0%, 9% and 18% and 28 days duration of moist and air curing, with the specimens immersed in a 3% NaCl solution for up to 1 year (Bonavetti et al., 2000; Irassar et al., 2006), showed that the chloride ingress into the concrete mixes increases with the air curing, and also that the rate of chloride ingress is greater for PLC concrete relative to PC concrete.

6.7 Exposure Temperature

Limited tests have been undertaken concerning how the temperature of a chloride-bearing environment may affect the penetration of chlorides into PLC concrete relative to PC concrete. The chloride measurements were available for the following test conditions: mortar specimens with w/c=0.5, limestone contents 0% and 20%, wet curing at 40°C for 3 weeks and immersion in artificial seawater with temperatures −1°C and 20°C for 100 days (Moukwa, 1989; Yamada et al., 2006). The studies came to similar conclusions, namely that (i) at lower temperature the chloride ingress into concrete is adversely affected by the inclusion of PLC and (ii) this is due to increased dissolution of $Ca(OH)_2$.

6.8 Limestone Fineness and Type of PLC (Inter-grinding or Blending)

The effects of GLS fineness on the chloride ingress into PLC concrete have been investigated over a fineness range of 200–1500 m^2/kg, GLS content 8.4%–50%, w/c 0.40–0.50, cement content 292–500 kg/m^3 and moist curing for 28–90 days. The results obtained were analysed and are plotted separately in terms of equal 28-day strength and equal w/c ratio of concrete in Figure 6.4 (a) and (b), respectively.

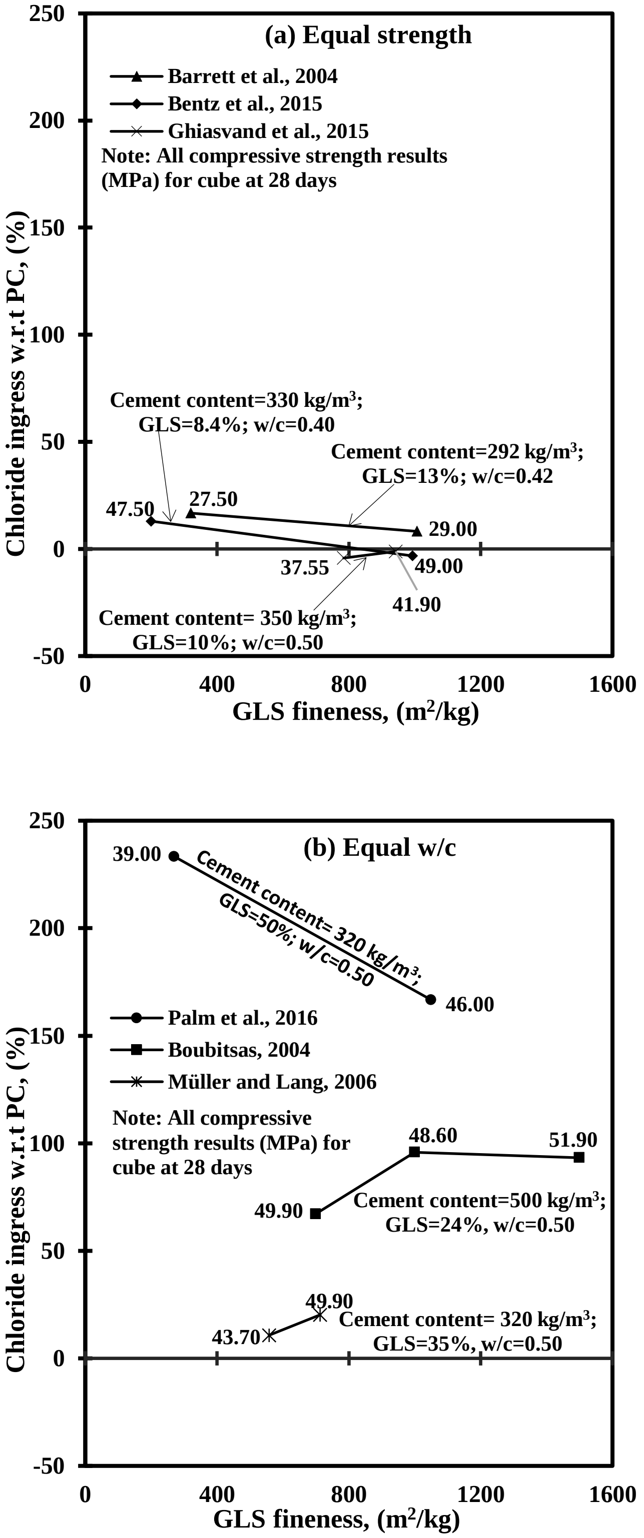


Figure 6.4: Influence of GLS fineness on chloride ingress in PLC concrete of equal strength design and w/c ratio with respect to PC concrete (Elgalhud et al., 2017b)

The relative measurements in Figure 6.4 show that, in general terms, regardless of whether the mixes were designed in terms of equal strength or equal w/c ratio, the effect of GLS fineness on the chloride ingress into concrete is insignificant up to 35% GLS content. The influence of fineness can be observed to be consistent with the compressive strength results, in that finer GLS results in slightly improved strength.

For mixes of equal strength [Figure 6.4 (a)], when GLS contents were in the range 8.4%–13%, which is relatively low, the results show that the relative chloride ingress in PLC was close to that of PC and there was a slight enhancement in the chloride ingress resistance of concrete due to the increased fineness of GLS. In contrast to the equal strength results, from the equal w/c ratio results [Figure 6.4 (b)], which at times, however, appear to be conflicting, there is some evidence to suggest that the chloride ingress into PLC concrete decreases to some extent with the increasing fineness of GLS.

In addition, the effects of PLC produced by two different methods, namely inter-grinding and blending, on chloride ingress have been studied, using GLS content at 10% (Ghiasvand et al., 2015). The fineness of the PLC varied from 3640 to 5980 cm^2/g and the results suggested that for this difference in GLS fineness the chloride ingress resistance was not significantly affected, irrespective of whether the PLC was produced by inter-grinding or blending.

6.9 Cement Content

The effects of total cement content on the chloride ingress into PLC concrete have been studied by Bertolini et al. (2007) and Lollini et al. (2014, 2016) using GLS up to 30%, w/c= 0.46, cement content 300–350 kg/m^3 and moist curing for 28 days. The chloride diffusion results for PLC concrete (13.6–23.5 × 10^{-12} m^2/s) were considerably higher than those for PC concrete (7.0–8.0 × 10^{-12} m^2/s) for all mixtures. As to be expected, owing to the narrow range of cement content employed, the effect on chloride ingress was found to be negligible in both PC and PLC mixes.

6.10 Combined Chloride and Sulfate Environment

Sotiriadis et al. (2014) and Yamada et al. (2006) reported on the chloride ingress into PC and PLC mixtures exposed to a combined chloride and sulfate–bearing environment using GLS 0%–35%, w/c 0.50–0.52, moist curing for 7 days, two test solutions [(a) artificial seawater with 0.28% SO_4^{2-} and 1.89%–2.11% Cl^- and (b) a solution containing 0.00%–0.10% SO_4^{2-} and 1.89%–2.11% Cl^-], exposure temperature of 5°C–20°C and immersion duration of 6–18 months. The results obtained showed that:

(i) The chloride measurements for PC and PLC with GLS content up to 15% were comparable.

(ii) PLC with GLS content of 35% had the highest chloride ingress.

(iii) In the presence of lower sulfate content high chloride contents were recorded, due to the higher amount of dissolved $Ca(OH)_2$ in comparison to seawater, in which the sulfate ions suppress the dissolution of $Ca(OH)_2$.

6.11 Aggregate Content and Particle Size

The effects of aggregate content and particle size have been examined by Wu et al. (2016), with the variables GLS 0%, 5% and 10% and w/c= 0.45, standard curing for 56 days and test samples prepared with varying aggregate content (0–1468 kg/m^3) and mean aggregate size (0.00–2.88 mm). In general, the chloride ingress results for PC and PLC showed similar trends. In comparison to PC, the inclusion of 5% GLS showed a minor reduction in chloride migration (by 5%–9%), whilst, though hard to justify and it could be due to some experimental errors, the results showed migration to increase noticeably (by 40%–45%) at GLS 10%. The increase in each aggregate volume content and particle size led to slight increases in chloride ingress in both PC and PLC mixtures, due to coarser pore structure and the sizeable presence of the aggregate–matrix interface.

6.12 Chloride Ingress: Concrete Strength Grade Effect

To study the relationship between compressive strength and chloride ingress into PLC concrete, the results used to create the Figures 6.1 and 6.2 were analysed in terms of chloride ingress into PLC concrete as a percentage of the corresponding PC concrete versus characteristic cube strength, as shown in Figure 6.5.

Figure 6.5 has been developed as described below:

- Characteristic cube strength was calculated from the measured strength using a variation coefficient of 6% given in ACI 301:2005 (ACI, 2005) for fair laboratory control class.

- The results obtained where the test mixes did not comply with the mix limitations of BS EN 206:2013 (BSI, 2013) for the chloride exposure class XS1 were not considered further in developing the figure.

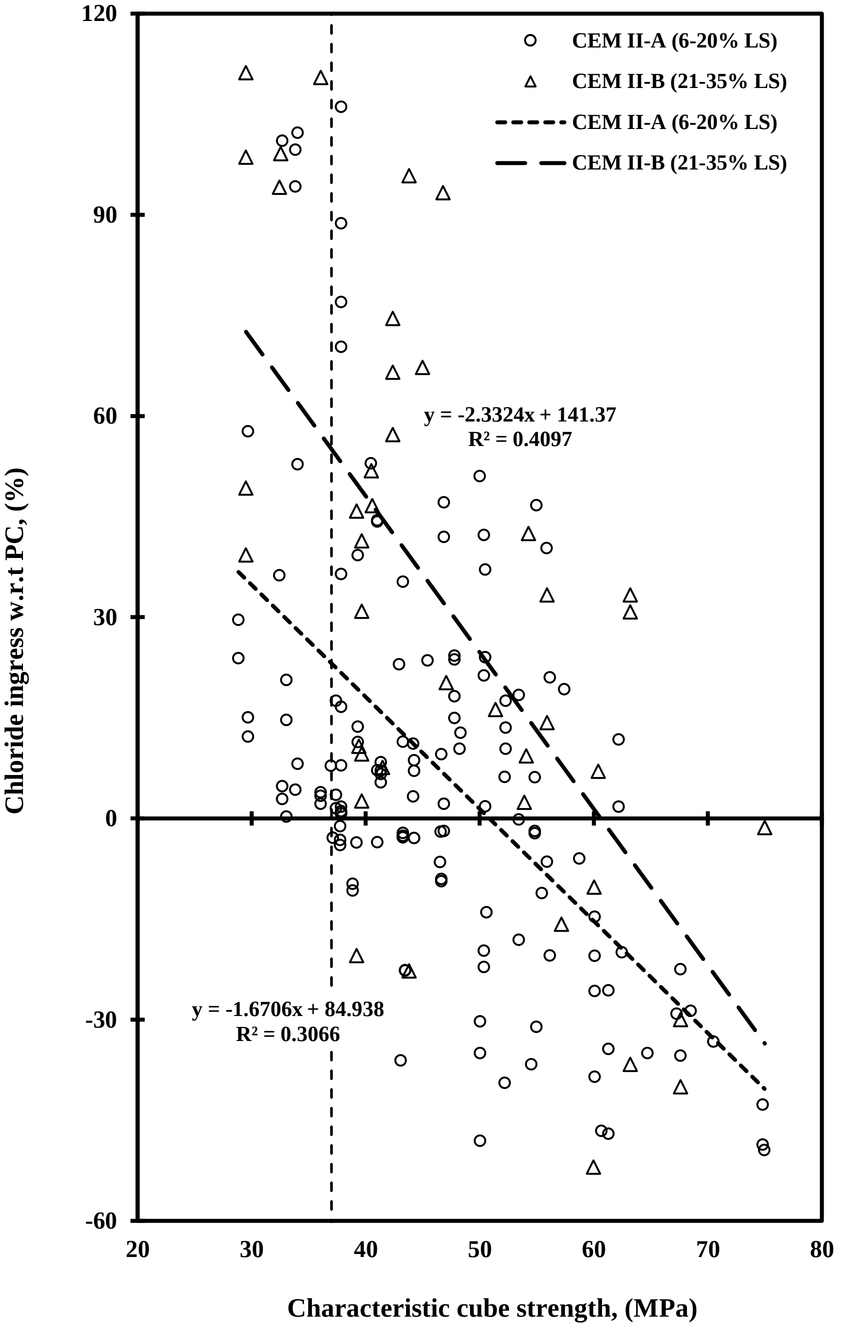


Figure 6.5: Chloride ingress in PLC concrete w.r.t. PC at different characteristic cube strengths (Elgalhud et al., 2017b)

Data of Figure 6.5 taken from Figures 6.1 and 6.2

- For convenience, a linear regression was applied in the analysis of the data. As the coefficients of correlation were generally poor, the trend lines obtained can be considered as of only qualitative value.

- For comparison purposes, the minimum characteristic strength of 37 MPa, for the XS1 exposure class recommended in Eurocode 2 (BSI, 2004), was chosen and identified using a dotted line.

The following important points are revealed by Figure 6.5:

- Chloride ingress increases with decreasing compressive strength and increasing GLS content of concrete. The relative chloride ingress for both CEM II/A (6%–20% GLS) and CEM II/B (21%–35% GLS) concretes can exceed the minimum cover of 35 mm specified in Eurocode 2 at the minimum characteristic strength of 37 MPa for exposure class XS1 (considering that the design working life is 50 years) (BSI, 2004).

- To have a chloride ingress similar to that of PC concrete at 37 MPa, the compressive strength of PLC concrete may have to be increased from 37 MPa to 50 MPa and 60 MPa for cements such as CEM II/A (6%–20% GLS content) and CEM II/B (21%–35% GLS content), respectively. Alternatively, the required minimum cover for PLC concrete at 37 MPa would have to be increased for concrete made with CEM II/A (6%–20% GLS) and CEM II/B (21%–35% GLS) cements.

6.13 Chloride Ingress into Concrete Specified in Terms of w/c Ratio

Looking from another perspective, the chloride ingress into PLC concrete specified in terms of w/c ratio is shown in Figure 6.6. The base data used here are those used in Figures 6.1 and 6.2 and were subjected to the screening process adopted previously for Figure 6.5. The recommended maximum w/c ratio of 0.50 for XS1 exposure class given in BS EN 206:2013 (BSI, 2013) was selected and is shown as a dotted line.

Figure 6.6 shows that for a given w/c ratio, chloride ingress increases with GLS content, and that the chloride ingress behaviour of concrete is similar to that shown in Figure 6.5, but at a slightly greater rate. Additionally, for a chloride ingress similar to that of CEM I concrete at w/c= 0.50, the mixes made with CEM II/A and CEM II/B with GLS would need to be designed with a reduced w/c ratio, of about 0.40 and 0.35, respectively. Alternatively, the required minimum cover (i.e., 35 mm) of PLC concrete at w/c= 0·50 would need to be increased for both CEM II/A (6%–20% GLS) and CEM II/B (21%–35% GLS) cements.

6.14 In-Situ Chloride Ingress Measurements

Fairly limited results have been obtained on this topic. In-situ chloride measurements were for concrete pavements constructed in two different locations in Canada during 2008 and 2009 (Hossack et al., 2014). The test conditions involved were: age at the time of measurement, 3 and 4 years; GLS content 0% and 12%; w/c ratio 0.37 and 0.44 and range of in-situ core strength 43–59 MPa. Although the effects of GLS on strength varied, the chloride measurements for both locations showed, in general, that PLC concretes had on average 20% higher penetration of chlorides than PC. This was attributed to the lower alumina content of PLC due to the dilution of C_3A and C_4AF with the addition of GLS, which reduces the capacity for chloride binding.

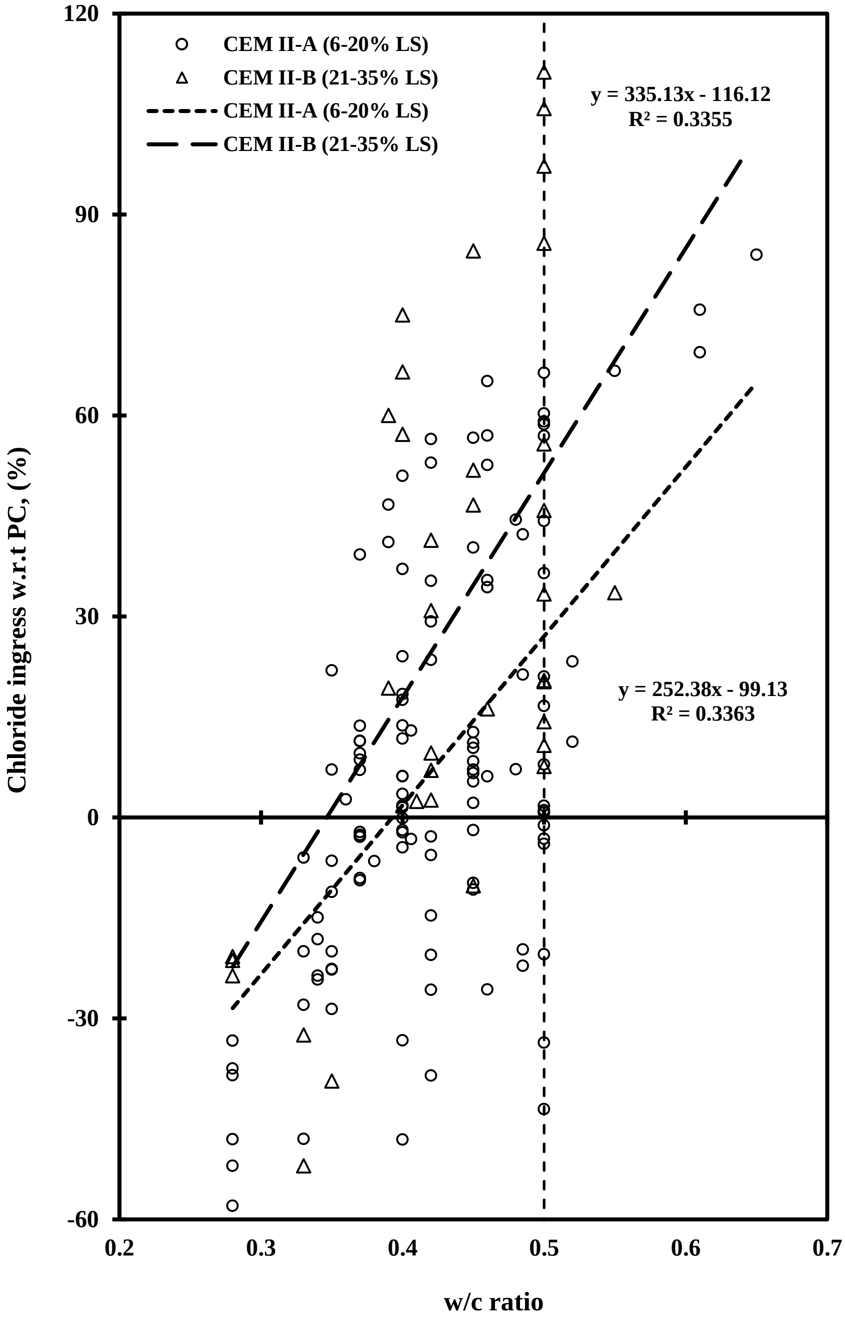


Figure 6.6: Chloride ingress in PLC concrete w.r.t. PC at different w/c ratios (Elgalhud et al., 2017b)

Data of Figure 6.6 taken from Figures 6.1 and 6.2

6.15 Influence of Limestone on Chloride-Induced Corrosion of Reinforcement

The effect of GLS addition on chloride-induced corrosion, though important, has not been reported widely. However, as the use of GLS is found to increase the susceptibility of concrete to chloride ingress, it is necessary to determine how this may influence the corrosion of steel reinforcement in PLC concrete. Only 13 studies have reported on the chloride-induced corrosion of PLC concrete, and their results show that chlorides can reach the steel reinforcement with sufficient concentrations (i.e., higher than 0.4% by cement mass, BS EN 206, 2013) and consequently the corrosion process could in principle be considered to have initiated. Additionally, owing to the complexity of the test methodology and the nature of the measurements, the results obtained could be examined only in a qualitative manner, as presented in Table 6.4.

The corrosion measurements obtained suggest that, in general, the test specimens used had cement blends of 0%–35% GLS, with w/c ratios of 0.42–0.72, and were subjected to chloride exposure for up to 5 years. The corrosion of steel reinforcement was measured using different methods, such as corrosion potential (mV), weight loss of reinforcement (g/m^2), corrosion current/density (mA/m^2) and corrosion rate (μm/year).

For the tests that conducted the assessment of PLC concrete with respect to the reference PC concrete (Table 6.4), the rate of corrosion of the concrete made with PLC was generally found to be higher than that of the corresponding PC concrete. It was also found that an increase in w/c reduced the differences between the corrosion results of the two set mixtures and that the type of curing did not produce a significant change, except for the mixture with the higher w/c and in the specimens cured with lime water (Batic et al., 2010; Batic et al., 2013). It has also been suggested that the corrosion of reinforcement in PLC concrete principally depends on the cement content, w/c ratio and fineness of the GLS (Diab et al., 2015; Diab et al., 2016)

In addition, some tests have assessed the corrosion behaviour of PLC concrete without testing PC concrete, using GLS 10%–20%, w/c 0.46–0.65, exposure duration up to 8 years and chloride concentration 3.5%–10.0% (Bertolini et al., 2002; Bertolini et al., 2004a; Bolzoni et al., 2006; Bolzoni et al., 2014; Brenna et al., 2013; Fayala et al., 2012; Garcés et al., 2006; Meira et al., 2014; Ormellese et al., 2006; Romano et al., 2013; Sistonen et al., 2008; Zacharopoulou et al., 2013). The overall outcome of these studies suggests that the use of PLC concrete leads to a moderate-to-high increase in the corrosion rate.

6.16 Improving PLC Performance in Practice

The effects of GLS addition on the chloride ingress into concrete can be lessened in a number of ways. Though extending the moist curing duration would certainly help greatly to improve the resistance of PLC concrete against chloride ingress by developing a less porous and less permeable concrete, to accomplish this in practice is made difficult by present construction practices. Other options for enhancing the resistance of PLC concrete to chloride ingress could be realised in the following ways:

(a) GLS content could be restricted to a smaller proportion, i.e., to a maximum of 15%. Such a cement will be in partial compliance with PLC of type CEM II/A (6%–20% GLS) in BS EN 197 (BSI, 2011). Though this option may be used, because it limits the replacement of PC content in the cement, it would have a negative impact on the carbon footprint of the cement industry.

(b) The porosity of the concrete could be enhanced by:

  (i) optimising particle packing by revising the proportions of coarse and fine aggregates and/or introducing the use of fillers (Dhir and Hewlett, 2008);

  (ii) developing a more effective use of GLS by adopting other additions such as small proportions of silica fume and metakaolin (Elgalhud et al., 2016).

(c) The specified characteristic strength of concrete could be increased by reducing its water/cement ratio, using a high-range water-reducing admixture. This option should enhance the durability and sustainability of the concrete (Dhir et al., 2000; Dhir et al., 2004; Dhir et al., 2006).

(d) The thickness of the concrete cover could be increased, as an additional obvious option. However, this will have an influence on the structural design and sustainability aspects, and is unlikely to be chosen by the design engineer.

Table 6.4: Summary of influence of GLS addition on chlorides induced corrosion (Elgalhud et al., 2017b)

REFERENCES	MAIN POINTS EMERGING
Batic et al., 2010	**Corrosion rate of PLC mixture higher than that of PC mixture and the increase in the w/c minimizes the differences between the corrosion results of the two mixtures.** ***Reinforcement corrosion unit: corrosion rate (i/µA cm^{-2})*** Cylinder specimen: 50×100 mm; concrete cover: 22 mm; GLS contents: 0 and 22%; w/c ratios: 0.50 and 0.65; moist curing: 28 days; exposure: immersion in a 3% NaCl solution; duration: 9 months; equal w/c mix.
Batic et al., 2013	**Concrete made with PLC showed greater corrosion rate than PC concrete and the increase in the w/c reduces the differences between the two mixtures. Moreover, the type of curing did not introduce significant change except for mixture with the higher w/c and cured with lime water.** ***Reinforcement corrosion unit: corrosion rate (i/µA cm^{-2})*** Cylinder specimen: 50×100 mm; concrete cover: 22 mm; GLS contents: 0 and 35%; w/c ratios: 0.50 and 0.65; air and wet (lime water) curing: 28 days; exposure: immersion in a 3% NaCl solution; duration: 9 months; equal w/c mix.
Bertolini et al., 2011; Lollini et al., 2015	**Corrosion activity of PLC concrete is higher than that of PC concrete.** ***Reinforcement corrosion unit: Rebar corrosion potential (mV).*** Prism specimen:60×250×150 mm; concrete cover: 15 mm; GLS contents: 0, 15 and 30%; w/c ratio: 0.61; moist curing: 28 days; exposure: ponding using 3.5% NaCl solution; duration: two years; equal w/c mix.
Deja et al., 1991	**The rate of reinforcement corrosion of PLC concrete is lower than that of PC concrete.** ***Reinforcement corrosion unit: rebar weight loss (g/m^2).*** Prism specimen: 40×40×160 mm; concrete cover: 22 mm; GLS contents: 0 and 5%; w/c ratio: 0·50; moist curing: 56 days; exposure: immersed in 23% NaCl solution; duration: 12 months; equal 28d strength mix.
Diab et al., 2015; Diab et al., 2016	**In general, the corrosion rate of PLC concrete is considered higher than that of PC concrete until certain level of GLS replacement (15%) after that it starts decrease until it become similar or lower than PC concrete at 20% and 25% of GLS addition. Furthermore, the corrosion activity of PLC concrete principally depends on the cement content, w/c ratio of the mix and the fineness of GLS.** ***Reinforcement corrosion unit: Corrosion rate (mm/year).*** Cylinder specimen: 75×150 mm; concrete cover: 31 mm; GLS contents: 0, 10, 15, 20 and 25%; w/c ratios: 0·48, 0.55 and 0.65; curing: in limewater for 6d, after that in air for 21d; exposure: immersion in 5% NaCl solution; duration: 9 months; equal 28d strength only for 10% GLS mixtures.
Moir and Kelham,1993; Matthews,1994; Livesey, 1991	**Corrosion rate of PLC (5%GLS) concrete is similar to PC concrete, whilst for the corrosion results of PLC (25%GLS) concrete its varying through time compared to PC concrete.** ***Reinforcement corrosion unit: percentage rebar weight loss (%).*** Prism specimen: 100×100×300 mm; concrete cover: 10 mm; GLS contents: 0, 5 and 25%; w/c ratio: 0.60; moist curing: 28 days; exposure: tidal zone; duration: up to 5 years; equal w/c mix.
Pavoine et al., 2014	**Corrosion rate of PLC concrete is higher than that of PC concrete.** ***Reinforcement corrosion unit: corrosion current (mA).*** Specimen: four concrete elements 1 m long, 100 mm thick, and 200 mm high sealed together to form a closed container; concrete cover: 25 mm; GLS contents: 0 and 10%; w/c ratios: 0.40 and 0.55; moist curing: 6 weeks; exposure: contained subjected to 5% NaCl solution; duration: up to three months; equal 28d strength mix.
Tsivilis et al., 2000; Tsivilis et al., 2002	**Corrosion rate of PLC concrete is lower than that of PC concrete.** ***Reinforcement corrosion unit: rebar weight loss (g/m^2).*** Prism specimen: 80×80×100 mm; concrete cover: 20 mm; GLS contents: 0, 10, 15, 20 and 35%; w/c ratios: 0.62 and 0.72; moist curing: 28 days; exposure: partially immersion in a 3% NaCl solution; duration: 12 months; equal w/c only for 35% GLS mixture.

6.17 PLC Performance in Terms of Pore Structure and Related Properties, Strength, Carbonation Rate and Chloride Ingress

To facilitate a meaningful comparison of the durability performance of PLC concrete, Figure 6.7 has been constructed to study collectively, relative to the corresponding PC concrete, the effect of GLS content in combination with PC on porosity and related properties (i.e., water absorption and sorptivity), compressive strength, carbonation rate and chloride ingress.

In developing Figure 6.7, some simple modifications have been carried out to the trend lines observed in Figure 6.1 and the previous Figures 4.1–4.5 and 5.1 presented in Chapters 4 and 5, respectively, to make it easier for the research to be adopted in practice. These modifications are based on the concept that the physical and chemical effects of the inclusion of GLS are mainly those of a filler (better packing of the pore matrix), of heterogeneous nucleation (improving the early strength) and of dilution (increasing the effective w/c), as suggested by Irassar (2009), though these effects rely on the amount and fineness of the GLS used in a mix (Sezer, 2012). The main change is the use of simple linear regression as opposed to polynomial regression and, though a degree of accuracy may have been lost in the process, the outcome has been to produce a useful tool that should allow to estimate the changes that may be expected with the use of GLS, in the pore structure of hardened concrete and its strength, carbonation and chloride ingress resistance.

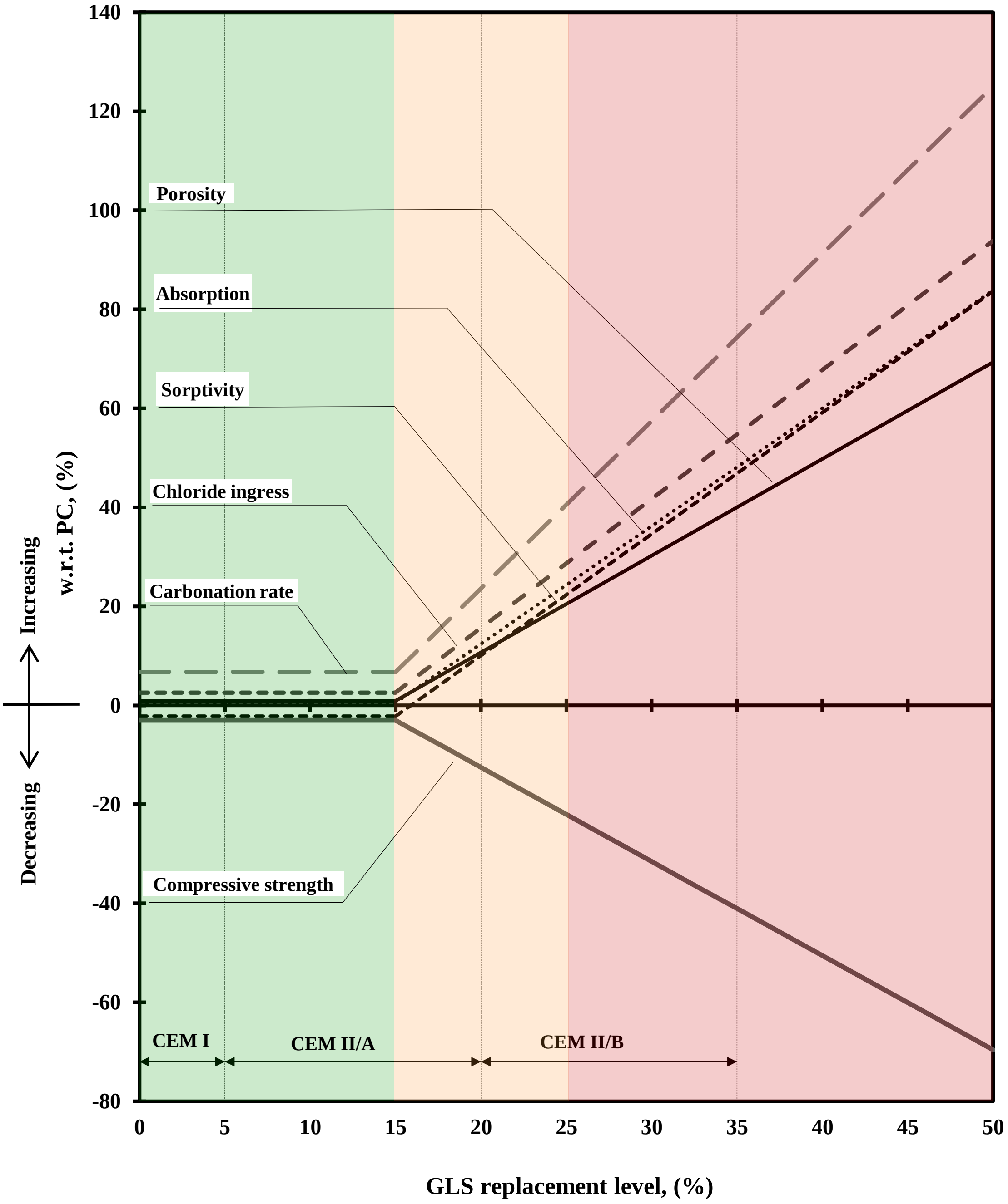


Figure 6.7: Mode of PLC performance in terms of pore structure and related properties, compressive strength, carbonation rate and chloride ingress (Elgalhud et al., 2017b)

Figure 6.7 suggests that, for practical purposes, it is feasible to accept that:

i. at up to 15% GLS content, its effect may be considered constant and almost neutral;

ii. an increase in GLS content beyond 15% gives rise to a progressive reduction in all the properties of concrete and, in this case, pore structure (in the form of porosity, water absorption and sorptivity), strength and durability (against carbonation and chloride ingress).

Table 6.5 shows that the trends of sorptivity and water absorption are mainly the same and are influenced by GLS slightly more than the porosity, which reflects the variance in the working mechanism of each of them. In addition, the sensitivity of PLC to carbonation exposure is higher than that to chloride ingress. This could be attributed to the pH of limestone/$CaCO_3$, which is between 8.5 and 10 (Chen and Yang, 2009; Hua and Laleg, 2009; Phung et al., 2015) and is lower than the pH of PC (i.e., 12.5–12.8) and is considered to decrease the pH of the resultant PLC (particularly at high GLS contents such as 35%).

In summary, it is proposed that though generally the use of GLS has some impact on the properties of concrete, it can be insignificant up to a maximum of 15% GLS content, which is below the maximum limit of 20% for CEM II/A Portland limestone cement (BSI, 2011) and which may need to be revised.

Table 6.5: Mode of PLC performance in terms of pore structure and related properties, strength, carbonation rate and chloride ingress (Elgalhud et al., 2017b)

Cement Type	GLS Content, (%)	WITH RESPECT TO PC, (%)					
		Porosity	Water Absorption	Sorptivity	Compressive Strength	Carbonation Rate	Chloride Ingress
CEM I	1-5	0.9	0.5	-2.0	-3.0	6.7	2.6
CEM II/A-L	6-15	0.9	0.5	-2.0	-3.0	6.7	2.6
	20	10.6	12.4	10.1	-12.5	23.6	15.6
CEM II/B-L	21	12.6	14.8	12.5	-14.4	27.0	18.2
	25	20.5	24.3	22.3	-22.0	40.5	28.6
	30	30.2	36.2	34.6	-31.6	57.4	41.5
	35	40.0	48.1	46.9	-41.1	74.3	54.7
-	40	49.7	60.0	59.1	-50.6	91.2	67.6
	45	59.5	71.9	71.3	-60.1	108.1	80.8
	50	69.3	83.8	83.6	-69.6	125.1	93.9

6.18 CONCLUSIONS

Based on the analysis, structuring and evaluation of the chloride measurements obtained, the following conclusions are made:

a. Combination of GLS with PC, within the bands of CEM II/A and CEM II/B cements in BS EN 197-1 (BSI, 2011), the results show that, in general, the chloride ingress of the concrete increases at an increasing rate as the GLS content increases. The rate of this increase and the significance thereof can vary with whether the PLC mix is designed on an equal strength or equal water/cement ratio basis, with the latter arrangement showing greater effect than the former; and likewise, the type and duration of curing (in terms of relative humidity and temperature), the exposure conditions and the fineness of GLS also tend to vary the magnitude and rate of the GLS effect on chloride ingress.

b. As follows from the above, these effects have been found to be more sensitive and significant with CEM II/B Portland limestone cement than with the CEM II/A type. This appears to support the approach adopted in the BS 8500-1:2006+A1:2012 standard (BSI, 2006), whereby CEM II/B does not appear to be suggested for use under chloride exposure conditions. Additionally, compliance with mix limitations for chloride exposure, as per BS EN 206-1:2013 (BSI, 2013), may have to be revised upward for PLC.

c. The limited in-situ chloride ingress measurements of concrete structures made with PC and PLC (12% GLS) over a period of 3–4 years showed that PLC concrete had a higher chloride ingress rate than the corresponding PC concrete. Additionally, the results showed that, owing to depassivation of reinforcement, the rate of corrosion in PLC concrete, upon chlorides reaching the reinforcement, was generally higher than that in PC concrete.

d. The results discussed in this chapter considered together with the two previous chapters (4 and 5) show that the effects of GLS addition to concrete on the pore structure in terms of porosity, absorption, sorptivity, strength and resistance to carbonation and chloride ingress are similar, though their magnitudes may be different.

e. For practical purposes, and in view of the outcomes of the two previous chapters, it is proposed that the effects of GLS content up to 15% on concrete performance may be assumed to be negligible, and to increase thereafter at a constant rate with increasing GLS content, and that in the light of this the maximum limit on GLS content of CEM II/A may be considered for revision from 20% down to 15%.

CHAPTER 7

STATISTICAL MODELLING OF CARBONATION OF PLC CONCRETE

7.1 Introduction

This chapter describes the statistical modelling work on the carbonation of Portland limestone cement (PLC) concrete using published carbonation data from 1986 to 2017. A computational approach (through multiple linear regression) was adopted to create an uncomplicated, yet effective, model. The generated model allows one to predict the carbonation depth of PLC concrete as a function of a number of factors which are considered statistically significant in the explanation of the carbonation phenomenon.

7.2 Literature Review

This review discusses the development of the models for estimating the carbonation of concrete that includes ground limestone (GLS) in combination with Portland cement. Although several models have been proposed, it was found that some of the notable work in this field was carried out in the 1980s by several researchers, such as Tuutti, 1982; Ho and Lewis, 1987; and Papadakis et al., 1989.

Different types of models for estimating the carbonation of concrete have been proposed, including:

1. **Mathematical models,** which are the most common type and describe the phenomenon of carbonation using mathematical theories and expressions, as by Papadakis et al.,

1991; Aiki and Kumazaki, 2012; Kashef-Haghighi et al., 2015; Kumazaki, 2014; Liang et al., 2002; Bakker, 1993, and Jiang et al., 2000.

2. **Numerical models,** such as those developed by Saetta and Vitaliani, 2004; Zha et al., 2015, and Pan et al., 2015. These types of models are slightly different from the mathematical models in that they utilise computational methods that are mainly computer dependent.

3. **Empirical models**, which are based essentially on experimental measurements in the laboratory or on site, as carried out by Alexander et al., 2007.

4. **Statistical models**, as undertaken by Garcia-Lodeiro et al., 2014; Monteiro et al., 2012, and Silva et al., 2016, which employ multiple regression of a number of parameters to generate predictive relationships.

5. **Simulations and artificial neural networks** based on the machine learning methods, such as those reported by Kwon and Song, 2010; Li and Lu, 2010; Lu and Liu, 2009; Dai and Shui, 2010; Liu et al., 2008, and De Jesus et al., 2017.

On the other hand, the studies that dealt with the modelling of the carbonation of concrete made with cement incorporating GLS are summarised and presented in Table 7.1.

Table 7.1: Summary of previous prediction models of carbonation resistance of PLC concrete from the literature

REFERENCE	PREDICTION MODEL TYPE	PARAMETERS INVOLVED
Demis and Papadakis, 2011; Demis and Papadakis, 2012; Papadakis and Demis, 2011 ; Demis et al., 2014	Mathematical (Physicochemical) model founded on Papadakis et al. 1991; Papadakis et al. 2007	- $Ca(OH)_2$. - C-S-H - CO_2 concentration.
Faustino et al., 2014	Mathematical model developed based on the EHE “Code on Structural Concrete”, 2008 (Spanish Standard)	- Environment conditions. - Porosity. - Binder type. - Compressive strength.
Faustino et al., 2017a; Faustino et al., 2017b;	Mathematical model established from the Portuguese Standard LNEC E465 2009.	- CO_2 concentration. - Relative humidity. - Curing conditions. - Wet/dry cycle influence
Hyvert et al., 2010	Mathematical model based on Bary and Sellier, 2004; Thiery et al., 2007	- Microstructure of concrete. - Concrete chemical composition.
Bucher et al., 2017	Mathematical based on Hyvert et al., 2010	
Marques and Costa, 2010 ; Marques et al., 2013	Mathematical model developed from CEB, 1997	- Relative humidity of the concrete. - Exposure class. - Calcium oxide of the hydrated cement matrix
Ta et al., 2017	Numerical model based on Klopfer, 1978	- Mix design. - Relative humidity. - CO_2 concentration. - Temperature exposure - Initial curing period
Taffese et al., 2015	Model created through the use of artificial neural networks or machine learning methods.	- Concrete mix design. - Fresh and hardened properties of concrete - Carbonation period. - Environmental and curing conditions.
Wang, 2017	Numerical model grounded on Demis et al., 2014	- Relative humidity.

It can be seen from Table 7.1 that the previous research work on modelling of carbonation for PLC concrete was essentially started around 2010. The studies listed in the table are different types of models, but mostly mathematical. In addition, the theoretical parts of these models are verified by a limited number of experimental test results, which could be considered a limitation of the work undertaken.

Furthermore, different parameters were considered in each of the reported models, such as concrete mix design, concrete properties, curing conditions and exposure conditions. There also is no consensus on the procedure of predicting and determining the carbonation of concrete.

The literature also revealed that statistical modelling has not been applied to PLC concrete carbonation. This was the main reason for deciding to use this approach with the large volume of experimental data produced over the past 32 years that was sourced for the work described in Chapter 5.

7.3 Statistical Modelling

As mentioned earlier, the purpose of this work was to propose an uncomplicated linear model for predicting PLC concrete carbonation depth, based on a large amount of published test results, and using a statistical method, which has not been attempted before in this area. The Statistical Package for the Social Sciences (SPSS) software was utilised to establish the model.

7.3.1 Linear Regression Analysis

Regression analysis is a strong method that can be applied to report on different research questions. In this study, multiple linear regressions were utilised to treat the carbonation measurements sourced, to create the best-fitting line over the data points. The word "multiple" refers to more than one input independent variable (it is also sometimes called a predictor variable). Thus, the aim is to fit a plane rather than a line, i.e., joining all the input variables by accompanying a constant number multiplied by each independent variable, and then taking the algebraic summation of these variables (Dey et al., 2000) as shown below:

$$y = A_0 + A_1 \times x_1 + A_2 \times x_2 + \ldots + A_n \times x_n$$

Where

y represents the dependent variable (predictor), which in this case is the depth of carbonation (d);

A_0, A_1, …, A_n are the regression coefficients (constant numbers);

x_1, x_2, ..., x_n are the independent variables, in this case the GLS replacement level, exposure time, 28-day compressive strength and CO_2 concentration.

7.3.2 Model Variables

The independent variables, which are associated directly and indirectly with carbonation, have been examined and analysed in this study as follows:

- Variables related to the concrete mix design and concrete properties: cement content, ground limestone content, water/cement ratio and 28-day characteristic cube strength

- Variables related to the curing: curing conditions and period

- Variables related to the exposure conditions and type: relative humidity, temperature, carbon dioxide concentration, indoor/outdoor and protection from the rain (i.e., sheltered or unsheltered)

There are various statistical ways to nominate which independent variables are to be involved in generating a model (Samal et al., 2008). The method employed in this study to select the variables is the step-wise method (one of the most common methods, which includes or removes one independent variable at each step), which allowed only the statistically significant variable to be applied. Thus, by eliminating the statistically insignificant variables, a higher potential to obtain a model with a credible degree of accuracy can be expected (Pires et al., 2008).

7.3.3 Tools for Examining a Fit

The step-wise method comprises different statistical tools, and these have been applied to assess the goodness of fit of the model. The tools used in this case were as noted below (Dey et al., 2000):

- Coefficient of correlation (R): This ranges from −1 to 1. The closer to 1 this measure is, the stronger is the relation between the variables studied.

- Coefficient of determination (R-squared): This value is the square of R and it computes the proportion of variation of the output (dependent values) explained by the independent variables in the model. Thus, the higher the value of R-squared the better the model.

- R-squared adjusted: This is a revised form of R-squared, that has been modified for the number of input variables in the model, which makes it sometimes preferred over the first.

- Analysis of variance: This is a statistical technique used to test differences between two or more means, where the inferences about means are made by analysing variance.

- The F-value (Fisher–Snedecor test): There are different uses for the F tests, and one of the common practices is to check the theory that a suggested regression model fits the data well.

- P-values: These are probabilities, whose values are always between 0 and 1. When a P-value is very small (usually ≤ 0.05), it means the result is significant and the null hypothesis can be rejected, whilst if the P-value is large (typically >0.05), the result is nonsignificant and the null hypothesis cannot be rejected.

- Equality line: This is determined and plotted by two parameters: slope equals 1 and intercept equals zero. This line is used to check the range of validity of the proposed model, where the closer the trend line of the tested model is to the equality line the better.

7.3.4 Data Used in the Modelling

The experimental measurements of carbonation depth obtained and used to produce a model to estimate carbonation depth in PLC concrete were in total 2335. The studies used to gain the experimental data to build the model, published over the period 1986–2014 (2093 results were gained representing 90% of the total data), were Abualgasem et al., 2014; Ali and Dunster, 1998; Alunno-Rosetti and Curcio, 1997; Assie et al., 2006; Assie et al., 2007; Balayssac et al., 1995; Balcu et al., 2012; Barker and Matthews, 1994; Baron, 1986; Batic et al., 2013; Bertolini et al., 2007; Bertolini et al., 2008; Bertolini et al., 2009; Bertrandy and Poitevin, 1991; Bolzoni et al., 2006; Bolzoni et al., 2014; Cangiano and Principallo, 2010; Catinaud et al., 2000; Chowaniec and Karen, 1992; Collepardi et al., 2004a; Corinaldesi et al., 2004; Courard et al., 2005; Courard et al., 2014; Dhir et al., 2004; Dhir et al., 2007; Diamanti et al., 2013; Drouet et al., 2010; Figueiras et al., 2009; Franzoni et al., 2013; Galan et al., 2010a; Galan et al., 2010b; Galan et al., 2012; Guiglia and Taliano, 2013; Holt et al., 2009; Holt et al., 2010; Hossack et al., 2014; Hussain et al., 2013; Ingram and Daugherty, 1992; Kaewmanee and Tangtermsirikul, 2014; Kargol et al., 2013; Kjellsen et al., 2005; Krell, 1989; Kuosa et al., 2008; Kuosa et al., 2012; Kuosa et al., 2014; Livesey, 1991; Lollini et al., 2014; Manns et al., 2001; Marques et al., 2013; Matthews, 1994; McNally et al., 2012; Meddah et al., 2014; Meira et al., 2014; Moir and Kelham, 1993; Moir and Kelham, 1999; Müller et al., 2006; Müller et al., 2014; Mwaluwinga et al., 1997; Nielsen et al., 2014; Nieuwoudt et al., 2012; Parrott, 1994; Parrott, 1996; Perlot et al., 2013; Pomeroy, 1993; Proske et al., 2013; Proske et al., 2014; Rabehi et al., 2013; Ranc et al., 1991; Redaelli and Bertolini, 2014; Redaelli et al., 2011a; Redaelli et al., 2011b; Révay and Gável, 2003; Rostami et al., 2012; Rozière et al., 2011; Schmidt et al., 1993; Schmidt, 1992a; Schmidt, 1992b; Segura et al., 2013; Shao et al., 2013; Sistonen et al., 2008; Sprung and Siebel, 1991; Tezuka et al., 1992; Thienel and Beuntner, 2012; Thomas et al., 2010d; Thomas et al., 2013; Tschegg et al., 2011; Tsivilis et al., 2000a; Tsivilis et al., 2002b; Vandanjon et al., 2003, and Ylmen et al., 2013).

The data used to verify the generated model were sourced from studies of the past three years, 2015–2017 (242 results, which represent 10% of the sourced data), and included Ahmed and Benharzallah, 2017; Bucher et al., 2015; Bucher et al., 2017; Carsana et al., 2016; El-Hassan and Shao, 2015; Faustino et al., 2017; Frazão et al., 2015a; Frazão et al., 2015b; Leemann et al., 2015; Lollini et al., 2016; Marzouki and Lecomte, 2017; Neves et al., 2015; Owsiak and Grzmil, 2015; Palm et al., 2016; Phung et al., 2015; Rio et al., 2015; Shi et al., 2015; Shi et al., 2016; Silva and Brito, 2015; Sotiriadis et al., 2017; Wang et al., 2017; Zhang et al., 2016, and Zhang et al., 2017).

The relevant information on the various parameters involved and comprising mix designs with different compressive strengths, curing and exposure conditions, is given below:

- Cement contents range between 215 and 540 kg/m^3
- GLS content ranges from 0 to 45%
- Water-to-cement ratios ranging from 0.30 to 0.79
- Characteristic cube strengths at 28 days ranging between 21 and 80 MPa
- Curing conditions:

  Type of curing: air and moist (i.e., relative humidity ≥90%)

  Curing periods between 3 and 365 days

- Exposure conditions:

  Exposure periods from 7 days to 5 years

  Relative humidity 38% to 90%

  Temperature 20°C to 30°C

  Carbon dioxide concentration 0.03% to 100%.

Around 44% of the sourced carbonation measurements are for natural indoor conditions, 11% are for natural outdoor sheltered and 7% are for natural outdoor unsheltered, whilst the rest, about 38%, are from concretes exposed to accelerated carbonation conditions.

It is worth mentioning that the values for some of the above information were missing in some of the studies used in this work. In such cases the studies were examined in detail to ascertain what the missing information would most likely be and accordingly assumptions were made to proceed with developing the model.

Owing to the small number of carbonation measurements available for both natural outdoor exposures and also some of the important information regarding the exposure conditions missing, such as the relative humidity and temperature, which were difficult to estimate, it was decided to work on only the natural indoor and accelerated exposures.

In addition, to improve the reliability of the sourced carbonation measurements, the data used for modelling were only for the moist curing and preconditioned specimens.

7.3.5 Development of Models

Although at first an attempt was made to develop a single model taking into account all the independent variables, as listed before, this was found to be statistically unworkable as for some of the variables their P-values were higher than 5%; these are curing duration, w/c ratio, cement content and exposure environment conditions (i.e., relative humidity, temperature and CO_2 concentration).

Thus, it was required to sort the data in a different manner, as explained below:

- The w/c ratio, cement content and curing duration parameters were excluded, but they were instead used in another equation for predicting the strength of PLC concrete and can be used in the carbonation model as required.

- Because relative humidity is in general a variable factor, its effect on the carbonation process can be difficult to gauge. Thus, the measurements used for modelling were confined to the range of 55% to 80% relative humidity, which is the most sensitive range affecting the carbonation of concrete (Neville, 1994). It is important to mention here that results outside 55%–80% relative humidity were small in number, less than 10% of the whole sourced data.

- Owing to the vast majority of the temperature information being within a quite small range of 20°C–30°C, its effect was considered not to be an influential factor in the model and accordingly the estimated carbonation depth of PLC concrete would be deemed for an exposure temperature range of 20°C–30°C.

- The rest of the data were split into two groups based on the type of carbonation exposure (i.e., natural indoor carbonation and accelerated carbonation) to have an individual model for each.

- Based on the information available, CO_2 concentration of exposure was assumed to be within the 0.03%–0.35% range for natural indoor exposure.

Working with the above considerations, models for estimating the depth of carbonation were developed as described below:

Model for Natural Indoor Exposure:

Table 7.2 presents a summary of the coefficients used in investigating the statistical validity of the first model. The analysis of the outcomes shows that 75.1% of the variability in the depth of carbonation is explained by the independent variables applied (i.e., GLS content, 28-day compressive strength and exposure time). Consequently, it is concluded that the produced model is statistically significant.

Table 7.2: Summary of the First Model[b]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate (S.D. of y about the regression line)
1	0.866[a]	0.751	0.748	2.407

a. Predictors/independent variables: (constant), exposure time, GLS content and compressive strength

b. Dependent variable: carbonation depth

In addition, Table 7.3 shows the analysis of variance of the first model. The F-value of this model is considerably higher than the critical value of F (which is 2.61). Therefore, the model is proved to hold a sufficient explanatory capability. Moreover, the P-value obtained (i.e., zero) for the whole model is less than 5% (the allowed), consequently showing that the GLS content, strength and exposure time (independent variables involved) are statistically significant in explaining the carbonation depth (dependent variable). Thus, it is essential to recognise the coefficients of the linear regression.

Table 7.3: Analysis of Variance Results of the First Model[a]

Model 1	Sum of Squared Deviation	Degree of Freedom (df)	Mean Squared Deviation	F	Significance (P-Value)
Regression	8364.567	3	2788.189	483.221	0.000[b]
Residual	4679.285	810	5.778	--	--
Total	13043.852	813	--	--	--

a. Predictors/independent variables: (constant), exposure time, GLS content and compressive strength

b. Dependent variable: carbonation depth

Table 7.4 shows the multiple linear regression coefficients of the first model. It is found that for each of the variables GLS content, strength and exposure time (the included independent variables), the P-value is lower than the allowed P-value (5%), which proves that they are all capable of explaining the carbonation depth (dependent variable).

Table 7.4: Coefficients of the Multiple Linear Regression of the First Model[a]

Model 1	Multiple Linear Regression Coefficients		Significance (P-Value)
	A	S.D. related to coefficients	
(Constant)	6.552	0.591	0.000
GLS content	0.044	0.014	0.002
Compressive strength	-0.120	0.014	0.000
Exposure time	2.641	0.104	0.000

a. Dependent variable: Carbonation depth

Based on the above, the first model for predicting the carbonation depth of PLC concrete for natural indoor exposure of moist-cured, preconditioned specimens, with exposure temperature 20°C–30°C, relative humidity for the exposure environment 55%–80% and CO_2 concentration between 0.03% and 0.35% can be expressed as follows:

$$d = 6.55 + (0.44 \times GLS) - (0.12 \times f_{cu}) + (2.641 \times T)$$

where

d is the carbonation depth in millimetres;

GLS is the ground limestone content in percentage of the whole cement content;

f_{cu} is the characteristic cube strength at 28 days (MPa);

T is the exposure time in years.

Model for Accelerated Carbonation:

In the model suggested for accelerated exposure it is found that the independent variables included are GLS content, strength, CO_2 concentration and exposure time. Table 7.5 gives a summary of the model, showing that 65.4% of the variability in the carbonation depth is explained by the four independent variables involved. Thus, it establishes that there is a good correlation between the variables of the model and it is statistically significant.

Table 7.5: Summary of the Second Model[b]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate (S.D. of y about the regression line)
2	0.809[a]	0.654	0.650	4.785

a. Predictors: (Constant), Exposure time, CO_2 concentration, GLS content and compressive strength

b. Dependent Variable: Carbonation depth

In addition, Table 7.6 shows the analysis of variance of the second model, which shows that the value of F of the model is higher than the critical value of F (which is 2.39). Consequently, the model possesses a satisfactory explanatory capability. Additionally, the determined P-value (i.e., zero) of the whole model is lower than 5% (allowed value), hence showing that GLS content, strength, CO_2 concentration and exposure time (the independent variables included) are statistically significant in explaining the carbonation depth (dependent variable). Therefore, it is necessary to identify the coefficients of the linear regression.

Table 7.6: Analysis of Variance Results of the Second Model[a]

Model 2	Sum of Squared Deviation	Degree of Freedom (df)	Mean Squared Deviation	F	Significance (P-Value)
Regression	8957.293	4	2239.323	98.091	0.000[b]
Residual	15982.885	700	22.834	--	--
Total	24940.179	704	--	--	--

a. Dependent variable: Carbonation depth

b. Predictors: (Constant), Exposure time, CO_2 concentration, GLS content and Compressive strength

Table 7.7 presents the coefficients of the multiple linear regression of the second model. It is found that for each of the variables GLS content, strength, CO_2 concentration and exposure time (the independent variables), the P-value determined is lower than 5% (the allowed P-value), which proves that all of the independent variables have the ability to explain the carbonation depth (dependent variable).

Table 7.7: Coefficients of the Multiple Linear Regression of the Second Model[a]

Model 2	Multiple Linear Regression Coefficients		Significance (P-value)
	A	S.D. related to coefficients	
(Constant)	7.014	2.303	0.003
GLS content	0.149	0.036	0.000
Compressive strength	-0.129	0.037	0.001
CO_2 content	0.100	0.024	0.000
Exposure time	20.036	2.291	0.000

a. Dependent variable: Carbonation depth

Based on the aforementioned, the second model for predicting the carbonation depth of PLC concrete for accelerated exposure of moist-cured, preconditioned specimens, with exposure temperature 20°C–30°C, relative humidity for exposure environment 55%–80% and CO_2 concentration ≥1% can be expressed as follows:

$$d = 7.01 + (0.149 \times GLS) - (0.129 \times f_{cu}) + (0.1 \times CO_2) + (20.04 \times T)$$

where

d is the carbonation depth in millimetres;

GLS is the ground limestone content in percentage of the whole cement content;

f_{cu} is the characteristic cube strength at 28 days (MPa);

CO_2 is the percentage carbon dioxide concentration;

T is the exposure time in years.

The other independent variables (i.e., w/c ratio, cement content and curing duration) were excluded from the previous proposed models because they were not statistically significant, for the allowed P-value (5%), to explain the (dependent variable) carbonation depth. Nevertheless, it was found that the excluded variables are statistically significant in explaining the 28-day compressive strength of PLC concrete. Therefore, a predictive relation can be described as follows to estimate the compressive strength as a function of these variables. It was found that 72.9% of the variability in the 28-day compressive strength is explained by these variables.

Compressive Strength Relationship:

$$f_{cu} = 104.148 - (0.288 \times GLS) - \left(122.725 \times \frac{w}{c}\right) + (0.021 \times CC) + (0.024 \times CP)$$

where

f_{cu} is the characteristic cube strength at 28 days (MPa);

GLS is the ground limestone content in percentage of the whole cement content;

w/c is the water-to-cement ratio;

CC is the cement content (kg/m^3);

CP is the moist curing period (day).

Based on the proposed models, the following points should be noted:

1. For both models, it is found that the exposure time, GLS content and compressive strength are explanatory variables, especially the last two, which express the effects of the pore structure of concrete on the ingress of CO_2, and hence the carbonation. Whilst, the concentration of CO_2 is found to be statistically significant in the second model.

2. The two models proposed show that each of the variables GLS content, CO_2 concentration and exposure time is directly proportional to the depth of carbonation, whilst the compressive strength has an inverse relationship with carbonation.

3. Regarding the compressive strength relationship, it is found that w/c ratio and GLS content are inversely associated with the compressive strength, i.e., the strength declines

as these variables increase, whereas an increase in curing period and cement content leads to a direct increase in the compressive strength.

4. The models work on the basis that the association between independent and dependent variables (carbonation depth) is linear, using linear equations in data estimation. Even though it is reported that the relationship between carbonation and some independent variables such as the compressive strength (Khan and Lynsdale, 2002) and the CO_2 concentration (Hyvert et al, 2010) is nonlinear, it is believed that this is compensated for by the fact that the generated models involve multiple variables, rather than the single influence of a certain variable being modelled.

5. The statistical relationships of all of the independent variables with the dependent variable studied are in agreement with the theoretical assumptions that clarify the effect of each of them.

7.3.6 Model Verification

It was found that each of the two models proposed are statistically significant. Figures 7.1 and 7.2 show the relationships between the measured (real) values and the values predicted (calculated) by the models. The fit lines of the two models generated are close to the line of equality. The first model obtained leads to a determination coefficient R^2 of 0.81, which indicates a good correlation between the values obtained and those predicted. On the other hand, the second model obtained leads to a determination coefficient R^2 of 0.74. Each of the two models demonstrates a satisfactory level of reliability and a reasonably good ability to describe the measured values.

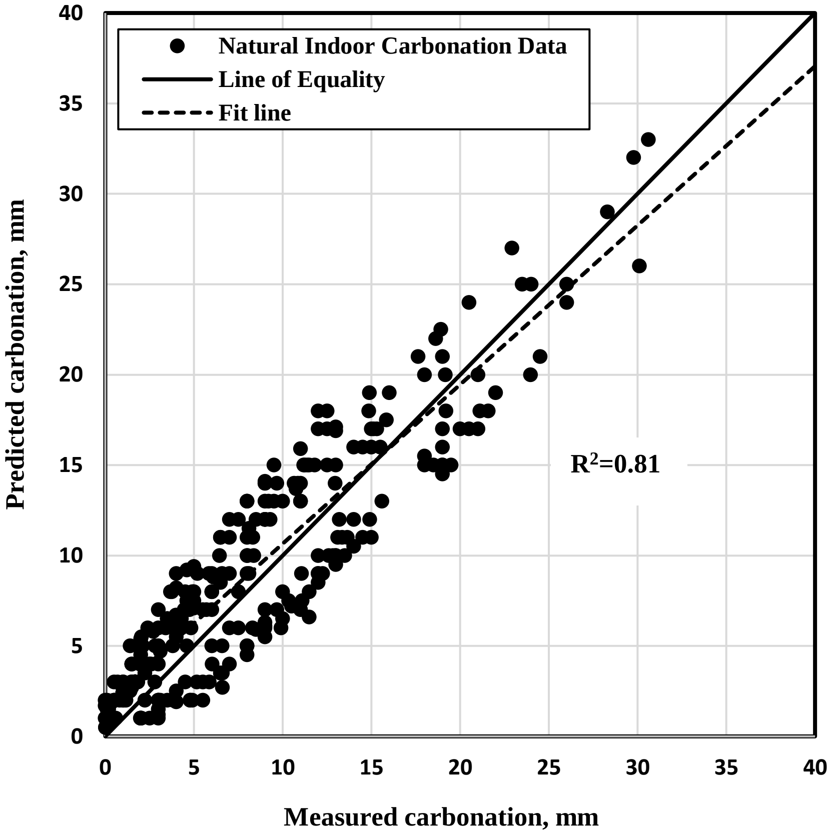


Figure 7.1: Relationship between the carbonation depth measure and that predicted by the first model (natural indoor carbonation)

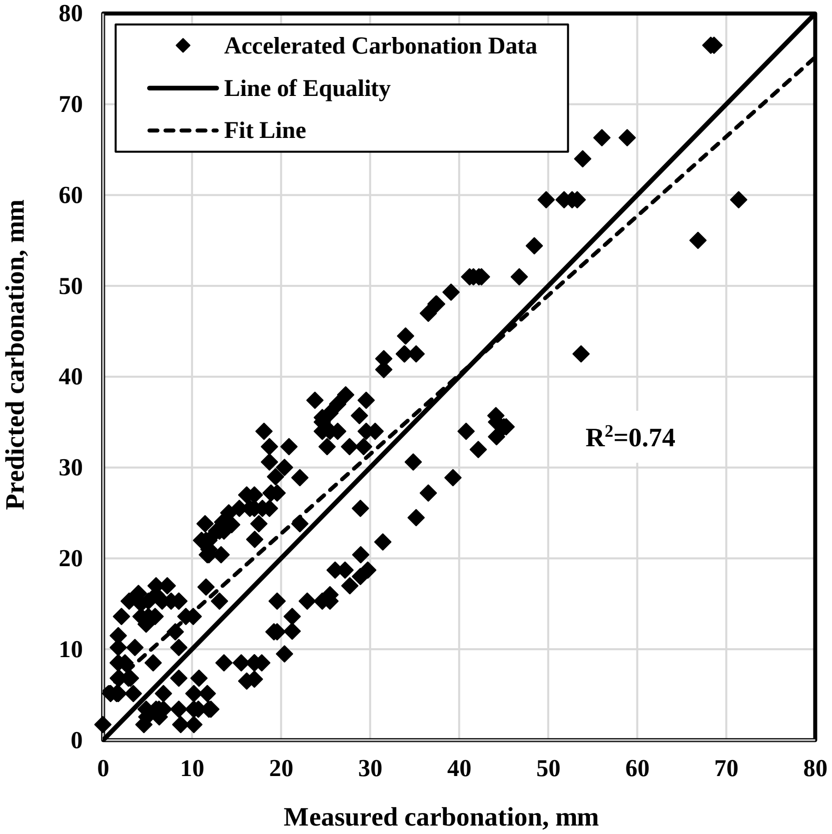


Figure 7.2: Relationship between the carbonation depth measure and that predicted by the second model (accelerated carbonation)

Furthermore, Table 7.8 presents some statistical markers (Dey et al., 2000) that can relate the measured values of the carbonation depth with the calculated values (predicted) obtained using the two proposed models. For each of the two models the mean value of the ratio between the measured and the predicted values was found to be close to 1, which signifies that the predicted values are comparatively close in most the cases.

Table 7.8: Statistical markers related to the calculation of the carbonation depth using the two models suggested

Statistical indicators	First Model		Second Model	
	Measured values (MV)	Predicted values (PV)	Measured values (MV)	Predicted values (PV)
Mean	10.29	11.78	14.98	18.95
Standard deviation	8.82	7.21	11.92	9.89
Cofficient of variation	0.85	0.62	0.79	0.53
Mean MV/PV	0.87		0.79	
Standard deviation MV/PV	0.75		0.72	
Coefficent of variation MV/PV	0.86		0.91	
Values where MV/PV > 1.3	16.2%		20.8%	
Values where MV/PV < 0.7	22.4%		24.1%	
Values where 0.7 ≤ MV/PV ≤ 1.3	61.4%		55.1%	

7.4 Conclusions

Based on the statistical modeling work in this chapter, the following conclusions can be made:

This work, based on a substantial amount of experimental results sourced from 121 publications, and covering a variety of parameters, is the first attempt at developing statistical modelling for estimating the carbonation of PLC concrete. Whilst workable, the two models developed offer scope for further development and/or refinement as more experimental data becomes available.

The sourced data were divided into two groups. The first consisted of information for natural indoor exposure and it was established that the statistically significant variables were the GLS content, 28-day compressive strength and exposure time, whilst the second group consisted of information for accelerated carbonation. In this model, the significant variables were the GLS content, 28-day compressive strength, CO_2 concentration of the exposure environment, and exposure time.

The predicted outcomes through the statistical modelling via the SPSS software are in agreement with the analytical systemisation results in suggesting that GLS addition has the potential to accelerate the rate of carbonation of PLC concrete under different exposure conditions.

CHAPTER 8

CONCLUDING REMARKS AND SUGGESTIONS FOR FUTURE RESEARCH WORK

8.1 Concluding Remarks

Based on the results obtained, discussions and findings of the analytical systemisation approach presented in Chapters 3 to 6 and the statistical modelling of the carbonation of Portland limestone cement (PLC) concrete in Chapter 7, although detailed conclusions have been presented at the end of each of these chapters, general concluding remarks can be drawn as follows:

1. The test results on the characteristics of ground limestone (GLS) and PLC specimens used for this study show that the overwhelming majority of these materials were in compliance with the permissible limits of the relevant international/national standards.

2. The physical and chemical effects of the inclusion of GLS are mainly identified as filler, heterogeneous nucleation and dilution effects. Also, $CaCO_3$ dissolved from GLS has the ability to react with aluminates (C_3A and C_4AF) to form calcium monocarboaluminate. In addition, GLS is considered an internal source of the carbonates required for the thaumasite sulfate attack.

3. The use of GLS up to 25% with Portland cement (PC) should not impair the pore structure, whilst the limit on GLS content for its effect on strength is likely to be lower, at about 15%. This should be considered where a higher proportion of GLS content is allowed in the standards.

4. The carbonation resistance of concrete decreases with increasing GLS content, within the range permitted by standard BS EN 197-1:2011. This effect, however, is less marked for concrete designed on a basis of equal strength compared to the corresponding PC concrete than for concrete designed on an equal water cement ratio (w/c) basis. Eurocode 2 standard specifications for XC3 carbonation exposure for characteristic cube strength of concrete (or its w/c ratio) may need to be reviewed for the addition of GLS. The response to accelerated carbonation, in 3%–5% carbon dioxide concentration, of PLC concrete is similar to that in natural indoor exposure. A conversion factor of one-week accelerated carbonation equal to 0.75-year natural indoor exposure was determined.

5. Similar to carbonation, the chloride ingress in concrete increases with increasing GLS content, within the range permitted in BS EN 197-1:2011. This effect, however, is less for the PLC concrete mixes designed for strength equal to the corresponding PC concrete mixes than for those designed on an equal w/c basis. The results showed that Eurocode 2 specifications for XS1 chloride exposure, in terms of characteristic cube strength of concrete, or w/c ratio, may need to be reviewed for the use of GLS with PC.

6. The effects of GLS in concrete on the pore structure in the form of porosity, absorption, sorptivity, strength and carbonation resistance and chloride ingress are similar, though their magnitude may be different. For practicality, it is proposed that the effects of GLS content of up to 15% on concrete performance may be assumed to be negligible, increasing thereafter at a constant rate with increasing GLS content, and that in light of this the maximum limit on GLS content of CEM II/A (as per BS EN 197-1:2011) may be considered for revision, where GLS content is reduced from 20% down to 15%.

7. The predicted carbonation depths of PLC concrete, through the statistical modelling via the SPSS software, are in harmony with the analytical systemisation results, in suggesting that GLS addition can potentially accelerate the rate of carbonation of PLC concrete under different exposure conditions. This suggests that the proposed models for estimating the carbonation of concrete are workable and offer scope for further refinement as more experimental data become available.

8.2 Suggestions for Future Research Work

Whilst this study has highlighted important aspects of the performance of PLC concrete in terms of pore structure and related properties, strength, carbonation resistance and chloride ingress, there are still other concerns requiring further research using the *analytical systemisation* method developed and used in this research. These are as follows:

1. Fresh properties: water demand, workability, stability, setting time, bleeding, heat of hydration, fresh density, air content and plastic settlement

2. Development of concrete strength: early strength development, tensile strength and flexural strength

3. Other permeation properties that were not covered in this study, i.e., permeability and diffusion

4. Deformation properties: plastic shrinkage, drying shrinkage, autogenous shrinkage, creep and modulus of elasticity

5. Potential durability to chemical attack: sulfate attack, alkali aggregate reaction and acid resistance

6. Resistance to physical attack, including freeze–thaw resistance, abrasion resistance, skid resistance, thermal expansion and exposure to elevated temperatures

7. Another subject that could be proposed is related to the use of GLS, not as a cement component but as a filler aggregate in concrete

In addition, some of the aspects examined in this study, where the experimental results obtained for PLC were limited, could be further investigated and are listed below:

- The effects of curing temperature on pore structure and related properties.
- The combined effects of carbonation and chloride exposure on durability of PLC concrete.
- The collective influence of chloride and sulfate environment on the durability of PLC concrete.
- The effects of temperature of chloride exposure and thereby chloride ingress.
- Carbonation-induced corrosion and chloride-induced corrosion of PLC concrete.
- The synergistic action of PLC with other uncommon types of additions as per BS EN197-1 in producing ternary cement systems, which possibly will enhance the performance of PLC. As a specific example, the use of GLS with cement kiln dust (CKD) on the durability of PLC concrete could be a worthy topic to be studied and researched. As CKD is a ready powder material, a solid and highly alkaline particulate, it could have the potential to enhance the durability and sustainability of PLC concrete.

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