

Durability of geopolymer concrete in marine environment

Author:

Noushini, Amin

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Durability of Geopolymer Concrete in Marine Environment

by

Amin Noushini

*A thesis submitted in fulfillment of the requirements for the degree of
Doctor of Philosophy*



School of Civil and Environmental Engineering
Faculty of Engineering
The University of New South Wales, Sydney, Australia

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Geopolymer binders which are produced by the reaction of solid aluminosilicate source materials such as fly ash, slag, and metakaolin with alkaline solutions represent a new class of inorganic polymer material with great potential to become a more sustainable alternative to Portland cement based binders.

Due to the inorganic nature of geopolymers, they are intrinsically fire resistant and have been shown to have high acid resistance far in excess of traditional cements. However, the long-term durability and factors affecting structural deterioration caused by exposure conditions such as marine environments have had limited examination. Structures are susceptible to a number of mechanisms of degradation such as chloride and carbonation induced steel reinforcement corrosion. It is generally accepted that concrete durability is (to a large extent) governed by the concrete resistance to the penetration of aggressive substances. In marine or coastal zones, the most harmful substances contain chloride ions.

This research work is aimed to experimentally investigate the microstructure, transport properties, chloride diffusion and carbonation of various types of geopolymer concrete including fly ash based, slag based and combined fly ash/slag geopolymer concretes. A systematic study on the effect of thermal curing and calcium content (sourced from slag) on the chloride diffusion resistance of geopolymers was conducted and results were interpreted by the means of nano and microstructural characteristics. The chloride binding capacity of low and high calcium content GPCs were investigated. The suitability of accelerated diffusion tests such as ASTM C1202 rapid chloride penetration test and NT BUILD 492 chloride migration test, initially developed for Portland cement concrete, has been investigated for geopolymer concretes and modification in test methods suggested and examined. Correlations between the modified ASTM C1202 data, the chloride migration coefficient and the chloride diffusion coefficient of geopolymers were established. Finally, performance-based recommendations for geopolymer concretes with various binders in marine environment were proposed.

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ABSTRACT

Geopolymer binders which are produced by the reaction of solid aluminosilicate source materials such as fly ash, slag, and metakaolin with alkaline solutions represent a new class of inorganic polymer material with great potential to become a more sustainable alternative to Portland cement based binders.

Due to the inorganic nature of geopolymers, they are intrinsically fire resistant and have been shown to have high acid resistance far in excess of traditional cements. However, the long-term durability and factors affecting structural deterioration caused by exposure conditions such as marine environments have had limited examination. Structures are susceptible to a number of mechanisms of degradation such as chloride and carbonation induced steel reinforcement corrosion. It is generally accepted that concrete durability is (to a large extent) governed by the concrete resistance to the penetration of aggressive substances. In marine or coastal zones, the most harmful substances contain chloride ions.

This research work is aimed to experimentally investigate the microstructure, transport properties, chloride diffusion and carbonation of various types of geopolymer concrete including fly ash based, slag based and combined fly ash/slag geopolymer concretes. A systematic study on the effect of thermal curing and calcium content (sourced from slag) on the chloride diffusion resistance of geopolymers was conducted and results were interpreted by the means of nano and microstructural characteristics. The chloride binding capacity of low and high calcium content GPCs were investigated. The suitability of accelerated diffusion tests such as ASTM C1202 rapid chloride penetration test and NT BUILD 492 chloride migration test, initially developed for Portland cement concrete, has been investigated for geopolymer concretes and modification in test methods suggested and examined. Correlations between the modified ASTM C1202 data, the chloride migration coefficient and the chloride diffusion coefficient of geopolymers were established. Finally, performance-based recommendations for geopolymer concretes with various binders in marine environment were proposed.

PREFACE

This thesis is submitted in fulfillment of the requirements for the degree of Doctor of Philosophy at the University of New South Wales (UNSW) in Sydney, Australia. The work described herein was performed by the candidate in the School of Civil and Environmental Engineering at UNSW. The candidate was supervised by A/Professor Arnaud Castel and Professor Raymond Ian Gilbert. The thesis has been supported by papers that have been submitted for consideration, accepted or published in internationally renowned journals and conferences. These papers are listed as follows.

- International Journal Publications

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2. Noushini, A., Hastings, M., Castel, A., Aslani, F. 2018, 'Mechanical and Flexural Performance of Synthetic Fibre Reinforced Fly-Ash Based Geopolymer Concrete', *Construction and Building Materials*, vol. 186, pp. 454-475.
3. Noushini, A., Castel, A. 2018, 'Performance-Based Criteria to Assess the Suitability of Geopolymer Concrete in Marine Environments Using Modified ASTM C1202 and ASTM C1556 Methods', *Materials and Structures*.
4. Noushini, A., Castel, A., Aldred, J., Rawal, A. 2018, 'Chloride Diffusion Resistance and Chloride Binding Capacity of Fly Ash-based Geopolymer Concrete', *Cement and Concrete Composites*.
5. Khan, M.S.H., Noushini, A., Castel, A. 2017, 'Carbonation of a Low-Calcium Fly Ash Geopolymer Concrete', *Magazine of Concrete Research*, vol. 69 (1), pp. 24-34.
6. Noushini, A., Castel, A. 2016, 'The Effect of Heat-Curing on Transport Properties of Low-Calcium Fly Ash-Based Geopolymer Concrete', *Construction and Building Materials*, vol. 112, pp. 464-477.
7. Noushini, A., Aslani, F., Castel, A., Gilbert, R.I., Uy, B., Foster, S. 2016, 'Compressive Stress-Strain Model for Low-Calcium Fly Ash-Based Geopolymer and Heat-Cured Portland Cement Concrete', *Cement and Concrete Composites*, vol. 73, pp. 136-146.
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9. Noushini, A., Castel, A., (under preparation), 'Performance-based Specification for Geopolymer Concrete in Marine Environment Using Chloride Diffusion and Migration Coefficients'.

10. Noushini, A., Castel, A., Aldred, J. (under preparation), 'Mechanical Performance and Chloride Diffusion Resistance of Fly ash, Metakaolin and Slag Based Geopolymer Concrete'.
 11. Noushini, A., Castel, A., Gilbert, R.I., Aldred, J. (under preparation), 'The Effect of Calcium Content on Creep and Shrinkage of Geopolymer Concrete'.
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 2. Noushini, A., Castel, A., Aldred, J. 2017, 'Chloride Diffusion and Chloride Binding Capacity of Geopolymer Concrete with Low, Moderate and High Calcium Contents', Concrete 2017 conference, Adelaide, Australia.
 3. Noushini, A., Castel, A. 2016, 'Porosity and Resistivity Measurement of Accelerated Cured Geopolymer and Conventional Concrete', *2nd International Conference on Concrete Sustainability (ICCS16)*, Madrid, Spain, pp. 759-770.
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 5. Noushini, A., Castel, A. 2015, 'A Resistivity-Based Approach to Indicate Chloride Permeability of Geopolymer Concrete', *Concrete 2015 conference*, Melbourne, Australia, pp. 1172-1181.
 6. Noushini, A., Babaei, M., Castel, A. 2015, 'The Effect of Heat-Curing on Mechanical Properties of Slag Blended Fly ash Based Geopolymer Concrete', *Geopolymers 2015*, Hernstein, Austria.

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Chapter 1

Introduction

1 INTRODUCTION

Concrete is the most widely used man-made material in the world. Ordinary Portland Cement (OPC), traditionally used as a binder in concrete, is associated with excessive consumption of natural resources and is a key contributor to global anthropogenic CO₂ emission. The majority of this emission is generated from the chemistry of OPC production (calcination of limestone) and not the production methods or technology. Consequently, the concept of OPC replacement with other more environmentally friendly cementitious materials has raised attention. Some industrial by-products such as fly ash (FA) and ground granulated blast furnace slag (GGBFS) are widely used as supplementary cementitious materials for partial replacement of OPC. Their prevalent use is attributed to their good cementitious and pozzolanic properties and relatively low price.

Geopolymer binders represent a new class of inorganic polymer material with great potential to become a more sustainable alternative to OPC binders. Although the concept of the alkali-activated cements was known as early as 1900s (Provis and Van Deventer 2014), geopolymers were first hypothesised by Davidovits in the late 1970s (Davidovits 1989). He conjectured that Aluminium (Al) and Silicon (Si) obtained from a geological source, or from by-products of industrial processes (e.g. fly ash and slag), had the potential to react with an alkaline liquid to form a strong polymer binder. It is now known that essentially any pozzolonic compound with a high Si and Al content in amorphous form, which is readily dissolved in an alkaline solution, will suffice as a geopolymeric precursor (Davidovits 2008).

Motivation behind the study of this material not only resides in its enhanced sustainability but also potentially superior engineering properties. The mechanical and structural properties of concrete made with geopolymer binders have been reported in many research publications to be comparable to that of OPC based counterparts (Kriven et al. 2003; Noushini et al. 2016b; Noushini and Castel 2016a; Palomo and Glasser 1992; Sarker et al. 2013; Xu and Van Deventer 2000). However, in spite of many studies dealing with the properties of geopolymer concrete (GPC), as with any new construction material, a thorough understanding of its long term performance is yet to be well documented. There are only a few published studies related to durability of

geopolymer concrete especially in marine environment (Babaee and Castel 2016; Chindaprasirt and Chalee 2014; Darmawan et al. 2013; Jaya Ekaputri et al. 2017; Kumar and Ramujee 2016; Kupwade-Patil and Allouche 2013; Ren et al. 2017; Tennakoon et al. 2017; Tittarelli et al. 2018; Wang et al. 2012; Yang et al. 2014; Zhuang and Xu 2017).

Premature deterioration of reinforced concrete structures has significant economic consequences relating to maintenance, repair or replacement of reinforced structures, as well as, environmental impacts and safety concerns (Costa and Appleton 1999; Zornoza et al. 2009). Reinforcing bar corrosion is the most common mechanism of deterioration of reinforced concrete structures which could happen either due to chloride diffusion or carbonation (Li 2011). In marine environments, reinforcement corrosion is predominantly due to chloride (Cl) ion penetration and depassivation of reinforcing bars (Andrade 1993; Li 2011). This will result in a loss of steel reinforcement cross section. Furthermore, due to the accumulation of high volume corrosion products, internal tensile forces generated eventually results in cracking, delamination and spalling of the concrete cover.

Concrete permeability and microstructure are the most important parameters which could control the rate of carbonation and chloride ion ingress and consequently affect the service life of the structure by controlling both corrosion initiation time and corrosion rate after depassivation of steel reinforcement.

This research work is aiming to experimentally investigate the microstructure, transport properties, chloride diffusion and carbonation of various types of geopolymer concrete including fly ash based, slag based and combined fly ash/slag GPCs. The key point is to better understand the long term performance of GPCs in marine environment and to investigate the possibility of establishing a relationship between accelerated and semi-natural durability test methods. The outcome of this research work can contribute significantly in the development of a performance-based recommendation for geopolymer concrete.

This thesis is organised into 8 chapters as follows;

Chapter 1 provides an introduction to the work including brief background information regarding the topic and the objectives of the study

Chapter 2 presents a comprehensive review of the existing literature on the sustainability concerns of OPC and the potential for geopolymer to contribute towards the reduction in CO₂ emissions. The chemistry of geopolymers and previous investigations on durability of geopolymer concrete in marine environment is reviewed. The lack of studies in methodical way on durability of geopolymer in marine environment is highlighted.

Chapter 3 discusses the experimental program including the materials, the methodology and test methods used in this research.

In Chapter 4, results obtained for the mechanical and transport properties of various GPCs are discussed in details and comparisons are made. The microstructural results are also presented in this chapter.

Chapter 5 is dedicated to the chloride related durability test results and discussion. The accelerated and semi-natural chloride diffusion tests results are presented and the chloride binding capacity of the geopolymer concrete is assessed.

Chapter 6 presents the accelerated and natural carbonation test results obtained on geopolymer concretes. Microstructural assessments (i.e. XRD) are reported to understand the carbonation mechanism and product formation in geopolymer concrete.

Chapter 7 provides performance-based recommendations to be used to estimate/evaluate the long term performance of geopolymer concretes of different type. It becomes evident that the test methods originally designed for the durability assessment of OPC concrete are not always compatible with geopolymer concrete since the chemistry and mechanisms of degradation are significantly different. The provided information can be used to develop a comprehensive database for standardisation and durability assessment of geopolymer concrete.

Finally, in Chapter 8, conclusions are drawn, some recommendations are made and direction for future research is suggested.

References to literature cited in this thesis and the appendices are presented at the end of the thesis.

Chapter 2

Literature Review

2 LITERATURE REVIEW

2.1 Sustainability issues of cement industry

Anthropogenic CO₂ emissions are recognised as the major contributor to climate change which is widely accepted as a real threat to the ecology of our planet. Manufacture of Portland cement which is the traditional binder for concrete production accounts for approximately 5% of the global CO₂ emissions. The production of 1 tonne of Portland cement directly generates 0.55 tonnes of CO₂ and requires the combustion of carbon-fuel to yield an additional 0.4 tonnes of carbon dioxide (Davidovits 2008). Since the cement manufacture is already quite efficient and the majority of the emission is a direct result of the calcinations of limestone, substitution of limestone with an alternative calcium source would appear to be the only solution for CO₂ emission reduction. However, no other source of calcium has been identified that would be capable of supplying more than a small fraction of the cement industry needs.

Therefore, the most viable solution is the partial replacement of Portland cement with other suitable more environmentally friendly materials such as fly ash (FA) and ground granulated blast furnace slag (GGBFS). FA and GGBFS are by-products of other industries. Fly ash is mainly being produced by burning pulverized coal in power plants. Since coal is a major fuel for energy production in power plants and is currently supplies around 30% of primary energy and 41% of global electricity generation (WCA 2012), hundred million tons of fly ash is being produced every year. The largest coal producing countries are China, the USA, India, Australia and the Russian Federation (Heidrich et al. 2013). It is estimated that there are over 850 Giga tonnes of proven coal reserves worldwide; which is enough to last more than 130 years at current rates of production (WCA 2012). From the data in 2010 (Heidrich et al. 2013), the worldwide production of coal combustion products (CCPs) was 780 Million tonnes which consists of more than 660 Million tonnes of fly ash (85% of CCPs). The world average effective utilization of CCPs is about 53% that is yet a limited utilization rate. GGBFS is produced by quenching molten iron slag (a by-product of iron and steel-making) from a blast furnace in water, to produce a granular product that is then dried and ground into a fine powder.

Since the FA and GGBFS are produced regardless of whether being reused or dumped, the replacement of Portland cement with these supplementary cementitious materials (SCMs) directly reduces the CO₂ emissions related to concrete production. However, there is a limited extent for the substitution of ordinary Portland cement (OPC) with these SCMs due to their effect on concrete properties particularly at early age strength.

Instead of blending fly ash and slag with OPC, these SCMs can be activated by alkaline solutions to fully replace OPC. This new type of material is called geopolymer, a new class of inorganic polymer material with great potential to become a more sustainable alternative to OPC binders.

2.2 Geopolymer background and chemistry

Geopolymers are a class of amorphous aluminosilicate materials, composed of cross-linked alumina (AlO₄⁻) and silica (SiO₄) tetrahedra to form polysialates, with an alkali metal ion to balance the negative charge of Al³⁺ in IV-fold coordination. The empirical formula proposed is:

$$M_n\{-(\text{SiO}_2)_z\text{-AlO}_2\}_n \cdot w\text{H}_2\text{O} \quad (2-1)$$

where M is a monovalent cation such as K or Na, n is a degree of polycondensation and z is between 1 and 3 or higher.

The term ‘geopolymer’ was first introduced by Davidovits in 1979 to represent the inorganic polymers resulting from geochemistry. Geopolymers like other polymers are macromolecules with definite size and molecular weight (Davidovits 1989). For instance, the polymerization number of K-poly(sialate-siloxo) type geopolymer $(\text{-Si-O-Al-O-Si-})_n$ is stated by Davidovits (Davidovits 2008) to be in the range of $512 < n < 8000$. This yields a molecular weight (MW) of $60,000 < \text{MW} < 850,000$ or a particulate dimension of 5 to 15 nm (50 - 150 Å) as measured by Kriven et al. (Kriven et al. 2003). Geopolymer consists of nanoparticulates which are separated by nanoporosity whose features are of the order of 3 to 10 nm (Davidovits 2008). It is the accumulation of these geopolymeric micells (individual nanoparticulates) that forms the geopolymer matrix. Davidovits, who first applied the term geopolymer to the alkali aluminosilicate binders (Davidovits 1991), pioneered the use of calcium-free systems based on calcined clays (Metakaolin).

The study on fly ash based geopolymer was first introduced in 1993 (J. Wastiels et al. 1993). Wastiels et al. (1993) found that the relative proportions of sodium and silica had a significant effect on the compressive strength of mortar samples (3.1 to 63.1 MPa). They observed a high compressive strength and good acid resistance for fly ash based geopolymer concretes. van Jaarsveld et al. (1999) characterised fly ash based geopolymers for stabilisation and immobilisation of toxic heavy metals. This study was the first to develop relationship between composition, mechanical properties and leaching of heavy metals in geopolymeric materials. The microstructure and mechanical properties of low calcium fly ash based geopolymers have been comprehensively studied by many researchers since 1999 following the pioneering works of Palomo et al. (1999).

The first attempts on the alkali activation of GGBFS has happened in 1940 by Purdon who discovered that the alkali addition to slag results in a rapid-hardening binder (Purdon 1940). The alkali-activated slag cements were used in large scale construction as early as the 1950s (Davidovits 2008). In 1959, Glukhovsky studied the mechanism of alkali activation of aluminosilicate raw materials including GGBFS (Glukhovsky 1959). Since then, many researchers have elaborated on and extended Glukhovsky's works. However, the complexity of slag chemistry as it relates to geopolymer formation is yet to be further investigated.

2.3 Geopolymerisation mechanism

2.3.1 Fly ash based geopolymers

The aluminosilicate contents (SiO_2 and Al_2O_3) in fly ash exist in both amorphous and crystalline phases. The crystalline phases are chemically stable and do not dissolve during geopolymerisation (Van Jaarsveld et al. 1998). Therefore, the analysis of geopolymerisation mechanism of fly ash based geopolymers is complicated due to the presence of significant amount of crystalline phases such as mullite, quartz and hematite. The crystalline phases may shield and cover some glassy aluminosilicate phases and prevent them to be readily accessible for alkali dissolution reactions.

Based on the conceptual model presented by Duxson et al (2007b), the geopolymerisation mechanism of fly ash based geopolymers consists of five stages; dissolution, speciation equilibrium, gelation, reorganization and polymerization-

hardening. The dissolution stage starts when FA particles been attacked by alkaline solution as shown in Figure 2-1 (Fernández-Jiménez et al. 2005). During this stage, the breakdown of the covalent bonds Si-O-Si and Al-O-Al in the glass occurs and ions (silicon and aluminium) pass into the solution (Palomo et al. 1999). Consequently, the reaction product is made both inside and outside the shell of the FA particle. This will continue until the FA particle is fairly consumed. A dense matrix is then formed when the alkaline solution penetrates the interior space of larger spheres and fills them up with reaction product. At this time, precipitations of reaction products occur.

If the rate of dissolution is low, some portions of smaller FA particles are covered with the reaction products within the precipitation stage. To avoid the formation of protective crust around undissolved FA particles which prevents the contact with alkaline solution, Law et al. (2014) recommended the use of an alkaline solution with modulus ratio of equal to 1 ($M_s=1.0$). The dissolution process should be quick enough to let most of the FA particles to react before precipitation starts.

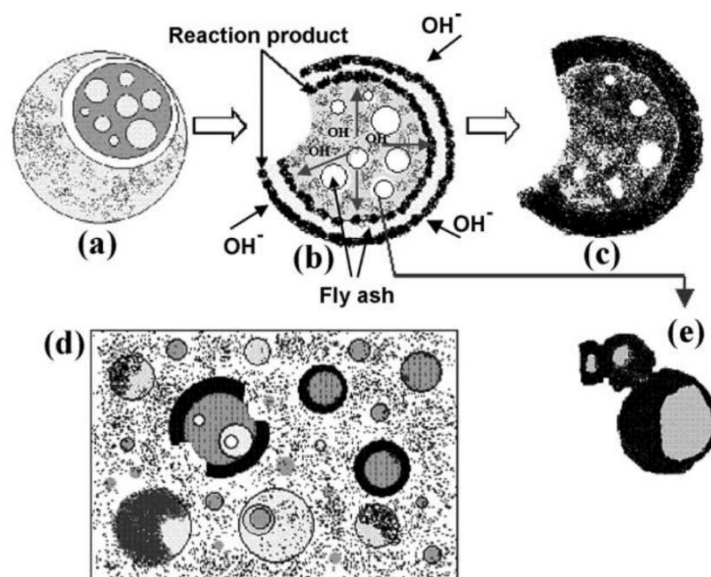


Figure 2-1. Descriptive model of geopolymerisation of fly ash (Fernández-Jiménez et al. 2005)

The mineralogy of the fly ash has significant influence on the properties of the resulting geopolymer (Davidovits 2008; Fernández-Jiménez and Palomo 2003; Steveson and Sagoe-Crentsil n.d.). The amorphous (glassy) content of fly ash has stated to be the key contributor to the reactivity and degree of geopolymerisation. The aluminosilicate contents (SiO_2 and Al_2O_3) in fly ash exist in both amorphous and crystalline phases. The

crystalline phases are chemically stable and do not dissolve during geopolymerisation and will be incorporated into the matrix of the final product (Van Jaarsveld et al. 1998). It has been shown that through the geopolymerisation, the amorphous structure of the fly ash particles is converted to a compact alkali (Na or K) aluminosilicate structure (Fernández-Jiménez and Palomo 2003, 2005). For a constant amount of fly ash used, higher amorphous content yields higher mechanical properties, since the amorphous content is the phase essentially feeding the geopolymerisation reactions (Criado et al. 2007a). Thus the amorphous content of the fly ash has to be measured and taken into account in the design and synthesis of the geopolymer concrete.

The fly ash particle size and unburnt carbon content has also shown to affect the properties of the resulting geopolymer concrete. Fly ashes with smaller particle size demonstrated to have a higher degree of reactivity and thus higher compressive strength. The amount of unburnt carbon presents in the fly ash (referred to as “loss on ignition (LOI)”) has an undesirable effect on geopolymer concrete. The high LOI of fly ash increases the electrical conductivity of concrete, increases the water demand due to reduced workability, entrains more air into the concrete and affects concrete aesthetic by leaving traces of black colour on concrete surface (Ha et al. 2005; Neville and Brooks 1987; Ryan 1989).

Lee and van Deventer (2003) studied the reaction mechanism and performance of geopolymers using FTIR and leaching experiments. It has been observed that the concentration of soluble silicate was critical in determining the nature of the product that would form and thus the mechanical performance. They observed that at low concentrations of dissolved silica a highly polymerised structure formed, with little interparticle bonding. On the other hand, with a higher quantity of soluble silicate in alkaline solution, much stronger interparticle bonding was observed.

The importance of dissolved silica in controlling the nature of the reaction products in geopolymer has been demonstrated in some other research works (Criado et al. 2007a, 2008). It was found that fly ash based geopolymers made with little or no dissolved silica in the alkaline solution contained significant amount of zeolites. The crystalline content of the reaction products decreased significantly by increasing the quantity of dissolved silica within the alkaline solution.

2.3.2 Slag based geopolymers

The overall geopolymerisation mechanism of slag based geopolymers is similar to one explained previously for fly ash based geopolymers, although there are differences in the properties of the final product. The considerable amount of calcium in the matrix of slag based geopolymers leads to the production of some form of calcium silicate hydrate with partial substitution of aluminium, also known as C-(A)-S-H (Myers et al. 2013; Wang and L.Scrivener 1995; Yip and van Deventer 2003). The alkali activation of GGBFS results in an aluminium and alkali substituted calcium silicate hydrate with a tobermorite-based structure (similar to the structure of C-S-H gel in OPC system) with some degree of cross-linking (Myers et al. 2013). C-(A)-S-H gel is also accompanied by secondary aluminium and/or magnesium-rich reaction products (Myers et al. 2013; Provis and Bernal 2014; Wang and L.Scrivener 1995; Yip and van Deventer 2003).

2.3.3 The role of alkaline solution in geopolymerisation

The impact of alkaline solution concentration/alkalinity on the properties of fly ash or slag based GPCs is of great importance. According to the conceptual model proposed by Duxson et al. (Duxson et al. 2007a), for fly ash based geopolymers (with low calcium content), higher alkalinity levels lead to a higher dissolution rate and consequently availability of more aluminate and silicate species to form the aluminosilicate network. Therefore, a higher mechanical strength is expected.

For high-calcium content systems such as slag based GPCs, high alkalinity levels can hinder the formation of the C-(A)-S-H gel and reduce the mechanical strength as the calcium solubility reduces due to supersaturation of the system with regard to portlandite (Ca(OH)_2) (Nath and Sarker 2014; Provis and Bernal 2014).

Yip et al. (Yip et al. 2005) studied the effect of alkalinity and calcium content on the formation of C-S-H gel in blended metakaolin and GGBFS systems using SEM. They reported the possibility of coexistence of C-S-H gel and aluminosilicate (geopolymer) network at low alkalinity levels and at sufficient GGBFS content. On the other hand, at high alkalinity levels of above 7.5 M, the geopolymer gel appeared to dominate the matrix accompanied by some calcium precipitates. The effect of alkali and calcium content on the formation of C-(A)-S-H gel and performance of fly ash/slag blended geopolymers requires further investigation.

2.3.4 *The role of curing condition on geopolymerisation*

Temperature or heat curing is known as the reaction accelerator for geopolymerisation (Palomo et al. 1999). According to the research performed by Pangdaeng et al. (2014), it has been found that temperature curing (TC) is the most effective curing method for GPCs among all the curing methods investigated. Pangdaeng et al. (2014) reported that temperature cured specimens at 40 °C for a period of 24 h, demonstrated higher compressive strength and lower porosity and water absorption in comparison with those of cured under vapour-proof membrane curing (MC) and wet curing (WC) conditions at the ambient temperature (23 °C). Generally, if all the factors remain constant, the temperature increase results in a higher mechanical strength (Hardjito et al. 2004; Palomo et al. 1999).

Many studies have been performed so far on the behaviour of geopolymer at different curing temperatures (Alvarez-Ayuso et al. 2008; Bakharev 2006; Hardjito et al. 2004; Nasvi et al. 2012; Sindhunatavan et al. 2006; Somna et al. 2011). Sindhunatavan et al. (2006) stated that an increase in temperature from 30 to 75°C increases the polycondensation of geopolymer, reduces the setting time and increases the strength. On a research (Guo et al. 2010) conducted on properties of low calcium fly ash GPC, it has been observed that the compressive strength of the specimens cured for 8 hours at 75 °C was almost equal (slightly higher) to the strength after 7 days of curing at 23 °C (35.6 MPa compared to 34.5 MPa, respectively). The same observation has also been reported by other researchers (Vora and Dave 2013) showing that increasing the curing temperature (up to 90 °C) and curing time lead to higher compressive strength of low calcium fly ash based GPC. Görhan and Kürklü (2014) found that apparent porosity and water absorption of low calcium fly ash based GPC samples decreased by increasing the heat curing time at 85 °C from 2 h to 24 h.

However, in a research conducted by Rovnanik (Rovnaník 2010) on the effect of heat curing on the pore structure of Na-based metakaolin geopolymers using mercury intrusion porosimetry (MIP) test, a systematic increase in pore size and cumulative pore volume was observed by increasing the curing temperature. The maximum pore volume in ambient-cured samples lied between 7 and 20 nm in diameter, whereas the bulk of pores were between 20 and 50 nm for heat-cured samples. The larger pore sizes observed in heat-cured samples were attributed to the rapid formation of the network which leads to a less ordered structure, while the ambient curing appeared to favour the

formation of a denser structure through a slower development of the aluminosilicate network where the reaction products could gradually fill up the pores and reduce the porosity.

In some research work, a resting period is applied between finishing the casting of specimen and starting of the heat curing. For instance, a rest period of 60 minutes after casting was applied by Hardjito et al. (2004) and specimens were then oven cured at 60°C for 24 hours and results were compared with those were oven cured at the same temperature immediately after casting, with no resting period. However, results reported by Hardjito et al. (Hardjito et al. 2004) show that applying a rest period before heat curing has very little effect on strength of geopolymer concrete.

It is observed that there is a point in geopolymerization at which temperature-controlled kinetics are inhibited (Sindhunatavan et al. 2006). Other researchers (Alvarez-Ayuso et al. 2008; Hardjito et al. 2004; Nasvi et al. 2012) have also found that the optimum curing temperature for higher reactivity and better geopolymerization lies between 60 and 90°C. However, increasing the curing temperature from 75 to 90°C did not show any significant gain in the compressive strength (Hardjito et al. 2004).

Although the importance of curing conditions on mechanical and microstructural properties of fly ash based geopolymers have been previously reported in several research works (Criado et al. 2005; Kovalchuk et al. 2007), their effect on durability, specifically chloride diffusion, has been insufficiently studied.

2.4 Durability of geopolymer concrete

Due to the inorganic nature of geopolymers, they are intrinsically fire resistant and have been shown to have exceptional thermal stability far in excess of traditional cements (Barbosa and MacKenzie 2003). Fly ash based geopolymers exhibited better frost resistance than OPCC (Provis and Deventer 2009). However, the long-term durability and factors affecting structural deterioration caused by exposure conditions such as marine environments have had limited examination (Bernal et al. 2011). Structures exposed to marine environments are susceptible to a number of mechanisms of degradation such as chloride and carbonation induced steel reinforcement corrosion.

The alkalinity of the concrete pore solution leads to formation of a thin passive layer surrounding the steel bars which prevents oxidation of steel (Glass et al. 2000).

However, under certain circumstances, passivity is lost and corrosion occurs. The corrosion products are expansive and typically cause cracking and spalling of the concrete (Ahmad 2003), leading to loss of structural performance. Loss of passivity usually occurs due to one of two factors, the presence of chloride ions or loss of pore solution alkalinity. Once the chloride concentration at the level of steel reinforcement reaches the chloride threshold level, the pH is considered to be low enough to result in the destruction of the passive layer (Ahmad 2003). This point is referred to as depassivation state. Loss of alkalinity in OPC concrete can also be a result of carbonation, although leaching of hydroxides by fresh water can also occur as well.

2.4.1 Chloride induced corrosion

Reinforcing bar corrosion is the most common mechanism in the deterioration of reinforced concrete structures (Li 2011). It is generally accepted that concrete durability is (to a large extent) governed by the concrete resistance to the penetration of aggressive substances. In marine or coastal zones, the most harmful substances contain chloride ions. In such a complex environment, chloride ions ingress concrete due to a combination of various mechanisms, which include permeation, absorption (or capillary suction) of chloride-carrying water and diffusion in the pore water of concrete (Mejía et al. 2003). In a completely water-saturated concrete, chlorides penetrate by pure diffusion mechanism due to the concentration gradient. However, in the case of partially saturated concrete, chloride ions penetrate by absorption, capillary forces or dissolving in the maritime fogs micro drops (Andrade 1993).

A schematic diagram of the process of corrosion-induced deterioration is given in Figure 2-2. The service life of reinforced concrete structures can be modelled as summation of two phases; corrosion initiation time (t_0) and corrosion propagation time (t_1) (Kyösti Tuutti 1982). The time taken for the chloride ions to transport through the matrix pore network and reach the threshold in which the passive film will breakdown and corrosion starts is called “corrosion initiation time”. The second stage of the deterioration process that involves corrosion development is then called “corrosion propagation phase”. Corrosion initiation time usually takes a long time to happen depending on chloride diffusion resistance of the concrete or corrosion resistance of steel. Once the corrosion starts (second of phase – corrosion propagation) the process can be very rapid resulting in cracking and severe damage to the structure.

There are five key transport mechanisms for chloride ions in permeating the concrete structure to reach the steel reinforcement and initiate corrosion (Song et al. 2010). These include:

- Diffusion under the influence of a concentration gradient
- Absorption due to capillary action
- Migration in an electric field
- Pressure-induced flow
- Wick action (when water absorption and water vapour diffusion are combined)

Each of these mechanisms reflects concrete exposed to a different situation, and consideration is required to understand the driving force of chloride ions in each use. Surface mechanisms contribute little to transporting chlorides to the depth of concrete and chloride transport through the concrete to reach steel reinforcement is mainly governed by diffusion and capillary action through the porosity. Most of the models used for corrosion initiation time prediction are developed based on the resistance of concrete to chloride ion diffusion (Boddy et al. 1999; Ehlen et al. 2009). As such, this thesis will focus on evaluating the concrete resistance to chloride diffusion to assess concrete durability in a marine environment

The time taken by the chloride ions to reach the rebar and trigger corrosion depends on factors such as; mechanism of intrusion, external concentration of the chlorides, the transport rate of Cl^- ions into concrete, the microstructure of the material and the matrix chloride binding capacity (Andrade 1993; Mejía et al. 2003).

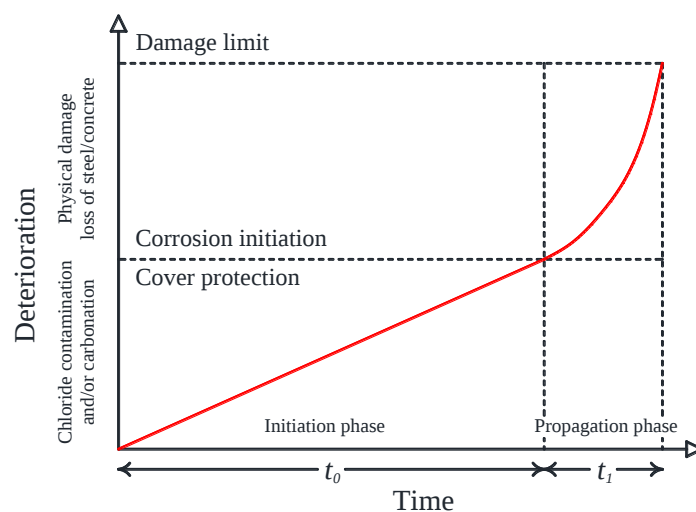


Figure 2-2. corrosion-induced deterioration model of reinforced concrete (Kyösti Tuutti 1982)

There are two main mathematical models used to describe diffusion of chloride ions through concrete; Fick's Second Law and Nernst-Planck Equation.

Fick's Second Law predicts the time-dependant special ion concentration in a semi-infinite medium. It is an essential tool for the prediction of chloride ion content and diffusion coefficients in concrete. However the model requires saturation and state conditions. The equation used to model ion diffusion is:

$$C(x,t) = C_s \left(1 - \operatorname{erf} \frac{x}{2\sqrt{Dt}} \right) \quad (2-2)$$

where $C(x,t)$ is the chloride concentration at depth x from the surface, C_s is the chloride concentration at the surface, D is the diffusion coefficient (measured experimentally), erf is the error function, and t is the time of exposure to the chloride environment.

The equation can be used in combination with the prescribed chloride threshold limit to predict the time of exposure or depth of chloride ions required to initiate corrosion of the steel reinforcement, but can only be used under steady state conditions.

Bazant (1979) proposed a model to determine the initiation time of corrosion based on Fick's law:

$$t_0 = \frac{1}{12D} \left[\frac{c}{1 - (C_{th}/C_s)^{0.5}} \right]^2 \quad (2-3)$$

where t_0 is the corrosion initiation time in s, D is the diffusion coefficient in m^2/s , C_{th} is the chloride threshold in %, C_s is the surface chloride in %.

Zhang and Lounis (2009) proposed a model estimating the corrosion initiation time as shown in eq. (2-4).

$$T_i = \frac{d_c^2}{4D \left[\operatorname{erf}^{-1} \left(1 - \frac{C_{th}}{C_s} \right) \right]^2} \quad (2-4)$$

where T_i is the corrosion initiation time, C_s is the surface chloride concentration, C_{th} is the chloride threshold, D is the diffusion coefficient, d_c is the depth of concrete cover and erf is the error function.

The Nernst-Planck equation describes the transport process of each ion in an ideal solution as shown eq. (2-5). This can be interpreted as diffusion due to the combination of three different mechanisms including diffusion, convection and electrical migration.

$$\frac{\partial(C_i + S_i)}{\partial t} = \text{div} \left(D_i \nabla C_i + z_i D_i \left(\frac{F}{RT} \nabla \phi \right) C_i \right) \quad (2-5)$$

where D_i is the diffusion coefficient, C_i is the concentration, z_i the charge number of the diffusing ion i , F is the Faraday's constant, R the gas constant, T the temperature, ϕ is the electrostatic potential, and S_i is the bound ion concentration.

It worth noting that the diffusion coefficient of concrete is a time-dependent parameter which reduces with time due to the ongoing cement hydration and pore refinement (Bamforth and Price 1993; Bentz et al. 1996; Luping and Gulikers 2007). Song et al. (2008) introduced a mathematical model to determine the diffusion coefficient as a function of time as shown in eq. (2-6).

$$D_t = D_0 \left(\frac{t_0}{t} \right)^m \quad (2-6)$$

where D_t is the diffusion coefficient at time t , D_0 is the diffusion coefficient at time t_0 , t_0 is the standard time (28 days or 1 year) and m is a constant.

While Nernst-Planck equation is a much more complex model, it allows the chloride ion concentration to be determined when an electrical potential is applied. As such, an integrated form of this equation is used to calculate the diffusion/migration coefficient for the Nordtest NT BUILD 492.

There is relatively limited literature available regarding the chloride diffusion in geopolymer concrete. Kupwade-Patil and Allouche (2013) and Muntingh (2006) reported the high resistance to chloride ingress of fly ash based geopolymer binders. Kupwade-Patil and Allouche [49] reported that the low calcium fly ash (Class F) geopolymer concrete heat cured at 80°C for 72 hours has lower chloride diffusion coefficients, chloride content and porosity compared to Class C fly ash geopolymer concrete and their counterpart OPC concrete which have higher calcium contents; on the other hand, Lloyd et al. (2010) stated that the presence of calcium is essential to lower

the permeability of pore system and prevent alkali from leaching and consequent pH drop which can lead to depassivation of embedded reinforcement.

Lloyd et al.'s statement is in agreement with findings of Ma et al. (2013) where a high water sorptivity rate which could be indicative of a high chloride diffusivity was reported for fly ash based geopolymer samples. Provis et al. (2012) also emphasized the importance of the presence of slag in the matrix to reduce the porosity of geopolymers. The high porosity of geopolymer aluminosilicate networks suggests high mass transfer rates, and as a result, high chloride diffusivities in low-calcium fly ash based geopolymer, at least compared to OPC-based binders, which contradicts results of some of the aforementioned studies.

For slag based geopolymers (also called alkali-activated slag binders), there is a better correlation between the reported pore structure observations and chloride diffusivity. Roy et al. (2000) showed that the chloride diffusion coefficient of slag based geopolymers can be as low as half of that of OPC binders. Similarly, Ma et al. (2016) reported lower chloride diffusivity in slag based geopolymer concretes than in OPC concretes. The chloride diffusivity values, however, decreased by increasing the alkali content, contradicting the better development of C-(A)-S-H gel at lower alkalinity levels as discussed in Section 2.3. A sensitivity of the chloride diffusion coefficient to the alkali concentration and modulus ratio (molar ratio of silicate to alkalis) was reported in their study.

The involvement of a wide range of variables in terms of both compositional parameters and experimental techniques mandates a systematic approach in which the effects of variables on the chloride diffusion and performance of geopolymer concrete are considered. In lieu of such an approach, and considering the often contradictory reported results in the literature, the performance of geopolymer structural concretes in chloride contaminated environments can be still a source of ambiguity for both the research community and general practitioners.

2.4.2 Carbonation

Carbonation is a significant issue for OPC concrete. Atmospheric CO₂ can dissolve in concrete pore water, forming carbonic acid. Carbonic acid may then attack calcium containing phases, particularly portlandite, resulting in neutralisation of the alkalinity of

the pore solution. As the concrete pore solution becomes less alkaline, embedded steel may corrode (Ahmad 2003).

In OPC binders the hydration products such as Portlandite Ca(OH)_2 provide a buffer effect. However, fly ash based geopolymers (with low calcium content) or slag based geopolymers (with high calcium content) do not have a substantial amount of Portlandite. The pore solution OH^- concentration is of importance during the carbonation process (Bernal et al. 2013b; Lloyd et al. 2010).

Bernal et al. (2013) investigated the carbonation of fly ash and GGBFS based geopolymers. According to their results, precipitation of alkali salts from the pore solution is the main reaction during the carbonation of aluminosilicate networks. The type of precipitated alkali salt was suggested to depend on the partial pressure of the ambient carbon dioxide. Under natural exposure, carbonates were identified as the main carbonation product, while bicarbonates were observed at elevated carbon dioxide concentration which is normally used to accelerate the carbonation process in laboratory conditions. Decalcification of C-(A)-S-H gel was also reported as a major reaction in calcium-rich geopolymers. The structure of carbonated aluminosilicate network remained rather unaltered based on nuclear magnetic resonance spectroscopy results. On the other hand, Puertas et al. (2006) and Bernal et al. (2015) reported substantial structural strength degradation and increase in porosity, particularly when the sodium silicate is used in the manufacture of calcium-rich geopolymers.

The artificial decline of the pH and alteration of the formed carbonation products were also further emphasised by Bernal et al. (2012), and confirmed by pH measurement of carbonated and uncarbonated fly ash based geopolymers under various carbon dioxide concentration by Khan et al. (2017). Bernal et al. (2012) developed a thermodynamic model which was capable of predicting the pH of alkaline solutions of various alkali concentrations after carbonation under different concentrations of carbon dioxide. According to their calculation, the declined pH level under natural carbonation was high enough to keep the reinforcement passivated, even for low concentration of alkalis in the activator solution. However, no further experimental verification including pH measurements or electrochemical assessment of a reinforced system was provided to complement the theoretical results.

Although it seems that there is a general consensus on the adverse effect of application of accelerated carbonation techniques on the service life estimation of geopolymer binders, the extent of pH drop due to the accelerated carbonation under different carbon dioxide concentrations are less investigated in the literature.

2.5 Durability testing

Measuring the performance of concrete structure in its natural service environment is the most reliable method to evaluate durability however it can take up to few several decades to collect sufficient data. Accelerated testing methods can be developed in order to predict, within a reasonable time, the durability of concrete under the conditions expected in service. However, accelerated tests invariably have some degree of errors which often increases as the degree of acceleration increases.

One of the test methods generally accepted to provide realistic data on concrete resistance against chloride penetration is the ponding or the diffusion tests standardised in America as ASTM C1556 and in Europe as Nordtest NT BUILD 443. The diffusion test is relatively slow but provides data which are representative of the properties of concrete irrespective of changes to the binder (Shi 2004a).

Another more rapid test method is the Chloride Migration Test standardised as Nordtest NT BUILD 492. This test provides good correlation with the ponding test for OPC concrete in a more reasonable timeframe (Chiang and Yang 2007).

Rapid chloride penetration test (RCPT) which has been first developed by Whiting (1981) and standardised as ASTM C1202, is an eminent test method using an electrical field to measure the chloride penetrability of concrete. A potential difference of 60 V DC is applied through a 50 mm thick concrete disc over a 6 h period and the total charge passed, in coulombs, is used as an indication of chloride permeability of concrete (refer to Table 2-1). Although the RCPT is relatively simple and quick, the high voltage used could cause heating and microcracking of the test specimen and the total current passed corresponds to the movement of all the ions (not only the Cl^- ions) in the pore solution of the concrete. Considering the above mentioned uncertainties, the RCPT method may only be used as an approximate indication of concrete permeability.

Table 2-1. Comparison between RCP and SR values to determine chloride ion penetrability in accordance with ASTM C1202-12 and AASHTO TP 95-11 criteria

Chloride ion penetrability	Charge passed [coulombs] RCP test - ASTM C 1202	Surface resistivity [$k\Omega$ -cm] SR test - AASHTO TP 95
High	> 4000	< 12
Moderate	2000 – 4000	12 – 21
Low	1000 – 2000	21 – 37
Very low	100 – 1000	37 – 254
Negligible	< 100	> 254

Surface resistivity (SR) test is another accelerated test method which is increasingly being used, to assess the permeability of concrete and its resistance to chloride ion penetration. The test has been standardised as AASHTO TP 95 which consists of measuring the resistivity of water-saturated concrete cylinders using a 4-pin Wenner probe array.

Resistivity is an intrinsic property of a material that indicates how resistant the material is to the flow of ionic current. The factors that mainly influence the resistivity of concrete are similar to those that affect its permeability (Nadelman and Kurtis 2014). When a voltage is applied to concrete, it creates an electric potential gradient which drives the flow of ions through the concrete. The ions flow through the complex and multi-scale porosity in the concrete matrix structure. Although the flow of ions through the aggregate and hardened binders is also possible, it plays a smaller role due to the higher resistivity of these materials (Nadelman and Kurtis 2014).

As it is graphically illustrated in Figure 2-3, the concrete containing less interconnected pores with a more tortuous path will have a higher electrical resistivity as it would be more difficult for ions to pass through these kinds of pore network. Accordingly, the measurement of concrete electrical resistivity is a good indication of its permeability since both properties are mainly controlled by the characteristics of the pore network. More compact microstructure which tend to have more complex and refined pore network result in a higher tortuosity and a lower permeability, whereas, less-dense microstructure (e.g. resulting from a higher water to binder ratio) would have greater porosity, lower tortuosity and higher permeability (Nadelman and Kurtis 2014).

It also worth mentioning that to some extent, other factors including pore solution chemistry, temperature and humidity can also highly affect concrete's resistivity (Sengul and Gjorv 2008).

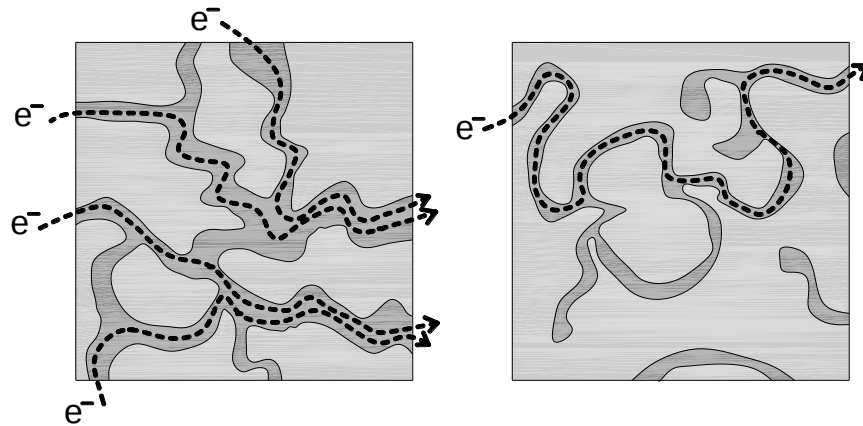


Figure 2-3. Schematic representation of electron flow through saturated concrete mixtures: (left) highly porous microstructure; (right) dense microstructure (Nadelman and Kurtis 2014).

Previous research works (Chini et al. 2003; Kessler et al. 2008; Lu 1997) have demonstrated that resistivity test results can be related to chloride diffusivity and also to chloride ion penetrability of OPC concrete. Furthermore, since SR test is non-destructive and can be conducted on the same specimen at different ages, changes in resistivity over time can be used to evaluate the rate of microstructure development, pore refinement and strength development.

There is no doubt that careful consideration is necessary when applying accelerated tests when interpreting results to examine the durability of concrete with various binder compositions (e.g. type of cement, type and amount of SCMs, etc). It is clear that far greater caution should be exercised when applying accelerated tests developed for OPC concrete to a material with a very different chemistry such as geopolymer concrete. Therefore, these tests shall carefully be examined when used for geopolymer concretes and correlations be studied and re-established.

Materials, Methods and Experimental Program

3 MATERIALS, METHODS AND EXPERIMENTAL PROGRAM

This chapter provides a description of the performed experimental work. The materials used are all described. The equipment and experimental methods used are detailed. The specific developments or modifications of existing test methods to be met for geopolymer concrete are also provided in this chapter.

3.1 Materials

Several geopolymer mixes were studied using various aluminosilicate source materials and alkaline solutions. Portland cement concrete mixes using Ordinary Portland Cement (OPC) also known as general purpose (GP) cement in Australia were also tested for comparison purpose.

A large portion of geopolymer studies to date have focused on metakaolin or a single source of fly ash as the aluminosilicate source material. The use of metakaolin may have benefits for laboratory investigations as it has a simpler chemistry (van Deventer et al. 2007). However, due to the high surface area of metakaolin, due to thin and flat particle shape, a large amount of water is required to form a workable paste. Moreover the high porosity of metakaolin based geopolymer is known to have a strong influence on durability. In practise, fly ash (FA) is preferred predominantly due to its relatively lower price.

Given the broad range of physical and chemical attributes of fly ashes from different sources, it was considered appropriate to study samples representative of a range of materials available. Three Australian fly ashes were used to prepare mixes G1 to G19 and were selected because of their differing properties. The Eraring fly ash branded as Blue Circle Fly Ash by Boral was sourced from Eraring Power Station in New South Wales, Australia. The Callide fly ash branded as Kaolite High-Performance Ash (HPA) by Cement Australia was obtained from Callide Power Station in Queensland, Australia. The Gladstone fly ash was sourced from Gladstone power station in Queensland, Australia.

Ground granulated blast furnace slag (GGBFS) was also included since the addition of GGBFS to fly ash based GPCs has shown to be beneficial in improving the strength and

regulating the setting time (Li and Liu 2007). So, it is of interest to study the effect of GGBFS on durability performance of geopolymers. The GGBFS used in this study was supplied by Australian Steel Mill Services (ASMS), Port Kembla, New South Wales, Australia. A European GGBFS supplied by ECOCEM, France was also used.

3.1.1 Characterisation of aluminosilicate materials

The chemical and physical characterisation of binder materials used in geopolymers is of a major important. Changes in the binder materials during reactions are also of significance. However, the accurate characterisation of fly ash is difficult, due to its heterogeneous nature at sub micron scale and the presence of both crystalline and amorphous phases (Hemmings and Berry 1988).

The chemical compositions of the binders as determined by x-ray fluorescence (XRF) analysis are listed in Table 3-1.

Table 3-1: Chemical compositions of aluminosilicate source materials by x-ray fluorescence analysis (wt.%)

Oxides	OPC	Eraring FA	Callide FA	Gladstone FA	ASMS GGBFS	ECOCEM GGBFS
SiO ₂	19.7	66.56	45.14	47.94	31.52	36.62
Al ₂ O ₃	4.9	22.47	33.32	25.68	12.22	10.15
Fe ₂ O ₃	3.3	3.54	11.99	14.66	1.14	0.36
CaO	64.6	1.64	4.13	4.11	44.53	42.88
K ₂ O	0.4	1.75	0.13	0.67	0.33	0.36
Na ₂ O	0.2	0.58	0.07	0.81	0.21	0.34
MgO	1.0	0.65	1.37	1.36	4.62	6.65
MnO	-	0.06	0.23	0.19	0.36	0.34
P ₂ O ₅	-	0.11	0.56	1.21	0.02	0.01
TiO ₂	-	0.88	2.19	1.40	1.03	0.54
SO ₃	2.4	0.10	0.48	0.19	3.24	1.26
LoI	3.3	1.66	0.41	0.69	0.79	1.89
Surface area [m ² /kg]	-	433	659	872	556	515
Amorphous content [%]	-	85.2	83.6	81.4	95.8	-

The particle size distribution of the aluminosilicate source materials was determined by laser diffraction technique using a Malvern Mastersizer 2000 instrument. The powders were dispersed in water and sonified prior to analysis on the instrument. The results are presented in Figure 3-1. As it is illustrated, Callide FA and then Gladstone FA are the finest, followed by GGBFS and Eraring FA. A considerable volume of Callide and Gladstone FA particles are about 5-6 µm in diameter, as opposed to 30 µm diameter of the majority of Eraring FA particles.

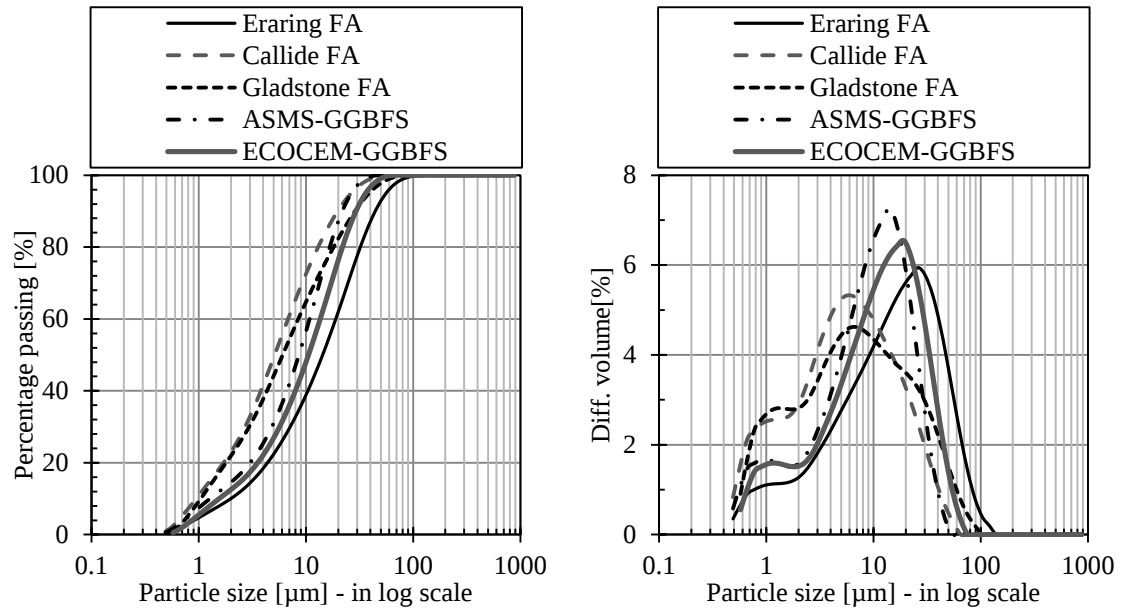


Figure 3-1: Aluminosilicate source materials particle size distribution

The specific surface area of the aluminosilicate source materials was measured using a Micromeritics TriStar Plus instrument. The technique uses nitrogen physisorption to generate adsorption/desorption isotherms from which the specific surface area is calculated. Prior to analysis, the samples were degassed at 150°C for 3 h. The Brunauer, Emmett and Teller (BET) theory is used to assess the specific surface area. The BET surface area of Eraring FA, Gladstone FA, Callide FA, ASMS-GGBFS and ECOCEM-GGBFS are 433, 659, 872, 556 and 515 m²/kg, respectively.

The amorphous content of the raw materials was also measured using X-ray diffraction (XRD), specifically the spike method (5 wt.% Zinc oxide been used) as shown in Table 3-1. Crystalline phases in the fly ash samples consisted of Mullite (Al_{2.17}O_{4.89}Si_{0.78}), Quartz (SiO₂), Magnetite (Fe₃O₄) and Hematite (Fe₂O₃) whereas the crystalline phases in slag were Gypsum (CaH₄O₆S) and Hatrurite (Ca₃O₅Si) with some traces of Quartz..

Scanning electron microscopy (SEM) images of some of the raw materials are given in Figure 3-2.

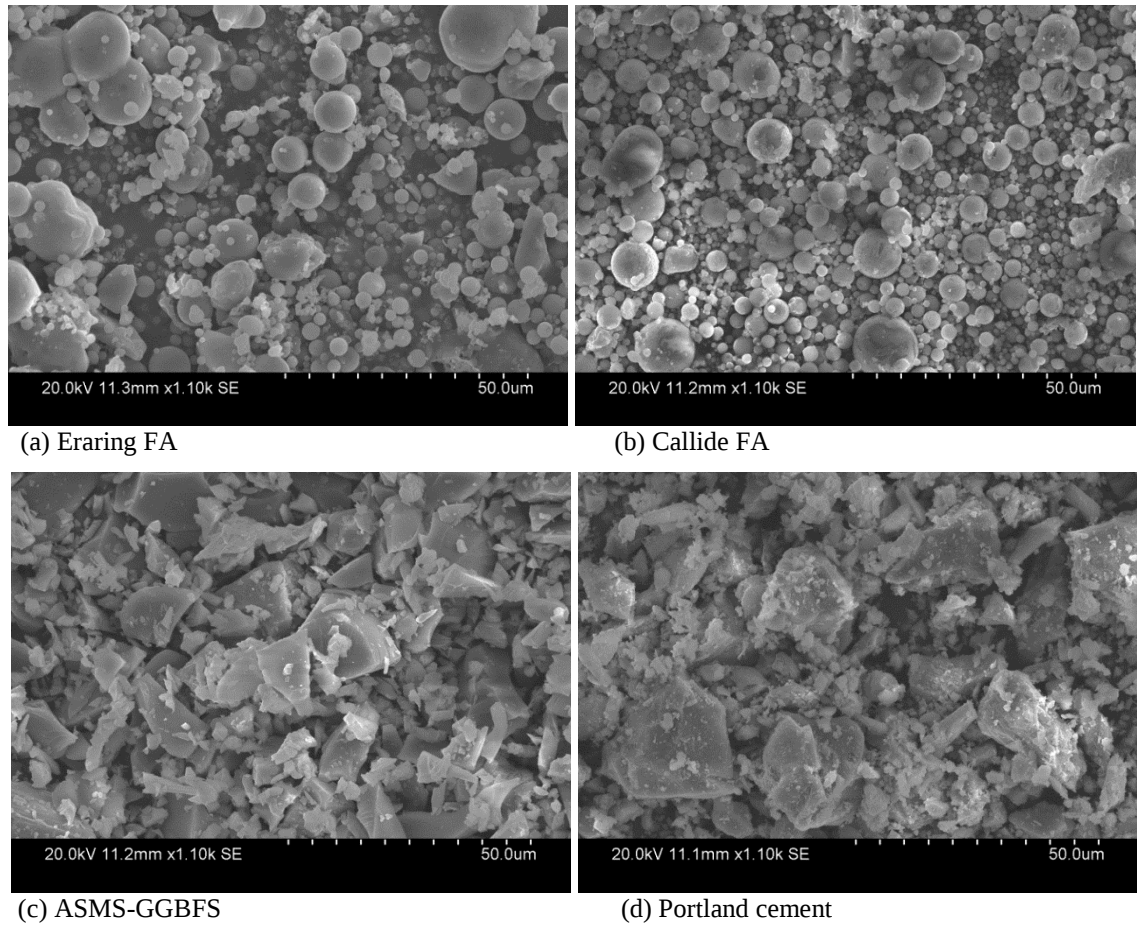


Figure 3-2: SEM images of the raw materials

3.1.2 Alkaline solution

The alkaline solution used is a mixture of technical grade NaOH pellets of 98% purity and commercially available sodium silicate solution. The NaOH pellets have a molecular weight of 40 and a specific gravity of 2.1. The NaOH pellets were dissolved in tap water to prepare NaOH solution. The sodium silicate solution has a chemical composition by mass of 14.7% Na_2O , 29.4% SiO_2 and 55.9% H_2O with a modulus ratio of 2 ($M_s = \text{SiO}_2/\text{Na}_2\text{O} = 2$) and a specific gravity of 1.53.

NaOH and Na-silicate solutions were mixed in proportions to form alkaline solutions at different concentrations and modulus ratios. After mixing, the alkaline solution was allowed to cool to ambient temperature and equilibrate (~24 h) prior to preparation of the specimens.

The typical modulus ratio used in geopolymer fabrication is within the range between 1.0 to 2.0, where $M_s = 1.0$ represent a more caustic solution with high content of

reactive species whereas $M_s = 2.0$ presents a more user friendly but less reactive species. The alkaline solution modulus can be modified by the addition of sodium or potassium hydroxide. Davidovits (2008) suggested modulus values higher than 1.45 which would be more user friendly and suitable for construction purposes.

3.1.3 Aggregate

Crushed basalt aggregates and natural river sand were used in all geopolymer mixes. Course aggregates were sourced from Peats Ridge quarry in NSW, Australia, with a maximum nominal size of 10 mm and 20 mm and water absorption of 0.8% and 0.6% respectively. Fine aggregates consisted of both manufactured and natural river sand. The manufactured sand, with water absorption of 1.1%, was the remaining material leftover from the rock crushing process at Peats Ridge Quarry. After crushing, the sand is washed and properly graded before distribution. The manufactured sand was mixed with Nepean river sand sourced from New South Wales, Australia, to produce a well-graded fine aggregate. The specific gravities of the basalt aggregates and Nepean river sand are 2.96 and 2.59 respectively. Sydney fine sand with specific gravity of 2.65 and water absorption of 1.5 was used for the manufacture of some of the mixes. All aggregates were prepared to saturated surface dry (SSD) condition prior to batching. The individual and combined aggregate grading curves are shown in Figure 3-3.

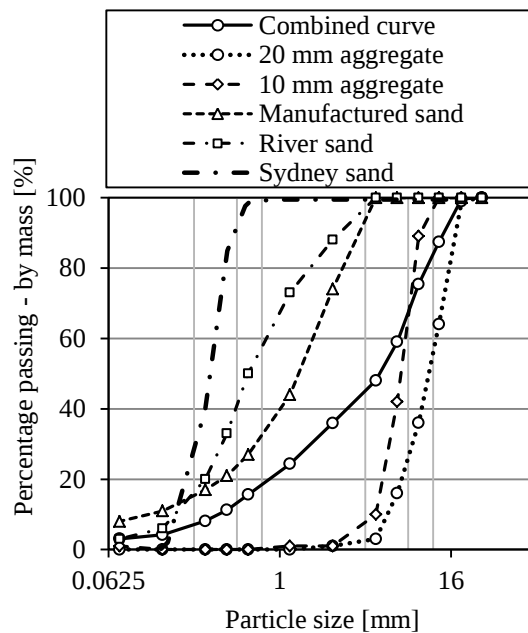


Figure 3-3: Aggregates grading curves

3.2 Mixing and curing

The mix proportioning of the materials, was carried out by mass. The aggregates were prepared to saturated surface dry (SSD) condition prior to batching. Using a pan mixer, the aluminosilicate source materials, alkaline solutions and water were mixed for 5 minutes to achieve a uniform paste. The aggregate were then gradually added and further mixed for 5 minutes. Freshly mixed concrete was placed into moulds and compacted using an external vibrating table to achieve proper consolidation and to minimise the amount of the entrapped air arising within the mix. Meanwhile, the mass per unit volume test were also performed following AS 1012.5.

One hour after casting, sealed specimens (in individual plastic bags) were moved either to the oven or to the controlled room for curing. After completion of the heat curing, samples were demoulded and stored in plastic bags in a controlled room at a temperature of $23 \pm 2^{\circ}\text{C}$ until the testing date. The ambient cured samples were demoulded after 72 hours and stored in plastic bags in a controlled room at a temperature of $23 \pm 2^{\circ}\text{C}$ until the testing date.

The reason for sealing specimens in plastic bags instead of leaving them exposed to a high humidity environment as stipulated by Australian Standard AS 1012 to avoid leaching of alkali from the samples. Free water settling or condensing on the surface of samples could result in leaching of alkali and formation of a poorly cured surface layer. Sealed curing resulted in surfaces with minimal deviation from the bulk properties.

3.3 Test methods

A range of instruments and techniques were used to examine various properties of the raw materials, geopolymer pastes and concretes. The mechanical performance of GPCs was examined through compressive strength and modulus of elasticity tests at different ages. The transport properties and porosity of geopolymers were measured using water absorption, apparent volume of permeable voids (VPV), sorptivity, mercury intrusion porosimetry (MIP) and saturated resistivity tests. Durability was measured using accelerated chloride migration, chloride permeability and chloride diffusion tests, as well as, carbonation. Microstructural assessments were carried out on paste samples using scientific tools, namely; SEM, EDS, XRD, FTIR and NMR. A summary of all test methods used in this thesis is provided in Table 3-2.

Table 3-2: Summary of test methods

Test method/technique used	Property measured
Compressive strength test	Mechanical performance
Compressive stress-strain test	Mechanical performance
Modulus of elasticity (MOE) test	Mechanical performance
Volume of permeable voids (VPV) test	Pore structure/connectivity
Sorptivity test	Capillary pore network
Mercury intrusion porosimetry (MIP)	Pore size distribution
Surface and bulk resistivity test	Pore connectivity/pore solution resistivity
Rapid chloride permeability test (RCPT)-modified	Charge passed – indicative of Chloride penetrability
Chloride migration test	Chloride penetration resistance
Chloride diffusion test	Chloride penetration resistance
Water soluble chloride measurement	Free chloride (for chloride binding capacity)
Acid soluble chloride measurement	Total chloride (for chloride binding capacity)
pH measurements of the leachate	Leaching of alkali
Accelerated and natural carbonation test	Carbonation resistance
Nuclear magnetic resonance (NMR) spectroscopy	Silico-aluminate species characterisation
Powder X-ray diffraction (XRD)	Phase determination
Scanning Electron Microscopy (SEM and EDS)	Microstructural and chemical analysis
Fourier-transform infrared spectroscopy (FTIR)	Chemical bond in Si-Al microstructure

3.3.1 Compressive strength and elastic modulus

The compressive strength of 100 × 200 mm standard cylinders was measured at different ages of 1, 3, 7, 28 and 56 days using a 3000 kN universal testing machine. Specimens were tested under a load rate controlled condition with a load rate equivalent to 20 ± 2 MPa compressive stress per minute, following the Australian Standard AS 1012.9. All the cylinders were ground flat on both ends before performing the tests.

The compressive stress-strain behaviour of the specimens was also studied. Uniaxial compressive load was applied and the axial and circumferential strain was recorded by means of extensometers/strain gauges mounted on the specimen as shown in Figure 3-4. Testing was performed under closed-loop displacement control. The displacement control system allows a more controlled evaluation of the post-failure strain response. Specimens were loaded in pure uniaxial compression at a constant displacement rate of 0.2 mm/min and were instrumented with an axial and radial extensometer.

The static chord modulus of elasticity was calculated based on the data recorded, in accordance with the Australian Standard AS 1012.17. The Young's modulus was determined as the secant modulus, measured at a stress level equal to 40% of the compressive strength of concrete.



Figure 3-4: Longitudinal and circumferential gauges attached to the specimen

3.3.2 Water absorption and volume of permeable voids (VPV)

The water absorption and volume of permeable voids (VPV) tests were carried out using 100 mm diameter and 50 mm thick specimens cut from the standard cylinders following ASTM C642-13 standard test method. Due to the concerns in oven-drying hardened geopolymer concretes at temperatures around 100°C as a pre-conditioning step prior to the determination of permeability-related properties, the standard ASTM C642-13 method was slightly modified. The oven-drying was initially conducted at 50°C rather than 105°C until no significant mass change is observed (mass change of less than 0.5% within 24 h). Upon the completion of the ASTM C642 standard

procedure, the samples were oven-dried again at 105°C to obtain the oven-dry mass for calculations.

For the slag based geopolymer or slag/fly ash blend geopolymer with high contents of slag (> 50 wt. %), which contain water in fairly different structural environments compared to the OPC concrete, the ASTM C462 procedure prescribed for testing OPC based materials must be applied with care (Ismail et al. 2013b). The matrix microstructure may change and C-A-S-H product may dehydrate during the pre-conditioning stage, when strictly following the standard methods defined for Portland cement concrete (Ismail et al. 2013a; b). However, for geopolymer concretes with higher contents of low calcium fly ash (> 75 wt.%), this effect would not be observed when heating up to around 100°C. For the fly ash based geopolymer systems, temperatures up to 100°C only leads to the evaporation of the free water. This will not cause significant damage to the polymer structure, except for some limited shrinkage (Davidovits 2008) and this free water removal is not as damaging as the removal of chemically bound water from slag based geopolymer binders (Ismail et al. 2013a).

Davidovits (Davidovits 2008) stated that the hardened geopolymer contains three types of water; the physically bonded water (free water), the chemically bounded water and the hydroxyl groups OH. Physically bonded water is the water generated during the geopolymerization reaction as part of the resultant products (Davidovits 1999; van Jaarsveld et al. 2002). The chemically bounded water exists in the geopolymer gel, also known as ‘zeolitic water’, whereas, the hydroxyl groups OH is presented at the surface and edges of each geopolymeric micelle. For the fly ash-based geopolymer concretes, the physically bonded water evaporates in the temperature range of 20–100°C. Further heating of the geopolymer concrete to temperatures above 100°C leads to removal of the chemically bonded water and the hydroxyl groups OH from the geopolymer structure, occurring due to the dehydration and dehydroxylation processes. The chemically bonded water evaporates at temperature range of 100–300°C, and finally the dehydroxylation of the OH groups take place at temperatures above 300°C to 800°C (Davidovits 2008; Duxson et al. 2007b). Thermo-physical test results (Abdulkareem et al. 2014) of fly ash-based geopolymer indicated that both dehydration and dehydroxylation processes are the main reason behind destruction of the geopolymer microstructure, which for fly ash based geopolymer systems takes place in temperatures beyond 100°C.

To determine the water absorption, the oven-dried samples at 50°C were immersed in water until constant mass was reached. Using Eq. (3-1) the absorption of the test samples was then determined.

$$Absorption(\%) = \frac{W_w - W_d}{W_d} \times 100 \quad (3-1)$$

where W_w is the mass of surface-dry sample after immersion in g and W_d is the mass of oven-dried samples in g.

In order to measure the VPV, the oven-dried samples at 50°C have been vacuum saturated following the method recommended by ASTM C1202. The specimens were placed in the vacuum chamber with the vacuum pump running for 3 hours. The chamber then filled up with sufficient de-aerated water to cover the samples and vacuumed for one additional hour. The specimens were then left soaking under water at the atmospheric pressure for 18 hours and their mass was recorded. After finishing of the vacuum saturation, the specimens' apparent mass in water been determined to work out the samples volume. At the end, the samples were oven-dried at 105°C. The volume of permeable voids was calculated using Eq. (3-2);

$$VPV(\%) = \frac{W_s - W_d}{W_s - W_b} \times 100 \quad (3-2)$$

where W_s is the mass of saturated surface-dry sample in g, W_d is the mass of oven-dried sample in g and W_b is the apparent mass of sample in water after vacuum saturation in g.

3.3.3 Sorptivity

The sorptivity test was conducted after 28 days. The test specimens were 100 mm diameter discs which are 50 mm thick, cut from moulded cylinders. Specimens underwent preconditioning prior to the test. Concrete discs were first vacuum-saturated based on the method defined by ASTM C1202. The mass of saturated specimens was measured, and discs were placed in the environmental chamber at a temperature of $50 \pm 2^\circ\text{C}$ and the relative humidity (RH) of $80 \pm 3\%$ for 3 days. After 3 days, each specimen was placed inside a separate sealed container and stored in a controlled room at $23 \pm 2^\circ\text{C}$ for 15 days. After finishing the preconditioning procedure, the specimens' diameter and mass were recorded, and the side surfaces were sealed using aluminium foil tape.

The top end of the specimens was also sealed by means of a loosely attached plastic sheet secured with elastic bands. The reason for insulating the side and top surfaces is to avoid additional penetration of the water and its evaporation from the sample during the measurement and to ensure that the water penetrates only through the bottom surface.

Sorptivity test specimens were then placed on the supports and the pan filled with tap water to reach 3 mm above the bottom surface of the sample. The mass of the absorbed water is calculated by measuring the mass of the sample in specified time intervals, as defined in ASTM C1585, since the initiation of the test and up to 9 days. The absorption is calculated using Eq. (3-3);

$$I = \frac{m_t}{a \times d} \quad (3-3)$$

where I is the absorption, m_t is the change in specimen mass in g at the time t , a is the exposed surface area in mm^2 and d is the density of the water in g/mm^3 (ASTM C1585-13).

The initial sorptivity (S_i) is determined from the slope of the line that is the best fit to the water absorbed against the square root of time from 1 min up to 6 hours. The linear least-squares regression analysis of the plot of I versus $\text{time}^{0.5}$ should be done to obtain this slope. The correlation coefficient (R^2) should not be less than 0.98. The schematic arrangement of the sorptivity test is shown in Figure 3-5.

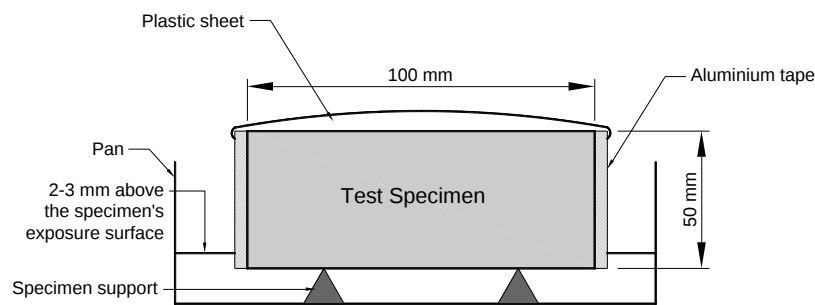


Figure 3-5: Schematic of the sorptivity test procedure

3.3.4 Mercury intrusion porosimetry (MIP)

In MIP, a non-wetting fluid (mercury) is forced into the pore space of a porous material by application of pressure. The smaller the pore size, the larger the pressure required to achieve intrusion. As the pressure applied is increased, the volume of mercury which intrudes into the pores increases according to the distribution of pores size. Measuring

the applied pressure and the intrusion volume, the pore size distribution can be calculated.

The MIP results for OPC and geopolymer pastes should be interpreted with cautions. For materials with a variety of pore sizes, such as OPC and geopolymer binders, the error induced by the mechanism known as “ink-bottle effect” is large (Diamond 2000; León y León 1998). A further problem with MIP which introduces uncertainty is the requirement for the sample to be thoroughly dried before analysis. It is generally accepted that the drying process causes changes in the pore structure and size distribution (Gallé 2001).

3.3.5 Surface and bulk resistivity

The surface resistivity test has been performed in accordance with the standard procedure AASHTO TP 95-11 after 28 days of age. The test consists of measuring the resistivity of vacuum-saturated 100×200 mm cylinders by use of a 4-pin Wenner probe array as shown in Figure 3-6 and Figure 3-7. An alternative current potential difference is applied at the outer pins of the Wenner array resulting in current flow in the concrete. The resultant potential difference between the two inner pins is measured and used to calculate the resistivity of the concrete specimen. Resistivity (ρ) can be obtained using Eq. (3-4).

$$\rho = R \frac{A}{L} = 2\pi a R = 2\pi a \frac{V}{I} \quad (3-4)$$

where ρ is resistivity in $\text{k}\Omega\cdot\text{cm}$, R is resistance in $\text{k}\Omega$, A is area of the element in cm^2 , L is the length of element in cm, and a is the spacing between the probs in cm (Morris et al. 1996).

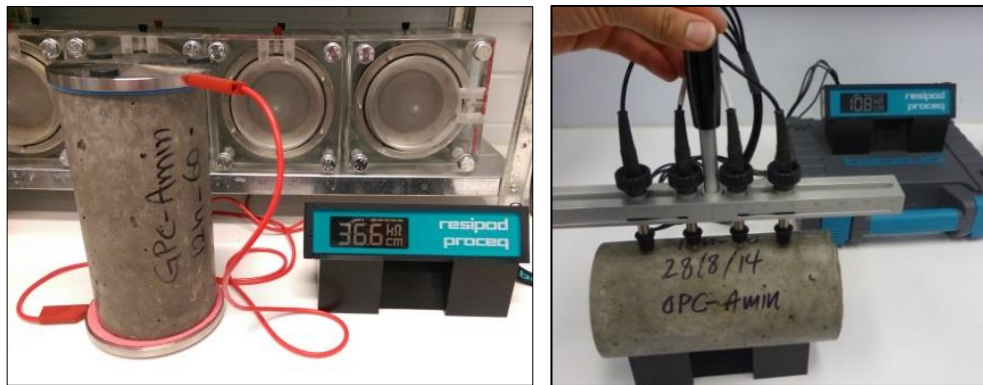


Figure 3-6: Bulk resistivity (left) and surface resistivity (right) measurement

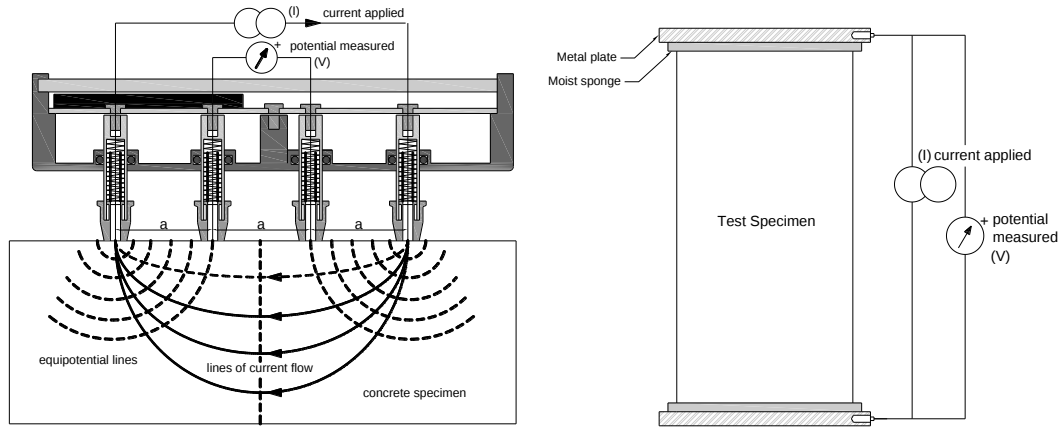


Figure 3-7: Schematic of surface and bulk resistivity apparatus (AASHTO TP 95-11)

The bulk (uniaxial) resistivity was measured using Proceq Resipod equipment at the age of 28 days. The test specimens are 100 × 200 mm concrete cylinders which have already been tested for the surface resistivity. A set of two round stainless steel plate electrodes was used with thin sponges as shown in Figure 3-6 and Figure 3-7. The wet sponges were placed at the top and bottom interfaces of the concrete sample to assure good electrical contact between the metal plate electrodes and the cylindrical concrete specimen. The total resistance measured ($R_{measured}$) were subsequently corrected for the contributions of these sponges following Eq. (3-5), by treating the system as series.

$$R_b = R_{measured} - R_{top-sponge} - R_{bottom-sponge} \quad (3-5)$$

The bulk resistivity (ρ_b) of the specimens could then be calculated according to Eq (3-6).

$$\rho_b = R_b \cdot K = R_b \times \frac{A}{L} \quad (3-6)$$

where K is given as the geometry factor and is equal to specimen's cross section area divided to its length.

The bulk resistivity of the concrete samples was measured in vacuum-saturated condition, as well as, at various moisture contents. After measuring the resistivity in saturated condition, specimens underwent a drying procedure. The resistivity and mass of the specimens was measured at specified time spans. Specimens were first dried in the standard laboratory condition ($23 \pm 2^\circ\text{C}$ and 50% RH) for 7 days and then dried in an oven at a temperature of 50°C for another 7 days. Since the temperature is significantly affecting the resistivity, specimens were cooled in the air for 12 hours,

prior to performing the measurements. At the end, specimens were oven-dried at 105°C for 72 hours to determine the dry mass. The moisture content at each resistivity reading is calculated by using the below formula.

$$MC_x = \frac{m_x - m_d}{m_d} \quad (3-7)$$

where MC_x is the moisture content, m_x is the mass of specimen at the time of resistivity measurement and m_d is the dry mass.

3.3.6 Modified RCPT/ASTM C1202

The ASTM C1202 test often referred to as rapid chloride penetration test (RCPT) was deemed a failure for most of the geopolymer concrete specially for low calcium content geopolymers. Therefore, a modified version of ASTM C1202 test method was used to measure the resistance of geopolymer concrete samples to chloride ion penetration. The modification made to ASTM C1202 test method is related to the applied voltage. Since the geopolymer samples had a high electrical conductivity, a lower voltage of 10 V was found to be more suitable rather than the suggested 60 V voltage. The high conductivity of the GPC samples was observed during the trial tests, showing an initial current of more than 500 mA when 60 V voltage was applied. Tests were run for 6 h and the current were measured every minute using PROOVEit software from Germann Instruments. The total charge or Coulombs passed was then calculated from the area under the current vs time curve.

For both ambient and heat-cured geopolymer concretes, after the age of 28 days, three 50 mm specimens were cut from the middle section of three identical 100 × 200 mm cylinders. The top 25 mm and bottom slice of each cylinder were thrown away. The side surface of the 50 mm concrete discs were coated using Parchem Emer-Proof Aqua Barrier and allowed to dry for 24 h. The samples were then vacuum saturated using a vacuum desiccator following the ASTM C1202 procedure. The vacuum saturated specimens were then placed in the test cell using rubber gaskets to prevent leakage of the solutions during the test. The cells were then filled with 3.0% NaCl (30 g NaCl in 970 g water) and 0.3 N NaOH solutions (12 g NaOH pellets in 1 L water).

3.3.7 Chloride migration

The Nordtest NT Build 492 test method is used to determine the chloride migration coefficient for the non-steady-state condition by using an external voltage to drive chloride ions into the sample and measure the chloride penetration depth. The test samples are 50 mm thick concrete discs cut from the 100 × 200 mm cylinders (similar to RCPT samples). Three test specimens were used for each identical GPC and specimens were vacuum saturated prior to test. The PELCON instrument was used to run the test. The catholyte solution was 10% NaCl (100 g NaCl in 900 g water) and the anolyte solution was 0.3 N NaOH. A 30 V electrical potential was applied axially across the specimen and the initial current was recorded. Based on the observed initial current, the voltage and test duration were adjusted following recommended values from NT BUILD 492. The test initial and final currents and temperatures were recorded. The specimen was then axially split and 0.1 M silver nitrate (16.99 g AgNO₃ in 1 L water) was sprayed on the freshly split section. Silver nitrate reacts with both chloride ions (Cl⁻) and hydroxyl groups (OH) to form white silver chloride (AgCl) and dark brown silver oxide (Ag₂O).

The chloride penetration depth was measured from the white silver chloride precipitation, after which the chloride migration coefficient can be calculated using an integrated form of Nerst-Planck equation;

$$D_{nssm} = \frac{0.0239(273+T)L}{(U-2)t} \left(x_d - 0.0238 \sqrt{\frac{(273+T)Lx_d}{U-2}} \right) \quad (3-8)$$

where D_{nssm} is chloride migration coefficient in $\times 10^{-12} \text{ m}^2/\text{s}$, U is applied voltage in V, T is the average of initial and final temperature in °C, L is the thickness of the sample in mm, x_d is the average penetration depth in mm and t is the test duration in h.

3.3.8 Chloride diffusion

Chloride diffusion test was conducted using ASTM C1556 test method (similar to NT BUILD 443). The test specimens were 100 mm (diameter) × 50 mm (height) discs cut from standard 100 × 200 mm cylinders, after 28 days of age. After preparation, the test specimens were immersed in 16.5% aqueous NaCl solution for 35 days. Following completion of the exposure duration, the powder samples were obtained by grinding off material in layers parallel to the exposed surface. The grinding was performed using

Germann Instruments' Profile Grinder. The grinding area was 73 mm in diameter adjusted at the center of the exposure surface. The concrete samples were ground up to 25 mm depth with increment of 1 mm. The powders were collected in sealed plastic vials to be used for chloride analysis. The apparent chloride diffusion coefficient was then determined using the non-linear regression analysis recommended in ASTM C1556.

The acid soluble chloride (total chloride) content of the powder samples were determined based on ASTM C1152 test methods as explained in section 3.3.9. The chloride profile of each concrete sample was then plotted to be used for apparent chloride diffusion coefficient determination.

The apparent chloride diffusion coefficient was determined by fitting Eq. (3-9) to the plotted acid-soluble chloride profile by means of a non-linear regression analysis using the method of least squares.

$$C(x,t) = C_s - (C_s - C_i) \operatorname{erf} \left(\frac{x}{\sqrt{4D_a t}} \right) \quad (3-9)$$

where $C(x,t)$ is the chloride concentration measured at depth x and exposure time t in mass %, C_s is the chloride concentration at the exposure surface (boundary condition) that is determined by the regression analysis in mass %, C_i is the initial chloride concentration of the concrete sample at time $t=0$ in mass %, x is the depth below the exposed surface in m, t is the exposure time in seconds, D_a is the apparent diffusion coefficient in m^2/s and erf denotes the error function described in Eq. (3-10).

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-u^2) du \quad (3-10)$$

3.3.9 Free and bound chloride measurements

Chloride ions that have penetrated the concrete can exist as either free or bound chloride ions. Since the free chloride ions are water soluble, in the presence of moisture, they are able to diffuse through the pore solution of the concrete to reach the steel reinforcement bars and trigger steel corrosion. The majority of the bound chloride do not contribute to the corrosion of steel reinforcement (Arya et al. 1990). In Portland cement concrete, some physically bound chlorides, which are adsorbed by C-S-H and interlayer species,

can be removed by water (leaching) (Arya et al. 1990). However, the chemically bound chlorides cannot be removed since they are water insoluble (Beaudoin et al. 1990; Justnes 1998). The AFm phase (alumina, ferric oxide, monosulfate) reacts with chloride to form Friedel's salt (calcium chloroaluminate hydrate) which is not a reversible reaction in aqueous solution (Arya et al. 1990; Birnin-Yauri and Glasser 1998; Justnes 1998).

Accordingly, all the free chlorides and a fraction of the bound chlorides are water soluble. In other words, the water soluble chloride is more than just the free chloride (Haque and Kayyali 1995; Ishida et al. 2008; Otsuki et al. 1992). Yuan et al. (2012) reported that the pore solution extraction method could be a direct measure of free chlorides and indicated that it is approximately 80% of water soluble chloride.

In this study, all the water soluble chlorides are referred to as free chloride since authors believe that all the water soluble chlorides, regardless of being free chloride or a fraction of physically bound chlorides which could be water soluble, contribute to the steel corrosion.

The acid soluble chloride (total chloride) and water soluble chloride (free chloride) content of the powder samples were determined based on ASTM C1152 and ASTM C1218 test methods except that a 3.5 g sample was used rather than 10 g sample recommended in the ASTM test methods. The final volume of solution was adjusted to a maximum of 60 mL to comply with the volume limit of the utilised titration apparatus. Also, instead of using a magnetic hot plate to boil the solution, an ultrasound bath was used. The applied modifications were proved to make no significant difference on the test results through trial examinations.

For acid soluble chloride measurement, a 3.5 g powder sample was dispersed in 10 mL milli-Q water. 20 mL of dilute nitric acid (20% concentration ($1 \text{ HNO}_3:2.5 \text{ H}_2\text{O}$), dilution of Sigma Aldrich reagent grade 70% nitric acid) was slowly added. 1 mL of hydrogen peroxide (30% solution) was slowly added to treat the interference of sulfides (if any) which can produce erroneously high test results (ASTMC1218 2008). The solution was then placed in an ultrasound bath (VWR Symphony 142-0081, 35kHz) at 60°C for 15 min. The solution was then filtered using Advantec 5B filter papers with a pore size of 5-10 microns in a Buchner funnel and suctioned filtration flask. The filter paper, funnel and flask were rinsed with milli-Q water. The final volume of the solution

was approximately 60 mL. The filtrate solution were cooled down to the room temperature and placed inside the potentiometric titration machine. A Metrohm 855 Robotic Titrosampler using silver nitrate solution was used to determine the chloride content based on the ASTM C114 (section 21) reference test method. The chloride content was calculated using Eq. (3-11).

$$Cl, \% = \frac{3.545[(V_1 - V_2)N]}{W} \quad (3-11)$$

where V_1 is the millilitres of 0.05 N $AgNO_3$ solution used for sample titration, V_2 is the millilitres of 0.05 N $AgNO_3$ solution used for blank titration, N is the exact normality of 0.05 N $AgNO_3$ solution and W is the mass of sample in g.

For the water soluble chloride measurement, a 3.5 g powder sample was dispersed in 30 mL milli-Q water. The solution was placed in the ultrasound bath at 50°C for 15 min and then allowed to stand 24 h at ambient temperature. The solution was again placed in the ultrasound bath at 50°C for 15 min. The solution was filtered using Advantec 5B filter papers with a pore size of 5-10 microns in a Buchner funnel and suctioned filtration flask. The filter paper, funnel and flask were rinsed with milli-Q water. The final volume of the solution was approximately 60 mL. 2 mL of dilute nitric acid (20% concentration) and 1 mL of hydrogen peroxide (30% solution) was slowly added to the filtrate. The solution were cooled down to room temperature and placed inside the Titrosampler to determine the water soluble chloride content.

3.3.10 SEM and EDS analysis

Scanning Electron Microscopy (SEM) allows examination of the surface topology of a sample using a Secondary Electron (SE) detector, or limited compositional information using a Back Scattered Electron (BSE) detector. Microscopes fitted with an X-ray spectrometer (usually an Energy Dispersive Spectrometer, EDS) allow detailed chemical information to be obtained from small volumes (a few μm^3) of the sample.

Microstructural analysis was performed using a Hitachi S-3400N SEM. Specimens were cold mounted in an epoxy resin and were polished using consecutively finer sand paper prior to final preparation using 3 micron and 1 micron diamond paste on cloth. Specimens were coated in carbon for better surface conductivity prior to the test.

A Quantax 400 energy dispersive X-ray spectrometer (EDS) was also coupled with the SEM to determine chemical/elemental composition. The hardware was run from two computers utilising the Esprit 1.9 software. The microscope parameters that were used for the EDS analysis were as follows; accelerating voltage: 15 keV, probe current: 50, working distance: 10 mm, Input counts: 1000 ± 300 cps, scan time 100s.

3.3.11 Powder X-ray diffraction (XRD)

X-ray Diffractometry (XRD) is a method for identifying and characterising crystalline materials. Each crystal has a unique diffraction pattern, so that comparison of experimental diffraction patterns with the patterns of known compounds allows unambiguous identification. XRD was used extensively for characterisation of raw materials and analysis of changes in geopolymer samples.

X-ray diffractograms of specimens were collected on a Phillips X'Pert Pro diffractometer with Cu-K α radiation generated at 40 mA and 45 kV, using BBHD optics with $\frac{1}{2}^\circ$ Div. slit and 1° Anti Scatter slit, 10 mm beam mask and 0.04 rad soller slit. Specimens were step scanned from 5 to $70^\circ 2\theta$ at $0.026^\circ 2\theta$ steps integrated at the rate of 130 s per step.

Phase identification was carried out by comparing diffraction patterns to the ICDD PDF4 database of powder diffraction files from the International Centre for Diffraction Data, using HighScore Plus software.

3.3.12 Solid-state nuclear magnetic resonance (NMR) spectroscopy

Geopolymer paste powders were tested for silicon (^{29}Si) and aluminium (^{27}Al) magic angle spinning nuclear magnetic resonance (MAS NMR). The samples were prepared by milling the hardened geopolymer paste to less than 75 microns using an ESSA tungsten carbide ring mill. The samples were packed in 4 mm zirconia rotors fitted with a Kel-F cap and spun to 14 kHz MAS in a 4 mm HX double resonance probehead. The spectra were acquired on a standard bore Bruker AVANCE III spectrometer with a 16.4 Tesla superconducting magnet, operating at frequencies of 139 MHz, 182.5 MHz and 700 MHz for the ^{29}Si , ^{27}Al and ^1H nuclei respectively. The ^{29}Si NMR spectra were acquired with spin-echo sequence, using a $7.5 \mu\text{s}$ 90° pulse width and a relaxation delay of 1000 s to ensure full relaxation of the signal. 64-80 transients were co-added to yield spectra with sufficient signal-to noise, which corresponded to a measurement time of

18-22 hours per spectrum. The Spinal64 scheme was used for ^1H heteronuclear decoupling with a field strength of 100 kHz during acquisition. The ^{29}Si peak of Kaolin at -91.2 ppm was used as a secondary reference for the ^{29}Si chemical shifts. The ^{27}Al spectra were acquired with a single pulse sequence and a pulse width of 2 μs , a relaxation delay of 0.3-1 s, and 512-4096 scans. The ^{27}Al chemical shift was referenced to a 1 M solution of $\text{Al}(\text{NO}_3)_3$ set to 0 ppm. The ^{29}Si spectra were fit using Gaussian line shapes with the DmFit software (Massiot et al. 2002).

3.3.13 Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectra of geopolymer paste samples were obtained with a Spotlight 400 FTIR spectrometer using transmittance mode in the range of 500–1600 cm^{-1} at a resolution of 1.0 cm^{-1} .

3.3.14 pH measurements of the leachate

The leaching of the alkali metals was investigated by measuring the pH of the leaching solution of raw materials and hardened geopolymer paste by diluting 5 g of fine powder in 50 g purified deionised water (Milli-Q water). For hardened geopolymer paste, the powder is prepared by crushing and grinding the hardened paste in a metal mortar and pestle prior to test. The powder is then screened using an 850 micron sieve. The process of crushing and grinding was completed in less than 5 min to minimise the risk of carbonation which can potentially influence the pH. The pH of the leaching solution is measured at 1, 5 and 10 min after powder addition following the recommended practice by Davidovits (Davidovits 2011). The solution was stirred during the first 5 min. It has been observed that the pH was almost constant after 5 min. The pH of the fresh paste leachate is also determined following the same method by diluting 5 g fresh paste in 50 g milli-Q water.

**Mechanical, Transport and
Microstructural Properties of
Geopolymer Concrete**

4 MECHANICAL, TRANSPORT AND MICROSTRUCTURAL PROPERTIES OF GEOPOLYMER CONCRETE

This chapter provides the experimental results and discussion on mechanical and transport properties and microstructural characteristics of various studied GPCs. During this study, it has been found that the calcium content in geopolymer concrete plays a significant role on rheology, mechanical performance and microstructure of the GPCs. Therefore, the investigated GPCs in this thesis are categorised in two main groups of low calcium content GPCs (containing less than 25% slag in their binder) and medium/high calcium content GPCs (containing more than 25% slag in their binder).

4.1 Low calcium content GPCs

Fly ash is a preferred aluminosilicate source material for geopolymerisation compared to slag, predominantly because fly ash is available in large quantities and due to its relatively lower price. In this section, the properties of 8 different GPCs with slag/total binder ratio of 0%, 10%, 15% and 25% are studied. These GPCs are labelled as G1 to G8 and their composition is presented in Table 4-1. The influence of various parameters on the mechanical, transport properties and microstructure of low calcium content GPCs are studied as follows:

- The effect of thermal curing on the mechanical performance and microstructure of low calcium content GPCs is comprehensively studied using mix G1.
- The influence of alkaline solution concentration (i.e. $\text{SiO}_2 + \text{Na}_2\text{O}$ /binder ratio) on the performance of low calcium content GPCs is investigated using mixes G2, G3 and G4.
- The influence of low percentage of slag addition (i.e. 10% and 25% of total binder) on the performance of fly ash based GPCs is investigated using mixes G5 to G8.

Table 4-1: Mix proportions of low calcium content GPCs

Materials	G1	G2	G3	G4	G5	G6	G7	G8
20 mm aggregate	0	613	613	613	613	613	673	673
10 mm aggregate	1221	350	350	350	350	350	384	384
Crushed sand	0	525	525	525	525	525	577	577
River sand	0	262	262	262	262	262	288	288
Sydney sand	621	0	0	0	0	0	0	0
Eraring FA	272	260	260	260	400	360	0	0
Callide FA	78	0	0	0	0	0	0	0
Gladstone FA	0	80	80	80	0	0	410	307
ASMS GGBFS	38	60	60	60	0	40	0	103
NaOH pellets	20.0	20.6	18.5	16.5	20.6	20.6	11.4	11.4
Na-silicate	139	143	129	114	143	143	178	178
Free water	48.6	50.1	58.1	66.1	50.1	50.1	48.2	48.2
MR ¹ (SiO ₂ /Na ₂ O)	1.15	1.15	1.15	1.15	1.15	1.15	1.5	1.5
SiO ₂ + Na ₂ O/Binder ²	0.21	0.21	0.19	0.17	0.21	0.21	0.22	0.22
Water ³ /Solid ⁴	0.27	0.27	0.27	0.27	0.27	0.27	0.30	0.30
GGBFS content [%]	10	15	15	15	0	10	0	25
Curing temperature [°C]	23-90	75	75	75	75	75	23	23
Heat-curing duration [h]	8-24	18	18	18	18	18	N.A.	N.A.

¹ Molar ratio of the alkaline solution² Binder = fly ash (FA) + GGBFS³ Water = free water + water in Na-silicate solution⁴ Solid = Binder + dissolved components of Na-silicate solution (i.e. SiO₂ and Na₂O) + NaOH pellets

4.1.1 Effect of thermal curing on mechanical properties of fly ash-based GPCs

The effect of 3 thermal curing temperature of 60°C, 75°C and 90°C and 4 thermal curing duration of 8h, 12h, 18h and 24h plus ambient curing on compressive strength and modulus of elasticity of GPC containing 10% slag is studied (refer to Figure 4-1).

An OPC concrete (C1) containing the same amount of binder (388 kg/m³) as GPC G1 and same amount of aggregates and water to binder ratio of 0.45 has been made and cured in water for the comparison purpose.

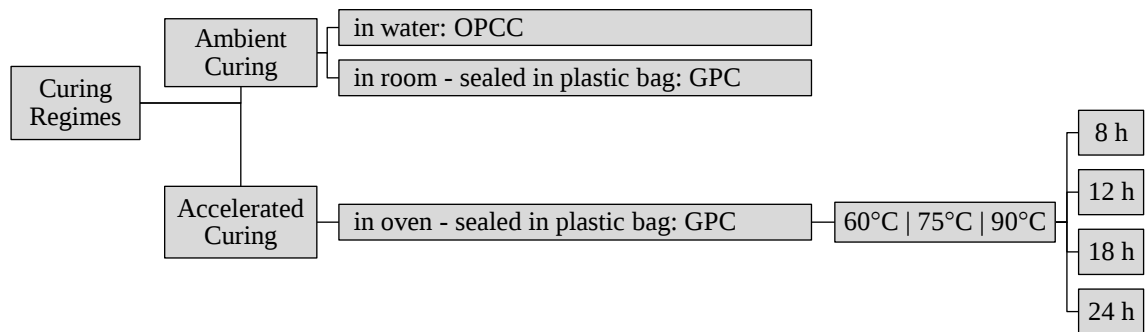


Figure 4-1: Curing methods applied for GPC and OPCC specimens

The compressive strength and modulus of elasticity of GPCs and OPCC measured at 1, 3, 7 and 28 days for the different curing condition are presented in Table 4-2. Three specimens were tested to determine the compressive strength. The coefficient of variation (standard deviation divided by the mean value) of all the test results is below 5%.

The compressive strength of GPCs increased with the increase in the curing temperature from 60°C to 90°C. The reason for this increase is that, at higher temperature, the geopolymerization degree is higher which results in the formation of higher amount of reaction products (Rovnaník 2010). The fly ash grains does not fully dissolve when coming into contact with the alkaline solution and the reactions are initially taking place at the surface layer of the solid particles to form primary geopolymer gel (Barbosa et al. 2000). The further geopolymerization rate is then controlled mainly by the diffusion of hydroxide and silicate ions through the primary geopolymer gel, which is affected mainly by curing temperature and duration at the early-stage of the reactions (Rovnaník 2010).

Table 4-2: Compressive strength and modulus of elasticity of low calcium content GPCs

Mix ID	Curing method	Compressive strength [MPa ± SD]				Elastic modulus [GPa]
		1-day	3-day	7-day	28-day	28-day
C1	Water	18.4±0.1	35.8±1.1	46.7±0.1	64.5±1.2	35.0
G1-1	Ambient	2.9±0.1	8.3 ± 0.4	15.0±0.1	41.7±0.9	19.3
G1-2	60°C-8h	18.6±0.9	25.5±0.7	28.0±1.0	27.4±0.9	13.5
G1-3	60°C-12h	29.7±1.4	36.3±1.1	37.2±0.8	37.8±0.3	16.6
G1-4	60°C-18h	40.8±0.8	42.7±0.5	44.6±0.2	45.6±0.4	20.3
G1-5	60°C-24h	43.6±1.6	49.0±1.0	49.7±0.3	50.0±0.8	22.9
G1-6	75°C-8h	45.2±1.9	45.7±1.1	44.7±0.1	44.8±0.2	20.4
G1-7	75°C-12h	50.5±0.8	52.2±1.3	55.2±1.1	53.9±0.5	22.8
G1-8	75°C-18h	55.9±1.1	59.8±1.9	59.5±0.1	60.0±0.1	24.4
G1-9	75°C-24h	60.2±0.3	62.1±2.9	62.8±0.4	62.3±0.2	25.9
G1-10	90°C-8h	51.1±0.1	48.5±2.4	51.9±0.1	52.2±0.7	23.5
G1-11	90°C-12h	54.1±1.9	57.2±0.1	56.0±1.0	58.6±0.9	23.9
G1-12	90°C-18h	56.0±0.6	61.8±0.6	59.1±0.5	59.8±0.2	25.1
G1-13	90°C-24h	60.5±1.3	60.8±1.6	63.3±0.1	60.7±1.2	25.8

The compressive strength of the geopolymer concretes cured for a short period of time (8 hours and 12 hours), increases with the increase in the curing temperature from 60°C to 90°C. However, for a longer period of heat curing (18 hours and 24 hours) the highest strength is achieved at 75°C. Heat curing at 90°C for more than 12 hours leads to a 28-day strength reduction. Other researchers (van Jaarsveld et al. 2002; Komnitsas and Zaharaki 2007) observed that curing geopolymer concrete for a longer period of time at elevated temperatures weakens its microstructure resulting in a lower compressive strength. Among all the different curing durations and temperatures, the

GPC cured at 75°C for a period of 24 hours shows the highest compressive strength at 28 days achieving 62.3 MPa. However, reducing the heat curing duration from 24 hours to 18 hours does not lead to a significant reduction in strength (around 4% reduction). As a result, 18 hours heat curing at 75°C could be considered as the optimum economical heat curing condition for low-calcium FA-based geopolymer concrete. Heat curing at 60°C appears not to be a suitable option for the geopolymer concrete.

The unfavourable effect of thermal curing on the long term compressive strength of OPC concrete is a well-known fact. Several studies have shown that the high rate of reaction due to the increased curing temperature results in coarser pore structure and increased porosity, non-homogeneous and less uniform distribution of hydration products and micro-cracking which adversely affect the long term compressive strength of the OPC concrete (Bentur et al. 1979; Goto and Roy 1981; Kjellsen 1996; Kjellsen et al. 1990, 1991; Mouret et al. 1999; Sellevold 1974; Skalny and Odler 1972; Verbeck and Helmuth 1968).

However the results of this study show that thermal curing has no detrimental effect on the long term compressive strength of low calcium content GPCs. This is in line with Palomo et al. (1999) and Fernández-Jiménez et al. (2005) investigations concluding that thermal curing increases the long-term compressive strength of fly ash based GPCs.

Figure 4-2 shows the compressive strength development of ambient and heat-cured GPCs up to 28 days. Results show that the curing temperature has a significant influence on the compressive strength development rate of fly ash-based GPCs. For samples cured at 23°C, the strength development rate is approximately 20 times lower than the heat-cured samples. Among the heat-cured samples, increasing the curing temperature and duration increases the initial rate of strength development. The specimens cured at 75°C and 90°C approximately obtained their 28-day compressive strength just after finishing the heat curing period.

Therefore, for precast applications, where high early-age strength is required and thermal curing is commonly applied, low calcium FA-based GPCs appears to perform better than OPC concrete in term of both early and long term compressive strength. The geopolymer mix G1 cured at 75°C and 90°C for 8 to 24 hours reached more than 90% of the 28 days compressive strengths after 1 day with values ranging from 45.2 to 60.5 MPa.

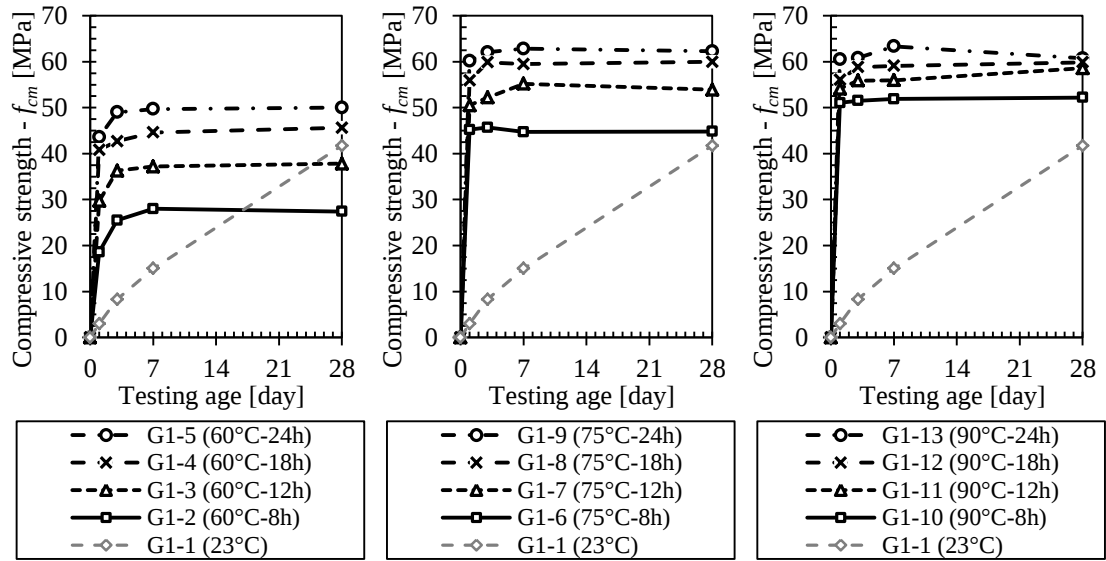


Figure 4-2: Compressive strength development of low calcium GPCs (Noushini and Castel 2016b)

Figure 4-3 shows the modulus of elasticity (MOE) results. Fly ash-based GPCs have much lower MOE than that of OPCC. The low modulus of elasticity of the fly ash based GPC is attributed to the lower modulus of elasticity of the geopolymer paste compared to OPC paste (Pan et al. 2011). For a similar strength level, Fernández-Jiménez et al. (Fernández-Jiménez et al. 2006) found that the elastic modulus of geopolymer concrete is approximately 50% of that of a comparable Portland cement concrete. However, the results of the current study show that, the GPC cured at 75°C for 24 hours is showing an elastic modulus of 25.9 GPa which is 74% of that of standard lime-water cured OPCC.

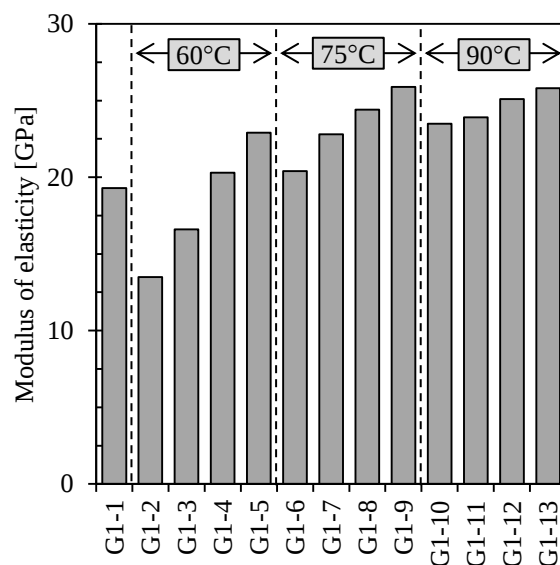


Figure 4-3: Effect of thermal curing on modulus of elasticity of low calcium content GPCs

Based on the regression analyses of the experimental results presented in Table 4-2, the below model is proposed to determine the modulus of elasticity of low calcium content GPCs.

$$E_{GPC} = -11400 + 4712 \sqrt{f_{cm}} \quad (4-1)$$

where E_{GPC} is the modulus of elasticity of GPC in MPa and f_{cm} is the mean compressive strength of GPC in MPa.

The proposed model is compared with ACI 363R (1992) and AS3600 (2009) design codes. Figure 4-4 shows the modulus of elasticity versus compressive strength of the GPC, as well as, the recommended relationship based on the ACI and AS design codes. The ACI 363R (1992) and AS3600 (2009) models are not suitable for predicting the modulus of elasticity of ambient and heat-cured fly ash-based GPCs while the proposed model reasonably predicts the modulus of elasticity of the GPCs tested in this study ($R^2=0.976$).

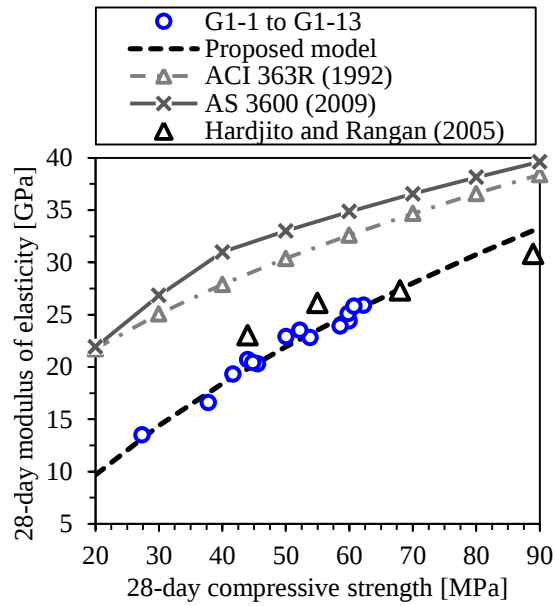


Figure 4-4: Modulus of elasticity versus compressive strength for low calcium content GPCs

4.1.2 Effect of thermal curing on transport properties of fly ash-based GPCs

The water absorption, volume of permeable voids (VPV), sorptivity and resistivity of GPC mix G1 cured at different thermal conditions are illustrated in Table 4-3.

Table 4-3: Water absorption, VPV, sorptivity and resistivity of OPCC and low calcium content GPCs at 28 days

Mix ID	Curing method	Water absorption [%]	VPV [%]	Sorptivity coefficient [$\times 10^{-3}$ mm/s ^{0.5}]	Surface resistivity [k Ω .cm]	Bulk resistivity [k Ω .cm]
C1	Water	5.0	13.5	2.4	12.5	5.3
G1-1	Ambient	5.4	14.7	4.5	2.5	0.97
G1-2	60°C-8h	6.0	15.5	-	1.8	0.63
G1-3	60°C-12h	5.7	15.3	6.4	2.1	0.77
G1-4	60°C-18h	5.6	15.4	4.9	2.6	0.98
G1-5	60°C-24h	5.7	15.2	4.6	3.5	1.19
G1-6	75°C-8h	5.7	15.6	-	3.0	1.15
G1-7	75°C-12h	5.5	15.2	3.8	4.0	1.48
G1-8	75°C-18h	5.6	13.8	3.6	4.4	1.67
G1-9	75°C-24h	6.0	13.7	3.1	5.0	1.73
G1-10	90°C-8h	5.7	15.4	-	3.0	1.10
G1-11	90°C-12h	5.8	14.1	4.4	3.2	1.35
G1-12	90°C-18h	5.7	13.7	4.0	3.8	1.53
G1-13	90°C-24h	5.7	13.7	3.9	4.0	1.62

The apparent volume of permeable voids (VPV) show that for fly ash-based GPCs, inappropriate heat accelerated curing such as curing temperatures lower than 75°C and curing durations lower than 18 hours would increase the VPV. The optimum VPV is obtained for GPCs cured for 18 and 24 hours at 75 and 90°C.

Sorptivity curves of the GPCs are shown in Figure 4-5. Sorptivity represents the material's ability to absorb and transmit water through the matrix by capillary suction. Sorptivity curves usually consist of two stages; starting by a sharp linear increase in sorption followed by a semi-exponential decay. In the initial stage (early times), capillary pores are dominating the sorption process while at the secondary stage, the gel pores govern the rate of water absorption (Martys and Ferraris 1997). In another word, larger size pores control the initial rate of water absorption and smaller pores control capillary suction at the later times.

The decrease in sorption rate with time may be due to several factors. Firstly, the water in contact with the concrete fills up the larger pores, then runs into smaller pores which slows down the rate of sorption. Based on the parallel tube models of porous media, the average velocity, V , of the fluid for a capillary tube could be obtained from Darcy's law

as shown in Eqn. (4-2). Since the flow rate (V) is proportional to the tube radius (r), porous media with smaller pores will absorb a liquid slower than larger pores.

$$V = \frac{r}{4\pi l} \gamma \cos \theta \quad (4-2)$$

Second, even if capillary pores form a strongly connected network through the specimen, such as through the interfacial transition zone (ITZ) around the aggregates, the ingress of water may still be slowed as the pore internal pressure increases. The entrapped air in the pore space compresses and the pore pressure rises when water enters the pore until the air/water interface reaches a stable or metastable configuration (equilibrium); this phenomenon lowers the ingress rate of water entering into the pore network. When equilibrium is reached in the large pore network, any further ingress of moisture would be controlled by capillary transport through the gel pores or moisture diffusion in the capillary and gel pores (Martys and Ferraris 1997).

As shown in Figure 4-5, most of thermal cured GPCs did not reach saturation even after 9 days, showing a low rate of capillary absorption, except for the ones cured for 8 and 12 hours at 60°C. The GPC cured at 60°C for 8 hours (G1-2) reached saturation after only 2.5 hours and samples cured for 12 hour at 60°C (G1-3) after 2 days. These results show that the lack or insufficient duration of heat curing for fly ash-based geopolymer concrete results in a more connected or less tortuous pore network. Furthermore, the total amount of water absorbed at the end of the test is decreasing by increasing the curing duration up to 24 hours (except for G1-2 and G1-3) and curing temperature up to 75°C. Heat curing at 90°C slightly increased the total absorbed water. It can be concluded that for low calcium fly ash-based GPCs, increasing the curing temperature up to 75°C and the curing duration up to 24 hours, reduces the total water taken up by sorption probably due to the reduced capillary pore size as a result of the formation of a more densified gel. The OPC concrete showed a lower rate of water sorption and a lower total amount of capillary absorbed water compared to all GPCs.

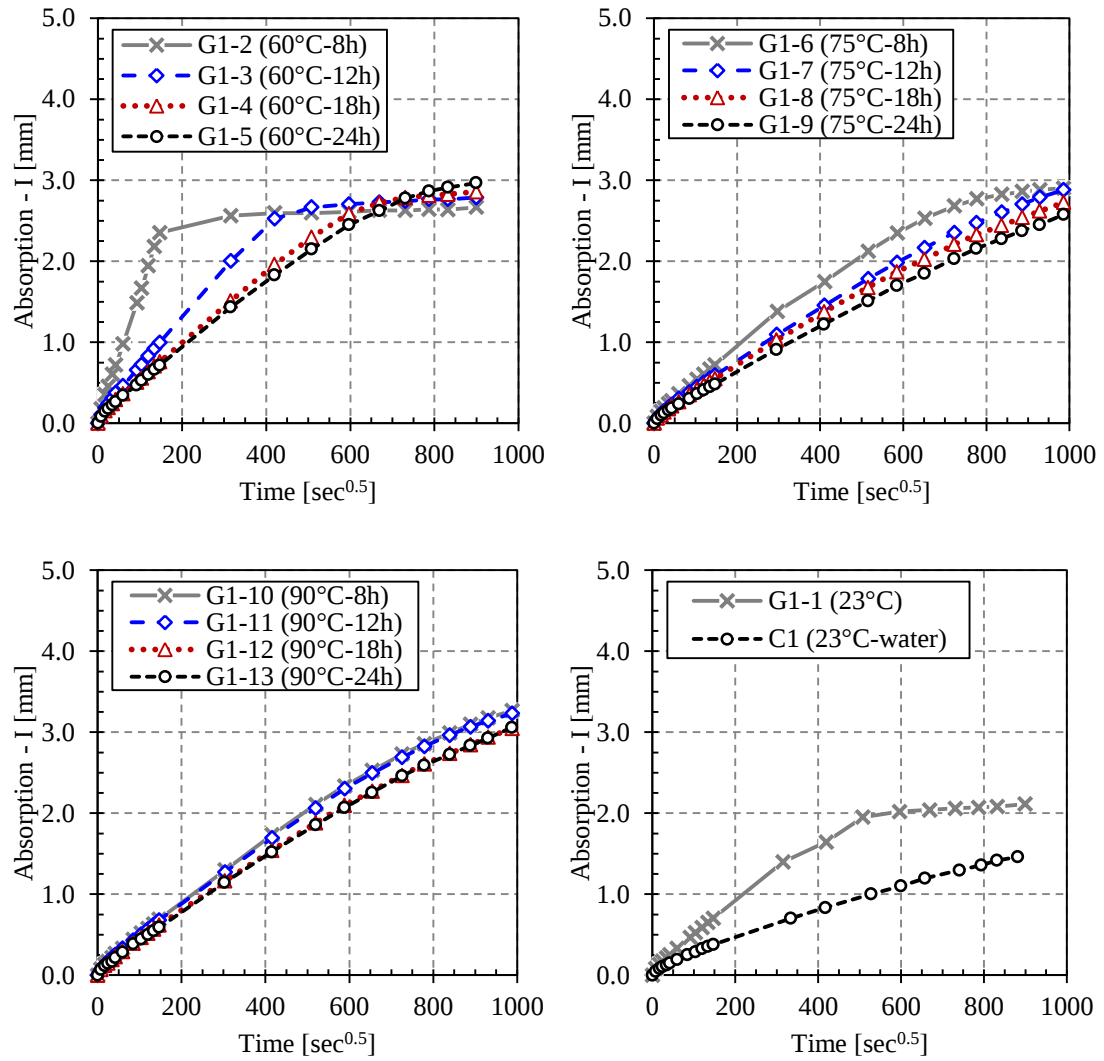


Figure 4-5: Capillary sorptivity of GPCs and OPCC as a function of time

Capillary sorption is associated with the total porosity, the tortuosity and size of the pore network (Ismail et al. 2013c). To better understand the pore size distribution of the tested specimens, mercury intrusion porosimetry (MIP) was performed on a couple of selected samples. One geopolymer and one Portland cement paste sample having the same composition as the GPCs and OPC concrete used in this study (excluding aggregate) have been prepared. The geopolymer paste was cured at 75°C for 18 hours and the Portland cement paste was cured in water at 23°C. The MIP results are presented in Figure 4-6.

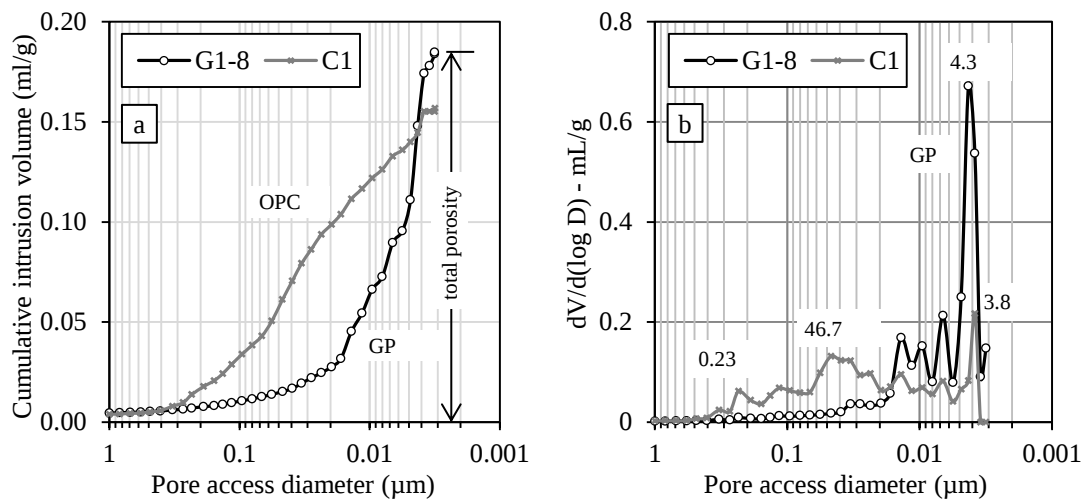


Figure 4-6: Pore structure distribution of heat-cured fly ash based geopolymer and ambient cured OPC mortars determined by mercury intrusion porosimetry (MIP)

The total porosity (open pores) of samples could be calculated using the volume of mercury intruded at the maximum experimental pressure as shown in Figure 4-6-a. The total volume of intruded mercury for OPC paste is lower than that of the geopolymer paste (0.155 compared to 0.185 ml/g). This shows lower total porosity for OPC compared to the thermal cured geopolymer which is in line with the total water absorbed at the end of the sorptivity test. The total water absorbed at the end of the sorptivity test was lower for ambient cured OPC concrete compared to the GPC cured at 75°C for 18 hours (2 mm versus to 2.6 mm –Figure 4-5).

The pore size distribution of the geopolymer sample in comparison with that of OPC paste is shown in Figure 4-6-b. The curve for heat-cured geopolymer presents several peaks reflecting pore sizes with diameter in the range of 3 to 13 nanometres with a critical or threshold peak at around 4 nm. These can be referred to the gel pores as earlier reported by Ma et al. (Ma et al. 2013). For the heat-cured geopolymer sample, no other significant peaks representing the larger size pores (capillary pores) have been observed but were observed in OPC mortar. GPC microstructure is distinctly different from that of cement paste. The homogeneous gels occupying most of the bulk space and the formation of the typical capillary pores (which can generally be observed in cement paste) could not be found in the geopolymer sample.

Although doubts exists on the accuracy of MIP method to reflect the true pore size distribution of cement based materials (Diamond 2000), the permeability and diffusion characteristics of materials are reported (Cook and Hover 1999) to be closely related to

the threshold pore diameter. The threshold pore diameter has been defined as the diameter of pore that completes the first connected pore pathway in materials (Cui and Cahyadi 2001).

The surface resistivity of GPCs as shown in Table 4-3 increased by increasing the curing temperature and duration with the highest resistivity recorded for G1-8. The strong correlation between surface resistivity of saturated specimens and sorptivity coefficient for GPCs is showed in Figure 4-7, indicating that the pore structure significantly influences the resistivity. Lower sorptivity coefficient which means lower capillary porosity and higher tortuosity of the pore structure results in an increased resistivity.

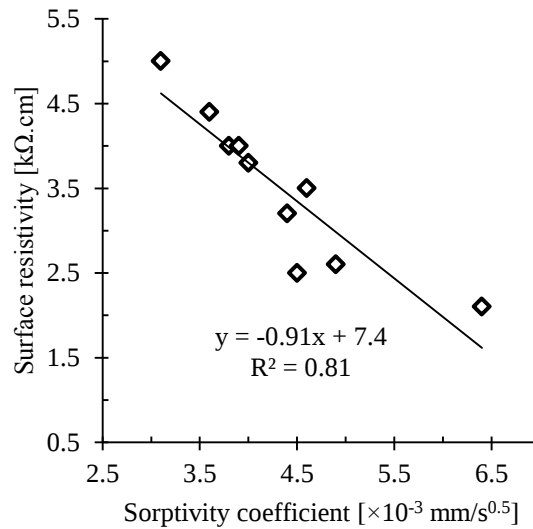


Figure 4-7: Correlation between surface resistivity and sorptivity coefficient of GPCs

In addition to the pore structure, the pore solution chemistry is also playing a significant role on the conductivity/resistivity of the concrete. Geopolymer concrete contains a lot of free metallic ions in the pore solution abandoned from the alkaline solution used in the mix. As mentioned before, increasing the curing temperature and duration, results in the formation of higher amounts of reaction products. This means that more metallic ions (i.e. Na^+ in the current case) will be bound into the geopolymer matrix and the concentration of metallic ions will decrease.

The combined effect of Na^+ decrease in the pore solution, lower capillary pores and increased tortuosity of geopolymer matrix by applying higher curing temperatures for longer period, led to an increased resistivity of geopolymer concretes.

To further support this statement, alkali metals leaching has been investigated by measuring the pH of hardened geopolymer paste leachate. The geopolymer paste powders were mixed with deionised water at a solid to water mass ratio of 1:10 (5 g powder, 50 g water) and pH of the solution were measured after 10 minutes. Table 4-4 shows the pH values of the leaching solutions of fresh and hardened geopolymer pastes. The pH of the fresh geopolymer paste leachate was notably high due to the very high pH of the alkaline solution used in the fresh geopolymer mixture. The pH of the hardened geopolymer pastes leachate decreased with time (3 to 28 days) and at the same age by increasing the curing temperature and duration. The reason for the decreasing trend in the pH of the geopolymer leachate is that the source of initial high pH (e.g. alkali metals) has decreased with time, being consumed during the geopolymerisation process. By ageing or increasing the curing temperature or duration, more reaction products have been developed; therefore more Na^+ has been captured inside the geopolymer matrix for the charge balance and less free Na^+ are available in the pore solution.

Table 4-4: pH values of leaching solutions of fresh and hardened geopolymer paste

Mix ID	Curing method	pH of leaching solution			
		Fresh paste	Hardened paste		
			3-day	7-day	28-day
C1 (paste)	Water	12.42	12.71	12.72	12.72
G1-1 (paste)	Ambient	12.68	12.64	12.50	12.29
G1-2 (paste)	60°C-8h	12.68	12.29	12.27	12.15
G1-3 (paste)	60°C-12h	12.68	12.20	12.18	12.14
G1-4 (paste)	60°C-18h	12.68	12.17	12.14	12.12
G1-5 (paste)	60°C-24h	12.68	12.16	12.14	11.98
G1-6 (paste)	75°C-8h	12.68	12.15	12.10	11.98
G1-7 (paste)	75°C-12h	12.68	12.10	12.06	11.96
G1-8 (paste)	75°C-18h	12.68	12.08	12.02	11.91
G1-9 (paste)	75°C-24h	12.68	12.07	12.00	11.90
G1-10 (paste)	90°C-8h	12.68	12.15	12.08	11.98
G1-11 (paste)	90°C-12h	12.68	12.09	12.05	11.96
G1-12 (paste)	90°C-18h	12.68	12.05	12.02	11.90
G1-13 (paste)	90°C-24h	12.68	12.04	12.02	11.88

The pH values of the leaching solutions of geopolymers prepared by thermal curing are in all cases lower than those cured at ambient temperature (refer to Figure 4-8). This shows that, in ambient cured samples, more alkalis are available to the leaching process. The excessing alkali in ambient cured samples could be an indicator of the lower degree of geopolymerisation leading to a lower amount of reaction products forming. This is confirmed by the lower compressive strength of the ambient cured samples compared to

heat-cured geopolymers especially at early age (up to 3 days). Similar observations have been previously reported by Zhang et al (Zhang et al. 2014).

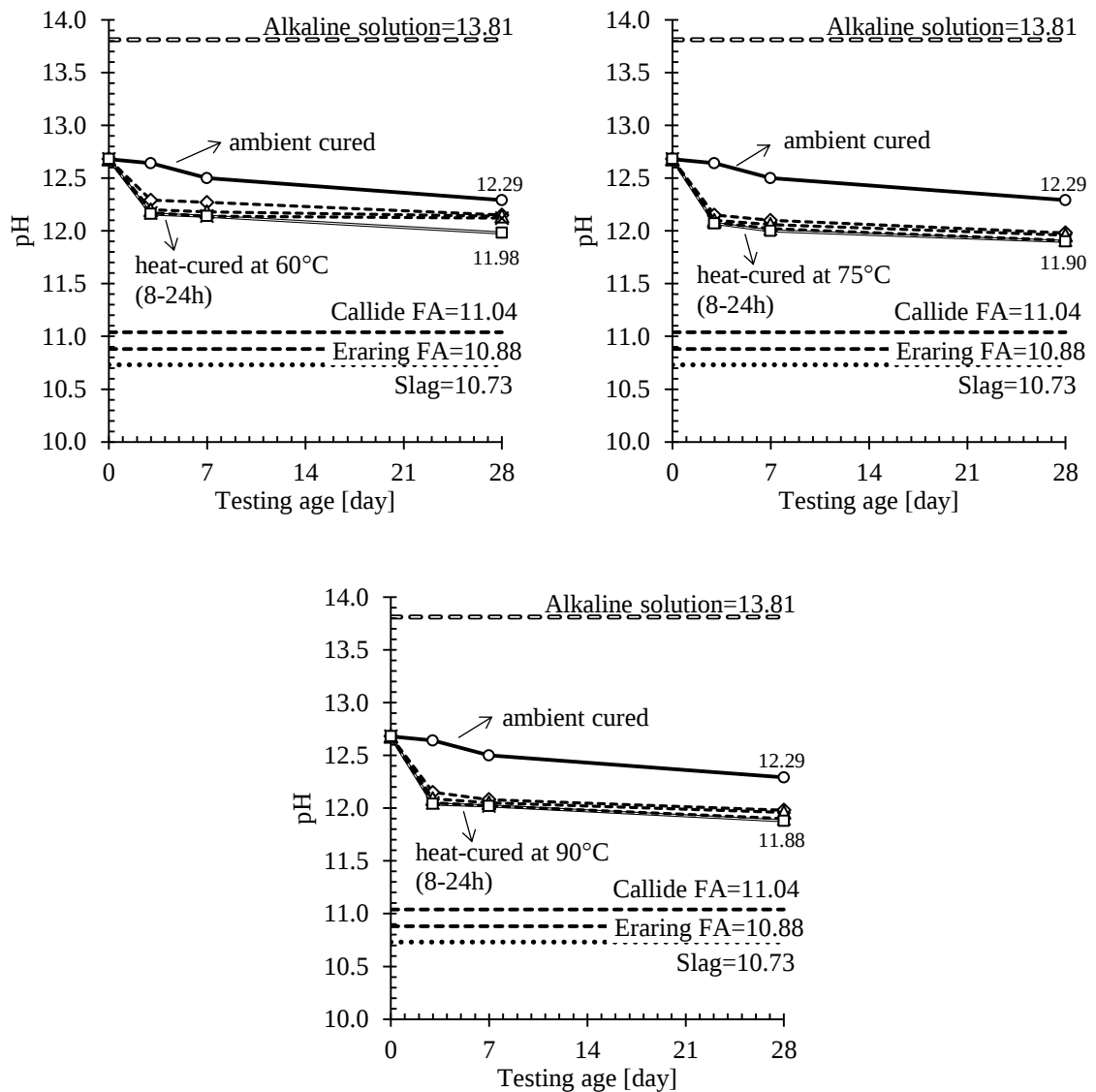


Figure 4-8: The pH values of the leaching solutions of thermal cured versus ambient cured geopolymers

Figure 4-9 shows the correlation between sorptivity, pH of the leaching solution and surface resistivity of fly ash based geopolymers. A good correlation exists between the capillary pore network characteristics (measured by sorptivity test), alkali metal concentration in the pore solution (indirectly measured through the pH of the leaching solution) and the resistivity of geopolymer concrete. The increase in resistivity has happened once the capillary pore network has refined and/or the concentration of alkali metals in the pore solution decreased. Combining the above mentioned together with

compressive strength, it can be concluded that for a particular fly ash based geopolymer mix design, increasing the curing temperature and duration lead to the formation of higher amount of geopolymer gel. This results in a more densified matrix with less capillary voids, less amount of free Na^+ and higher compressive strength. The geopolymer gel densification and reduction in free alkali metals also increases the resistivity of the pore solution and the concrete.

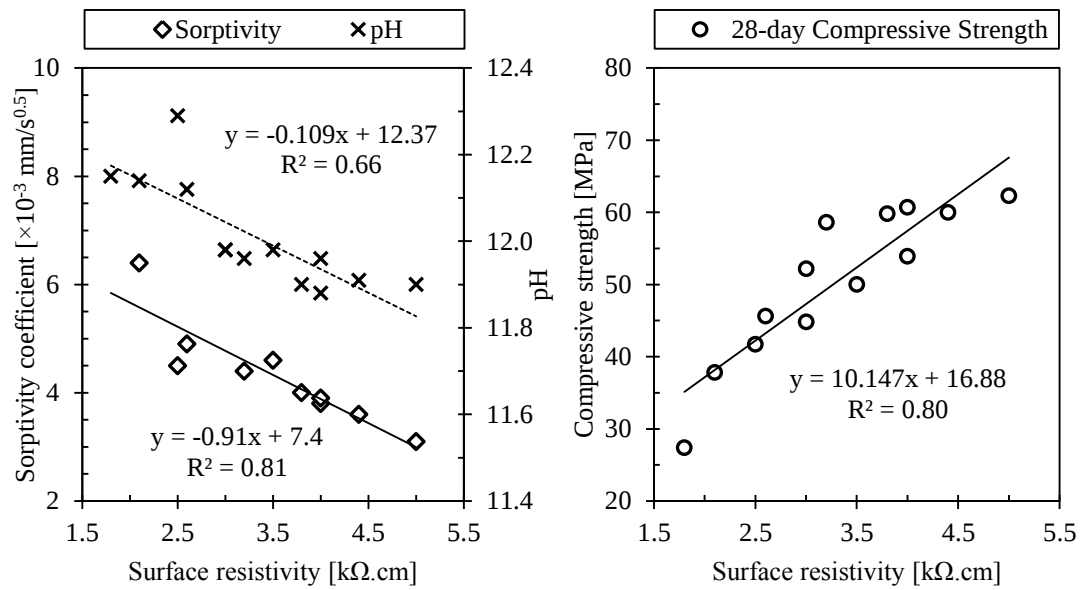


Figure 4-9: Correlation between sorptivity coefficient, pH of leaching solution and surface resistivity of fly ash based geopolymers

4.1.3 Effect of thermal curing on the microstructure of fly ash-based GPCs

The SEM micrographs of all studied geopolymer pastes synthesized under various thermal conditions showed a high proportion of un-reacted or partially reacted fly ash spheres and agglomerated slag particles (selected micrographs are presented in Figure 4-10). Although the quantification of un-reacted particles was unfeasible using the available microscope software, it is expected that by increasing the curing temperature from 60°C to 90°C and curing duration from 8 h to 24 h, a better dissolution of aluminosilicate source materials should have happened which resulted in a higher compressive strength as discussed before. However, this could not be clearly proven using SEM and further examination using solid-state ^{29}Si and ^{27}Al MAS NMR is required to identify the formed species.

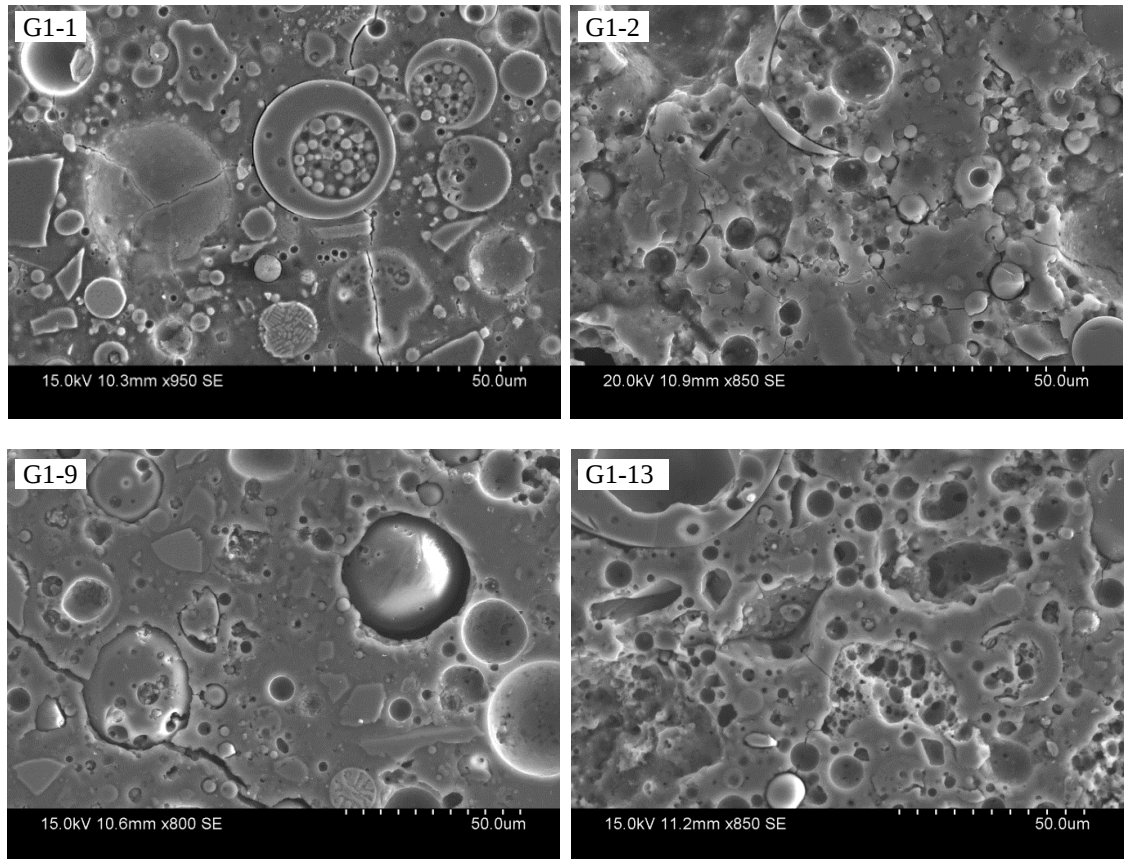


Figure 4-10: SEM Images of geopolymer samples at the age of 28 days

Figure 4-11 shows the interfacial area between the aggregate and the aluminosilicate gel matrix for GPC. No major defects or high porosity at interfacial transition zone (ITZ) can be observed, meaning that the bond between the geopolymer matrix and the aggregates is of a good quality.

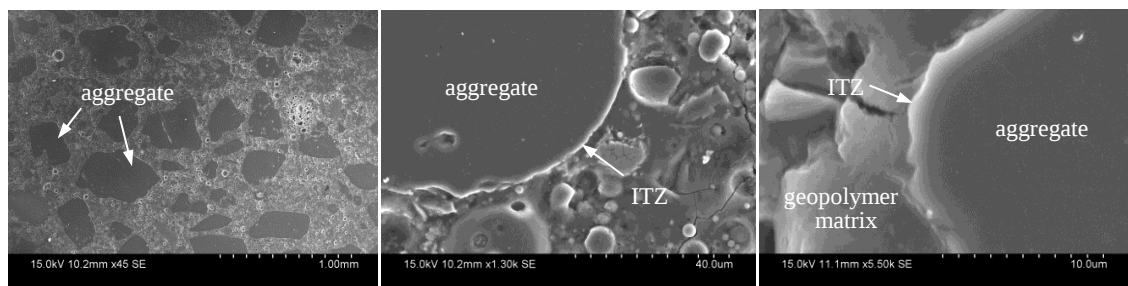


Figure 4-11: SEM micrographs of the interfacial transition zone (ITZ) in geopolymer concrete samples

The EDS spot analysis was performed on the matrix of each geopolymer sample to provide semi-quantitative elemental data. The analysis points were carefully selected to be on the surface of the reaction products and not on the un-reacted particles. An example of the chosen spot for EDS analysis and acquired spectrum is given in

Figure 4-13. For each geopolymer sample, a minimum of 30 points were targeted and analysed. A large variation in the weight percentage of individual elements has been observed throughout the paste which indicates significant variation in elemental composition at different locations of geopolymer paste. However, as expected, the weight percentage of major elements (Si, Al, Ca, Na, K, Mg, S, Fe and O) in the structure of geopolymer paste from various samples were similar due to the use of the same material and mix proportion. Based on the EDS analysis, the Si/Al ratio of the geopolymer pastes is found to be ranging between 3.0 and 3.9 with no systematic trend and correlation to the curing temperature and duration (refer to Figure 4-12).

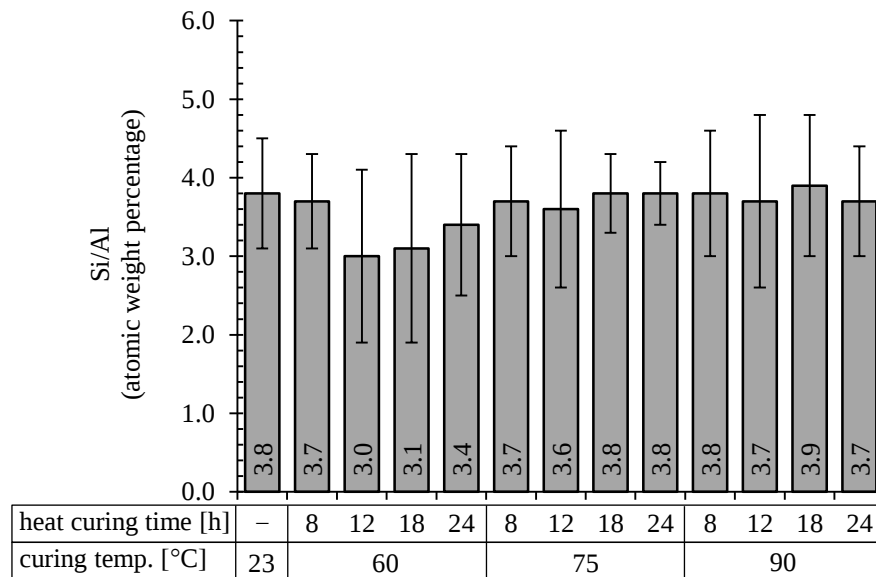


Figure 4-12: Si/Al ratio of GPCs cured at various temperatures and durations

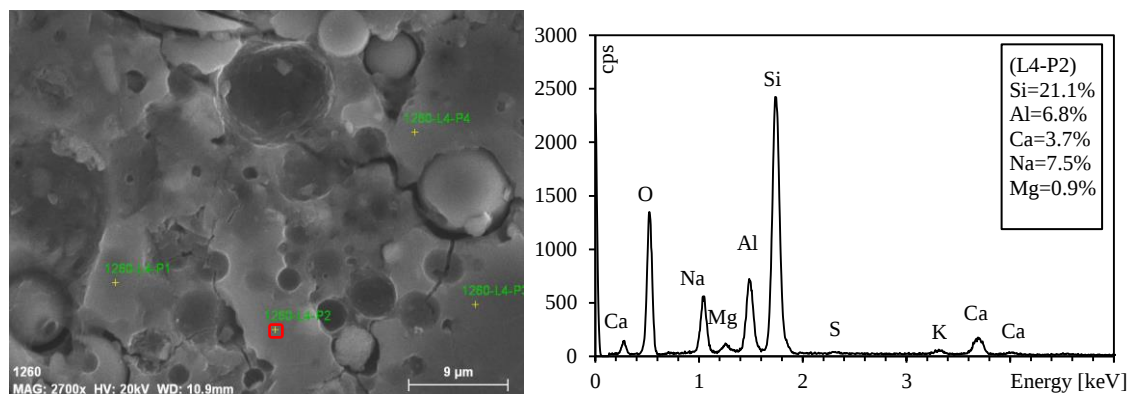


Figure 4-13: SEM micrograph of analysed section and selected EDS spectrum

Figure 4-14 shows the diffractograms of the geopolymers as well as the initial aluminosilicate source materials. The results of XRD analysis of the geopolymer pastes indicated that the main phases are amorphous geopolymer structures as indicated by the broad hump from 15 to 35° 2θ and crystalline quartz, mullite, magnetite, hematite and calcite. These crystalline phases were also found in the initial fly ash and slag, and apparently remained unaltered after geopolymerisation due to their unreactive nature. The geopolymer structure which can also be referred to as N-(C)-A-S-H network results from the dissolution, coagulation and reorganisation of the glass structure in fly ash and slag. Similar findings have been previously reported in other research works (Criado et al. 2005).

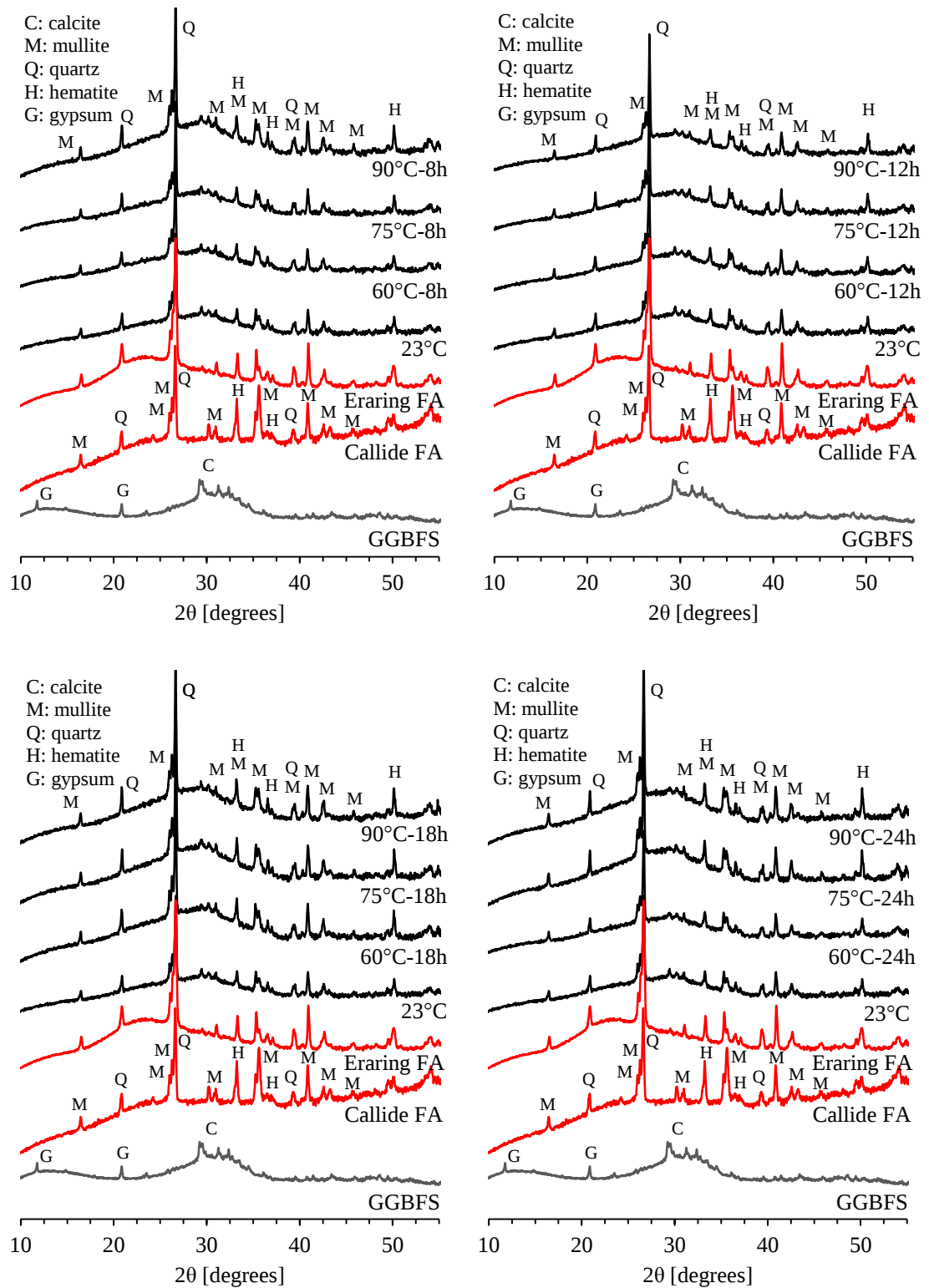


Figure 4-14: XRD pattern of geopolymer pastes cured at different temperatures and the initial aluminosilicate source materials

Figure 4-15 shows the infrared spectroscopic results of the aluminosilicate source materials used as geopolymer precursors, as well as, the geopolymer pastes. The fly ash spectrum contains a broad hump between $850\text{--}1250\text{ cm}^{-1}$ centred at 1050 cm^{-1} , which is

associated with Si-O and Al-O bond asymmetric stretching vibrations. This provides information on the degree of crystallinity of the sample (Criado et al. 2007b). The signal appearing at around 792 cm^{-1} is also attributed to quartz and mullite.

The GGBFS contains only one wide and intense band centred at approximately 855 cm^{-1} which represents the calcium silicate amorphous phase. The FTIR results match well with the phases found in the XRD patterns.

The ambient and heat-cured geopolymers consist of an intense band centred at $\sim 973\text{--}983\text{ cm}^{-1}$, which depends on the heat curing regime. The intensity of the peak was almost constant for all synthesized geopolymers. The shift of the main band in fly ash (1050 cm^{-1}) to smaller wave numbers ($973\text{--}983\text{ cm}^{-1}$) along with the increase of intensity corresponds to dissolution, silica solubilisation and polycondensation processes, with partial substitution of SiO_4^{4-} with AlO_4^{5-} groups in the newly formed network. The valence compensation is achieved by Na^+ ions. No significant difference in the FTIR spectra of ambient and heat-cured geopolymers was observed. This is due to the nature of the FTIR test. FTIR is a high sensitivity but low resolution technology (compared to NMR for instance which has a low sensitivity but high resolution). As a result, FTIR could not capture the difference in the types of silicate species forming depending on the different curing conditions. For this reason, the solid-state ^{29}Si and ^{27}Al MAS NMR test has been carried out.

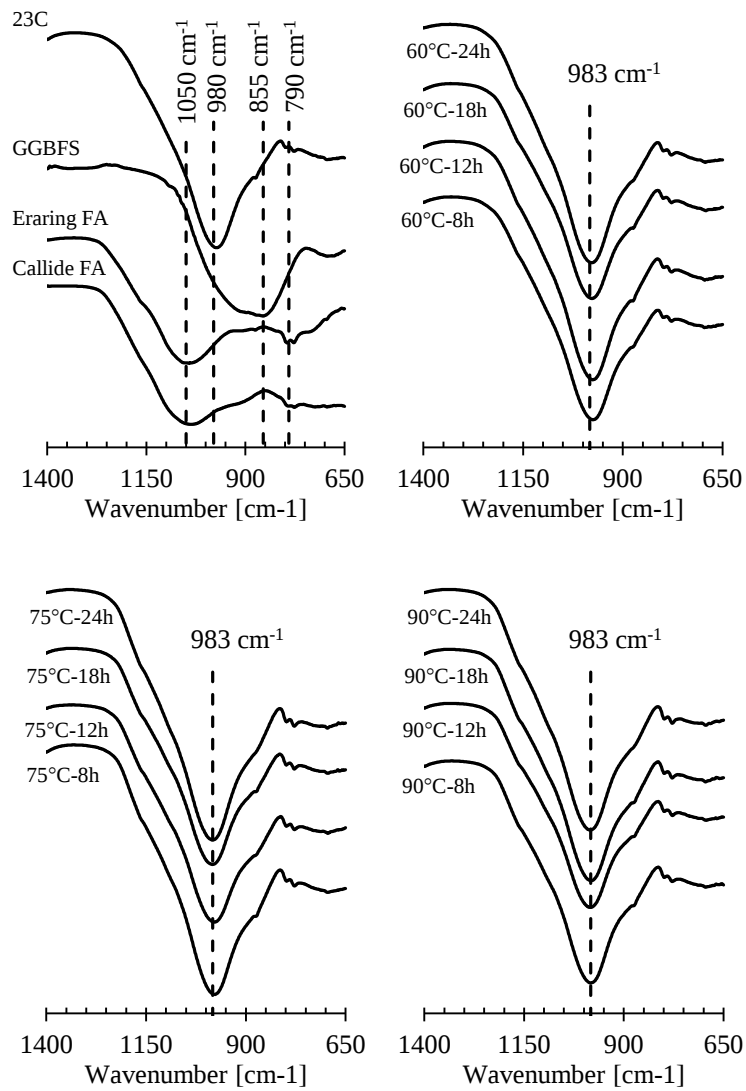


Figure 4-15: FTIR spectrum of the aluminosilicate source materials and synthesized geopolymers

Figure 4-16 shows the ^{29}Si and ^{27}Al MAS-NMR spectra of the initial aluminosilicate source materials. Deconvolution of the ^{29}Si MAS NMR signal for GGBFS and fly ash, yield resolved sites, whose relative populations are tabulated in Table 4-5.

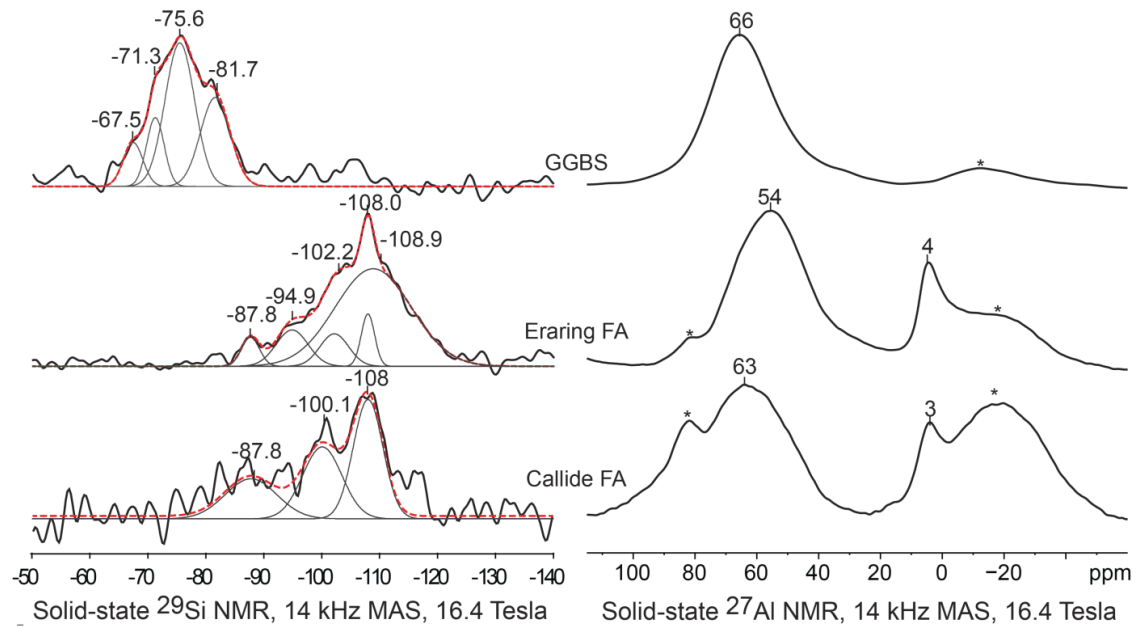


Figure 4-16: Solid-state ^{29}Si and ^{27}Al MAS-NMR of the initial aluminosilicate source materials. Bold lines are the experimental spectra. For the ^{29}Si NMR spectra, the dashed lines (red) are the overall fit to the experimental spectra, while the thin lines are the individual components to the fit.

Table 4-5: Quantification summary of Q^n species identified in ^{29}Si MAS-NMR spectra of alumina silicate source materials

Sample ID	Site type and positions (ppm)									
	-67.5 Q^0	-71.3 Q^0	-75.6 Q^1	-81.7 $\text{Q}^2(2\text{Al})$	-87.8 Q^2 $\text{Q}^3(3\text{Al})$ $\text{Q}^4(4\text{Al})$	-94.9 $\text{Q}^3(1\text{Al})$ $\text{Q}^4(3\text{Al})$	-100.1 Q^3 $\text{Q}^4(1\text{Al})$ $\text{Q}^4(2\text{Al})$	-102.2 Q^3 $\text{Q}^4(1\text{Al})$	-108.0 Q^4	-108.9 Q^4
Eraring FA	-	-	-	-	5±5%	11±5%	-	9±5%	7±5%	69±5%
Callide FA	-	-	-	-	25±25%	-	34±25%	-	42±25%	-
GGBFS	10±4%	13±4%	47±4%	30±4%	-	-	-	-	-	-

The ^{29}Si MAS-NMR spectrum of GGBFS contains a broad peak with resolved components at -67.5 ppm, -71.3 ppm, -75.6 ppm and -81.7 ppm. The primary component is the -75.6 ppm peak which corresponds to akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) glass, which is Q^1 silicate species (Kirkpatrick 1988). The second major peak at -81.7 ppm corresponds to a solid solution gehlenite glass ($\text{Ca}_2(\text{Al}_2\text{Si})\text{O}_7$) which are $\text{Q}^2(2\text{Al})$ silicate species (Davidovits 2011). The additional smaller peaks at -67.5 ppm and -71.3 ppm are assigned to Q^0 species which are likely to be the calcium-rich silicate phases. However, it is important to point out that the Q^0 species do not have the appropriate ^{29}Si chemical shifts of the di- and tri-calcium silicates (C_2S and C_3S) present in ordinary Portland cements (Rawal et al. 2010), nor is there any evidence of C_2S or C_3S observed in the x-ray diffraction. It is likely that these Q^0 species are either a disordered glassy calcium

silicate phase or more likely local disordered species within the akermanite glass structure.

In contrast to the GGBFS, the ^{29}Si NMR spectrum of the Eraring FA is dominated by the Q^4 species. Specifically, the deconvolution indicates components at -87.8 ppm, -94.9 ppm, -102.2 ppm, -108.0 ppm and -108.9 ppm. The sharp signal at -108.0 ppm is assigned to crystalline quartz (Q^4 silicate) while the signal at -87.8 ppm is assigned to mullite ($\text{Q}^4(4\text{Al})$ silicate) (Davidovits 2011; Palomo et al. 2004), which is consistent with the observed X-ray diffraction pattern (Figure 4-14). Additionally the peaks at -94.9 ppm and -102.2 ppm observed for Eraring fly ash correspond to different vitreous Q^3 and Q^4 species as indicated in Table 4-5. By far the most prevalent silicates species (69 %, Table 4-5) in the Eraring FA is the resonance centred at -108.9 ppm. Unlike quartz, which has a well resolved sharp lineshape, the -108.9 ppm peak has a very broad lineshape indicative of a disordered structure. Cristobalite cannot be assigned to this species based on the fact that ^{29}Si NMR does not match with the expected chemical shift of cristobalite (Davidovits 2011), the peak is too broad to be due to a crystalline phase and that there is no evidence for this in the X-ray diffraction results. Most likely, the -108.9 ppm signal is associated with the glassy spheres observed in the SEM micrographs of fly ash (Noushini et al. 2016a).

The ^{29}Si MAS-NMR spectrum of the Callide FA sample has a significantly reduced signal to noise ratio as compared to the GGBFS and Eraring FA, due to its very high Fe content (12 wt.%, Table 3-1). The low signal to noise ratio is reflected in the large error bars associated with the peak integrals in Table 4-5, and this prevents peak assignment with a high degree of resolution. None the less, for the Callide FA, three distinct regions are observed in the ^{29}Si NMR spectra, assigned to -87.8 ppm for crystalline mullite, -100.1 ppm corresponding to the starting vitreous materials and -108.0 is associated with quartz. All signals are broadened compared to the Eraring FA signal due the presence of high amounts of iron in the sample. Although XRD quantification indicates that Callide fly ash has a high volume of glass component, however the low signal intensity precludes observation of the broad peak of the $\text{Q}^4(0\text{Al})$ glass species.

The difference in the aluminate speciation of the raw materials is observed in the ^{27}Al MAS-NMR plotted in Figure 4-16. The broad resonance in the ^{27}Al NMR spectrum (centred at 66) of GGBFS reflects the highly disordered tetrahedral configuration within the akermanite and gehlenite glass (Davidovits 2011). No six-coordinate aluminate

species were observed in GGBFS spectrum. In comparison for the Eraring FA, ^{27}Al NMR spectrum shows a broad component centred at 55 ppm associated with a disordered tetrahedral four-coordinate aluminate, and a relatively narrower signal centred at 4 ppm corresponding to an octahedral six-coordinate aluminate species. While peaks at ~50 ppm and 4 ppm have been previously assigned to aluminate species in mullite (Davidovits 2011), we note that, in the present case, the ratio of the peak intensity between the four and six coordinate aluminate species precludes complete assignment of the 55 ppm peak to a mullite environment, which here is assigned to the disordered vitreous phase. For Callide FA, the tetrahedral four coordinate aluminate species are centred at 64 ppm, while the octahedral six-coordinate aluminate species are centred at 3 ppm. The high intensity of the spinning side band in the ^{27}Al NMR spectrum of the Callide FA is due to the high iron content. For both fly ashes, the octahedral environments are significantly less distorted which coupled with the reduced second-order quadrupolar broadening associated with octahedral symmetry, yields significantly narrower peaks. These peaks are mainly associated with the presence of mullite in fly ash (Davidovits 2011; Palomo et al. 2004).

Figure 4-17 shows the ^{29}Si and ^{27}Al MAS-NMR spectra of an ambient cured geopolymer paste (G1-1), as well as two selected heat-cured geopolymer pastes (G1-2 and G1-9). The heat-cured geopolymers are the paste fraction of the concrete samples that yielded the lowest (G1-2, 27.4 MPa) and highest compressive strength (G1-9, 62.3 MPa) after 28 days. The Eraring FA spectrum which consists of 70% of the total geopolymer precursor is also included for comparison.

Figure 4-18 shows the ^{29}Si and ^{27}Al MAS-NMR spectra of geopolymer samples cured at 75°C for different curing periods of 8 to 24 hours, and thus specifically represents changes in the molecular structure as a function of heat curing time.

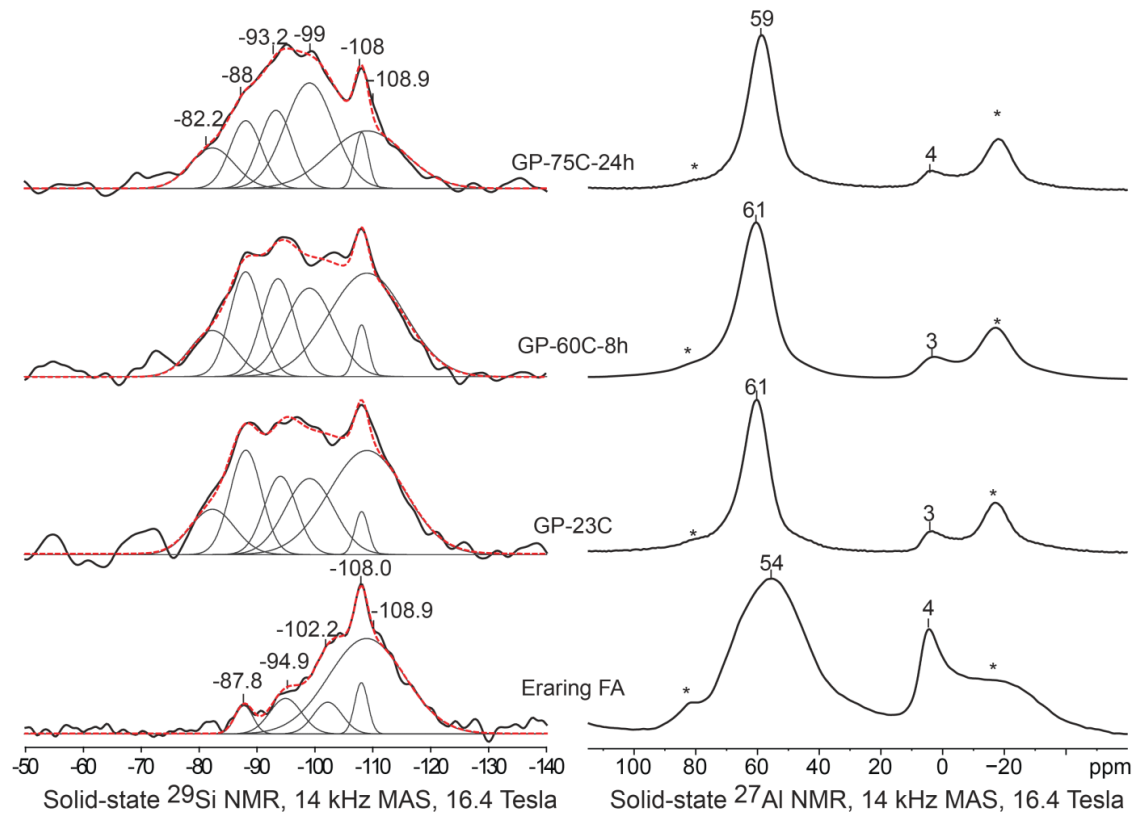


Figure 4-17: Solid-state ^{29}Si NMR and ^{27}Al MAS NMR showing influence of ambient and heat-cure on the structure of geopolymer samples. Bold lines are the experimental spectra. For the ^{29}Si NMR spectra, the dashed lines (red) are the overall fit to the experimental spectra, while the thin lines are the individual components to the fit. The spectra of Eraring FA, which is the primary component of the geopolymer samples is replotted for comparison.

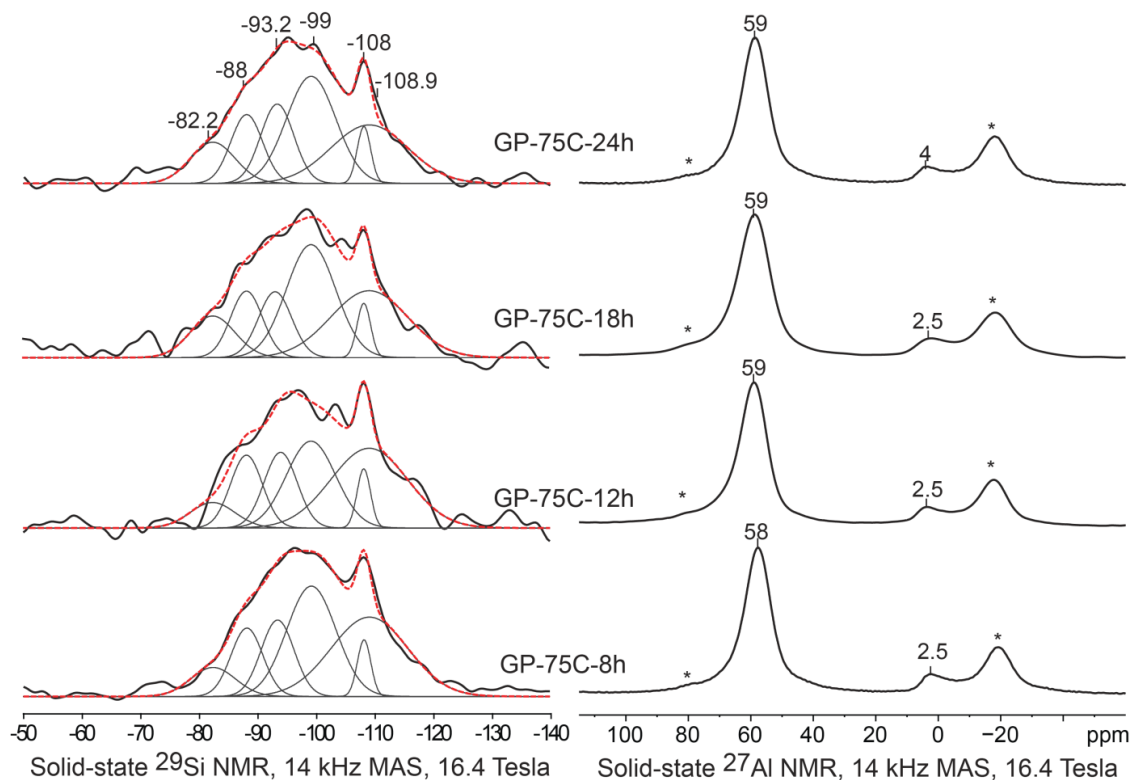


Figure 4-18: Solid-state ^{29}Si NMR and ^{27}Al MAS NMR showing influence of varying heat-cure time (8 h–24 h at 75 °C) on the structure of geopolymer samples. Bold lines are the experimental spectra. For the ^{29}Si NMR spectra, the dashed lines (red) are the overall fit to the experimental spectra, while the thin lines are the individual components to the fit. The spectra of G1-9 is replotted for comparison.

The ^{29}Si NMR spectra of all geopolymers show strong resonances within -80 to -120 ppm. For all the cured pastes, there is negligible signal centred at -75 ppm indicating that the slag is almost completely reacted away. For deconvolution, the ^{29}Si NMR spectrum of the G1-9 was first fit using the Dmfit software, and the resulting peak parameters were fixed for all subsequent fits, allowing only their relative intensities to vary. This allows to quantitatively monitor the specific changes associated with the different aluminosilicate species as a function of the curing process. The deconvolution of geopolymer paste samples identified a total of six peaks of which the peaks at -88 ppm, -108 ppm and -108.9 ppm were assigned to the mullite, quartz and glass respectively, from the residual un-reacted fly ash. Additionally, new signals at -82.2, -93.2 and -99 ppm, were associated with the geopolymer paste. The distinct assignments and the relative integrals of the different silicate species are tabulated in Table 4-6. Due to the inherent uncertainty associated with the chemical shifts of aluminosilicates, at present the new signals are assigned to multiple different species. For example, the signal at -82.2 ppm is assigned to either Q^1 or $\text{Q}^2(2\text{Al})$ or $\text{Q}^4(4\text{Al})$. Although, it is complicated to distinctly assign a signal to a specific species, the current deconvolution

can effectively monitor the collective change on the spectra as a function of different curing protocols.

The ^{27}Al NMR spectra of the geopolymer pastes in Figure 4-17 and Figure 4-18 contain two peaks. The peak centred at around 59 - 61 ppm is attributed to Al(IV) configuration while the signal at around 4 ppm (3 - 4 ppm) is assigned to Al(VI) configuration as before. The key difference between the ^{27}Al NMR spectra of the raw materials and the geopolymer pastes is that the signal of the four-coordinate aluminates is much narrower in the geopolymer pastes, indicating the formation of more ordered and less distorted aluminate tetrahedral during the geopolymerisation process. This characterises well condensed aluminosilicate networks (Davidovits 2011). Importantly, the signal of the octahedral aluminate (~ 4 ppm) is not much changed compared to the neat fly ash, indicating that the mullite phase in the raw materials is not significantly altered during the geopolymerization.

The quantification of the different silicate species from the ^{29}Si NMR presented in Table 4-6 allows to measure the combined influence of the different heating protocols on the overall structure of the material. The primary trend observed is the reduction of the signal intensity of -108.9 ppm component with increasing curing temperature and time as compared to the neat fly ash. For the fly ash, the -108.9 ppm signal constitutes $\sim 69\%$ of the silicate species, while in the cured geopolymer pastes, the values range between 26% to 39%, which indicates that the glassy component of the fly ash is significantly consumed in the geopolymerization process. In contrast, the signal of the quartz (-108 ppm) is effectively the same for all the geopolymer pastes, indicating that the quartz reacts very little, even at elevated temperatures. We note that the signal at -88 ppm has a relative fraction of 12% to 16% of the total silicate species. In the raw materials, the -88 ppm signal assigned to mullite only constituted to 5% of the total silicate, and since additional mullite cannot be formed in the geopolymerization process, the -88 ppm signal must therefore have contributions from silicate species newly formed during the geopolymerization process.

Table 4-6 shows that the signal at -99 ppm corresponds to the primary silicate ($\text{Q}^3/\text{Q}^4(1\text{Al})$) species formed during the geopolymerization, and varies in relative concentration from 18% -32%. No significant change was observed for the -82.2 ppm and -93.2 ppm signals as a function of the different heat curing regimes. Thus, the

primary changes associated with the geopolymerization are the reduction in the intensity of the -108.9 ppm peak and the increase in the intensity of the -99 ppm peak.

The systematic increasing trend in the quantity of species formed at -99 ppm and the decreasing trend of glassy component at -108.9 ppm observed in Table 4-6, clearly highlight the effect of curing temperature and duration on the geopolymer structure, which correlates strongly to the compressive strength of the geopolymer concrete. The decrease in $Q^4(0Al)$ from 39% for G1-1 and G1-2, to 26% for G1-9, i.e. 13 % drop, clearly shows that extended high temperature curing enable better dissolution of the glassy component, thereby enhancing the overall geopolymerization reaction. The fact that the -99 ppm signal undergoes an expected concomitant ~10% increase further validates this observation. Thus, the key mechanism in the improvement of the mechanical strength is the increase in the formation of the -99 ppm silicate species which enhances the three-dimensional crosslinks in the paste and improves bond with the aggregate. We note from Table 4-6 that in compositional profile, G1-1 (i.e. ambient cure) has a very similar structure to GP-60C-8h. Yet, the associated geopolymer concretes have significantly different compressive strengths, i.e 41.7 MPa for G1-1C and 27.4 MPa for G1-2. The difference in the compressive strength is due to the macro-structural differences in the geopolymer structure developed at different curing temperature. Although the short curing duration of 8 h at 60°C appeared to make no significant difference in chemical composition of the resulting geopolymer, it affected the physical and macro-structural properties of the geopolymer paste and concrete as shown Table 4-2 and Table 4-3. The porosity of the geopolymer paste synthesised at 60°C is higher than that of the ambient cured GPCs hence the less compact structure of G1-1 resulted in a lower compressive strength. The effect of heat curing on density of geopolymers has also previously be reported by Rovnanik (2010).

The effects of varying curing time at elevated curing temperature above 75 °C seem to be more significant. Within the limits of measurement, Table 6 indicates that for the G1-5 to G1-9, the silicate structures after 8 h and 12 h of cure are very similar as are the structures after 18 h and 24 h of cure. This similarity agrees well with their respective compressive strengths as seen in Table 4-2. Thus from current data, it appears that significant changes tend to occur in steps within the curing geopolymer system. In particular the most significant change was observed with regards to the enhanced dissolution of the glassy component.

Table 4-6: Quantification summary of Qⁿ species identified in ²⁹Si MAS-NMR spectra of geopolymer pastes

Sample ID	Site type and positions (ppm)					
	-82.2 Q ¹ Q ² (2Al) Q ⁴ (4Al)	-88.0 Q2 Q3(3Al) Q4(4Al)	-93.2 Q3(1Al) Q4(3Al)	-99.0 Q3 Q4(1Al) Q4(2Al)	-108.0 Q ⁴ (0Al) quartz	-108.9 Q ⁴ (0Al) glass
G1-1	10%	16%	13%	18%	3%	39%
G1-2	10%	15%	14%	19%	3%	39%
G1-6	7%	12%	14%	30%	4%	33%
G1-7	7%	14%	15%	25%	5%	36%
G1-8	11%	12%	12%	32%	4%	29%
G1-9	11%	13%	15%	31%	4%	26%

4.1.4 Effect of alkaline solution concentration on performance of fly ash based GPC

The influence of alkaline solution concentration (i.e. SiO₂+ Na₂O/binder ratio) on the performance of low calcium content GPCs is investigated using mixes G2, G3 and G4. Reducing the amount of soluble silicate and alkali in the mix resulted in reduced mechanical properties as shown in Figure 4-19.

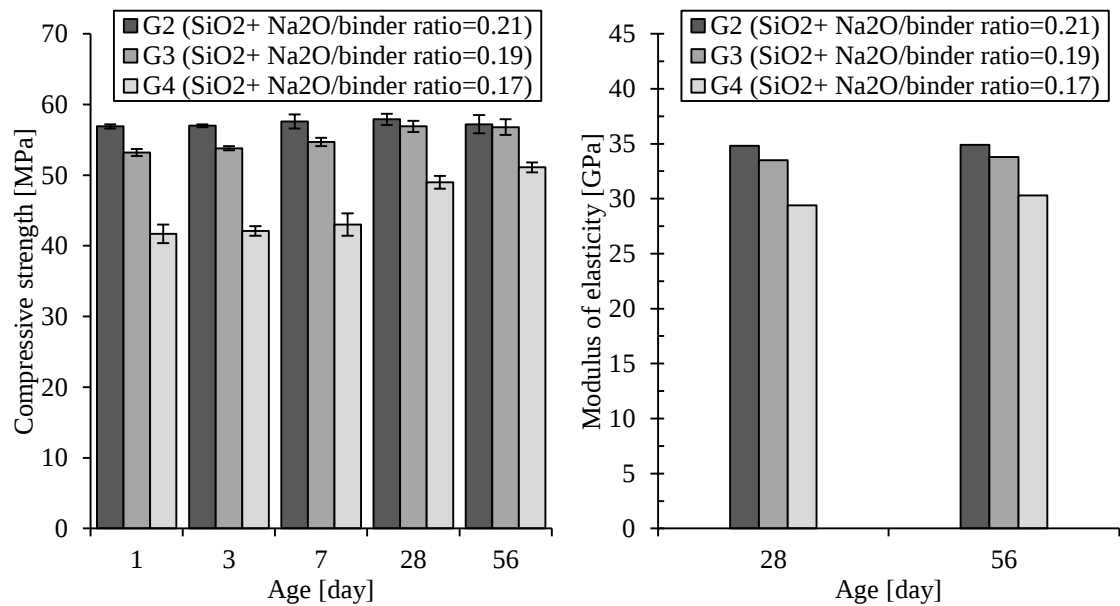


Figure 4-19: The effect of alkaline solution concentration on mechanical properties

As presented in Table 4-7, the reduction in alkaline solution concentration led to an increased porosity and reduced electrical resistivity for fly ash based GPCs.

Table 4-7: The effect of alkaline solution concentration on 28-day water absorption, VPV, sorptivity and resistivity of fly ash based GPCs

Mix ID	Water absorption [%]	VPV [%]	Sorptivity coefficient [$\times 10^{-3}$ mm/s ^{0.5}]	Surface resistivity [k Ω .cm]	Bulk resistivity [k Ω .cm]
G2	5.2 $\pm$ 0.4	13.3 $\pm$ 0.2	3.6 $\pm$ 0.2	9.0 $\pm$ 0.1	3.6 $\pm$ 0.1
G3	5.8 $\pm$ 0.1	14.5 $\pm$ 0.1	5.2 $\pm$ 0.2	6.0 $\pm$ 0.5	2.6 $\pm$ 0.1
G4	6.3 $\pm$ 0.1	17.2 $\pm$ 0.2	10.2 $\pm$ 0.6	3.3 $\pm$ 0.1	1.4 $\pm$ 0.1

4.1.5 Effect of low slag content on properties of fly ash-based GPCs

The influence of low percentage of slag addition (i.e. 10% and 25% of total binder) on the performance of fly ash based GPCs is investigated in mixes G5 to G8.

G5 and G6 were heat-cured at 75°C for 18 hours. G5 was made with 100% fly ash while G6 had 10% GGBFS. G7 and G8 were ambient cured at 23°C. G7 is a 100% fly ash based GPC while G8 has 25% GGBFS as binder.

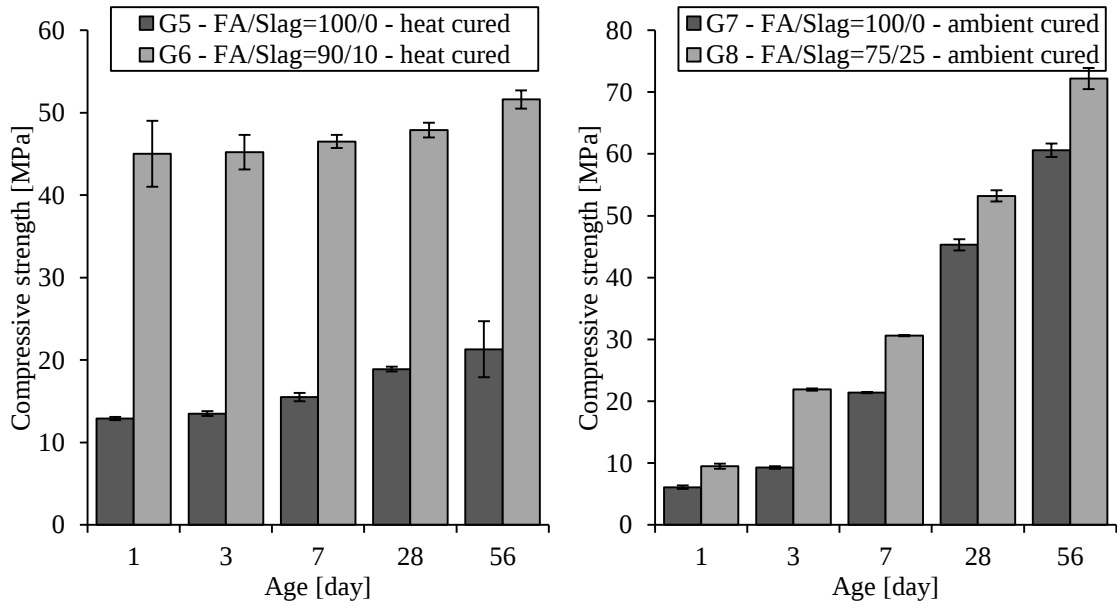


Figure 4-20: The effect of slag addition on compressive strength of fly ash based GPCs

The fly ash based GPCs with 10% and 25% slag demonstrated higher compressive strength at all ages. The effect of slag addition on compressive strength is more pronounced for the heat-cured GPCs compared to the ambient cured GPC. The increased strength by the addition of slag to fly ash based GPCs is due to the formation of C-S-H and C-A-S-H structures in addition to the geopolymer network (Diaz et al. 2010).

A lower total porosity and higher electrical resistivity were observed for fly ash based GPCs blended with 10% and 25% GGBFS as shown in Table 4-8. Provis et al. (2012)

investigated the microscale pore structure and tortuosity of blended fly ash and GGBFS GPCs using X-ray microtomography. They found that the increase in the pore network tortuosity and the decrease in total porosity by increasing the slag content were attributed to the pore filling effect of C-A-S-H gel.

Table 4-8: The effect of slag addition on 28-day transport properties of fly ash based GPCs

Mix ID	Water absorption [%]	VPV [%]	Sorptivity coefficient [$\times 10^{-3}$ mm/s ^{0.5}]	Surface resistivity [k Ω .cm]	Bulk resistivity [k Ω .cm]
G5	6.9 $\pm$ 0.4	19.8 $\pm$ 0.9	26.9 $\pm$ 1.2	1.3 $\pm$ 0.1	0.6 $\pm$ 0.1
G6	6.4 $\pm$ 0.1	17.3 $\pm$ 0.2	7.3 $\pm$ 0.2	5.3 $\pm$ 0.1	2.0 $\pm$ 0.1
G7	6.8 $\pm$ 0.3	17.3 $\pm$ 0.6	11.4 $\pm$ 0.5	2.7 $\pm$ 0.2	0.8 $\pm$ 0.0
G8	6.1 $\pm$ 0.2	10.0 $\pm$ 0.8	5.9 $\pm$ 0.4	4.4 $\pm$ 0.2	1.5 $\pm$ 0.1

4.2 High calcium content GPCs

The results presented in section 4.1 and the pore structure analysis of GPCs employing gas adsorption/desorption, MIP and Wood's metal intrusion revealed that the aluminosilicate network of fly ash based GPCs is highly porous with considerable pore blocking in the network (Duxson et al. 2005; Lloyd et al. 2009; Provis et al. 2012; Rovnaník 2010).

Provis et al. (2012) employed X-ray microtomography technique that allows direct assessment of the pore structure and tortuosity of blended FA and GGBFS binders. They observed a general improvement (i.e. finer pore development with higher tortuosity) in the pore structure as a consequence of GGBFS addition due to the pore filling effect of C-(A)-S-H gel, although their findings were restricted to microscale pores due to the technical limitations. A critical slag content of 25% was also reported; below this content, the calcium ions appeared to get absorbed into the aluminosilicate network and did not chemically bind the water and therefore, the pore filling effect was negligible. On the other hand, the formation of C-(A)-S-H gel was suggested to start dominating the binder at slag contents of 50% or higher.

In this section, the properties of 5 geopolymer concretes with slag/total binder ratio ranging from 0% to 100% with 25% increment are studied. These GPCs are labelled as G7 to G11 and their composition is presented in Table 4-9. All these mixes were ambient cured at 23°C in sealed plastic bags.

Table 4-9: Mix proportions of GPCs with various GGBFS content

Materials	G7	G8	G9	G10	G11
20 mm aggregate	673	673	668	660	660
10 mm aggregate	384	384	382	377	377
Crushed sand	577	577	572	566	566
River sand	288	288	287	283	283
Gladstone FA	410	307	205	103	0
ASMS GGBFS	0	103	205	307	410
NaOH pellets	11.4	11.4	5.2	5.2	5.2
Na-silicate	178	178	81	81	81
Free water	48.2	48.2	135.5	157.4	157.4
MR ¹ (SiO ₂ /Na ₂ O)	1.5	1.5	1.5	1.5	1.5
SiO ₂ + Na ₂ O/Binder ²	0.22	0.22	0.1	0.1	0.1
Water ³ /Solid ⁴	0.30	0.30	0.40	0.45	0.45
GGBFS content [%]	0	25	50	75	100
Curing temperature [°C]	23	23	23	23	23
Heat-curing duration [h]	N.A.	N.A.	N.A.	N.A.	N.A.

¹ Molar ratio of the alkaline solution² Binder = fly ash (FA) + GGBFS³ Water = free water + water in Na-silicate solution⁴ Solid = Binder + dissolved components of Na-silicate solution + NaOH pellets

The mechanical properties of GPC mixes (i.e. compressive strength, elastic modulus and stress-strain behaviour) with low and high GGBFS content are presented in Table 4-10 and Figure 4-21. An OPC concrete (labelled as C2) with 410 kg/m³ of Portland cement, water/binder ratio of 0.45 and similar aggregate content as of GPCs was made and tested for comparison. The chemistry of the alkaline solution and the water/binder ratio of the GPC mixes have been adjusted in order to control the setting time and workability.

Table 4-10: Compressive strength and elastic modulus of GPCs with low and high GGBFS content.

Mix	Curing method	Compressive strength [MPa ± SD]					Elastic modulus [GPa]	
		1-day	3-day	7-day	28-day	56-day	28-day	56-day
C2	Water	17.4±0.3	28.9±0.5	35.8±0.1	49.3±1.2	52.5±1.0	39.0	39.2
G7	Ambient	6.1±0.3	9.3±0.2	21.4±0.1	45.3±0.9	60.6±1.1	26.3	26.9
G8	Ambient	9.5±0.4	21.9±0.2	30.6±0.1	53.2±0.9	72.2±1.7	24.0	24.3
G9	Ambient	0.0	2.7±0.2	23.9±1.3	45.7±0.2	49.4±2.1	26.4	27.0
G10	Ambient	0.0	8.9±0.4	27.8±2.2	43.8±2.3	49.6±0.8	29.9	30.8
G11	Ambient	0.0	18.1±0.9	31.5±0.9	47.6±1.8	48.0±1.2	28.0	28.1

The stress-strain relationships presented in Figure 4-21 show that in the ascending branch of the curves up to the peak stress, the GPCs with higher GGBFS content have higher stress value for the same strain (higher stiffness). The higher stiffness of high calcium content GPCs is due to the formation of higher amount of C-(A)-S-H gel with high stiffness. This is also notable from the elastic moduli presented in Table 4-10

where G10 (75% GGBFS – 25% FA) with lower 28-day compressive strength compared to G8 (25% GGBFS – 75% FA) demonstrated a higher elastic modulus.

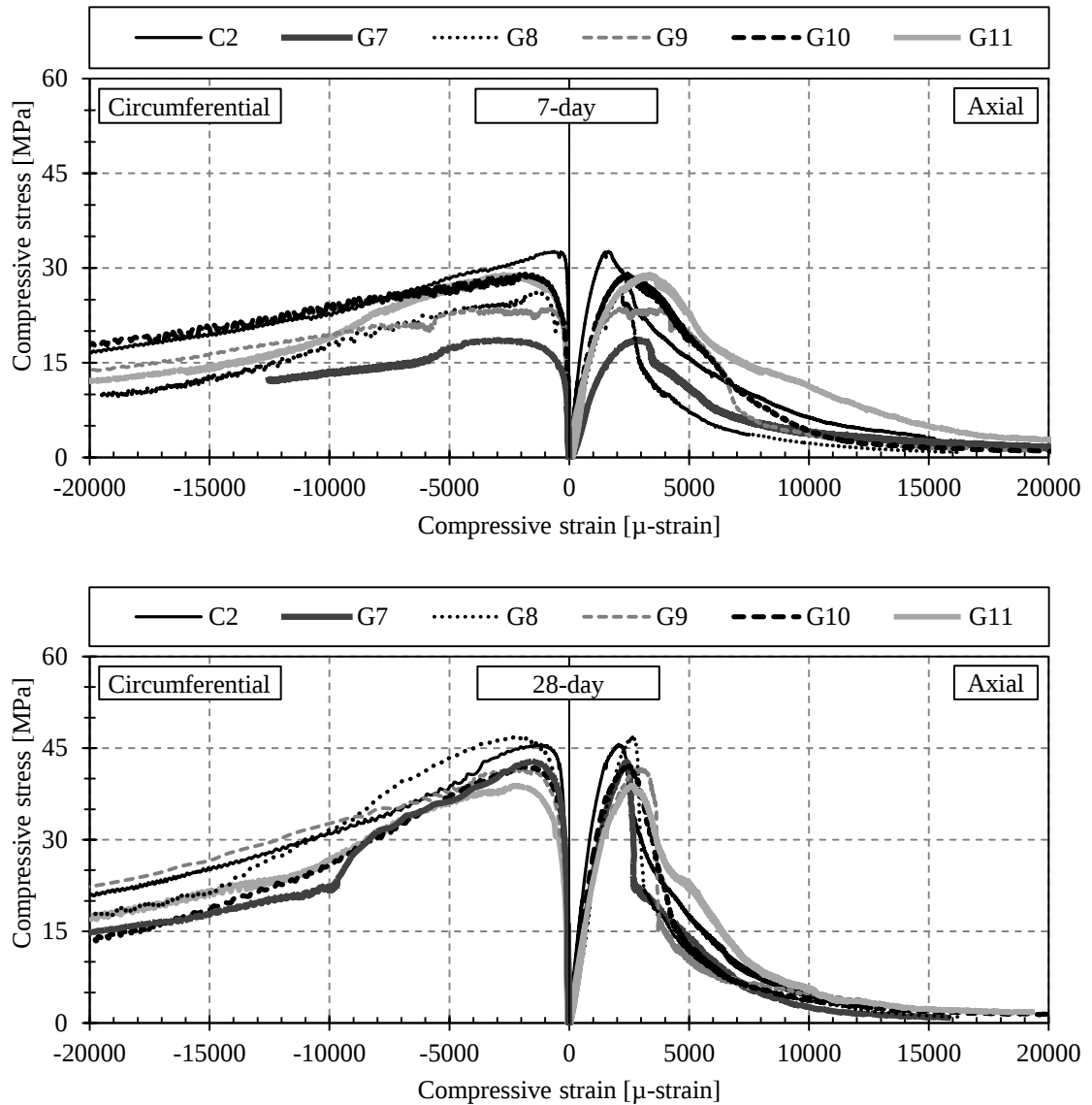


Figure 4-21: 7 and 28 days compressive stress-strain behaviour of low and high calcium content GPCs

The water absorption, volume of permeable voids (VPV), sorptivity and resistivity of the GPC mixes were measured and are illustrated in Table 4-11.

Table 4-11: Water absorption, VPV, sorptivity and resistivity of OPCC and GPCCs at 28 days

Mix ID	GGBFS/FA	Water absorption [%]	VPV [%]	Sorptivity coefficient [$\times 10^{-3}$ mm/s ^{0.5}]	Surface resistivity [k Ω .cm]	Bulk resistivity [k Ω .cm]
G7	0/100	6.8 $\pm$ 0.3	17.3 $\pm$ 0.6	11.4 $\pm$ 0.5	2.7 $\pm$ 0.2	0.8 $\pm$ 0.0
G8	25/75	6.1 $\pm$ 0.2	10.0 $\pm$ 0.8	5.9 $\pm$ 0.4	4.4 $\pm$ 0.2	1.5 $\pm$ 0.1
G9	50/50	8.1 $\pm$ 0.2	19.6 $\pm$ 0.2	6.3 $\pm$ 0.5	26.2 $\pm$ 0.9	10.3 $\pm$ 0.7
G10	75/25	8.8 $\pm$ 0.7	20.8 $\pm$ 1.4	4.9 $\pm$ 1.0	40.8 $\pm$ 2.6	16.0 $\pm$ 1.1
G11	100/0	8.8 $\pm$ 0.2	21.2 $\pm$ 0.4	3.6 $\pm$ 0.5	38.8 $\pm$ 3.8	15.8 $\pm$ 0.9

The reason for the higher water absorption and VPV of GPCs G9 to G11 with higher GGBFS content compared to G7 and G8 is probably related to the higher water/binder ratio of G9 to G11. The additional water used in mixes G9, G10 and G11 with more than 50% GGBFS, to maintain the workability of the fresh concrete, created extra voids which resulted in higher VPV and water absorption. The relationship between the VPV and water/binder ratio is shown in Figure 4-22. The VPV is increasing by increasing the water/binder ratio. For a same water/binder ratio of 0.3, the mix G8 with higher GGBFS content compared to G7 demonstrated a lower VPV and water absorption.

Despite the high volume of voids in GPCs with more than 50% slag, the presence of GGBFS resulted in refined capillary pore structure and increased tortuosity as reflected in water sorption results. A strong correlation exists between the sorptivity coefficient and slag content of GPCs G7 to G11 as shown in Figure 4-22. The effect of slag on the pore structure of GPCs is studied in details in the subsequent section.

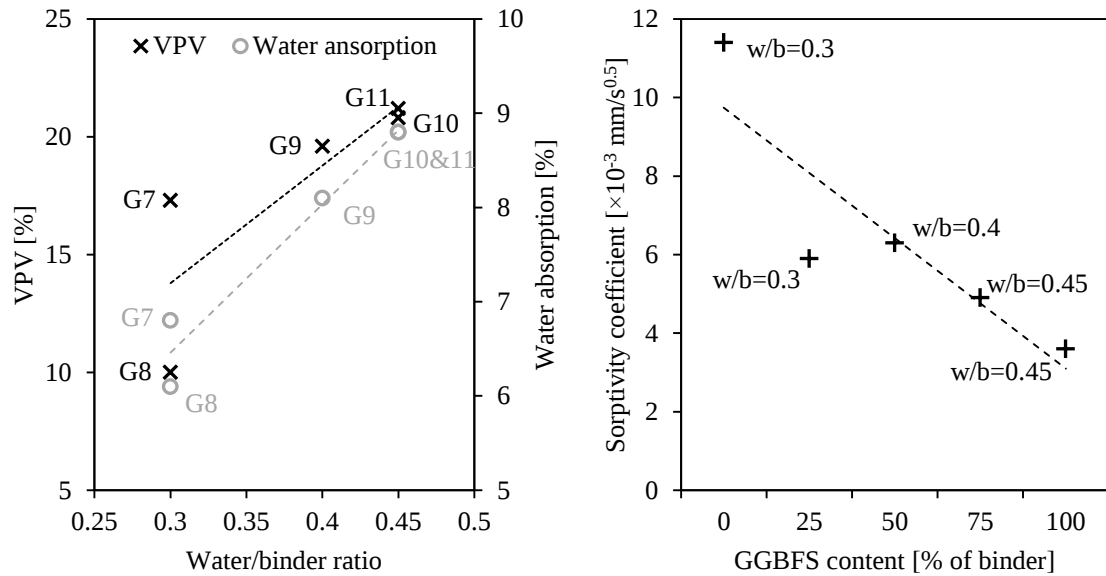


Figure 4-22: The relationship between transport properties of GPCs and mix parameters

As shown in Table 4-11, the electrical resistivity of GPCs has significantly increased by increasing the slag content. This is due to the simultaneous effect of the pore refinement and reduced metallic ion concentration (e.g. Na^+) in the pore solution of high calcium content GPCs. The use of low concentrated alkaline solution in high calcium content GPCs reduces the amount of free Na^+ present in the pore solution.

In geopolymers, the ideal proportion of SiO_4 tetrahedra to AlO_4 tetrahedra is 2:1 (Davidovits 2008). Therefore, if blast furnace slag is targeted as the sole aluminosilicate source, Al-Si tetrahedral geopolymer structure will not form due to the low Al content in GGBFS. When the alkali solution is sodium silicate, both Si and Al form tetrahedral in calcium aluminate silicate hydrates (C-A-S-H) geopolymer network, although this network will have a Si/Al tetrahedral ratio greater than 2. This deficiency can be compensated through the use of GGBFS in conjunction with fly ash, which leads to the formation of a higher proportion of AlO_4 tetrahedra, higher Si/Al tetrahedra ratio, and charge-balanced with Na^+ (Kumar et al. 2010; Nath and Sarker 2014).

Figure 4-23 shows the SEM micrographs of fly ash and GGBFS blended geopolymer pastes with various GGBFS content. Different surface morphologies are observed depending on the slag content and alkali level. G7 and G8 show a more homogeneous binding matrix compared with G9 and G10, which is due to the higher concentration of the alkaline solution and consequently higher rate of dissolution of the solid precursors.

Elemental analyses of the binding matrix are also conducted through point analysis, and the average values are presented in Table 4-12. Samples fabricated with concentrated alkaline solutions (G7 and G8), show higher Si/Al ratios, suggesting a higher rate of dissolution of aluminate and silicate species and incorporation in the matrix.

A noticeable difference in the macropore structure of geopolymers with low and high GGBFS content is evident. For the fly ash based GPCs with non or low GGBFS content, the large macropores or cavities are left by the dissolution of fly ash particles or surface dissolution of hollow fly ash particles (Ma et al. 2013). These spaces are not filled by the growth of the aluminosilicate network, due to either inability of the network to fill up the cavities despite the ongoing matrix development, or due to rapid setting and formation of the matrix before complete dissolution of the raw precursors (Duxson et al. 2005; Ma et al. 2013). The influence of rapid setting on the pore volume can get intensified for heat-cured samples where the reactions are accelerated. As it can be seen in the micrographs of Figure 4-23, no large pores (larger than $1\text{ }\mu\text{m}$) were observed for G9-P and G10-P samples. The lack of large macropores for calcium-rich geopolymer binders containing more than 50% GGBFS is supported by the results of MIP test discussed more in detail in the subsequent sections.

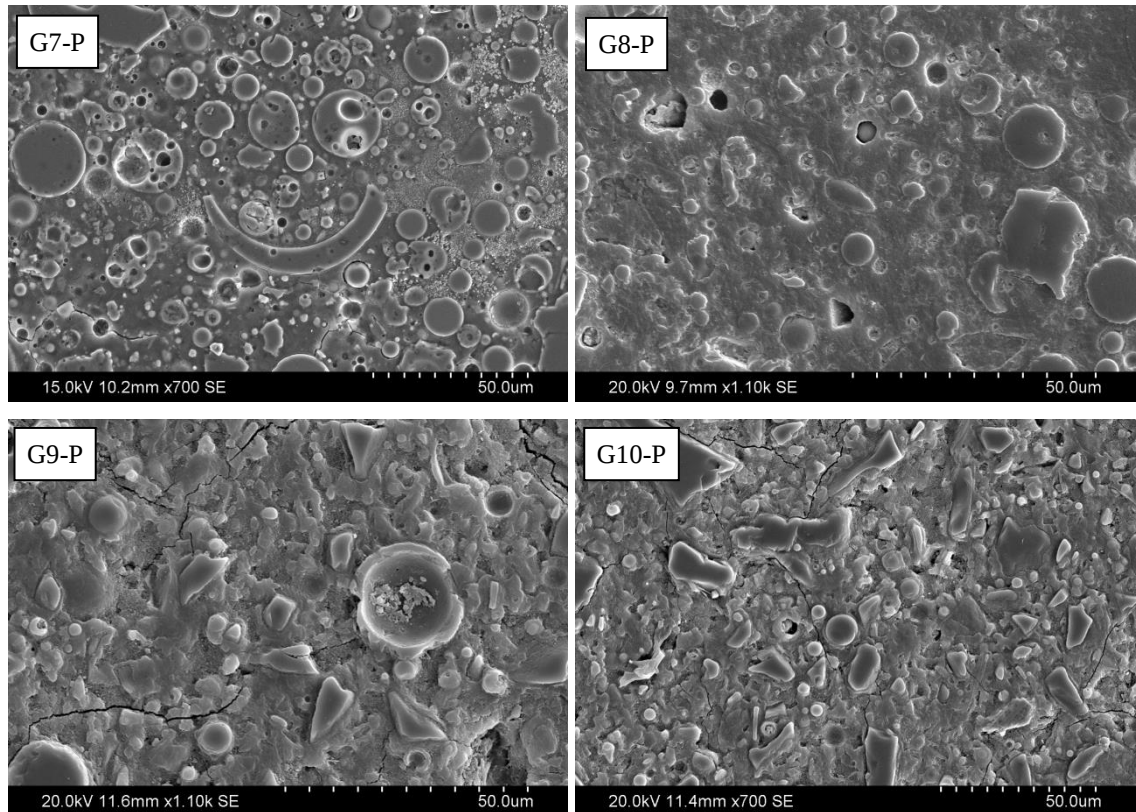


Figure 4-23: SEM micrographs of FA/GGBFS blended geopolymer pastes with various GGBFS content

Interpreting the effect of slag addition requires an understanding of the differences in reaction mechanisms between calcium-rich and aluminosilicate binders. The alkali activation of aluminosilicate precursors with an insignificant amount of calcium, such as FA and metakaolin, results in a highly cross-linked alkali aluminosilicate network (Bernal et al. 2013a; Davidovits 1989). The primary reaction product of calcium-rich GGBFS, on the other hand, is an alkali charge-balanced aluminium-substituted calcium silicate hydrate gel also known as C-(A)-S-H gel. Formation of calcium aluminates and calcium silicate hydrates is also possible. Also, depending on the alkali concentration, some degree of aluminosilicate network formation can also be expected in slag-rich binders (Hong and Glasser 2002; Myers et al. 2013; Wang and L.Scrivener 1995; Yip and van Deventer 2003).

In blended FA and GGBFS systems, Formation of C-(A)-S-H over aluminosilicate network depends on the availability of enough calcium in the mix and also the alkali concentration. Below a certain threshold, around 25% slag content according to Duxson et al. (2005), calcium ions get adsorbed into the aluminosilicate network via a charge balancing mechanism. Increasing the slag content above this threshold value appears to provide enough calcium to form C-(A)-S-H gel, critical to reduce the porosity and

increase the network tortuosity. Alkali concentration is another important factor in promoting the formation of the C-(A)-S-H gel. Presence of excessive amount of sodium hydroxide can inhibit the formation of calcium silicate hydrates by forming a thick layer of calcium hydroxide around the slag particles. Moreover, since the dissolution of silicate and aluminate species is slower in a less alkaline environment, formation of calcium silicate hydrates is promoted in a less alkaline environment, due to the initial lack of aluminates to form calcium aluminosilicates and calcium aluminates (Xu and Van Deventer 2002; Yip et al. 2005; Yip and van Deventer 2003).

The average Ca/Si ratios of geopolymer pastes (G8-P, G9-P and G10-P) synthesised from the paste fraction of concrete mixes G8, G9 and G10 with 25% to 75% GGBFS content are presented in Table 4-12. The Ca/Si ratio is increasing by increasing the slag content, which is indicative of the development of some form of C-S-H. A sharp rise in Ca/Si is notable by comparing G8-P and G10-P. While the slag content has increased by 50%, Ca/Si has increased by more than 87%. This non-proportional growth is attributed to the lower alkalinity of the alkaline solution that promotes the formation of silicate hydrates, as discussed before. Of interest is the comparison between the Ca/Si ratio of the studied geopolymers and the Portland cement paste reported by Yip and van Deventer (2003). The Ca/Si ratio of all geopolymers even mix G10-P with 75% GGBS is still far below that of Portland cement paste, suggesting the formation of aluminosilicate network along with the C-(A)-S-H gel under the alkali concentration level used.

Table 4-12: Elemental composition ratios of geopolymer with low and high calcium content

Mix ID	GGBFS/FA	Ms	Si/Al (wt. %) $\pm$ SD	Ca/Si (wt. %) $\pm$ SD
G8-P	25/75	1.5	2.26 $\pm$ 0.26	0.76 $\pm$ 0.08
G9-P	50/50	1.5	2.19 $\pm$ 0.21	0.97 $\pm$ 0.18
G10-P	75/25	1.5	2.13 $\pm$ 0.33	1.80 $\pm$ 0.31

MIP test was performed to investigate the pore structure of samples and results are presented in Figure 4-24. Caution needs to be exercised while interpreting the results of MIP test in binders with a considerable amount of inkbottle shaped pores where larger pores are only accessible through constrictions. This limited accessibility results in some errors as mercury cannot intrude all the pores, and as such, a finer pore structure in the absence of larger pores can be erroneously deduced from the results (Lloyd et al.

2009). Despite all inaccuracies, MIP can provide valuable information regarding the pore volume distributions, particularly for pores larger than 50 nm and up to 1000 nm.

Several interesting features can be found from the individual PSDs of low and high calcium content geopolymers as shown in Figure 4-24. Two main pore modes are distinguishable for samples with less than 50% GGBFS content. One associated with the bulk of fine mesopores, ranging from 3 nm to ~16 nm which is common for G7, G8 and G9. The second pore mode is associated with the larger mesopores and small macropores which for fly ash based geopolymer (G7) is ranging from 16 nm to ~500 nm and for geopolymers with 25% and 50% GGBFS ranging from 16 to ~150 nm.

For geopolymers with more than 50% GGBFS content, only one main pore mode is observed with no pores larger than ~20 nm. Lack of a second main peak is considered reasonable for G10 and G11 due to the presence of 75% and 100% GGBFS respectively.

The disappearance of pores larger than 150 nm in G8 and G9 compared with G7 and disappearance of pores larger than 20 nm in G10 and G11 compared to G7 to G9 and shifting the location of the main peak to ~3.4 nm demonstrates the systematic development of a finer pore structure by the addition of GGBFS to the binder.

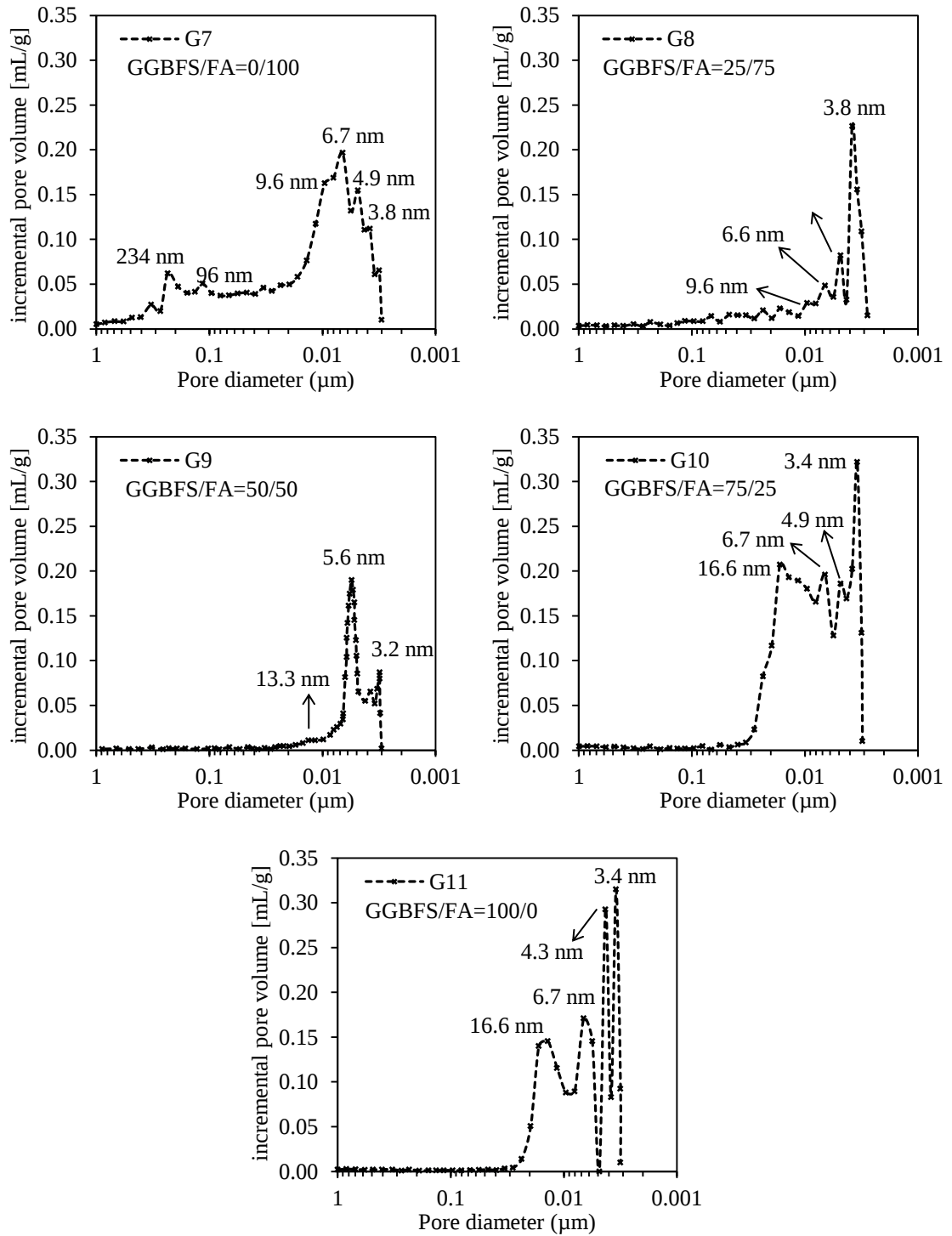


Figure 4-24: MIP results and pore size distribution of geopolymer samples with low and high slag content

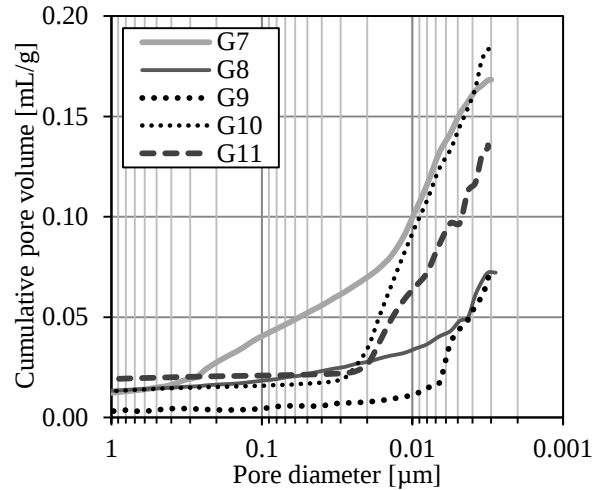


Figure 4-25: Cumulative pore volume of geopolymers with low and high slag content

4.3 Conclusion

The mechanical and transport properties and microstructural characteristics of various low and high calcium content GPCs with ambient and accelerated heat curing were investigated. The main outcomes are summarised as follows:

- The fly ash based GPCs benefit from the thermal curing in order to develop a more densified matrix. It has been observed that the thermal curing not only has no detrimental effect on the long term compressive strength of low calcium content GPCs, it results in fewer cavities and voids and reduces the water sorption of GPCs. This is due to the higher degree of dissolution of aluminosilicate sources at higher temperature as proved by the microstructural analysis.
- Although thermal curing is the preferred curing method for fly ash based GPCs due to the slow rate of strength gain at ambient temperature, it is possible to produce high strength (>50 MPa at 28 days) ambient cured fly ash based GPCs by blending fly ash with GGBFS. A critical GGBFS content of 25% of the binder mass has identified. However, beyond this value, the use of extra slag in high concentrated alkaline solution results in reduced workability and rapid setting of fresh GPC. For GPCs including more than 25% GGBFS, the concentration of the alkaline solution and the water to solid ratio requires adjustment as demonstrated in Table 4-9.
- The calcium content plays a significant role on mechanical performance and microstructure of the GPCs. In general, geopolymers with little or no calcium content are highly porous which is in line with previous observations in literature

(Duxson et al. 2005). On the other hand, geopolymers with considerable amount of calcium (i.e. high GGBFS content GPCs), show a very fine pore structure ~16 nm or less in diameter, with a relative lack of pores larger than 20 nm in the whole meso and macropore range. This particular pore size distribution leads to considerable pore-blocking effect.

- From the MIP test results, two vastly different pore structures can be inferred for low and high calcium content GPCs. The pore structure of low calcium fly ash based geopolymer binders is comprised of a rather uniformly distributed volume of pores over the whole mesopore and macropore range. On the other hand, high calcium content geopolymer binders (with $\geq 50\%$ GGBFS) have a considerably finer pore structure where the bulk of pores are smaller than 16 nm with a relative lack of larger pores. For blended FA and GGBFS systems, GGBFS replacement up to 25% helps to develop a finer pore structure, with two main distinguishable pore modes: one between 3 to 16 nm with a peak between 3 to 7 nm, and the other one between 16 and 150 nm. Formation of different sized pore groups in blended binders amplifies the pore blocking effect and to a larger extent, cavitation.
- Although attaining a very fine pore structure in high calcium content geopolymers can be an indication of less permeability, water sorption tests were conducted and demonstrated that the tortuosity of the pore structure of GPCs has significantly increased by including 50% GGBFS or more in the binder which led to a very low sorptivity coefficient. It can be concluded that high calcium content GPCs are considerably less porous and permeable compared to their fly ash based counterparts.

Chloride Diffusion in Geopolymer Concrete

5 CHLORIDE DIFFUSION IN GEOPOLYMER CONCRETE

Concrete durability is (to a large extent) governed by the concrete resistance to the penetration of aggressive substances. In marine or coastal zones, the most harmful substances contain chloride ions. Chloride induced corrosion is one of the main causes of the premature failure of concrete structures; it shortens the designated service life of buildings and infrastructures, leading to huge economic losses annually (Koch et al. 2002; Xi et al. 1994). During the initiation phase of corrosion, the chloride ions penetrate into the concrete and reach the surface of the steel reinforcement. The accumulation of chloride ions in considerable amount at the level of reinforcement break down the passive layer around the steel bars (Kyösti Tuutti 1982). After depassivation and during the second phase of corrosion which is called the propagation phase, the corrosion starts and the accumulation of rust around the bars lead to structural damages such as concrete spalling, delamination, loss of ductility of the bars, etc. While the reinforced concrete members can still sustain the applied loads during the initial stages of the propagation phase (Zhang et al. 2009), it is common practice and more conservative to limit the service life of the structure to the end of the initiation phase, i.e. the point where the reinforcement depassivates and corrosion starts.

Several factors determine the duration of the initiation phase of corrosion including the rate of diffusion of chloride ions which is influenced by the permeability of the concrete (physical absorption), the chloride binding capacity of the matrix and the stability of the passive film around the reinforcement which is indirectly measured by the concentration of chloride ions required to break the passive film (chloride threshold).

In geopolymers, depending on the precursor used, the final products can have considerably different nano/microstructures with different transport properties which broadly investigated in Chapter 4. Low calcium content geopolymers such as fly ash based GPCs, consist of amorphous aluminosilicate network with a porous nano/microstructure while the high calcium content geopolymer structures as of slag based GPCs have considerably finer pore structure (Hong and Glasser 2002; Myers et al. 2013; Wang and L.Scrivener 1995; Yip and van Deventer 2003). The type and concentration of the alkaline solution and the ratio of silicates to alkalis play an important role in the pore structure development and stability of the passive layer as it is

reported in a number of previous researches (Bastidas et al. 2008; J.S.J. van Deventer et al. 2006; Ma et al. 2016; Yu et al. 2017).

In this chapter, the chloride diffusion and chloride binding capacity of various geopolymer concretes with low and high calcium content were studied. The suitability of accelerated diffusion tests such as ASTM C1202 rapid chloride penetration test (RCPT) and NT BUILD 492 chloride migration test, initially developed for OPC concrete, has also been investigated for GPCs. The results of RCPT and chloride migration tests are compared with the bulk chloride diffusion test. The chloride binding capacity of low and high calcium content GPCs were investigated using XRD and FTIR analysis. The relationship between accelerated chloride resistivity tests and transport properties were examined and correlations developed where possible.

The composition of studied GPCs is presented in Table 5-1. The mechanical properties of mixes G1 to G11 have been provided in Chapter 4; Table 4-2, Table 4-10, Figure 4-19 and Figure 4-20.

Table 5-1: Mix proportions of low and high calcium content GPCs

Materials	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11
20 mm aggregate	0	613	613	613	613	613	673	673	668	660	660
10 mm aggregate	1221	350	350	350	350	350	384	384	382	377	377
Crushed sand	0	525	525	525	525	525	577	577	572	566	566
River sand	0	262	262	262	262	262	288	288	287	283	283
Sydney sand	621	0	0	0	0	0	0	0	0	0	0
Eraring FA	272	260	260	260	400	360	0	0	0	0	0
Callide FA	78	0	0	0	0	0	0	0	0	0	0
Gladstone FA	0	80	80	80	0	0	410	307	205	103	0
ASMS GGBFS	38	60	60	60	0	40	0	103	205	307	410
NaOH pellets	20.0	20.6	18.5	16.5	20.6	20.6	11.4	11.4	5.2	5.2	5.2
Na-silicate	139	143	129	114	143	143	178	178	81	81	81
Free water	48.6	50.1	58.1	66.1	50.1	50.1	48.2	48.2	135.5	157.4	157.4
MR ¹ (SiO ₂ /Na ₂ O)	1.15	1.15	1.15	1.15	1.15	1.15	1.5	1.5	1.5	1.5	1.5
SiO ₂ + Na ₂ O/Binder ²	0.21	0.21	0.19	0.17	0.21	0.21	0.22	0.22	0.1	0.1	0.1
Water ³ /Solid ⁴	0.27	0.27	0.27	0.27	0.27	0.27	0.30	0.30	0.40	0.45	0.45
GGBFS content [%]	10	15	15	15	0	10	0	25	50	75	100
Curing temperature [°C]	23-90	75	75	75	75	75	23	23	23	23	23
Heat-curing duration [h]	8-24	18	18	18	18	18	N.A.	N.A.	N.A.	N.A.	N.A.

¹ Molar ratio of the alkaline solution

² Binder = fly ash (FA) + GGBFS

³ Water = free water + water in Na-silicate solution

⁴ Solid = Binder + dissolved components of Na-silicate solution (i.e. SiO₂ and Na₂O) + NaOH pellets

5.1 Chloride binding examination

The chloride binding capacity of GPCs was investigated by comparing the total (acid soluble) and free (water soluble) chloride content in geopolymer concrete samples.

Figure 5-1 shows the relationship between free and total chlorides of GPCs G1 to G11 with low and high calcium content cured at various conditions, as well as the water-cured OPC concrete (w/b=0.45) after 35 days exposure in 16.5% NaCl solution (saline solution exposure recommended by ASTM C1556). For all geopolymer samples, there is a remarkably good match between the total and free chloride content, revealing poor chloride binding capacity through chemical reactions. The OPC concrete, on the other hand, showed a clear chloride binding capacity compared to GPCs due to the chemical reaction between the AFm phase (alumina, ferric oxide, monosulfate) of the matrix and the chloride ions with the formation of Friedel's salt.

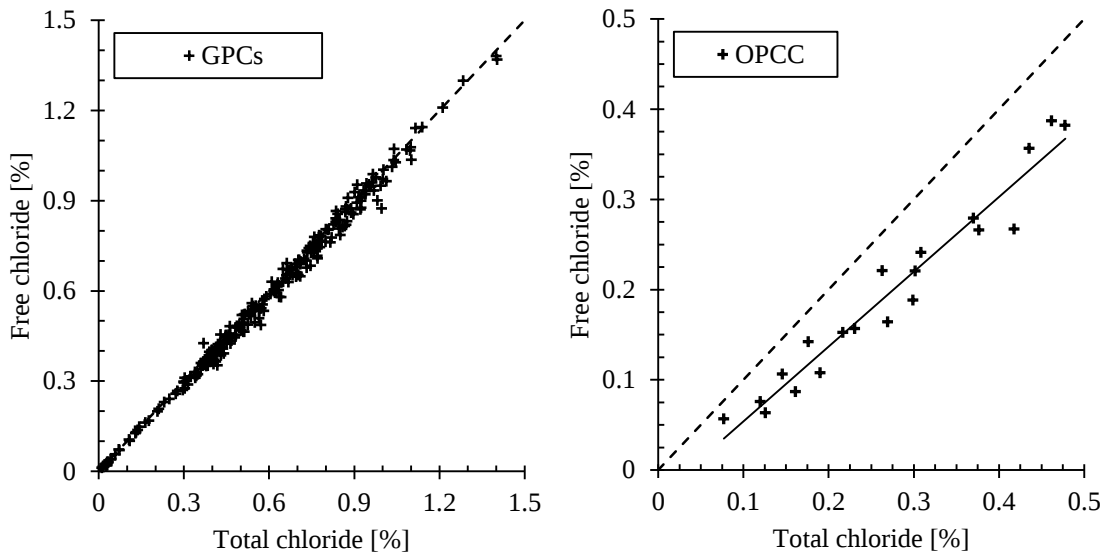


Figure 5-1: Relationship between free and total chloride of GPCs and OPCC after 35 days of exposure in 16.5% NaCl solution

The chloride binding capacity (C_b) was calculated by subtracting the free chloride content from the total chloride content, and dividing by the percentage of total chloride as shown in Eq. (5-1).

$$C_b = \frac{[(C_t - C_f) \times 100]}{C_t} \quad (5-1)$$

where C_t is the total chloride content and C_f is the free chloride content. The calculated chloride binding capacity of GPCs was close to zero where OPC demonstrated an average C_b of 29.8% which is variable between 20% to 40% through the depth of the sample (decreasing throughout the depth of the sample).

To further assess the chemical binding capacity of the geopolymer binders, the formation of new crystalline phases was investigated by X-ray diffraction of paste

samples fabricated with the same composition as the geopolymer concretes. Two sets of samples were prepared and tested. The samples were crushed paste with an average grain diameter of 10 mm. The first set of samples was immersed in 16.5% aqueous NaCl solution for a period of 35 days (similar to the exposure used for chloride diffusion test following ASTM C1556 test procedure). The second set of samples (control samples) was stored in sealed plastic bags for 35 days in a similar temperature (23°C) as that of samples exposed to chlorides (set one). At the end of the 35 days, the samples set one were removed from the NaCl solutions and quickly rinsed with distilled water to eliminate any surface contamination. Both set of samples were then dried in a sealed vacuumed desiccator stored in a 50°C oven for 24 hours and milled to less than 75 micrometers. The X-ray analysis of specimens was then carried out.

The XRD patterns of selected uncontaminated (intact) and chloride contaminated samples along with the identified phases are illustrated in Figure 5-2.

The diffraction patterns of OPC after exposure to NaCl solution shows some new peaks which are attributed to the formation of calcium chloroaluminate hydrate crystals ($\text{Ca}_2\text{Al}(\text{OH})_6(\text{Cl}, \text{OH}) \cdot 2\text{H}_2\text{O}$) known as Friedel's salt. However, there appeared to be no chemical reaction between geopolymer binders (low and high calcium content) and chloride ions as no new crystalline phases were observed. The only new peak observed in the diffraction patterns of the contaminated geopolymers is related to the crystalline NaCl (Halite) confirming the physical binding and encapsulation of the chlorides in the pore network of geopolymer matrices.

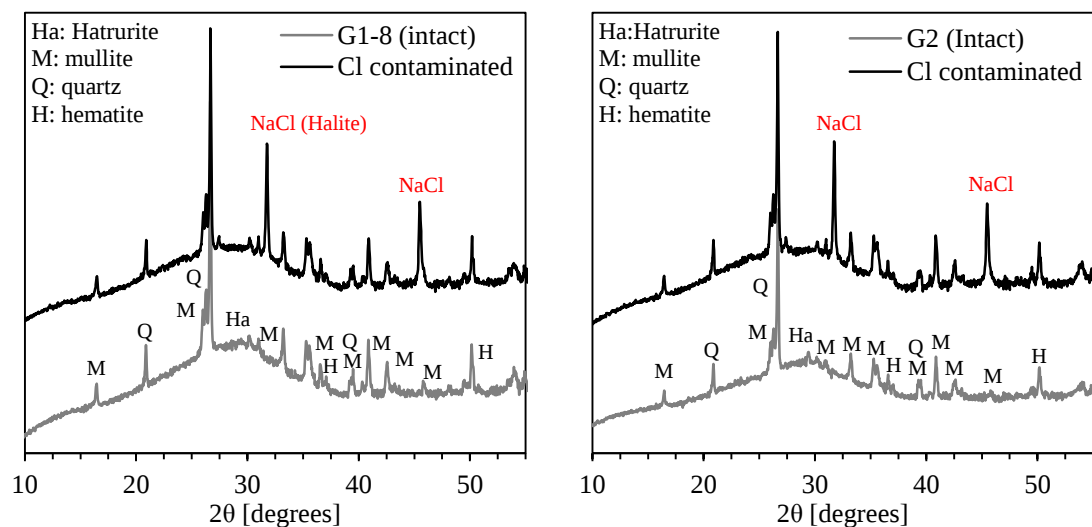


Figure 5-2: XRD patterns of OPC and geopolymer pastes before and after exposure to NaCl solution

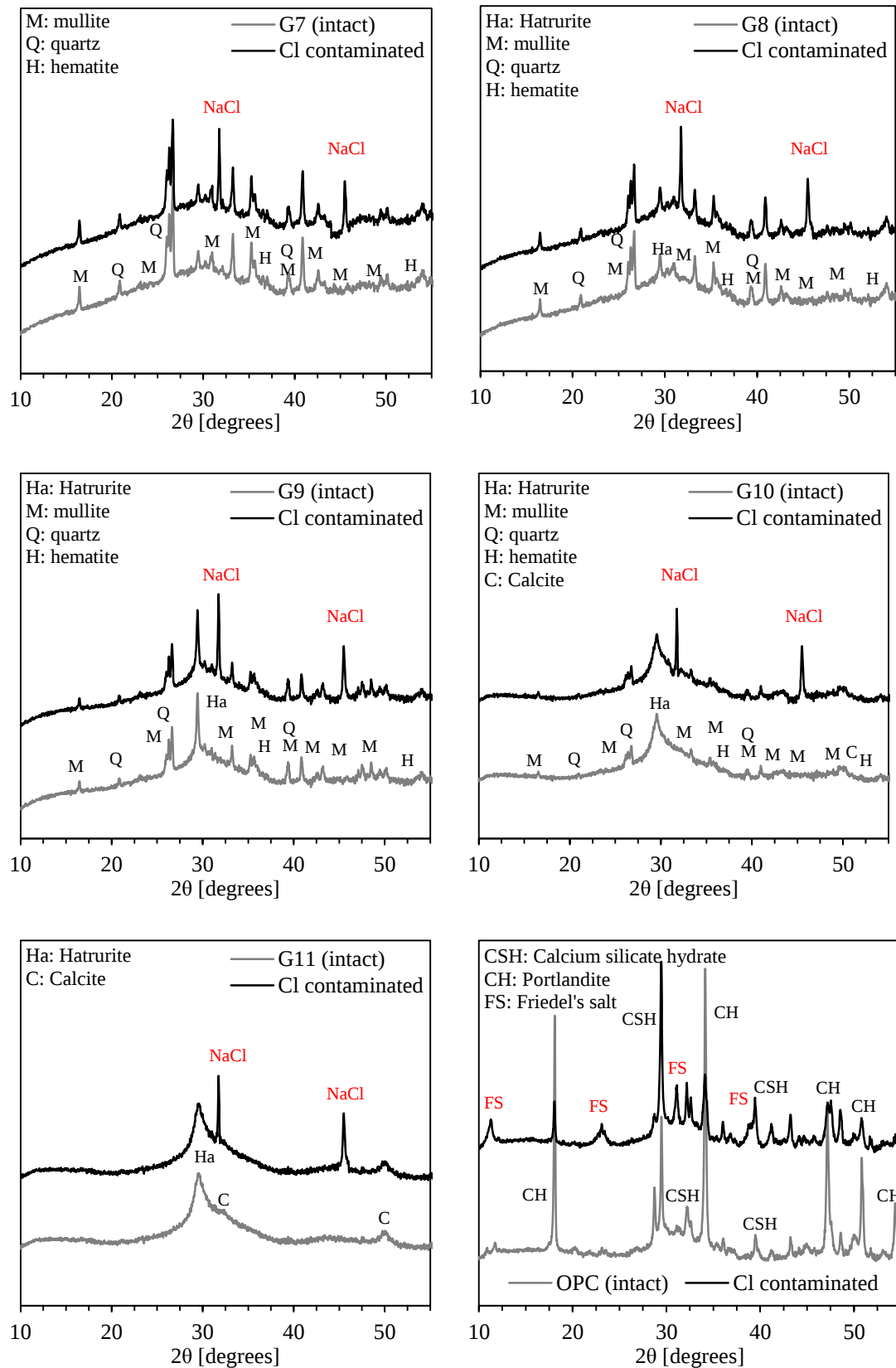


Figure 5-2: XRD patterns of OPC and geopolymer pastes before and after exposure to NaCl solution (continue)

5.2 Chloride diffusion coefficient

The chloride diffusion coefficient of concrete samples were determined by measuring the total (acid soluble) chloride contents after 35 days of exposure to 16.5% NaCl solution as explained in details in section 3.3.8 using a non-linear regression analysis. The total chloride diffusion profiles of GPCs G1 to G11 are shown in Figure 5-3. All heat cured low calcium content GPCs with less than 15% GGBFS content (i.e. G1-2 to G1-13 and G2 to G6) regardless of the heat curing condition showed a high level of chloride content (above 0.3% of concrete mass) even at the depth of 25 mm from the surface. The ambient cured GPCs (i.e. G1-1, G7 and G8) with up to 25% GGBFS content were also showing a similar low resistance to chloride diffusion. These low calcium content GPCs cover a wide range of mechanical performance with 28-day compressive strengths ranging from 27 to 62 MPa. On the other hand, high calcium content GPCs with more than 50% GGBFS content (i.e. G9, G10 and G11) demonstrated a high resistance to chloride diffusion.

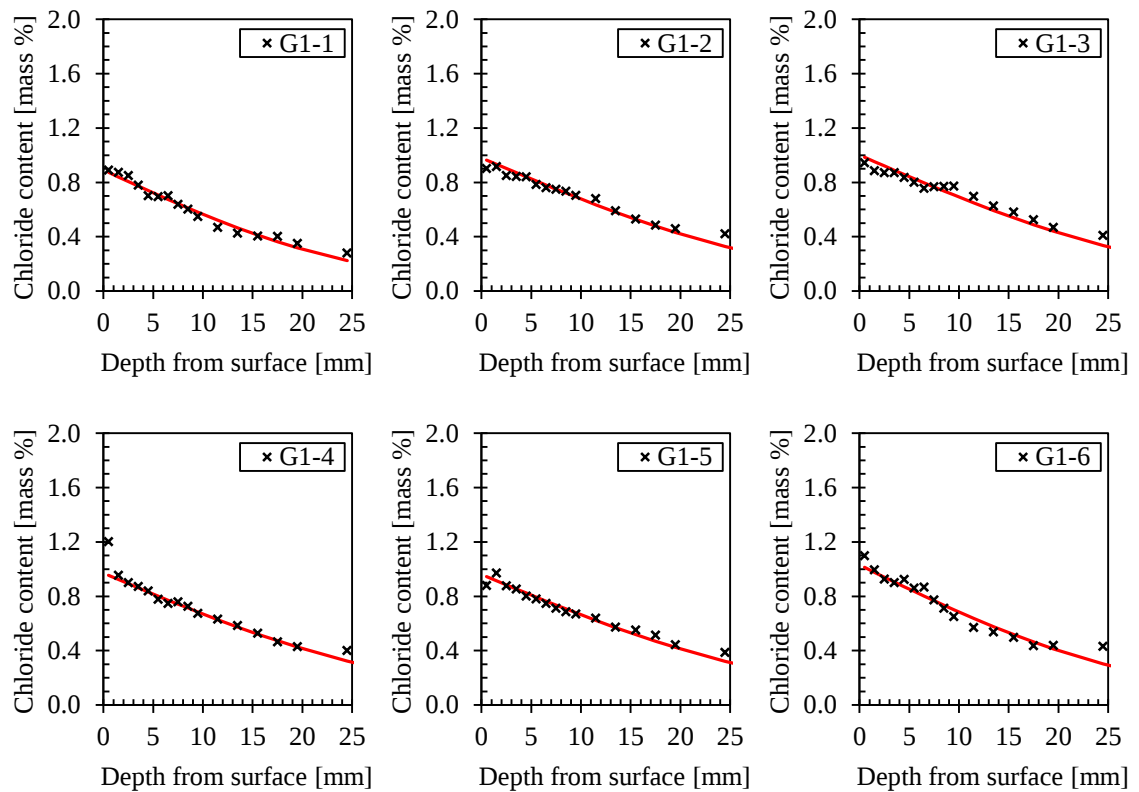
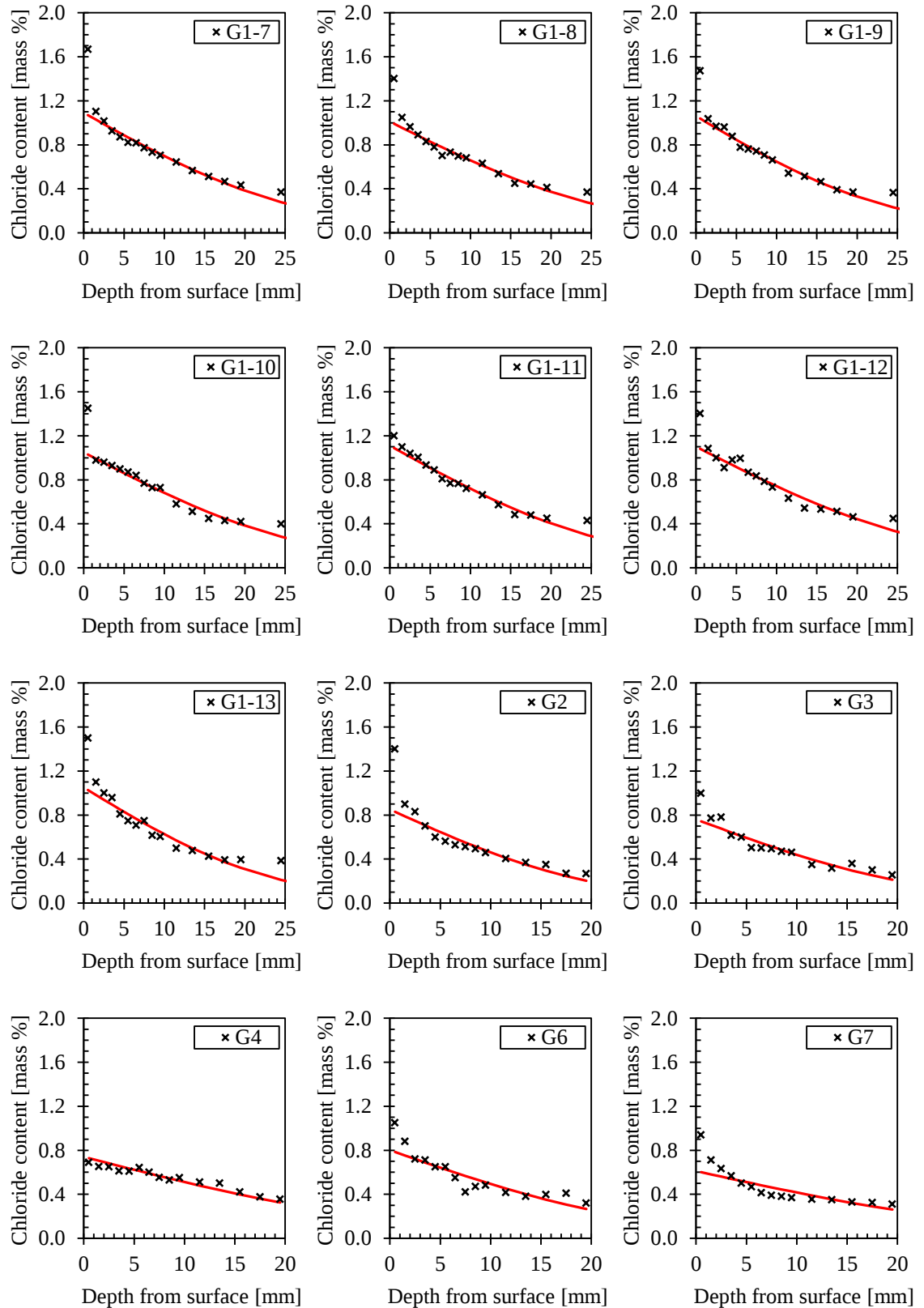


Figure 5-3: Total chloride (C_t) profiles of GPCs cured at various conditions

Figure 5-3: Total chloride (C_t) profiles of GPCs cured at various conditions (continue)

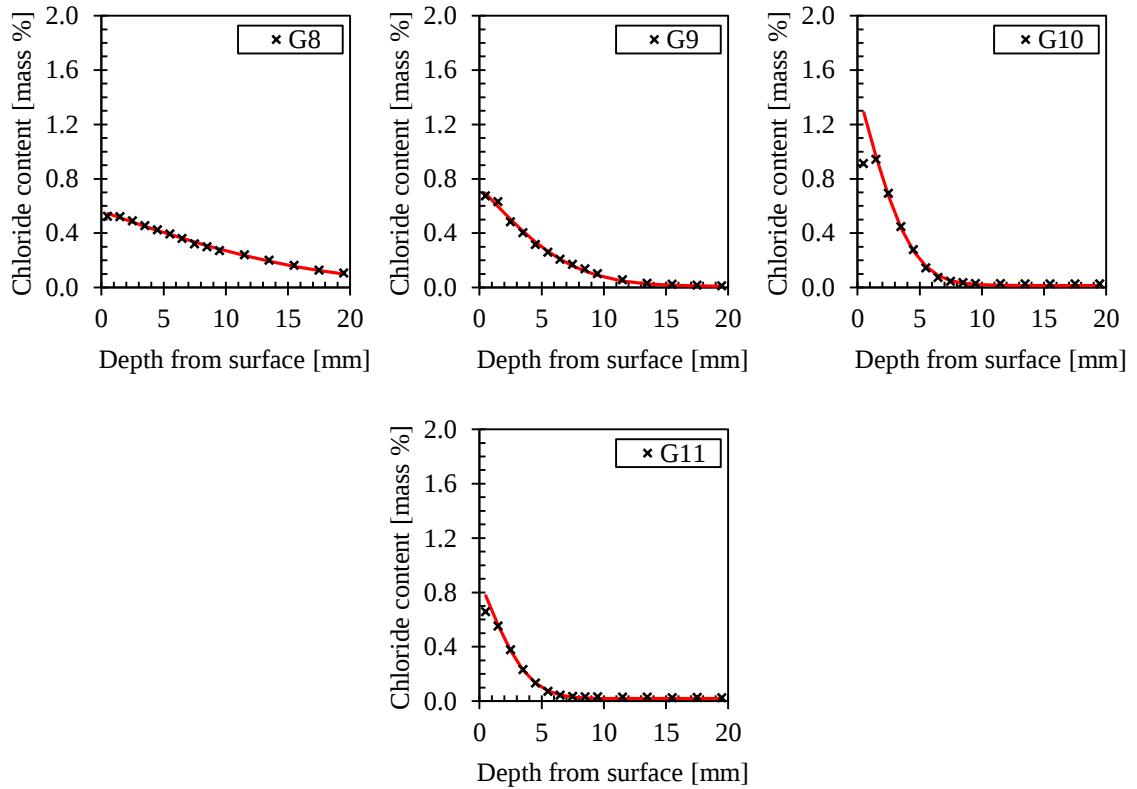
Figure 5-3: Total chloride (C_t) profiles of GPCs cured at various conditions (continue)

Table 5-2: Chloride diffusion coefficient of GPCs after 35 days exposure in 16.5% NaCl solution

Mix designation	GGBFS/FA [%]	C_i [%]	C_s [%]	D_a [$\times 10^{-12} \text{ m}^2/\text{s}$]	SSE*
G1-1	10/90	0.022	0.89	69.7	0.0167
G1-2	10/90	0.022	0.98	100.0	0.0167
G1-3	10/90	0.022	1.00	100.0	0.0287
G1-4	10/90	0.022	0.97	99.4	0.0089
G1-5	10/90	0.022	0.96	100.0	0.0130
G1-6	10/90	0.022	1.03	84.2	0.0359
G1-7	10/90	0.022	1.09	72.2	0.0210
G1-8	10/90	0.022	1.01	77.4	0.0295
G1-9	10/90	0.022	1.06	60.6	0.0290
G1-10	10/90	0.022	1.05	76.2	0.0272
G1-11	10/90	0.022	1.11	75.8	0.0304
G1-12	10/90	0.022	1.10	89.3	0.0424
G1-13	10/90	0.022	1.05	56.0	0.0786
G2	15/85	0.017	0.85	42.39	0.0414
G3	15/85	0.015	0.76	50.70	0.0349
G4	15/85	0.016	0.74	99.98	0.0150
G6	10/90	0.016	0.80	63.53	0.0631
G7	0/100	0.015	0.61	93.81	0.0556
G8	25/75	0.014	0.56	31.30	0.0007
G9	50/50	0.010	0.74	5.77	0.0030
G10	75/25	0.015	1.46	1.83	0.0022
G11	100/0	0.019	0.89	1.48	0.0007

*SSE: sum of squared errors

From the chloride profiles, the apparent chloride diffusion coefficient of GPCs were calculated and are presented in Table 5-2. All low calcium content GPCs with less than

25% GGBFS content demonstrated a very high chloride diffusion coefficient of more than $30 \times 10^{-12} \text{ m}^2/\text{s}$. This is worth noting that some of this low calcium content GPCs have a high 28-day compressive strength of over 60 MPa. The GPCs with more than 25% GGBFS content showed a very low chloride diffusion coefficient in the range of 1.5 to $6 \times 10^{-12} \text{ m}^2/\text{s}$. The 28-day compressive strength of these high calcium content GPCs is ranging between 44 and 48 MPa. This demonstrates that the compressive strength is not a relevant property to assess the durability performance of GPCs as shown in Figure 5-5. The presence of calcium in geopolymer matrix instead is critical to reduce porosity and increase the chloride diffusion resistance which is in agreement with the results obtained in Chapter 4.

Figure 5-4 shows the effect of GGBFS (source of calcium) content on the diffusion coefficient of GPCs. The decreasing trend of the diffusion coefficients by increasing the slag content is more notable by increasing the slag content from 25% to 50%, after which increasing the slag content does not significantly affect the chloride diffusion. Of interest is that the slag based GPCs demonstrated substantial lower diffusion coefficient compared to the fly ash based GPCs while having higher water/binder ratio. The water/binder ratio of all fly ash based GPCs was less than 0.3 and was 0.4 and 0.45 for slag based GPCs (refer to Table 5-1). The considerably lower diffusion coefficient of slag based GPCs despite having a high water/binder ratio of up to 0.45 is indicative of a finer pore structure with higher tortuosity compared to that of fly ash based GPCs, due to the pore filling effect of calcium silicate hydrate gel, formed due to the presence of slag in the blended geopolymer matrix as previously reported by Provis et al. (2012).

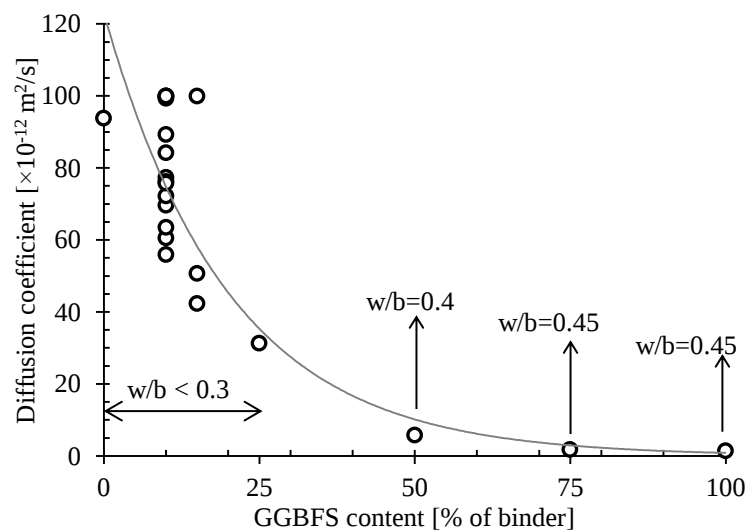


Figure 5-4: Correlation between GGBFS content and chloride diffusion coefficient in GPCs

As stated above and shown in Figure 5-5, there is no relationship between the compressive strength and chloride diffusion coefficient of low and high calcium content GPCs. For OPC concrete it is suggested that the volume of permeable voids (VPV) is a good measure of concrete's durability (Andrews-Phaedonos 1997; VicRoad 2007). However, in case of geopolymer concrete, no correlation has been found between the VPV and chloride diffusion coefficient as shown in Figure 5-5.

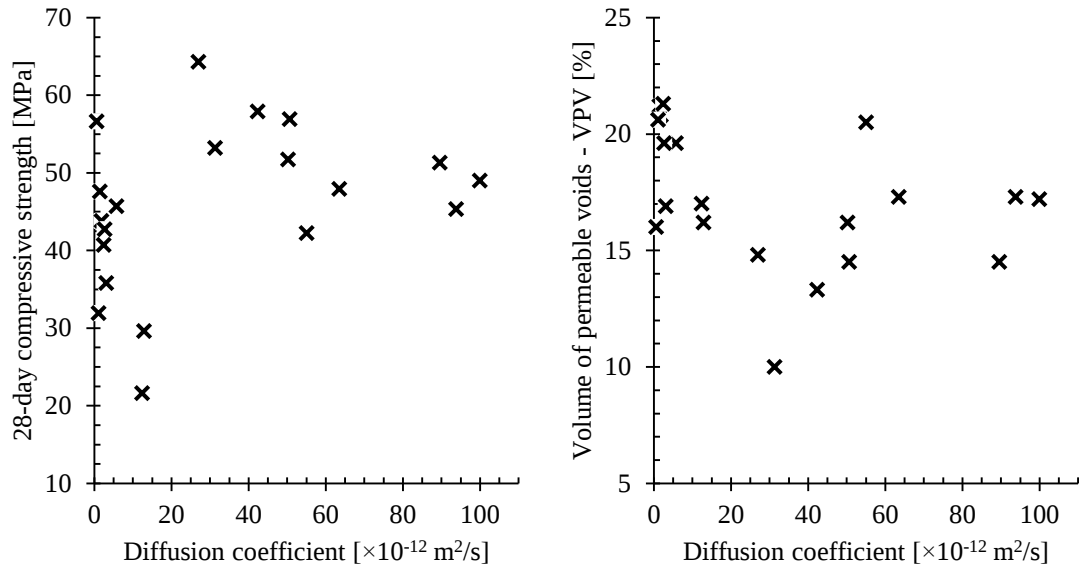


Figure 5-5: Correlation between: (left) compressive strength and chloride diffusion coefficient (right) VPV and chloride diffusion coefficient of GPCs

5.3 Rapid Chloride Penetration Test

The ASTM C1202 standard method also refers to as rapid chloride permeability test (RCPT) using 60 V was deemed a failure for all low calcium content GPCs with less than 50% GGBFS because of the high initial currents over 500 mA (refer to Table 5-3). Indeed, due to safety concerns and to avoid overheating of the samples during the test, the RCPT test apparatus designed to terminate the test if the current reaches 500 mA.

Since the ASTM C1202 standard test method was unable to measure the charge passed through the geopolymer concrete samples due to their low resistivity, modifications to the standard test method was made. The voltage applied across the sample was changed to 10 volts as opposed to the standard specification of 60 volts. Table 5-3 shows the results of RCPT test accompanied with ASTM C1202 standard test results. All GPCs with less than 50% slag content failed the standard ASTM C1202 test. The modified ASTM C1202 test was successfully completed for all different types of GPCs.

Table 5-3: Rapid chloride penetration test after 28 days

Mix	Curing method	ASTM C1202			Modified ASTM C1202		
		Applied voltage [V]	Charge passed [Coulombs]	Chloride penetrability	Applied voltage [V]	Test duration [hours]	Charge passed [Coulombs]
G1-1	Ambient	60	Failed	-	10	6	741
G1-2	60°C-8h	60	Failed	-	10	6	1610
G1-3	60°C-12h	60	Failed	-	10	6	1591
G1-4	60°C-18h	60	Failed	-	10	6	1533
G1-5	60°C-24h	60	Failed	-	10	6	1553
G1-6	75°C-8h	60	Failed	-	10	6	1467
G1-7	75°C-12h	60	Failed	-	10	6	1314
G1-8	75°C-18h	60	Failed	-	10	6	1201
G1-9	75°C-24h	60	Failed	-	10	6	1197
G1-10	90°C-8h	60	Failed	-	10	6	1421
G1-11	90°C-12h	60	Failed	-	10	6	1161
G1-12	90°C-18h	60	Failed	-	10	6	1103
G1-13	90°C-24h	60	Failed	-	10	6	817
G2	75°C-18h	60	Failed	-	10	6	577
G3	75°C-18h	60	Failed	-	10	6	876
G4	75°C-18h	60	Failed	-	10	6	1114
G5	75°C-18h	60	Failed	-	10	6	2706
G6	75°C-18h	60	Failed	-	10	6	1191
G7	Ambient	60	Failed	-	10	6	2266
G8	Ambient	60	Failed	-	10	6	1017
G9	Ambient	60	2272	Medium	10	6	206
G10	Ambient	60	1041	Low	10	6	146
G11	Ambient	60	930	Very low	10	6	136

The reduced voltage used will affect the test results which then cannot be compared to the ASTM C1202 recommended values indicating chloride ion penetrability. This issue will be addressed in Chapter 7 where calibrated RCPT values for GPCs will be defined for each durability category using modified RCPT method. However, the results can still be used for relative comparison of the GPCs performance.

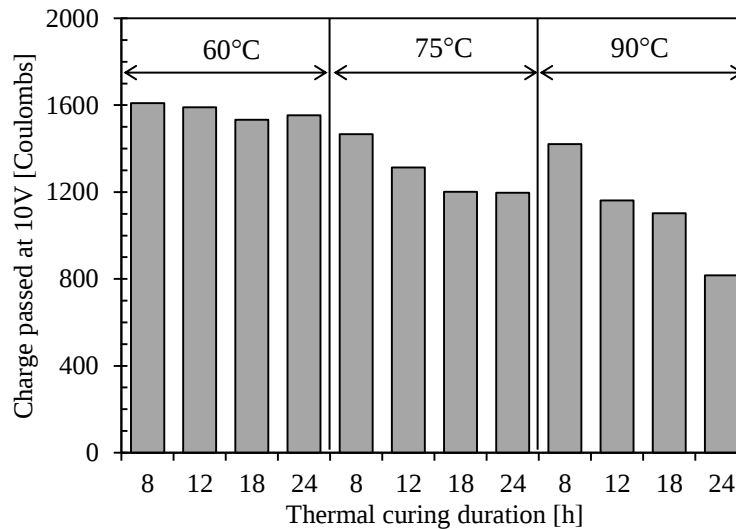


Figure 5-6: Effect of thermal curing on charge passed of low calcium content GPCs

The RCPT results for heat-cured low calcium content GPCs G1-2 to G1-13 are consistent with the mechanical and transport properties presented in sections 4.1.1 and 4.1.2. The total charge passed through the test specimens reduced by increasing the curing temperature and duration as shown in Figure 5-6. The relatively good correlation found between the charge passed and the resistivity of low calcium content GPCs as shown in Figure 5-7 confirms that the RCPT is significantly affected by the chemistry of the pore solution. Fly ash based geopolymer concretes contain lots of free metallic ions in the pore solution abandoned from the alkaline solution used in the mix. Increasing the curing temperature and duration, results in the formation of higher amounts of reaction products. This means that more metallic ions (i.e. Na^+ in the current case) will be bound into the geopolymer matrix and the concentration of metallic ions will decrease.

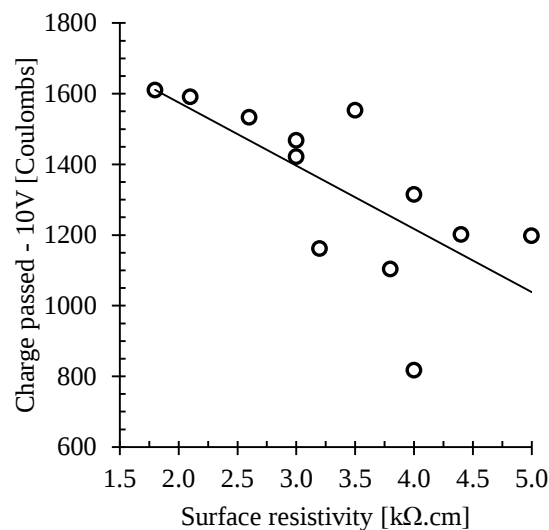


Figure 5-7: Correlation between charge passed and surface resistivity of fly ash based GPCs

The presence of free Na^+ in the pore solution has also been previously reported by other researchers (Bernal et al. 2012a) to have a significant effect on the total amount of charge passed. Any Na^+ present in the pore solution will counter-diffuse as the Cl^- ions are electrically driven through the pore network by the imposed electrical field gradient, leading to an increase in the charge passed (Bernal et al. 2011). In other words, the RCPT results for low-calcium fly ash-based GPCs appear influenced by the presence of Na^+ ions in the specimens and the porosity rather than directly the chloride transport. Rather than looking at only the ion of interest (the chloride ion), the RCP test measures all ions passing through the specimen. The combined effect of Na^+ decrease in the pore

solution, lower capillary pores and increased tortuosity of geopolymer matrix by applying higher curing temperature for longer period, led to a reduced charge passed.

It has been noted in literature that the ASTM C1202 results could be inconclusive for geopolymer concrete or indicates poor durability properties of the material due to the presence of mobile ions in the pore structure when in fact the transport properties demonstrate higher durability potential (Bernal et al. 2012a). Despite the existing concerns over the reliability of ASTM C1202 method to determine the durability of geopolymer concrete, the results of this study shows that the modified ASTM C1202 correlate well with the chloride diffusion coefficient of low and high calcium content GPCs (refer to Figure 5-8).

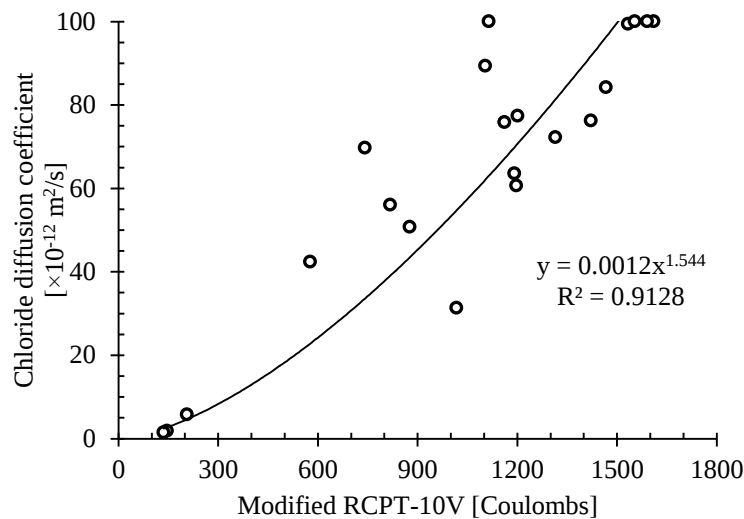


Figure 5-8: Correlations between total charge passed and chloride diffusion coefficient

The modified ASTM C1202 method introduced in this work can be used as a relatively good indicator of the chloride resistance for GPCs. However it is acknowledged that the RCPT is not ion specific and every metallic ions such as Na⁺ present in the pore solution (depends on the degree of availability of such ions in the pore structure) can interfere to the total charge passed and cause miss-leading results. Therefore, it is believed that running a reference or blank test prior to proceed with the modified RCPT can produce more reliable and less binder dependent test data.

For each set of geopolymer concrete samples, a set of 3 concrete discs can be tested following the modified ASTM C1202 protocol with distilled water as electrolyte in both cells instead of NaOH and NaCl solutions. The total charge passed in blank

measurement can be subtracted from the modified ASTM C1202 results to eliminate the effect of charge passed via other ions rather than chloride ions.

A pilot study on the above proposed method has been conducted on 5 selected geopolymer concretes; G7 to G11. These mixes are having a wide range of binder composition and alkaline solution concentration (e.g. different Na₂O content). G7 is made with 100% FA, G11 is made with 100% GGBFS and G8 to G10 were made with a mixture of FA and GGBFS. The result of blank modified RCPT is presented in Table 5-4. G7 and G8 with low GGBFS content and high amount of Na₂O in the alkaline solution demonstrated higher charge passed as opposed to high calcium content GPCs with low concentration of Na₂O (i.e. G9 to G11). However, the blank charge passed as a percentage of total charge passed increases by increasing the calcium content. This confirms the significant interference of the various ions in RCPT results.

Table 5-4: Blank modified RCPT results

Mix ID	GGBFS/FA	Na ₂ O content [% of binder]	Blank modified RCPT [Coulombs]	Modified RCPT (ref Table 5-3) [Coulombs]	Blank/total RCPT [%]
G7	0/100	8.8	267	2266	12
G8	25/75	8.8	193	1017	19
G9	50/50	4.0	86	206	42
G10	75/25	4.0	71	146	49
G11	100/0	4.0	82	136	60

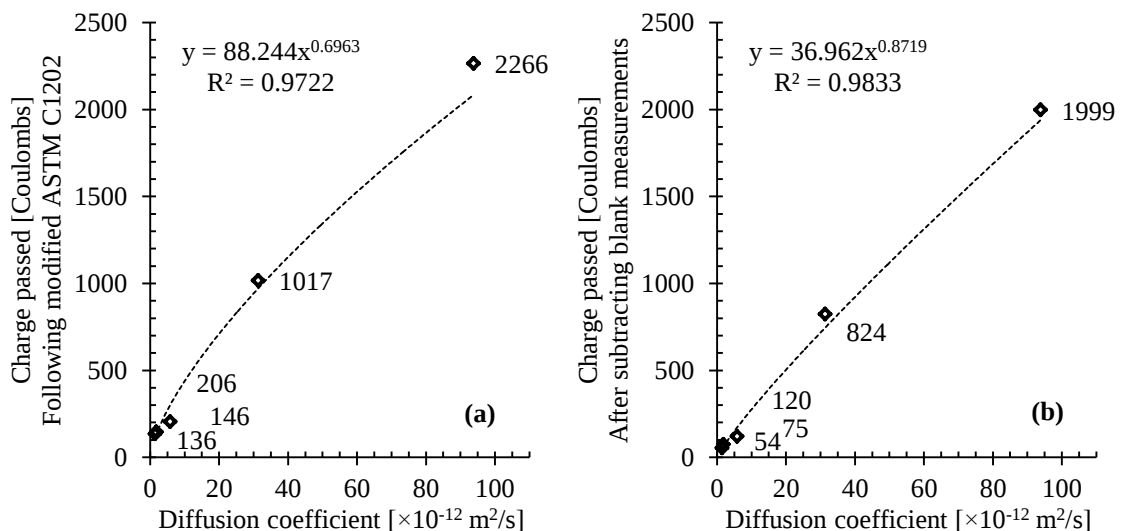


Figure 5-9: Correlations between total charge passed and chloride diffusion coefficient; (a) following modified ASTM C1202 method (b) following modified ASTM C1202 method after subtracting the blank measurement

Figure 5-9 shows the correlation between charge passed and chloride diffusion coefficient of GPCs G7 to G11. Figure 5-9 (a) includes the results of the modified

ASTM C1202 method while Figure 5-9 (b) includes the charge passed after subtracting the blank measurement. The R-squared value of modified ASTM C1202 after subtraction of the blank measurement is only marginally higher ($R^2=0.98$) compared to R^2 without blank measurement ($R^2=0.97$). This suggests that for GPCs including the blank measurement to the RCPT might improve the reliability of the test data and enhance the suitability of modified ASTM C1202 as a performance test method. However, the number of test specimens was very limited in this pilot study and a more comprehensive experiment has to be conducted in order to establish a conclusive statement.

5.4 Chloride migration test

The Nordtest NT Build 492 test method is commonly used to determine the chloride migration coefficient in non-steady-state condition by using an external voltage to drive chloride ions into the sample and measure the chloride penetration depth.

It's worth mentioning that the migration coefficient calculated from the silver nitrate colorimetric method may not be accurate enough to measure the chloride penetration depth in geopolymer concretes when exactly following the NT BUILD 492 formulation. An important parameter affecting the accuracy of the migration coefficient determination in Nordtest method is the chloride concentration at which the colour of the indicator changes (c_d). It has been recognized that hydroxyl ions (or pH value) have a great influence on the colorimetric measurements (Tang 1996; Yuan et al. 2008). In fact, silver nitrate can react with both chloride ions and hydroxyl ions to form white silver chloride (AgCl) and dark brown silver oxide (Ag_2O). When aqueous silver nitrate solution is sprayed on the surface of split concrete, the precipitates formed on the surface of concrete are a mixture of AgCl and Ag_2O . For every chemistry of pore solution, there is a critical point where the brown colour of the silver oxide covers the white colour of the silver chloride and forms the penetration front. The concentration of chloride ions at this critical point (penetration front) is labelled c_d .

The NT BUILD 492 suggests to use $c_d=0.07$ for OPC concrete. This value may be different for geopolymer concrete and has to be assessed experimentally.

Indeed, the silver nitrate colorimetric measurement is based on a chemical reaction, which can be influenced by the chemistry of concrete pore solution. Geopolymer

concrete has a different chemistry of pore solution compared to OPC concrete, which is not considered in NT BUILD 492 method.

The NT BUILD 492 recommends the value of 0.07 N for c_d for OPC concrete. However, previous studies showed that the concentration of the hydroxide ions (pH value) can significantly affect the c_d (Yuan et al. 2008, 2012). Andrade et al. (1999) studied the chloride concentration at the colour change boundary of various concretes made of OPC, slag, fly ash and silica fume. They reported a chloride concentration (% of total sample) at colour change boundary of 0.30, 0.27, 0.28, 0.03 for concretes made of Portland cement, slag, fly ash and silica fume, respectively. From the results reported by Andrade et al. (1999), it can be found that the reason for a lower chloride concentration at the colour change boundary of concrete made of pozzolonic materials (particularly silica fume) is due to a lower concentration of hydroxide ions or a lower pH value. This might be similar for geopolymer concrete with different pH values.

Figure 5-10 shows the pH values of aluminosilicate source materials and hardened geopolymer pastes compared to an OPC paste with a w/c of 0.45. The pH of all solid materials was examined by measuring the pH of a solution made of 5 g powder in 50 g distilled water.

The pH of all hardened geopolymer pastes is lower than that of the OPC paste. The fly ash-based GPCs are having the lowest pH ranging between 11.9 and 12.0 at 56 days of age. The pH of hardened geopolymer paste increased as more GGBFS is used in the mix. The slag-based geopolymer (i.e. G11 with 100% GGBFS binder) showed the highest pH value among all the geopolymers, very similar to that of OPC paste.

As shown in Figure 5-10, the pH of geopolymer pastes decreased with time. The reason for the decreasing trend of pH of the synthesized geopolymer is that the source of initial high pH (i.e. the alkaline solution) is decreasing with time and consumed during the geopolymerisation process. At early age large quantity of sodium hydroxide is available in the pore solution of the hardening geopolymer paste, reacting with fly ash and slag particles to become part of the geopolymer framework. The pH of the fresh OPC concrete was initially 12.42 and increased to 12.72 at 28 days.

The difference in pH between GPC and OPC concrete can lead to a different c_d value. Therefore, using the recommended value of $c_d=0.07$ for OPC concrete may underestimate the migration coefficient of GPCs specially for low GGBFS content

GPCs. Therefore the measurement of c_d for various geopolymer types is very important. Since the experimental measure of the chloride concentration at the silver nitrate boundary was not carried out during the course of this study, the c_d was determined according to the formula proposed by He et al. (2011) as shown in Eq. (5-2) assuming that all AgNO_3 reacts with Cl^- and OH^- at the colour change boundary.

$$C_{bd} = \frac{35.5P \times 1.6C_{\text{OH}^-} \times 100\%}{M_{\text{binder}}} \quad (5-2)$$

where C_{bd} is the chloride concentration at the colour change boundary, C_{OH^-} is the pore solution hydroxyl concentration before reaction and P is the mass ratio of AgCl to precipitates with AgCl and Ag_2O . The pore solution hydroxyl concentration (C_{OH^-}) varies according to the different proportions of GGBFS/FA, water/binder ratio and alkaline solution concentration, as reported by Lloyd et al (2010). The C_{OH^-} values used in this section is taken as the estimated values suggested by Ismail et al. (2013b) as shown in Table 5-5.

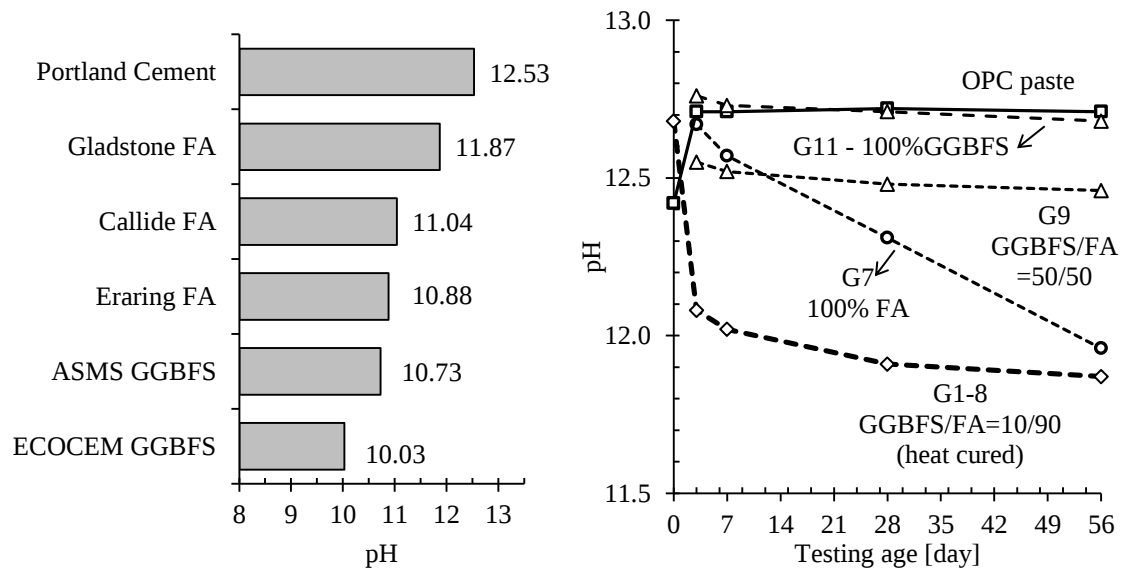


Figure 5-10: pH of aluminosilicate source materials (left) and geopolymer pastes (right)

Table 5-5: Estimated chloride concentrations at colour change boundary of GPCs

GGBFS/FA	SiO ₂ + Na ₂ O/Binder	Water/binder	Estimated C _{OH⁻} [mol/L]	C _{bd} [mol/L]
0/100	0.17 – 0.22	0.27 – 0.30	2.2	0.21
10/90	0.17 – 0.22	0.27 – 0.30	2.2	0.21
15/85	0.17 – 0.22	0.27 – 0.30	2.2	0.21
25/75	0.22	0.30	2.2	0.21
50/50	0.10	0.40	1.8	0.17
75/25	0.10	0.45	1.4	0.13
100/0	0.10	0.45	1.0	0.09

Figure 5-11 shows a typical chloride penetration depth measurement at the end of the migration test (NT BUILD 492). The chloride penetration front is marked by a red line in the figure and chloride ingress started from the top of the samples as shown. The scales on the side assist to assess the overall chloride penetration depth into the sample. The average penetration depth is then calculated to determine the chloride migration coefficient using Eq. (3-1). As noted in NT Build 492 method, the 10 mm edge is not included in chloride penetration front measurement due to the possible leak of test solutions through the sides of the test specimens.

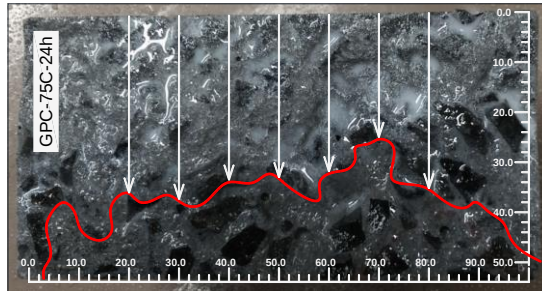


Figure 5-11: Chloride Penetration Depth (NT BUILD 492); test duration=24 h, voltage=10 V

The chloride migration coefficient of the ambient and heat cured GPCs along with the applied test voltage and duration are presented in Table 5-6.

Table 5-6: Chloride migration coefficient of GPCs after 28 days

Mix	GGBFS/FA	Curing	Voltage [V]	Duration [h]	Migration coefficient [$\times 10^{-12} \text{ m}^2/\text{s}$]
G1-1	10/90	Ambient	10	24	37.7
G1-2	10/90	60°C-8h	10	24	78.7
G1-3	10/90	60°C-12h	10	24	73.6
G1-4	10/90	60°C-18h	10	24	69.1
G1-5	10/90	60°C-24h	10	24	70.5
G1-6	10/90	75°C-8h	10	24	78.1
G1-7	10/90	75°C-12h	10	24	60.2
G1-8	10/90	75°C-18h	10	24	49
G1-9	10/90	75°C-24h	10	24	48.1
G1-10	10/90	90°C-8h	10	24	61.2
G1-11	10/90	90°C-12h	10	24	54.3
G1-12	10/90	90°C-18h	10	24	55.2
G1-13	10/90	90°C-24h	10	24	50.9
G2	15/85	75°C-18h	10	24	54.8
G3	15/85	75°C-18h	10	24	63.2
G4	15/85	75°C-18h	10	24	71.1
G5	0/100	75°C-18h	10	24	78.9
G6	10/90	75°C-18h	10	24	70.2
G7	0/100	Ambient	10	6	153.0
G8	25/75	Ambient	10	24	33.0
G9	50/50	Ambient	30	24	4.4
G10	75/25	Ambient	60	24	1.5
G11	100/0	Ambient	60	24	1.5

A very broad range of migration coefficients ranging between 1.5 and $141.4 \times 10^{-12} \text{ m}^2/\text{s}$ was observed for GPCs with low and high calcium content and various alkaline solution compositions. As shown in Figure 5-12, the migration coefficient of heat-cured fly ash based GPCs reduced by increasing the heat-curing temperature and duration. Among ambient cured GPCs, the best result was obtained when samples were cured for 18 and 24 hours at 75°C .

The fly ash based GPCs heat cured in similar condition (i.e. 18h at 75°C) with less than 15% GGBFS, the chloride migration coefficient reduces by increasing the GGBFS content. For samples with the same amount of slag (i.e. G2, G3 and G4 with 15% GGBFS), the lowest migration coefficient is obtained with high concentrated alkaline solution ($\text{SiO}_2 + \text{Na}_2\text{O}/\text{Binder} = 0.21$).

The migration coefficient of ambient cured GPCs significantly reduced by increasing the slag content. As mentioned earlier in this chapter, the presence of calcium in geopolymer matrix is critical to reduce porosity and increase the chloride resistance. The decreasing trend of the migration coefficients by increasing the slag content is more notable by increasing the slag content from 25% to 50%, after which increasing the slag content does not significantly affect the chloride diffusion.

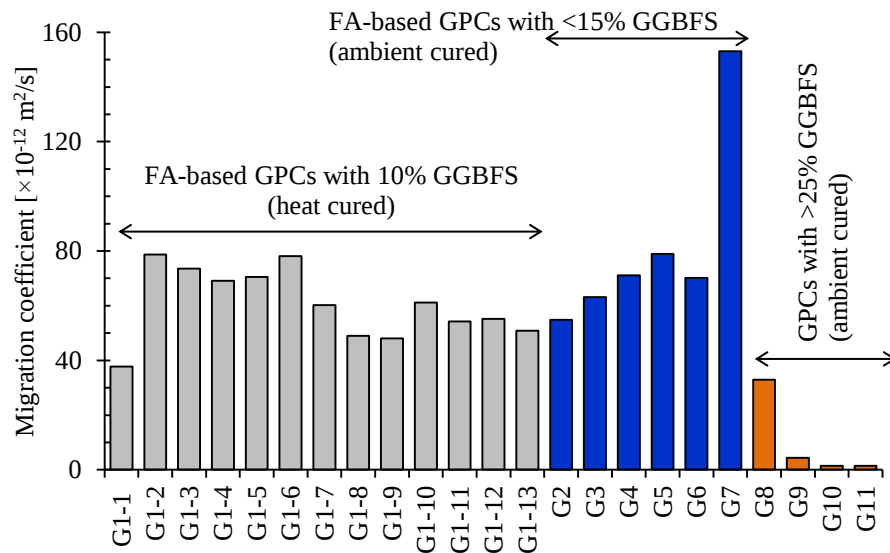


Figure 5-12: Chloride migration coefficient of low and high calcium content GPCs

Figure 5-13 depicts the relationship between the chloride diffusion coefficient and migration coefficient of low and high calcium GPCs. A good correlation ($R^2=0.97$) exist between the results of this two different tests. Comparing the relationship shown in

Figure 5-13 to that presented in Figure 5-8 demonstrate that the NT BUILD 492 test is a more reliable accelerated chloride testing for geopolymer concretes as opposed to the modified ASTM C1202.

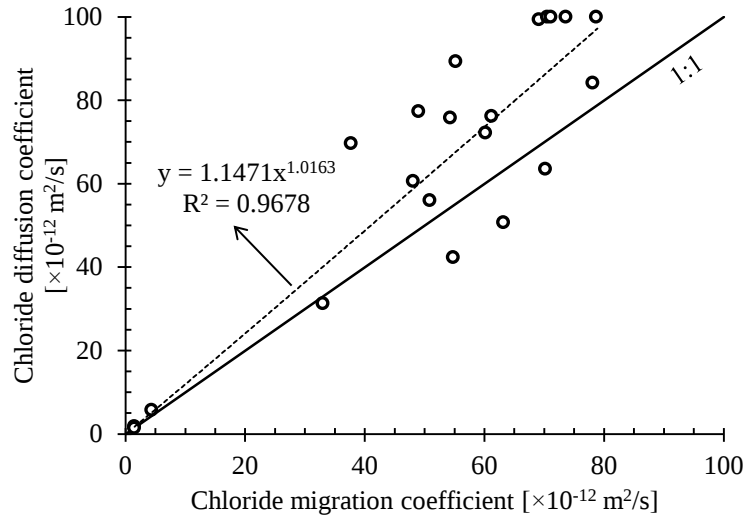


Figure 5-13: Correlations between total charge passed and chloride diffusion coefficient

Similar to the chloride diffusion coefficient, the significantly lower chloride migration coefficient of slag based GPCs is indicative of a finer pore structure with higher tortuosity compared to that of fly ash based GPCs. The pore filling effect of calcium silicate hydrate gel, formed due to the presence of slag in the blended geopolymer matrix, as previously reported by Provis et al. (2012), resulted into a very dense matrix and leading to high chloride penetration resistance.

5.5 Conclusion

The chloride resistance and chloride binding capacity of low and high calcium content GPCs have been examined thoroughly in this chapter. Two accelerated chloride penetration tests i.e. ASTM C1202 RCPT and NT BUILD 492 chloride migration tests has been investigated and results were compared to the chloride diffusion coefficient measured through the ponding test. The results show that:

- The acid soluble and water soluble chloride measurement and XRD analysis showed no chloride binding capacity and no chemical reaction between geopolymer binders of low and high calcium content and chloride ions. It appears that the geopolymer binder has no chloride chemical binding capacity.

- The influence of curing temperature and curing duration on chloride penetration resistance of low calcium content fly ash-based GPCs were studied. Twelve different heat curing regimes with three temperatures of 60, 75 and 90°C and four heat curing durations of 8, 12, 18 and 24 hours were applied to the specimens. All heat cured fly ash based GPCs with less than 15% GGBFS content demonstrated a very low resistance to chloride penetration. For fly ash based GPCs, among all the thermal curing conditions and over all the chloride-related durability tests, curing at 75°C for 18-24 hours provided the highest chloride resistance.
- In fly ash based GPCs, the inclusion of up to 25% GGBFS helps to develop a finer pore structure and increase the resistance to chloride penetration.
- The bulk diffusion test results of heat-cured samples showed that all the fly ash based GPCs with less than 25% GGBFS regardless of the curing condition had very high chloride content (above 0.3% of concrete mass) even at the depth of 25 mm from the surface. This is due to the highly porous microstructure and well-interconnected pore network of fly ash based geopolymer binders as demonstrated in Chapter 4.
- The ASTM C1202 RCPT could not be completed for the fly ash-based GPCs. The RCPT was deemed a failure at the voltage of 60 V for all the low calcium content GPCs with less than 25% GGBFS since the initial current readings were too high. A modification of the RCPT was successfully carried out by reducing the applied voltage to 10 volts. At each accelerated thermal curing temperature, the samples cured for a longer period demonstrated a lower charge passed (although it was not very significant at 60°C) which is consistent with the capillary absorption test results. The effect of curing duration on the charge passed became more significant at 75 and 90°C. The fly ash based samples with lower sorptivity coefficient and hence smaller capillary pores showed higher resistance to chloride penetration.
- The NT BUILD 492 chloride migration test is a suitable accelerated chloride penetration test for geopolymer concrete. A good correlation exist between the chloride migration coefficient and chloride diffusion coefficient of GPCs. However, the chloride concentration at the colour change boundary suggested in Nordtest should be calibrated for the chemistry of the pore solution of geopolymer concrete.

- The calcium content plays a significant role on chloride penetration resistance of GPCs. The chloride diffusion and migration coefficient of GPCs significantly reduced by the inclusion of higher amounts of GGBFS in the binder. A remarkable shift in chloride diffusion/migration coefficient occurs with 50% or more GGBFS content. The very fine pore structure of calcium rich geopolymers along with the high tortuosity of the pore network as measured by the water sorptivity in Chapter 4 result in a low permeability and a high chloride penetration resistance.

Carbonation in Geopolymer Concrete

6 CARBONATION IN GEOPOLYMER CONCRETE

6.1 Introduction

The carbonation process is detrimental to reinforced concrete, as carbon dioxide diffuses through the pore structure and reduces the alkalinity of the pore solution (Chang and Chen 2006; Pouhet and Cyr 2016). This can lead to the depassivation of reinforcing steel, leaving them prone to corrosion. There is relatively little existing knowledge on the carbonation process in geopolymer concretes. Bernal et al. (2013b) carried out a detailed microstructural analysis to investigate the effects of accelerated carbonation on alkali-activated FA and slag. However, their study only focused on powder samples, which revealed some important and fundamental aspects of carbonation chemistry, but the results are unlikely to represent the performance of concrete under natural exposure conditions. Law et al. (2014) measured the pH of extracted pore water in geopolymer mortar specimens exposed to 5% accelerated carbonation, and recommended a pH value of 11 to protect the reinforcing steel following carbonation. However, the pore solution extraction method is unlikely to provide the pore solution composition at the vicinity of the steel, required to assess the degree of depassivation. The accurate measurement of the pH profile along the depth of GPC cover under natural and accelerated carbonation conditions could be an alternative way to assess the passivity of steel in carbonated GPC.

In OPC concrete, the portlandite (Ca(OH)_2) provides a buffer effect in which the continuous dissolution of portlandite maintains a high pH level in the pore solution in case of neutralization of the OH^- ions during the carbonation process. Unlike the OPC binders, low-calcium content GPCs do not contain a considerable amount of portlandite as a reaction product; and, as a result, they might be more prone to the loss of alkalinity (Lloyd et al. 2010). During the Carbonation of low calcium GPCs, the main process is carbonation of the highly alkaline pore solution resulting in the formation of alkali carbonate/bicarbonate salts that precipitate from the pore solution. No significant change in the aluminosilicate gel nanostructure has been reported (Bernal et al. 2013b), yet some minor strength degradation was observed which intensifies by increasing the calcium content (Sufian Badar et al. 2014). On the other hand, high calcium content GPCs (as of alkali activated slag binders) experience carbonation of the pore solution,

followed by carbonation of secondary products and decalcification of calcium aluminosilicate hydrates C-(A)-S-H gel which can lead to considerable structural strength degradation and increasing the porosity particularly when sodium silicate is used as the alkaline solution (Bernal et al. 2015; Puertas et al. 2006). The carbonation of blends of fly ash and slag is similar to the carbonation of binders based on the individual precursors, where after the initial carbonation of the pore solution, the largely unaltered aluminosilicate network coexist with the decalcified C-A-S-H gel, along with various alkali-carbonate precipitates (Bernal et al. 2013b). Therefore, the pore solution alkalinity and composition plays a major role during the carbonation process of low and high calcium GPCs: a pore solution with enough alkalinity can keep the reinforcement passivated, and also prevents the structural alteration of the binder (in particular in Ca-rich binders) which only occurs after the initial exhaustion of the pore alkali content during the carbonation.

In this chapter, the pH profiles of various geopolymer concretes with low and high calcium content exposed to natural and accelerated carbonation are examined to provide a precise evaluation of the degree of carbonation in GPCs.

6.2 Experimental program

6.2.1 Materials, mixes and sample fabrication

Five geopolymer concrete mixes and one OPC concrete mix were prepared and tested using the materials described in Chapter 3 section 3.1. The mix proportioning of the raw material ingredients, as shown in Table 6-1, was carried out by mass. The aggregate's mass shown in Table 6-1 is in SSD condition. All the GPCs were ambient cured in sealed plastic bags until 28 days. The OPCC was standard cured in lime-water prior to testing. Standard 100 (diameter) × 200 (height) mm cylinders were cast and then cut into slices for carbonation testing. The mechanical properties of mixes G7 to G11 have been provided in Chapter 4; Table 4-10.

Table 6-1: Mix proportions of low and high calcium content GPCs and OPCC

Materials	OPCC2	G7	G8	G9	G10	G11
20 mm aggregate	681	673	673	668	660	660
10 mm aggregate	389	384	384	382	377	377
Crushed sand	584	577	577	572	566	566
River sand	292	288	288	287	283	283
Portland Cement (GP)	410	0	0	0	0	0
Gladstone FA	0	410	307	205	103	0
ASMS GGBFS	0	0	103	205	307	410
NaOH pellets	0	11.4	11.4	5.2	5.2	5.2
Na-silicate	0	178	178	81	81	81
Free water	184.5	48.2	48.2	135.5	157.4	157.4
MR ¹ (SiO ₂ /Na ₂ O)	N.A	1.5	1.5	1.5	1.5	1.5
SiO ₂ + Na ₂ O/Binder ²	N.A	0.22	0.22	0.1	0.1	0.1
Water ³ /Solid ⁴	0.45	0.30	0.30	0.40	0.45	0.45
GGBFS content [%]	0	0	25	50	75	100
Curing temperature [°C]	23 (water)	23	23	23	23	23
Heat-curing duration [h]	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.

¹ Molar ratio of the alkaline solution² Binder = fly ash (FA) + GGBFS³ Water = free water + water in Na-silicate solution⁴ Solid = Binder + dissolved components of Na-silicate solution + NaOH pellets

6.2.2 Conditioning prior to the carbonation test

All the samples were cured for 28 days prior to carbonation test. To achieve uniform moisture redistribution, the 28-day old concrete cylinders were kept in an environmental chamber for 2 weeks at a constant temperature of 23±2°C and 55% relative humidity. After the dry conditioning, a 20 mm section was removed from the top and bottom of each cylinder, and the remaining segment was cut into sections of 50 mm depth for subsequent carbonation testing.

6.2.3 Carbon dioxide exposure conditions

The 50 mm discs were sealed using aluminium tape along the perimeter, leaving the top and bottom of the samples exposed for carbon dioxide diffusion. For natural carbonation, the specimens were kept in an environmentally controlled room. For accelerated carbonation, the specimens were placed in a carbonation chamber with a carbon dioxide concentration of 1%. The exposure temperature and relative humidity in all cases were 23°C and 55%, respectively. The carbonation depth and pH profiles were analysed after 2, 4 and 8 and 12 weeks of accelerated exposure and 6 months of natural exposure.

The effect of carbon dioxide concentration on carbonation product formation has studied for a low calcium content GPC and results were published in details in (Khan et al. 2017b). In this study, XRD results revealed that natron (sodium carbonate) was the main carbonation product in GPC specimens exposed to natural carbonation and 1% accelerated carbonation (AC) for 6 weeks. Quantification of the crystalline phases showed that natron accounted for about 25% in both exposure conditions. The pH profiles measured for 18 months' natural carbonation and 1% AC for 6 weeks were very similar. Therefore, 1% AC demonstrated to reproduce well the chemistry of the natural carbonation. On the other hand, nahcolite (sodium bicarbonate) started to form just after 2 weeks at 3% AC and its crystalline proportion was 17 wt%, while the proportion of natron was only 6.3 wt%. A significant difference in pH reduction in carbonated GPC was observed when using 1% or 3% carbon dioxide. The minimum pH measured was around 9.8 using 1% carbon dioxide and around 9.2 using 3% carbon dioxide. As a result, the carbon dioxide content used to accelerate the natural chemistry of low-calcium FA GPC carbonation should not be more than 1% since the high carbon dioxide concentration (>1%) can lead to the transformation of natron to nahcolite. The XRD patterns of low calcium fly ash based GPCs exposed to 1% and 3% accelerated carbonation are presented in Figure 6-1.

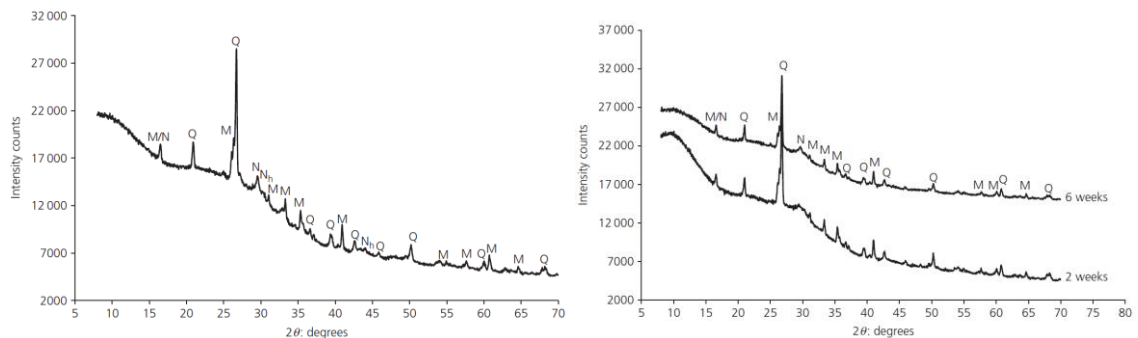


Figure 6-1: XRD patterns of geopolymer pastes exposed to; (left) 3% accelerated carbonation for (right) 1% accelerated carbonation for 2 and 6 weeks. M: Mullite, Q: Quartz, N: natron, N_h: nahcolite (Khan et al. 2017b)

6.2.4 pH profile and carbonation depth

pH profiles were obtained by combining the powder suspension method proposed by Räsänen and Penttala (2004) and pore solution extraction method proposed by Barneyback and Diamond (1981). For powder suspension method, the concrete powder was sampled every 1 mm over 25 mm depth of the specimens by using Germann Instruments' Profile Grinder. The powder was then mixed with de-ionised water with a

solid to liquid ratio of 1:10 (5 g solid + 50 g water) for ten min on a magnetic stirrer, and finally the pH of the solution was measured using a pH probe. The absolute values of the pH obtained from the suspension method might not be accurate, unlike the general trend which shows the variation of the pH values along the depth at different times. To calibrate the measured values, pore solution was extracted from uncarbonated paste samples with the same mix design and curing condition as the concrete specimens, but without any aggregate. pH of the extracted pore solution was directly measured by using a calibrated pH probe and then compared to the values obtained by using the powder suspension method for uncarbonated paste specimens. The difference between these two pH values was then used to calibrate the pH values obtained by powder suspension method along the profiles. Phenolphthalein indicator spraying was also done as a rapid test to assess the carbonation front penetration in the carbonated samples; each specimen was split, and 1% phenolphthalein was sprayed on the fractured surface.

6.3 Results and discussions

6.3.1 Mechanical and transport properties

The mechanical and transport properties of OPCC mix C2 and GPCs G7 to G11 are presented in Chapter 4 section 4.2 Table 4-10 and Table 4-11. All mixes are having a 28-day compressive strength in excess of 45 MPa (i.e. 45.7 MPa - 53.2 MPa).

6.3.2 Pore solution pH calibration

The pH values obtained from the pore solution extraction and powder suspension of uncarbonated OPCC and GPCs are presented in Table 6-2. As noted earlier, the difference between these two pH values is used to calibrate the pH values obtained by powder suspension method along the pH profiles of carbonated GPCs.

Table 6-2: Pore solution pH of uncarbonated geopolymers after 28 days

Mix ID	GGBFS/FA	pH from pore solution extraction – paste	pH from powder suspension – concrete (paste)
C2	100% OPC	13.40	12.80 (12.75)
G7	0/100	12.23	11.94 (12.32)
G8	25/75	12.46	12.05 (12.64)
G9	50/50	13.00	12.07 (12.52)
G10	75/25	13.35	12.17 (12.61)
G11	100/0	13.37	12.21 (12.71)

6.3.3 pH profile and carbonation fronts

The pH profile and the split GPC specimen sprayed with phenolphthalein indicator are shown in Figure 6-2 to Figure 6-6. The reported pH values in each pH profiles are post-calibration values obtained following the calibration method explained in section 6.3.2. The dark pink colour throughout the fractured surface of the specimen indicates uncarbonated areas. The pH profiles show that the pH of carbonated GPCs is higher for geopolymers with higher calcium content. The pH of carbonated GPCs G7 to G11 with 0%, 25%, 50%, 75% and 100% GGBFS content is ~10.75, ~11.0, ~11.45, ~11.7 and ~11.7 respectively. This follows the same trend as for uncarbonated GPCs shown in Table 6-2.

Figure 6-2 shows the pH profiles of the fly ash based GPC with 0% GGBFS content. For both accelerated and natural carbonation, the pH of fly ash based GPCs dropped to ~10.75 at 1 mm depth and then gradually converged to the uncarbonated value except for the sample exposed for 12 weeks to accelerated carbonation. The mix G7 partially carbonated throughout the whole depth when exposed to 1% carbon dioxide for 12 weeks. The pH at the depth of 25 mm of the sample was 11.7. Similar carbonation behaviour was observed for mix G8 with 25% GGBFS content except that G8 showed higher resistance to carbonation compared to G7.

GPCs G9 to G11 with more than 50% GGBFS content fully carbonated throughout the whole depth after being exposed to 1% CO₂ for 8 weeks.

Pore blockage plays an important role in controlling the diffusion of carbon dioxide through concrete. Natron has a very large molar volume (196.56 cm³/mol) compared to nahcolite (38.66 cm³/mol) and calcite (36.93 cm³/mol) (IEM - Institute of Experimental Minerology 2016). Natron therefore fills a large pore space and thus provides a significant degree of pore blockage in carbonated low-calcium content GPCs (Bernal et al. 2012b). The significant amount of natron formed in the 1% AC specimens might have slowed down carbon dioxide diffusion by enhancing the degree of pore blockage in fly ash based GPCs (with <25% GGBFS), and thus the pH profiles did not experience a significant drop.

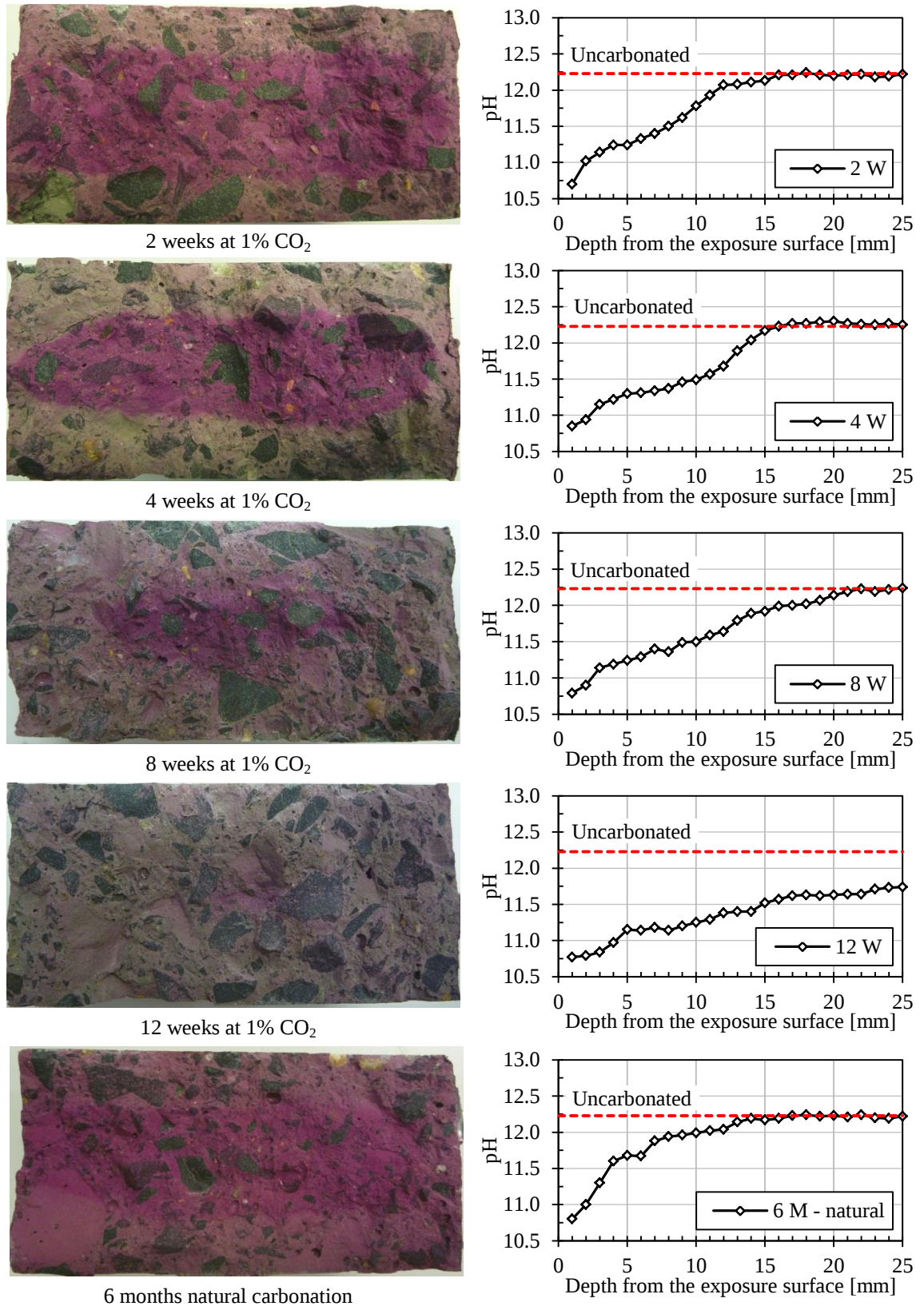


Figure 6-2: Carbonation fronts and calibrated pH profile of GPC G7 (GGBFS/FA=0/100)

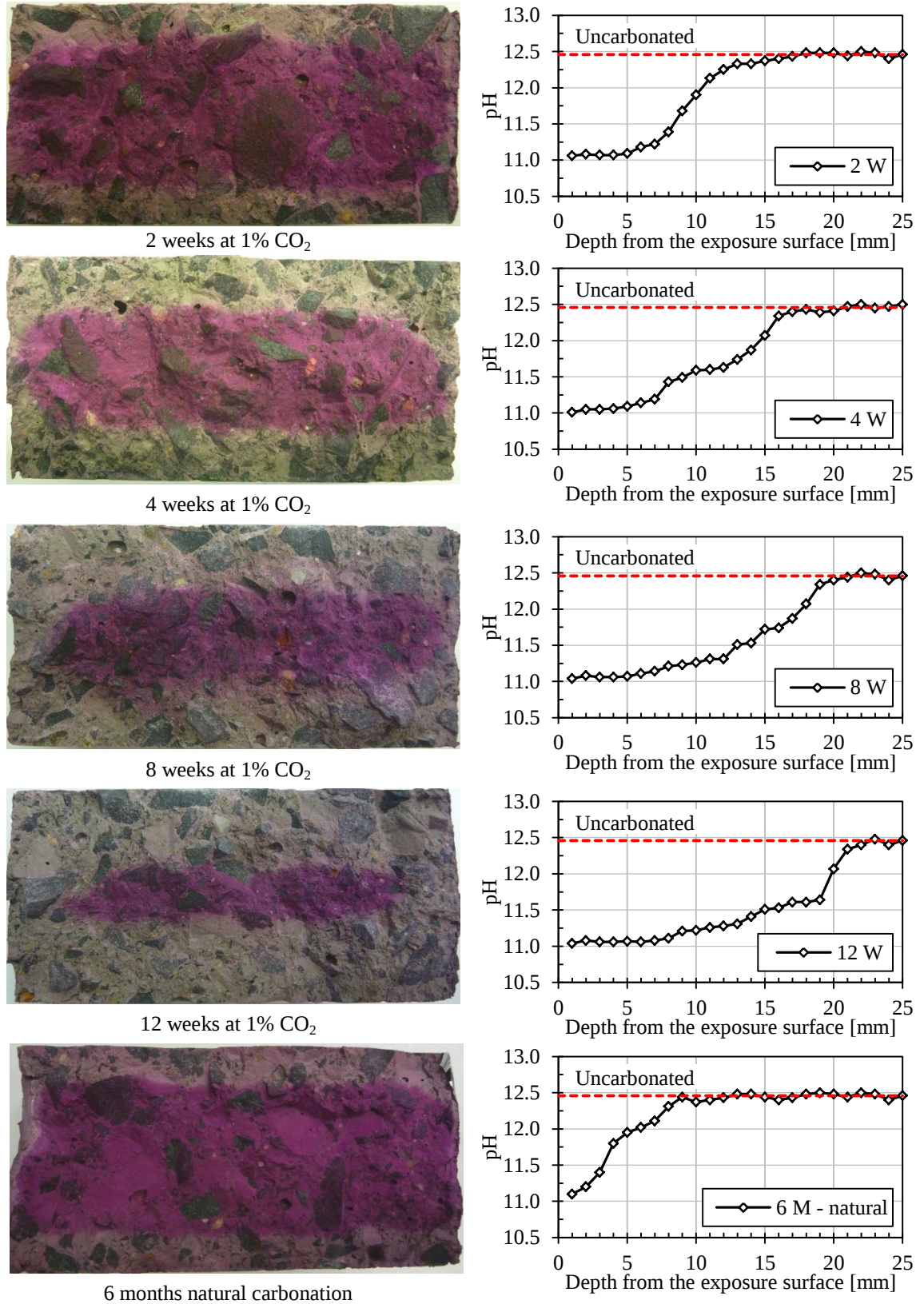


Figure 6-3: Carbonation fronts and calibrated pH profile of GPC G8 (GGBFS/FA=25/75)

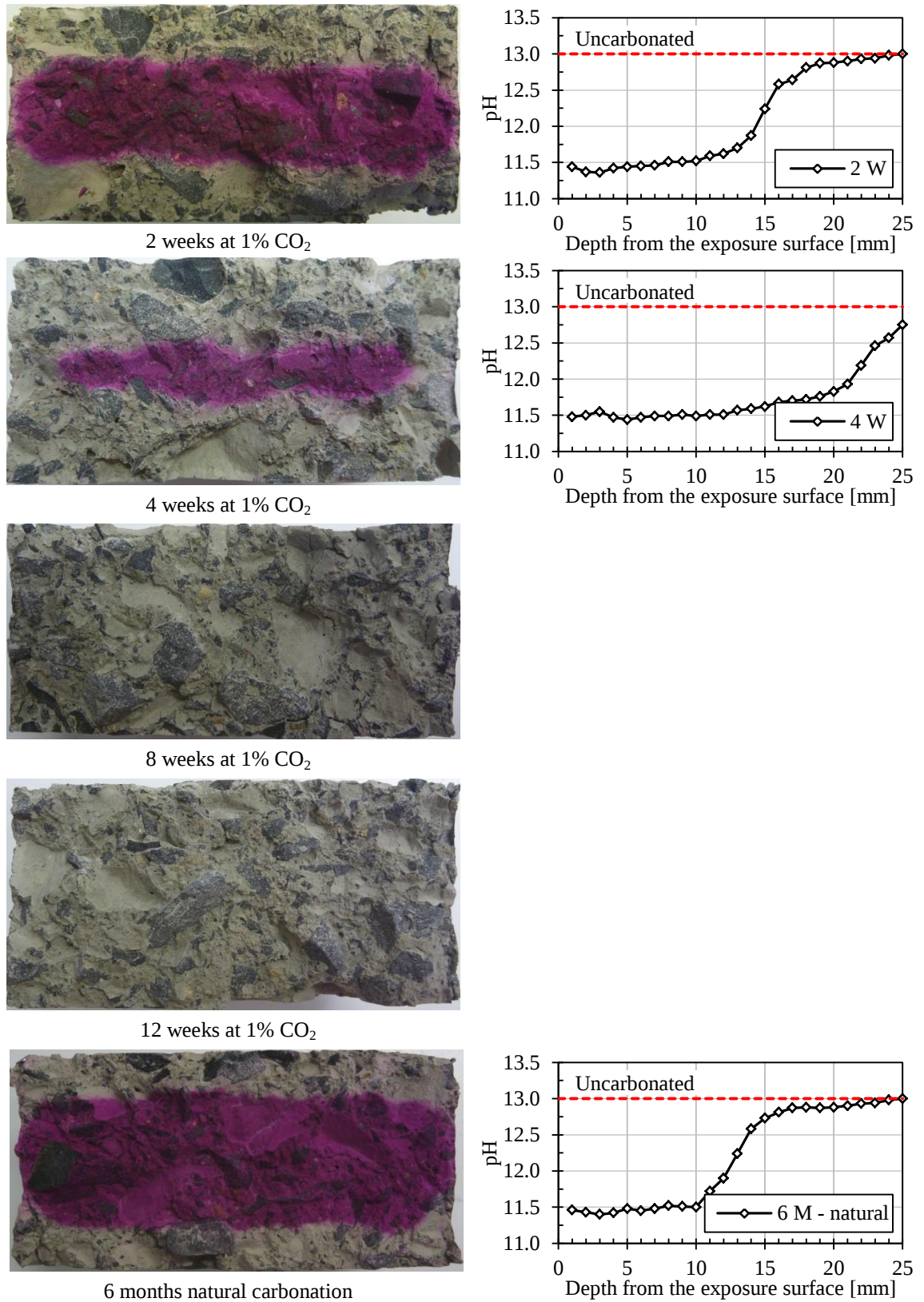


Figure 6-4: Carbonation fronts and calibrated pH profile of GPC G9 (GGBFS/FA=50/50)

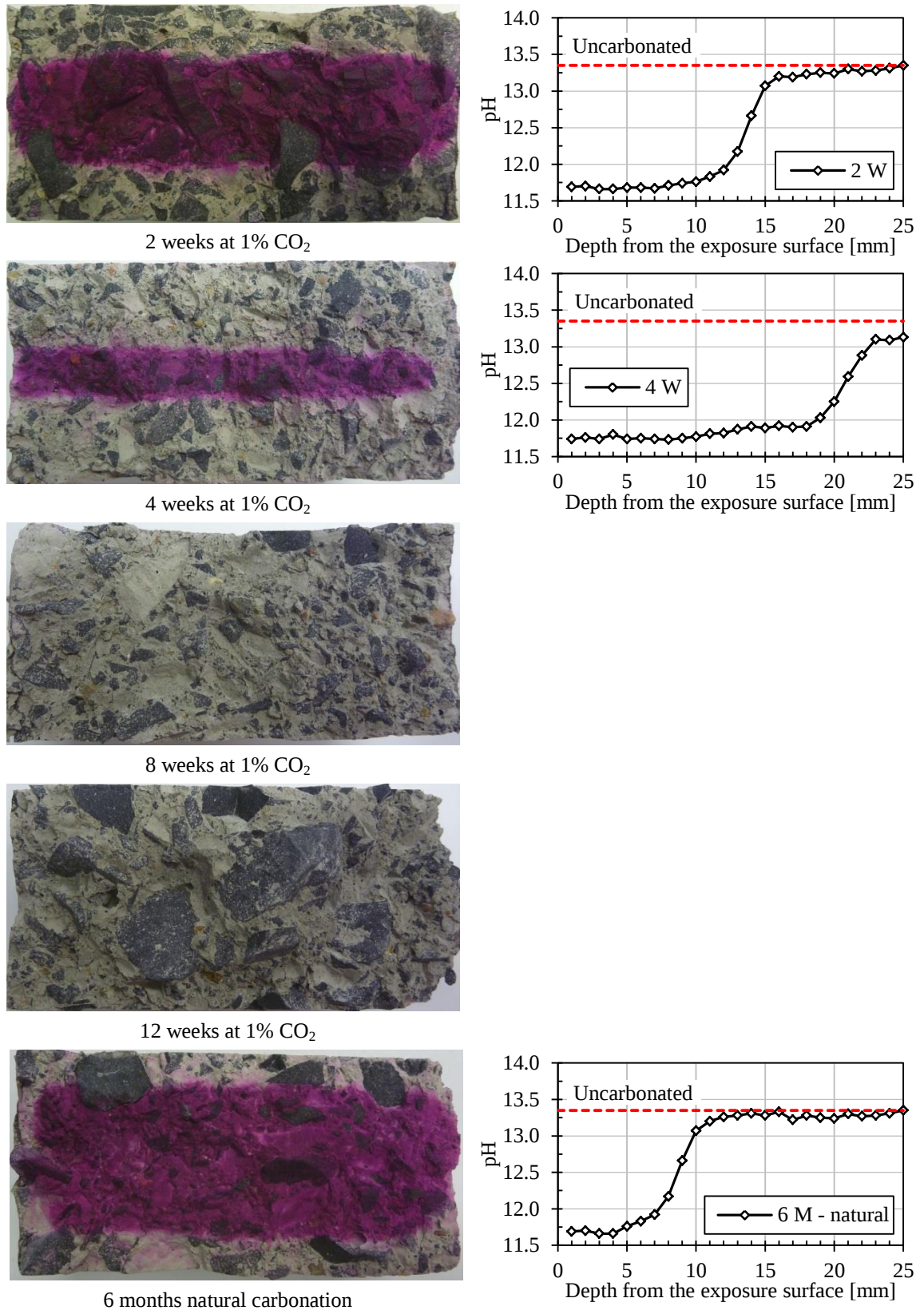


Figure 6-5: Carbonation fronts and calibrated pH profile of GPC G10 (GGBFS/FA=75/25)

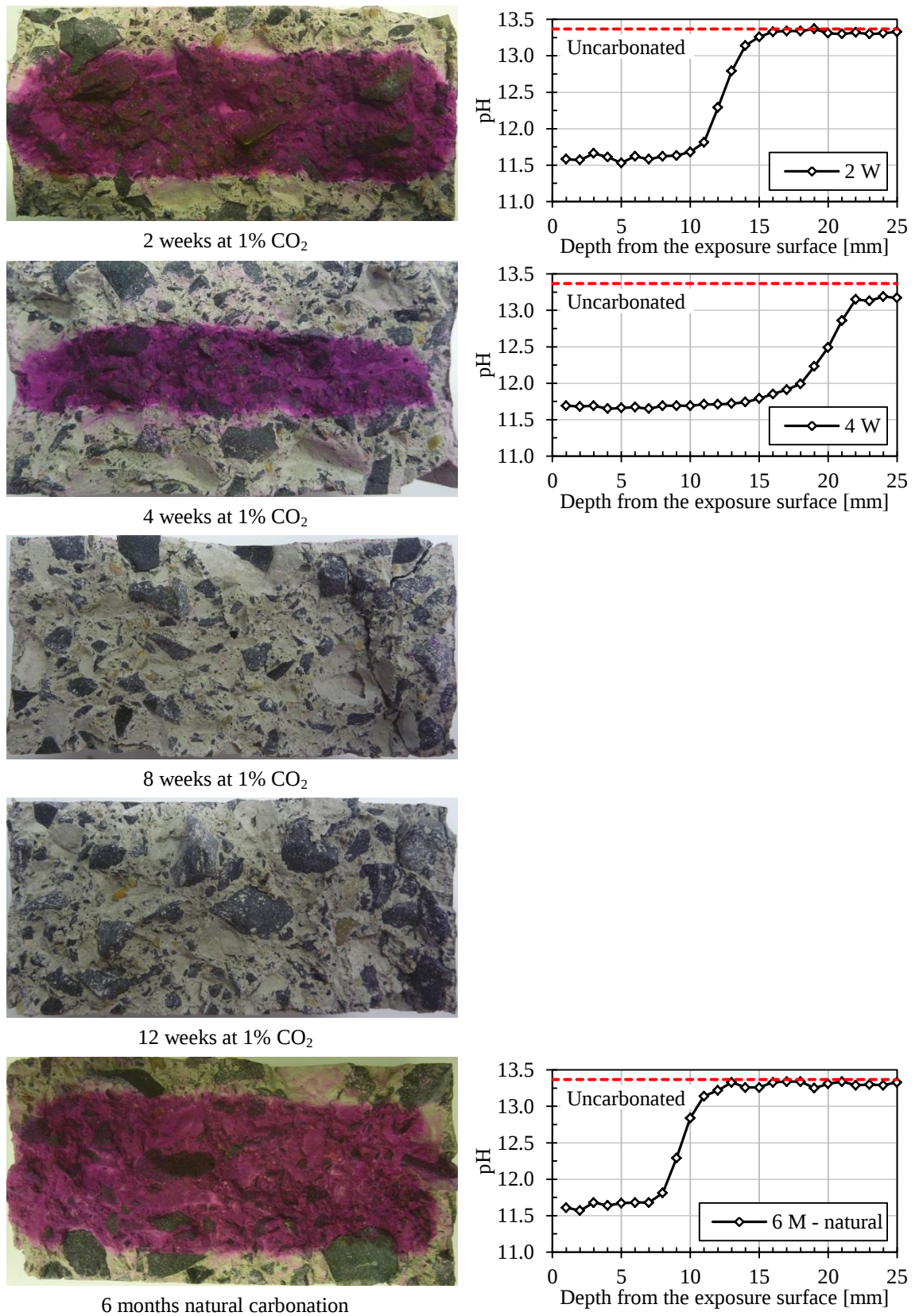


Figure 6-6: Carbonation fronts and calibrated pH profile of GPC G11 (GGBFS/FA=100/0)

Figure 6-7 shows the OPC concrete samples exposed to 1% carbon dioxide for 2 to 12 weeks. As expected and reported in literature (Chang and Chen 2006), a very clear border between the coloured (uncarbonated) and colourless (carbonated) zones is notable for OPCC when sprayed with phenolphthalein indicator. However, this was not the case for the fly ash based GPC mix G7. A faded colour was scattered throughout an elongated depth and the pH profile suggest that the pH of the partially carbonated zone is often >11.2 . By replacing fly ash with slag and increasing the calcium content of the GPCs, the partially carbonated zone has shrunk to a very narrow band similar to OPCC.

However, carbonation of the pore solution might or might not lead to the depassivation of reinforcement which depends on the extent of carbonation and pH reduction. Depassivation is imminent in OPCC when the pH of the carbonated binder falls below ~ 9 (Pourbaix 1974). In all the studied GPCs, the pH of the fully carbonated concrete was always more than 10.75 (10.75 to 11.7). Therefore, the pH drop in the partially/fully carbonated zone of GPCs may not be sufficient to destroy the passive film and initiate the corrosion during the service life of the structure. Further experimental work is required to assess the active phase of corrosion in carbonated GPCs.

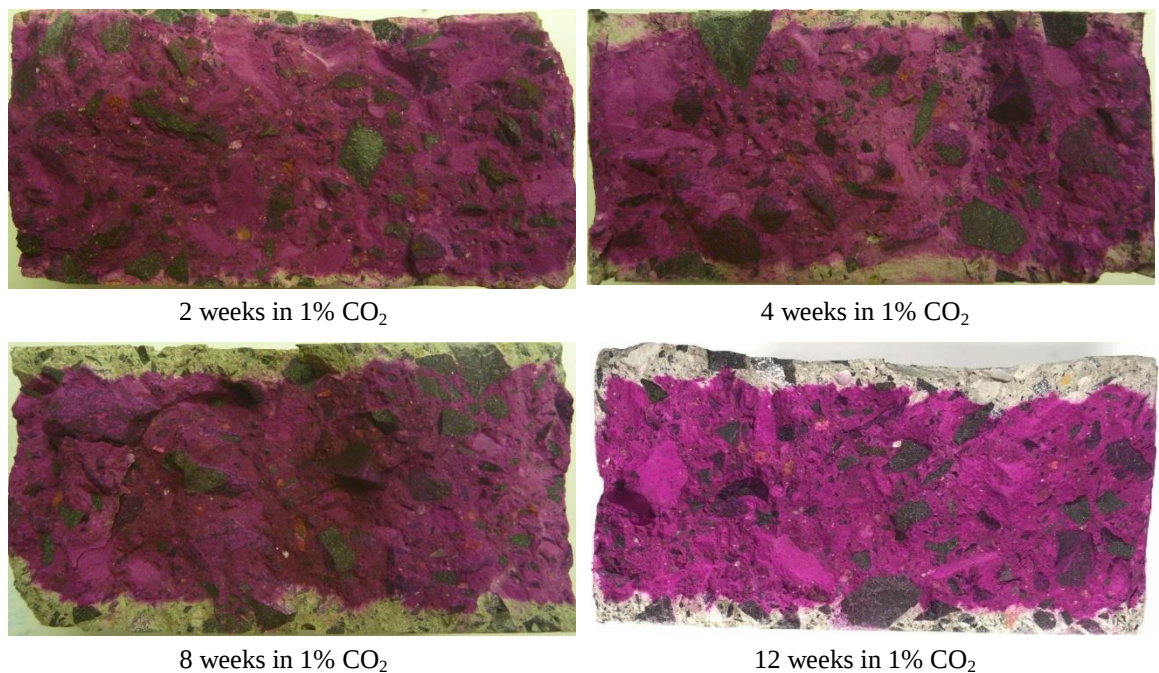


Figure 6-7: Carbonation fronts of OPCC mix C2 exposed to accelerated carbonation

6.4 Carbonation rate in GPCs

The diffusion process of carbon dioxide into concrete obeys Fick's law, which states that the carbonation depth proportionally varies with the square root of time (Bakharev et al. 2001). The carbonation front was measured at six different locations in each specimen. The average carbonation depth and the carbonation rate of low and high calcium content GPCs under accelerated and natural carbonation exposure conditions are presented in Table 6-3 and Figure 6-8. The carbonation rate of low and high calcium content GPCs was determined to be ranging between 10.0 and 18.5 mm/year^{0.5} under natural carbonation. This indicates that the natural carbonation process will take about 1 year to 4 years to reach the steel surface if a minimum concrete cover of 20 mm is considered. Studies looking at the carbonation of OPC concrete in natural conditions report that the carbonation rate can range from 2.0 to 3.6 mm/year^{0.5} for OPC concrete (Castel et al. 1999) and from 3.0 to 4.5 mm/year^{0.5} for blended FA and OPC concrete (Ho and Lewis 1987). This indicates 15 to 50 times higher carbonation rate for GPCs compared to OPCC. The highest carbonation resistance in both accelerated and natural carbonation exposure is observed for G8 with a blend of 25% GGBFS and 75% fly ash.

It should be noted that the faded purple zone (partially carbonated zone) in low calcium content GPCs G7 and G8 is counted as carbonated in the carbonation rate calculation. However, research (Babaei et al. 2018) tends to show that the pH of the partially carbonated zone is not low enough to lead to the depassivation of steel reinforcement. Further work is required to confirm that the faded purple zone should not be accounted in the determination of the carbonation front.

The natural carbonation process is rather slow. To assess the performance of concrete against carbonation, it is desirable to accelerate carbonation in order to curtail the duration of the test. From the accelerated and natural carbonation profiles obtained in the current study, the correlation below can be established between these 2 exposures;

- GPC G7 (GGBFS/FA=0/100): 6 weeks 1% accelerated carbonation can be equal to 6 months natural carbonation (requires validation by experimental testing)
- GPC G8 (GGBFS/FA=25/75): 2 weeks 1% accelerated carbonation is approximately equal to 6 months natural carbonation
- GPC G9 (GGBFS/FA=50/50): 2 weeks 1% accelerated carbonation is approximately equal to 6 months natural carbonation

- GPC G10 and G11 (GGBFS content > 75%): 1 week 1% accelerated carbonation can be equal to 6 months natural carbonation (requires validation by experimental testing)

Further experimental studies are required to investigate different accelerated carbonation durations or conduct longer natural exposure times (e.g. 12 to 18 months) to nominate a more accurate accelerate test time which replicates the carbonation associated with natural carbonation duration.

Table 6-3: Carbonation rate in low and high calcium content GPCs

Mix ID	GGBFS/FA	Exposure	Duration [day]	Carbonation depth [mm]	Carbonation rate [mm/year ^{0.5}]
G7	0/100	1% CO ₂	14	12 *	61.3
		1% CO ₂	28	14 *	50.5
		1% CO ₂	56	20 *	51.1
		1% CO ₂	84	25 *	52.1
		Natural	180	13 *	18.5
G8	25/75	1% CO ₂	14	9 *	46.0
		1% CO ₂	28	12 *	43.3
		1% CO ₂	56	14 *	35.7
		1% CO ₂	84	18 *	37.5
		Natural	180	7 *	10.0
G9	50/50	1% CO ₂	14	13.5	68.9
		1% CO ₂	28	19	68.6
		Natural	180	10.5	15.0
G10	75/25	1% CO ₂	14	13	66.4
		1% CO ₂	28	19	68.6
		Natural	180	8.5	12.1
G11	100/0	1% CO ₂	14	10.5	53.6
		1% CO ₂	28	17	61.4
		Natural	180	8	11.4
C2	100% OPC	1% CO ₂	14	1.5	7.7
		1% CO ₂	28	4	14.4
		1% CO ₂	56	5.5	14.0
		1% CO ₂	84	6	12.5
		Natural	-	-	2 – 3.6 **

* Including partially carbonated zone

** (Castel et al. 1999)

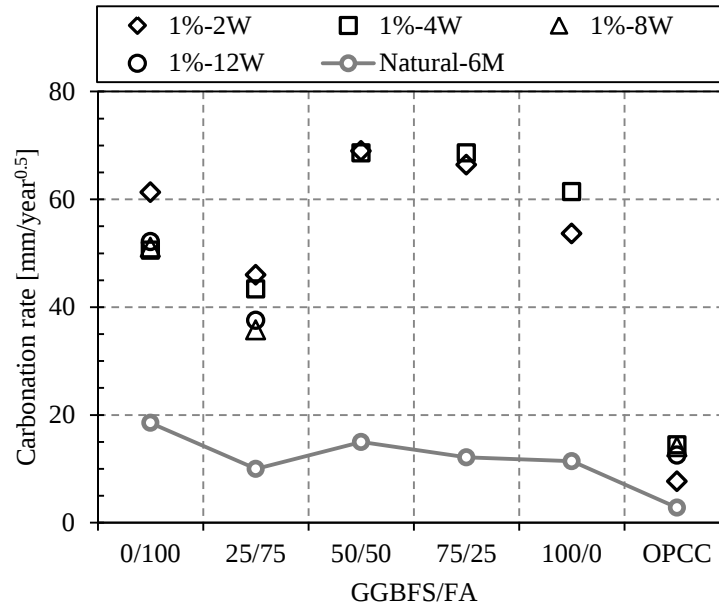


Figure 6-8: Carbonation rate of GPCs and OPCC

6.5 Conclusion

The pH of hardened uncarbonated geopolymer concrete can range between 12.2 and 13.4. The pH is increasing by GGBFS addition to the mix. The pH of carbonated GPCs is ranging between 10.8 and 11.7. The pH of carbonated high calcium content GPCs is higher than that of low calcium content GPCs.

All ambient cured GPCs of low and high calcium content provided a much higher carbonation rate as opposed to OPCC. However, the pH of the fully carbonated GPCs was always more than 10.8 that may still be high enough to sustain the passivity of steel reinforcement and avoid carbonation induced corrosion.

It appears that 6 weeks exposure at 1% CO_2 reproduces a similar carbonation penetration front as of natural carbonation for fly ash based GPCs with no GGBFS content. This is similar to fly ash based GPCs with 10% GGBFS content as reported by Khan et al. (2017b). For GPCs with 25% and 50% GGBFS content, 2 weeks accelerated carbonation reproduced 6 months natural carbonation. It is estimated that 1 week exposure at 1% CO_2 replicates 6 months natural carbonation for GPCs with more than 75% GGBFS content. However, the later requires validation through further experimental testing.

**Performance-Based
Recommendations for GPCs in
Marine Environment**

7 PERFORMANCE-BASED RECOMMENDATIONS FOR GPCS IN MARINE ENVIRONMENT

7.1 Introduction

A substantial roadblock to the implementation of geopolymer concrete is its durability. The need for suitable accelerated test methods to evaluate the long term performance of geopolymer concrete (GPC) in its designated environmental exposure is evident. In marine or coastal zones, the most harmful substance for reinforced concrete structures is chloride ion. The ASTM C1556 and its European equivalent Nordtest NT BUILD 443 (chloride diffusion test) have been widely used as the most reliable methods to assess the performance of concrete against chloride penetration. However, the chloride diffusion test takes around 6 weeks to complete (saline solution exposure, grinding and titration) and is a labour intensive process. The ASTM C1202 test (RCPT) is often used as a rapid test to evaluate the chloride penetrability of Ordinary Portland Cement concrete (OPCC). Good correlation exists between the total charges passed (Coulombs) through OPCC saturated concrete samples and the chloride diffusion coefficient (Andrade et al. 1999; Shi 2004b; Yang et al. 2002). However, no such evidence is available for GPCs. A modification to ASTM C1202 test method was successfully carried out in this study to adapt the test to various GPCs made with fly ash, ground granulated blast furnace slag (GGBFS) and metakaolin. The modified ASTM C1202 and chloride diffusion tests were conducted on a wide range of GPCs and a relatively good correlation was found between the total charges passed and the chloride diffusion coefficient. The test data and the proposed model can potentially be incorporated in performance-based standards to specify geopolymer concrete for different exposure condition.

The Nordtest NT Build 492 chloride migration test is another accelerated test method used to determine the chloride migration coefficient in non-steady-state condition by using an external voltage to drive chloride ions into the sample and measure the chloride penetration depth. Good correlation has been found between the chloride migration coefficient and chloride diffusion coefficient for OPCC. However, similar to what has been stated above for RCPT, there is not such data available for GPC.

This chapter aims to investigate the suitability of the modified RCPT and chloride migration tests to assess the chloride diffusion resistance of geopolymer concrete and to establish performance-based criteria to assess GPCs. The suitability and accuracy of each accelerated test method is assessed by comparison with the results obtained on the same geopolymer concrete using ASTM C1556 standard chloride diffusion test. Nineteen geopolymer concretes were tested using different aluminosilicate source materials including fly ash, GGBFS and Metakaolin, various alkaline solutions, water to binder ratios and aggregate. Two OPC concretes were tested and some test results from the literature considering blended cement-based concrete were used as bench mark.

7.2 Materials and mixes

Nineteen different geopolymer concrete mixes were prepared and tested using different aluminosilicate source materials (i.e. fly ash, GGBFS and metakaoline), alkaline solutions and aggregates as characterised in sections 3.1.1 to 3.1.3. The metakaolin (MK) used for mix G19 was made with a flash calcination process and supplied by Argeco, France. The chemical composition of MK as determined by XRF analysis is; $\text{SiO}_2=70.42$, $\text{Al}_2\text{O}_3=22.34$, $\text{Fe}_2\text{O}_3=2.34$, $\text{CaO}=0.49$, $\text{K}_2\text{O}=0.19$, $\text{Na}_2\text{O}=0.1$, $\text{MgO}=0.16$, $\text{TiO}_2=1.1$. The specific surface area of the MK was measured to be $14658 \text{ m}^2/\text{kg}$.

The mix proportioning of the raw materials, as shown in Table 7-1, was carried out by mass. The aggregate's mass shown in Table 7-1 is in SSD condition. G20 and G21 mixes are two commercial geopolymer concretes supplied by Wagners; Earth Friendly Concrete (EFC). A blend of GGBFS and fly ash is used in EFCs but, for confidentiality reasons, their proportion, provenance and chemical composition cannot be provided.

Table 7-1: OPC and geopolymer concrete mix designs [kg/m³]

Materials	OPCC1	OPCC2	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10	G11	G12	G13	G14	G15	G16	G17	G18	G19
20 mm aggregate	0	681	613	613	613	613	613	613	613	598	673	673	668	660	660	627	637	0	0	661	629
10 mm aggregate	1221	389	350	350	350	350	350	350	350	341	384	384	382	377	377	358	364	1220	1220	378	359
Crushed sand	0	584	525	525	525	525	525	525	525	512	577	577	572	566	566	538	540	0	0	567	539
River sand	0	292	262	262	262	262	262	262	262	256	288	288	287	283	283	269	273	620	620	284	270
Sydney sand	621	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Eraring FA	0	0	400	360	280	260	260	260	260	0	0	0	0	0	0	0	0	0	0	0	0
Callide FA	0	0	0	0	80	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Gladstone FA	0	0	0	0	0	80	80	80	80	425	410	307	205	103	0	114	114	205	182	0	0
ASMS GGBFS	0	0	0	40	40	60	60	60	60	0	0	103	205	307	410	341	341	205	273	0	0
ECOCCEM GGBFS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	320	0
Metakaolin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	350
Portland cement	388	410	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NaOH pellets	0	0	20.6	20.6	20.6	20.6	18.5	16.5	18.5	25.1	11.4	11.4	5.2	5.2	5.2	3.4	3.4	6.5	4.4	9.6	9.8
Na-silicate	0	0	143	143	143	143	129	114	129	157	178	178	81	81	81	55.6	68	45.5	68	9.6	261
Free water	175	184.5	50.1	50.1	50.1	50.1	58.1	66.1	64.3	35.0	48.2	48.2	135.5	157.4	157.4	188	167	138	147	145	47.7
MR ¹ (SiO ₂ /Na ₂ O)	N.A.	N.A.	1.15	1.15	1.15	1.15	1.15	1.15	1.15	1.10	1.5	1.5	1.5	1.5	1.5	1.5	1.6	1.15	1.5	0.32	1.67
SiO ₂ + Na ₂ O/Binder ²	N.A.	N.A.	0.21	0.21	0.21	0.21	0.19	0.17	0.19	0.22	0.22	0.22	0.1	0.1	0.1	0.06	0.07	0.06	0.08	0.04	0.36
Water ³ /Solid ⁴	0.45	0.45	0.27	0.27	0.27	0.27	0.27	0.27	0.28	0.24	0.30	0.30	0.40	0.45	0.45	0.45	0.42	0.37	0.38	0.45	0.41
GGBFS content [%]	N.A.	N.A.	0	10	10	15	15	15	15	0	0	25	50	75	100	75	75	50	60	100	N.A.
Curing temperature [°C]	23	23	75	75	75	75	75	75	75	23	23	23	23	23	23	23	23	23	23	23	23
	(water)	(water)																			
Heat-curing duration [h]	N.A.	N.A.	18	18	18	18	18	18	18	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.

¹ Molar ratio of the alkaline solution² Binder = fly ash (FA) + GGBFS³ Water = free water + water in Na-silicate solution⁴ Solid = Binder + dissolved components of Na-silicate solution (i.e. SiO₂ and Na₂O) + NaOH pellets⁵ G20 and G21 mixes are commercially provided geopolymer concretes (from an Australian supplier) and their composition is unknown to the authors.

7.3 Chloride diffusion coefficients

The chloride diffusion coefficient of OPCCs and GPCs is measured using the ASTM C1556 method. The chloride profiles of are shown in Figure 7-1 and Figure 7-2.

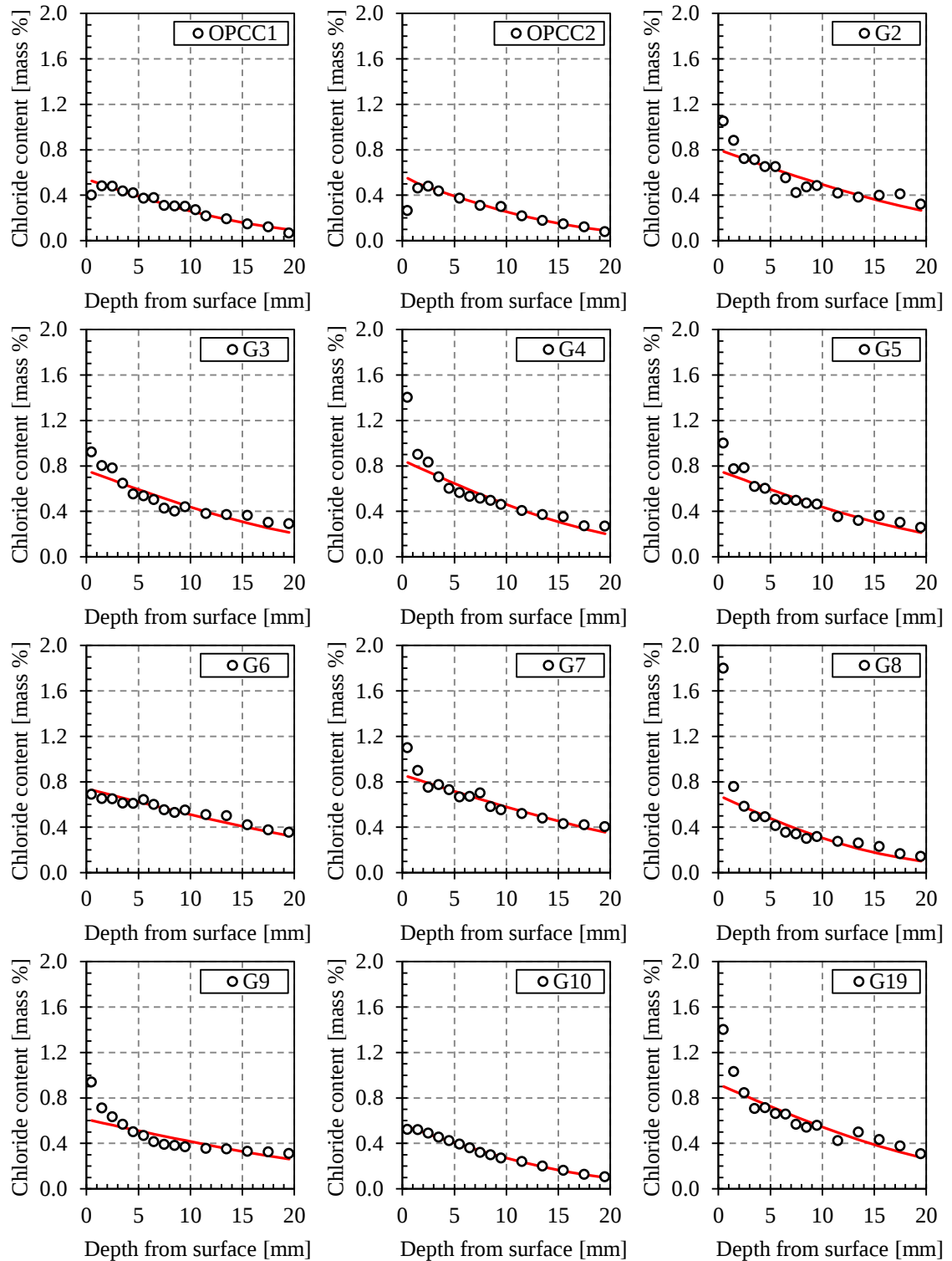


Figure 7-1: Chloride profiles of OPCCs and low calcium content GPCs

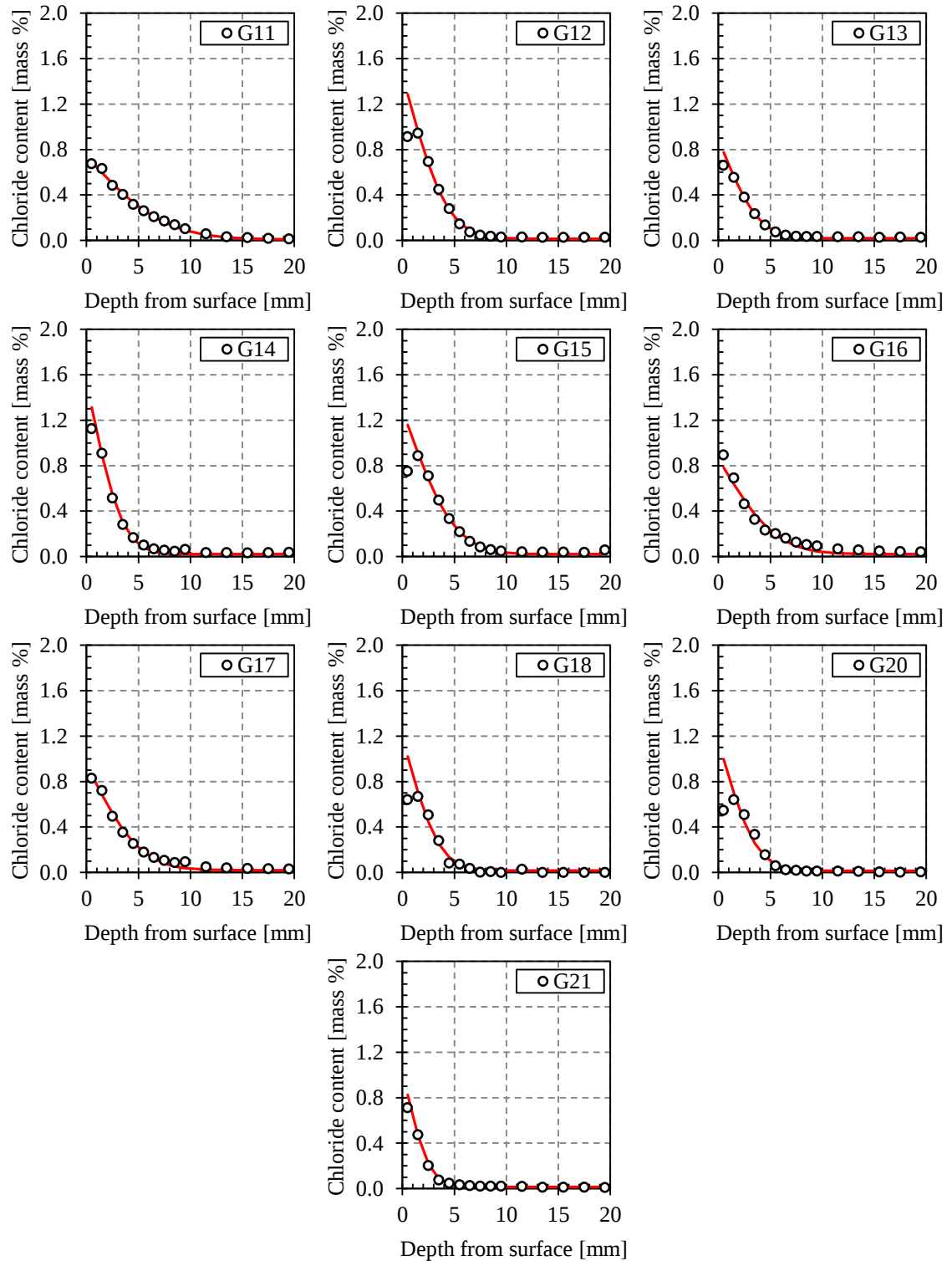


Figure 7-2: Chloride profiles of high calcium content GPCs after 35 days in 16.5% NaCl solution

The apparent chloride diffusion coefficients deduce from the chloride profiles are summarised in Table 7-2 for all concretes. All fly ash based GPCs and fly ash/slag blend GPCs with more than 75% fly ash and the metakaolin based GPC demonstrated a very low resistance to chloride diffusion with very high diffusion coefficients (i.e. $D_a >$

$27 \times 10^{-12} \text{ m}^2/\text{s}$). The chloride diffusion resistance of GPCs was significantly increased by increasing the GGBFS content in the mix. The lowest chloride diffusion coefficients were observed for mixes with more than 75% GGBFS.

Table 7-2: Chloride diffusion coefficient of GPCs and OPCCs after 35 days in saline solution

Mix designation	C_i [%]	C_s [%]	D_a [$\times 10^{-12}$ m^2/s]	Sum of squares [Mass%]
OPCC1	0.014	0.54	31.30	0.0044
OPCC2	0.015	0.55	28.81	0.0015
G2	0.016	0.80	63.53	0.0631
G3	0.019	0.76	50.25	0.0542
G4	0.017	0.85	42.39	0.0414
G5	0.015	0.76	50.70	0.0349
G6	0.016	0.74	99.98	0.0150
G7	0.015	0.86	89.59	0.0196
G8	0.018	0.68	27.02	0.0425
G9	0.015	0.61	93.81	0.0556
G10	0.014	0.56	31.30	0.0007
G11	0.010	0.74	5.77	0.0030
G12	0.015	1.46	1.83	0.0022
G13	0.019	0.89	1.48	0.0007
G14	0.022	1.54	1.15	0.0060
G15	0.021	1.29	2.47	0.0038
G16	0.022	0.86	3.11	0.0179
G17	0.020	0.95	2.7	0.0088
G18	0.016	1.19	12.45	0.0108
G19	0.017	0.92	55.10	0.0634
G20	0.015	1.16	12.95	0.0146
G21	0.014	1.03	0.62	0.0011

7.4 Modified ASTM C1202 test

The ASTM C1202 standard method also refers to as Rapid Chloride Permeability Test (RCPT) using 60 V was deemed a failure for most of the geopolymer concretes. Indeed, due to safety concerns and to avoid overheating of the samples during the test, the RCPT test apparatus is designed to terminate the test if the current reaches 500 mA.

Since the ASTM C1202 standard test method was unable to measure the charges passed through most the geopolymer concrete samples due to their low resistivity, modifications to the standard test method is proposed. The voltage applied across the sample is reduced to 10 volts as opposed to the standard specification of 60 volts. Table 7-3 shows the results of modified RCPT test together with ASTM C1202 standard test results. All GPCs with more than 75% fly ash content (G1 to G10) and the Metakaolin-based GPC (G19) failed the standard ASTM C1202 test. The modified ASTM C1202 test was successfully completed for all GPCs and OPCCs.

Table 7-3: Charge passed using ASTM C1202 standard (60V) and modified (10V) methods

Mix designation	ASTM C1202 RCPT			Modified RCPT		
	Applied voltage [V]	Charge passed [Coulombs]	Chloride penetrability	Applied voltage [V]	Test duration [hours]	Charge passed [Coulombs]
OPCC1	60	4545	High	10	6	458
OPCC2	60	4563	High	10	6	460
G1	60	Failed	-	10	6	2706
G2	60	Failed	-	10	6	1191
G3	60	Failed	-	10	6	1066
G4	60	Failed	-	10	6	577
G5	60	Failed	-	10	6	876
G6	60	Failed	-	10	6	1114
G7	60	Failed	-	10	6	1025
G8	60	Failed	-	10	6	581
G9	60	Failed	-	10	6	2266
G10	60	Failed	-	10	6	1017
G11	60	2272	Medium	10	6	206
G12	60	1041	Low	10	6	146
G13	60	930	Very low	10	6	136
G14	60	965	Very low	10	6	101
G15	60	630	Very low	10	6	99
G16	60	520	Very low	10	6	74
G17	60	719	Very low	10	6	104
G18	60	219	Very low	10	6	31
G19	60	Failed	-	10	6	1363
G20	60	1575	Low	10	6	173
G21	60	511	Very low	10	6	60

7.5 Chloride migration coefficient

The chloride migration coefficient of the ambient and heat cured GPCs along with the applied test voltage and duration are presented in Table 7-4. For the chloride migration coefficient calculation, the chloride concentration at the colour change boundary of GPCs was measured using He et al. (2011) proposed model and the pore solution hydroxyl concentration as suggested by Ismail et al. (2013b) as detailed in section 5.4.

Table 7-4: Chloride migration coefficient of OPCCs and GPCs

Mix	GGBFS/FA	Curing	Voltage [V]	Duration [h]	Migration coefficient [$\times 10^{-12} \text{ m}^2/\text{s}$]
OPCC1	100% OPC	Water	10	24	21.7
OPCC2	100% OPC	Water	10	24	18.6
G1	0/100	75°C-18h	10	24	78.9
G2	10/90	75°C-18h	10	24	70.2
G3	10/90	75°C-18h	10	24	58.2
G4	15/85	75°C-18h	10	24	54.8
G5	15/85	75°C-18h	10	24	63.2
G6	15/85	75°C-18h	10	24	71.1
G7	15/85	75°C-18h	10	24	55.7
G8	0/100	Ambient	10	24	62.2
G9	0/100	Ambient	10	6	153.0
G10	25/75	Ambient	10	24	33.0
G11	50/50	Ambient	30	24	4.4
G12	75/25	Ambient	60	24	1.5
G13	100/0	Ambient	60	24	1.5
G14	75/25	Ambient	60	30	1.0
G15	75/25	Ambient	50	24	0.7
G16	50/50	Ambient	60	24	0.7
G17	60/40	Ambient	50	24	1.8
G18	100/0	Ambient	60	48	0.6
G19	100% MK	Ambient	10	24	79.7
G20	Unknown	Ambient	40	24	1.8
G21	Unknown	Ambient	60	24	1.7

7.6 Performance-based specifications for durability design in marine environments

7.6.1 General

This section provides the minimum requirements for durability in marine environments. The recommendations are largely performance-based in that the required functional properties of the concrete are specified (including compressive strength) and limitations on concrete mix design or restrictions on binder type are not given. Given that geopolymer concrete does not have the same lengthy track record as Portland cement-based concrete, there are some uncertainties regarding long-term behaviour. With

ongoing research and practical experience with geopolymer concrete uncertainties will be resolved. Hence, this specification is viewed as a starting point and will be subject to revision as more information becomes available.

The requirements apply to steel reinforced and prestressed geopolymer concrete structures and members. The primary objective of this section is to provide guidance to enable engineers to conservatively specify geopolymer concrete for use in structures with a design life up to 50 years.

The procedure proposed is firstly to classify the severity of the environment to which the concrete surfaces are exposed to. For that exposure classification, a minimum geopolymer concrete performance is specified in terms of both minimum strength and resistance against chloride diffusion, and, a minimum concrete cover is then required. The basic principle is that where corrosion of the reinforcement, once initiated, is likely to be fast, higher levels of protection are required. More severe environments require increasingly better protection, and this is reflected by the requirement for better quality concrete and larger covers.

7.6.2 Exposure classifications

Exposure classification from the Australian Standard for design of concrete structures AS3600-2009 is used. AS3600-2009 specifies four exposure classifications involving chloride contamination, namely B1, B2, C1 and C2. Exposure classification B1 is applicable to near-coastal (1 km to 50 km from coastline) areas. Exposure classification B2 is for coastal zones within 1 km of the shoreline of large expanses of saltwater and for the permanently submerged surfaces of maritime structures in sea water. Exposure C1 and C2 are applicable to the surface of maritime structures in contact with sea water. Exposure classification C1 is for surfaces of maritime structures in spray zone (the zone from 1 m above wave crest level). The exposure classification C2 is for the surfaces of maritime structures in tidal/splash zone (the tidal/splash zone is directly below the spray zone and includes the zone 1 metre below the lowest astronomical tide (LAT) and up to 1 metre above the highest astronomical tide (HAT) on vertical structures, and all exposed soffits of horizontal structures over the sea (extracted from AS3600-2009 Table 4.3).

7.6.3 Minimum strength requirements

The performance-based specifications aim to assist engineers to specify in confidence geopolymer concrete. Even if the correlation between 28 days compressive strength of GPCs and their resistance to chloride diffusion is poor (refer to Figure 7-3) and should not be used as the only requirement to design for durability, strength remains a core aspect of almost all standards and so cannot be neglected. As a result, for members subject to exposure classifications B1, B2, C1 and C2, a minimum average compressive strength at 28 days is required for concrete as specified in Table 7-5.

Table 7-5: Required minimum 28 days average compressive strength for durability

Exposure classification	Minimum strength (MPa)
B1	35
B2	40
C1	40
C2	40

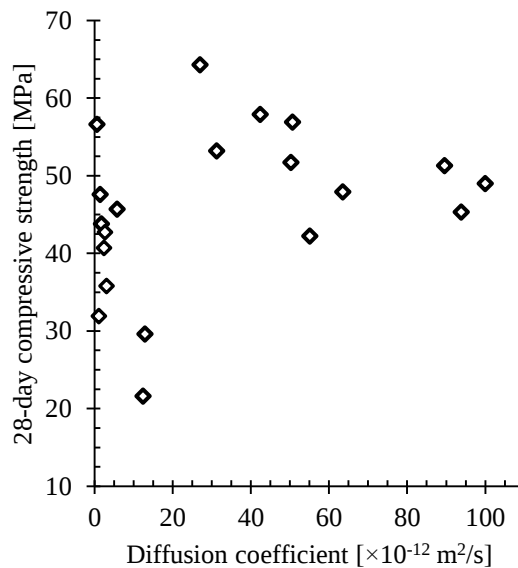


Figure 7-3: correlation between 28-day compressive strength and chloride diffusion coefficient of GPCs

7.6.4 Performance-based specifications using modified ASTM C1202 and ASTM C1556

The charges passing through the tested samples measured by using the modified ASTM C1202 test method proposed in section 5.3 is plotted against chloride diffusion coefficient in Figure 7-4 for all GPCs regardless their average compressive strength. Some additional test results obtained on several heat-cured low calcium fly ash geopolymers studied in section 5.3 were added as well. Overall, it is evident that a

minimum of 50% GGBFS content is required to achieve an acceptable resistance against chloride diffusion according to the tests carried out. Indeed, all GPCs with 50% GGBFS content or more performed much better than the OPC concretes (OPCC1 and OPCC2). It is worth noting that OPC mix design OPCC1 and OPCC2 achieved 4545 and 4563 Coulombs respectively using standard ASTM C1202 (using 60V) which categorises them as high chloride penetrability concretes according to ASTM C1202 classification (>4000 Coulombs).

Despite the existing concerns over the reliability of ASTM C1202 method to determine the chloride resistance of geopolymer concrete, a relatively good correlation ($R^2 = 0.81$) between charges passed and chloride diffusion coefficient of GPCs has been found in this study.

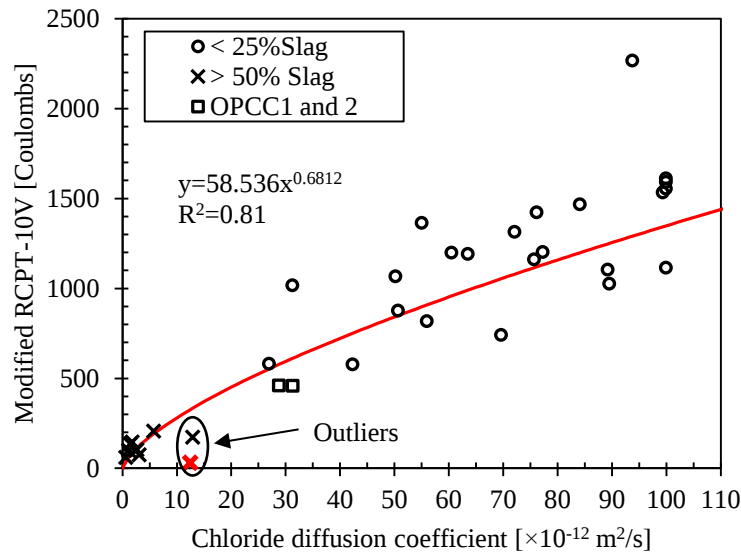


Figure 7-4: Correlations between total charge passing and chloride diffusion coefficient of GPCs regardless the compressive strength

Figure 7-5 shows the same results after eliminating concretes not achieving the minimum average compressive strength of 35 MPa (B1 exposure) which is the minimum strength for concrete exposed to marine environments according to Table 7-5. Minimum strength requirements allow to eliminate the outliers (see Figure 7-4) having low charges passing (modified ASTM C1202 test method), but higher chloride diffusion coefficient compared to other GPCs having a similar performance according to modified ASTM C1202. The elimination of test results associated with low strength GPCs improves the correlation between the RCPT and chloride diffusion coefficient as

noted by a higher $R^2=0.94$ as presented in Figure 7-5 as opposed to 0.81 showed in Figure 7-4.

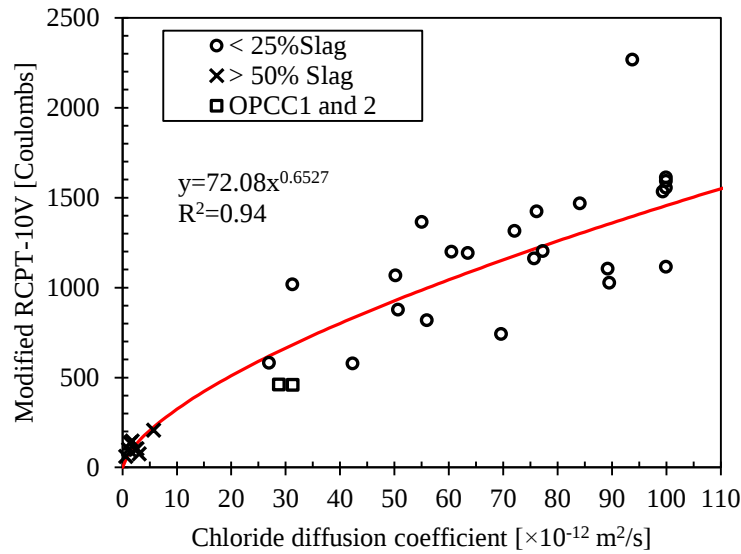


Figure 7-5: Correlations between total charge passing and chloride diffusion coefficient of GPCs after eliminating the mix designs not complying with compressive strength requirements

To calibrate both modified ASTM C1202 and ASTM C1556 performance-based requirements for GPCs for each exposure classification, appropriate reference concretes were selected based on experimental results available in the literature (Bjegovic et al. 2012; Maes et al. 2013; Tang and Sørensen 2001). Reference concretes were blended cement or Portland cement-based concretes tested in accordance to the standard ASTM C1556. Table 7-6 provides information on the binder composition, compressive strength when available and the chloride diffusion coefficient. In (Tang and Sørensen 2001), round-robin test results were reported involving several laboratories. As a result, a range of chloride diffusion coefficient values are provided in Table 7-6 for each concrete tested. Table 7-6 highlights the influence of SCMs content in improving the concrete resistance against chloride diffusion. Best performance is attributed to the mixes with 50% to 70% GGBFS or with 8% silica fume. Concretes without SCMs achieve chloride diffusion coefficients ranging between 8.1 and 34.0 ($\times 10^{-12} \text{ m}^2/\text{s}$), having compressive strengths ranging from 56 MPa to 63 MPa which is consistent with the performance of mixes OPCC1 and OPCC2.

Table 7-6: Binder composition, compressive strength and chloride diffusion coefficient of the reference concretes

Binder type	Concrete Mixes							
	M1 ¹	M2 ¹	OPC ²	BFS50 ²	BFS70 ²	Mix A ³	Mix B ³	Mix C ³
OPC (%)	100	65	100	50	30	92	100	30
GGBFS (%)	-	12	-	50	70	-	-	70
Fly ash (%)	-	18	-	-	-	-	-	-
Silica fume (%)	-	-	-	-	-	8	-	-
Limestone (%)	-	5	-	-	-	-	-	-
Total SCM, %	0	35	0	50	70	8	0	70
f_{c28} (MPa)	56	48	N/A	N/A	N/A	83	63	45
D_a ($\times 10^{-12} \text{m}^2/\text{s}$)	26.0	10.0	13.2	4.6	5.9	2.4 to 6.4	8.1 to 34	1.7 to 2.5

¹(Bjegovic et al. 2012) ²(Maes et al. 2013) ³(Tang and Sørensen 2001)

Based on the reference concretes performance presented in Table 7-6 and aiming to conservatively specify GPCs, performance-based requirements were defined for GPCs according to the standard ASTM C1556 bulk chloride diffusion test results obtained as follows:

- For extremely severe environments C1 and C2, the minimum required performance is a chloride diffusion coefficient inferior to $3 (\times 10^{-12} \text{m}^2/\text{s})$.
- For exposure classification B2, the minimum required performance is $6 (\times 10^{-12} \text{m}^2/\text{s})$.
- For exposure classification B1, performance requirement is set at $14 (\times 10^{-12} \text{m}^2/\text{s})$.
- GPCs with a chloride diffusion coefficient superior to $14 (\times 10^{-12} \text{m}^2/\text{s})$ should not be used in chloride environments.

The calibration of the performance-based requirements for modified ASTM C1202 test method for GPCs is presented in Figure 7-6. Figure 7-6 shows the same results as the ones already presented in Figure 7-5 but focusing on concretes with a suitable performance to be used in chloride environments. OPCC1 and OPCC2 are displayed as well in Figure 7-6. Modified ASTM C1202 performance-based requirements are defined based on both experimental results obtained in this study and the above proposed chloride diffusion coefficient requirement defined for standard ASTM C1556 test, as follows:

- For extremely severe environments C1 and C2, the maximum charges passed should be less than 120 Coulombs.
- For exposure classification B2, the required performance is 220 Coulombs.

- For exposure classification B1, performance requirement is set at 350 Coulombs.
- GPCs with charges passed superior to 350 Coulombs should not be used in chloride environments.

Table 7-7 summarises the performance-based requirements for both testing methods and all exposure classifications. It is acknowledged that the values proposed in Table 7-7 were calibrated using a limited number of experimental results involving almost only materials sourced in Australia. It is a baseline for future works involving international contributors to assess the suitability of the proposed requirements for non-Australian GPCs. This specification is viewed as a starting point and will be subject to revision as more information becomes available.

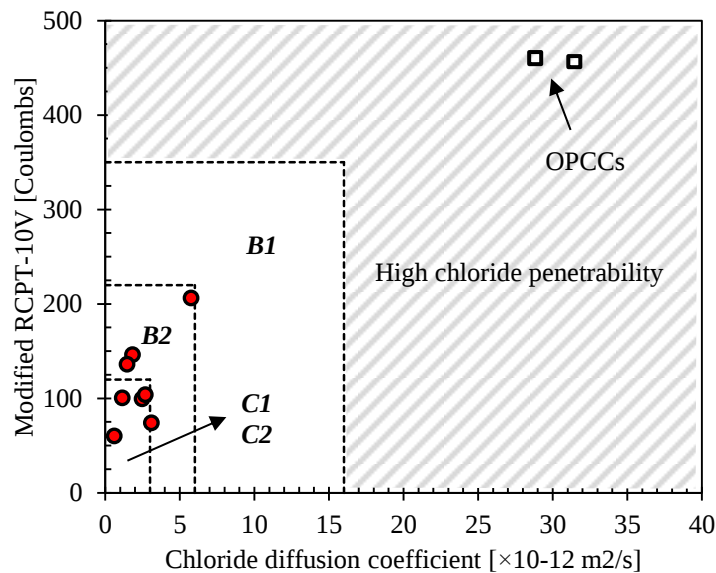


Figure 7-6: Calibration of the performance-based requirements for modified ASTM C1202 test method based on the new standard ASTM C1556 performance-based requirements proposed for GPCs

Table 7-7: Performance-based requirements for geopolymer concrete in chloride environments using modified RCPT and chloride diffusion coefficient

Exposure classification (as per AS 3600-2009)	Charge passed modified ASTM C1202* [coulombs]	Chloride diffusion coefficient ASTM C1556 [$\times 10^{-12} \text{ m}^2/\text{s}$]	chloride penetrability
-	≥ 350	≥ 16.0	High
B1	< 350	< 16.0	Medium
B2	< 220	< 6.0	Low
C1 and C2	< 120	< 3.0	Very Low

* Modified ASTM C1202: applied voltage 10 V, test duration 6 hours.

Equation (7-1) is proposed to estimate the chloride diffusion coefficients (ASTM C1556) of GPCs using results from modified ASTM C1202 test (Figure 7-5). Equation (7-1) should only be used for charges passed lower than 350 Coulombs.

$$D_a = 72.08C^{0.6527} \quad (7-1)$$

where D_a is the diffusion coefficient in $\times 10^{-12} \text{ m}^2/\text{s}$ and C is the charge passed using modified ASTM C1202 (10V) in Coulombs.

7.6.5 Performance-based specifications using NT BUILD 492 and ASTM C1556

The chloride migration coefficient measured using the NT BUILD 492 method is plotted against chloride diffusion coefficient in Figure 7-7 for all GPCs regardless of their average compressive strength. Some additional test results obtained on several heat-cured low calcium fly ash geopolymers studied in section 5.4 were added as well.

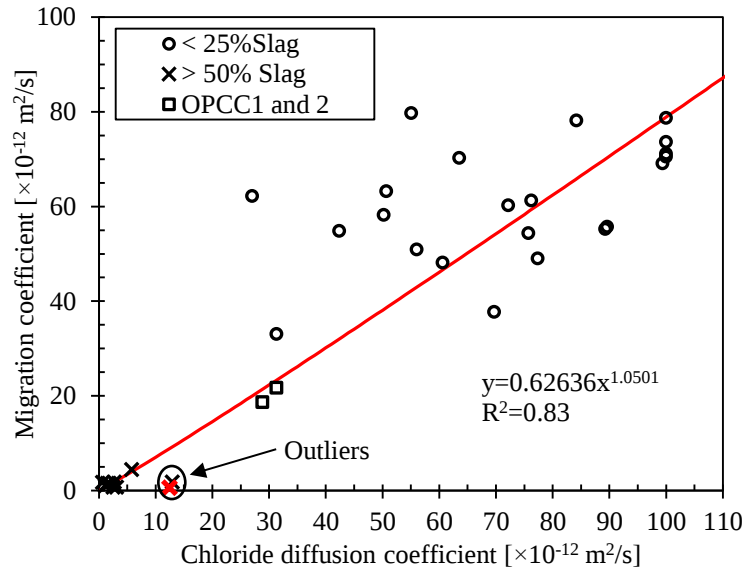


Figure 7-7: Correlations between chloride migration and diffusion coefficients of GPCs regardless of the compressive strength

Figure 7-8 shows the same results after eliminating concretes not achieving the minimum average compressive strength of 35 MPa (B1 exposure) which is the minimum strength for concrete exposed to marine environments according to Table 7-5. Minimum strength requirements allow to eliminate the outliers (see Figure 7-7) having low migration coefficients but higher chloride diffusion coefficient compared to other GPCs. The elimination of test results associated with low strength GPCs improves the correlation between the chloride migration and chloride diffusion coefficients as noted by a higher $R^2=0.92$ as presented in Figure 7-8 as opposed to 0.83 showed in Figure 7-7.

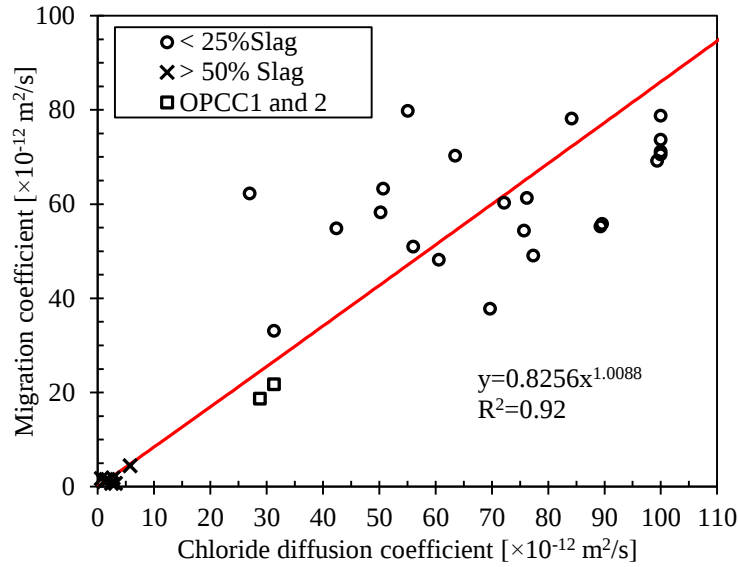


Figure 7-8: Correlations between chloride migration and diffusion coefficients of GPCs after eliminating the mix designs not complying with compressive strength requirements

The calibration of the performance-based requirements for NT BUILD 492 test method for GPCs is presented in Figure 7-9. Figure 7-9 shows the same results as the ones already presented in Figure 7-8 but focusing on concretes with a suitable performance to be used in chloride environments. OPCC1 and OPCC2 are displayed as well in Figure 7-9. The NT BUILD 492 performance-based requirements are defined based on both experimental results obtained in this study and the chloride diffusion coefficient requirement proposed in section 7.6.4, as follows:

- For extremely severe environments C1 and C2, the maximum chloride migration coefficient should be less than $2.5 \times 10^{-12} \text{ m}^2/\text{s}$.
- For exposure classification B2, the required performance is $5 \times 10^{-12} \text{ m}^2/\text{s}$.
- For exposure classification B1, performance requirement is set at $13.5 \times 10^{-12} \text{ m}^2/\text{s}$.
- GPCs with chloride migration coefficient superior to $13.5 \times 10^{-12} \text{ m}^2/\text{s}$ should not be used in chloride environments.

Table 7-8 summarises the performance-based requirements for both testing methods and all exposure classifications. As stated in section 6.6.4 it is acknowledged that the values proposed in Table 7-8 were calibrated using a limited number of experimental data and should be viewed as a starting point and are subjected to revision as more information becomes available.

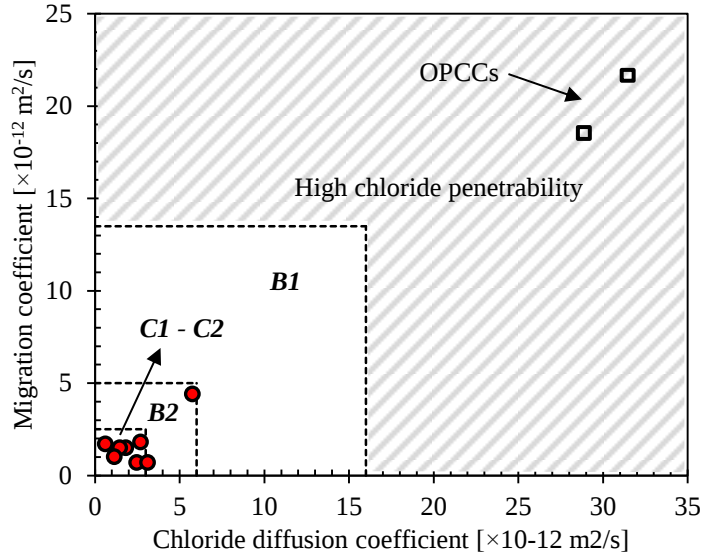


Figure 7-9: Calibration of the performance-based requirements for NT BUILD 492 test method based on the standard ASTM C1556 performance-based requirements proposed for GPCs

Table 7-8: Performance-based requirements for geopolymer concrete in chloride environments using chloride migration and diffusion coefficients

Exposure classification (as per AS 3600-2009)	Chloride migration Coefficient (NT BUILD 492) [$\times 10^{-12} \text{ m}^2/\text{s}$]	Chloride diffusion coefficient (ASTM C1556) [$\times 10^{-12} \text{ m}^2/\text{s}$]	chloride penetrability
-	≥ 13.5	≥ 16.0	High
B1	< 13.5	< 16.0	Medium
B2	< 5.0	< 6.0	Low
C1 and C2	< 2.5	< 3.0	Very Low

* Modified ASTM C1202: applied voltage 10 V, test duration 6 hours.

Equation (7-2) is proposed to estimate the chloride diffusion coefficients (ASTM C1556) of GPCs from the chloride migration coefficient test data.

$$D_a = 0.8256 D_{nssm}^{1.0088} \quad (7-2)$$

where D_a is the diffusion coefficient in $\times 10^{-12} \text{ m}^2/\text{s}$ and D_{nssm} is the chloride migration coefficient in $\times 10^{-12} \text{ m}^2/\text{s}$.

7.7 Conclusion

The following conclusions are drawn from this chapter:

- The ASTM C1202 standard test method (RCPT) failed to measure the charges passed through most of the GPCs tested. A modified version of RCPT using 10 V (as opposed to 60 V specified by standard ASTM C1202) successfully measured the charges passed through all GPC samples using a wide range of binders. A good

correlation was observed between modified ASTM C1202 and Standard ASTM C1556 chloride diffusion test results.

- The NT BUILD 492 standard chloride migration test appears to be a suitable method to evaluate the chloride penetration in GPCs of various binders and demonstrated a good correlation with the chloride diffusion coefficient. Care should be exercised when using standard formulation proposed in Nordtest method to calculate the migration coefficient of OPC based concretes. The chloride concentration at the colour change boundary suggested in NT BUILD 492 should be calibrated for the chemistry of the pore solution of geopolymer concrete.
- Performance-based recommendations are proposed for GPCs in marine environment. Both experimental results from this study and appropriate reference concretes from the literature were used to calibrate the modified ASTM C1202 chloride penetrability categorisation and chloride migration coefficient for GPCs. Guidance required to enable engineers to conservatively specify geopolymer concrete for use in structures exposed to chloride environments with a design life of 50 years is proposed.

Summary and Conclusions

8 SUMMARY AND CONCLUSIONS

8.1 Concluding remarks

The chloride diffusion and carbonation which are the main durability concerns for reinforced concrete structures have been extensively investigated for geopolymer concretes. The evaluation of transport properties and diffusion mechanism in geopolymer binders are more complicated as opposed to Portland cement based systems due to the high dependency of properties of the final product on raw material characteristics, compositional parameters and applied curing regime.

The examination of geopolymer mix parameters showed that the increase in alkali content of the alkaline solutions leads to the development of more homogeneous binders due to the higher rate of dissolution of aluminosilicate precursors. A higher dissolution rate, suggests the availability of more aluminate and silicate species which can be incorporated into the matrix and results in a higher Si/Al ratios. Increasing the geopolymer formation at higher silicate contents was attributed to the enhancement of depolymerisation of Si-O-Si and Si-O-Al bonds. Higher Si/Al ratio of the matrix is indicative of the formation of more porous geopolymer gel (as in fly ash based geopolymers) as a result, increasing the alkali content or the soluble silicate content leads to an increase in mesopore volume. Apart from affecting the pore structure development of the aluminosilicate networks, the alkalinity of the alkaline solution can also hinder or promote the formation of calcium silicate hydrates when there is calcium (as in slag based geopolymers) in the matrix.

The effect of thermal curing and calcium content on mechanical, transport properties, chloride diffusion and microstructural characteristics of various GPCs were investigated. The thermal curing not only has no detrimental effect on the long term compressive strength of low calcium content GPCs, but densifies the geopolymer matrix leading to fewer cavities and voids and reducing the water sorption rate. This is due to the higher degree of dissolution of aluminosilicate sources at higher temperature as proved by the microstructural analysis. Although thermal curing is the preferred curing method for fly ash based GPCs due to the slow rate of strength gain at ambient temperature, it is possible to produce high strength (>50 MPa at 28 days) ambient cured

GPCs by blending fly ash with GGBFS. A critical slag content of 25% of the binder mass has been identified as an optimal blend.

Although an increasing trend in chloride diffusion resistance of fly ash based GPCs has been observed by applying proper thermal curing, all the studied GPCs with less than 25% GGBFS content demonstrated very high chloride diffusion coefficient in excess of $40 \times 10^{-12} \text{ m}^2/\text{s}$. The pore structure of low calcium content geopolymers is characterised by an almost uniformly distributed volume of pores over the whole mesopore (2 nm – 50 nm) and macropore (> 50 nm) ranges. The highly porous microstructure and well-interconnected pore network of fly ash based geopolymers reduces the chloride diffusion resistance and makes this type of GPCs unsuitable for marine environment.

Calcium content plays a significant role on the durability performance and microstructure of the GPCs. Geopolymers with little or no calcium content are highly porous. On the other hand, the geopolymers with considerable amount of calcium show a very fine pore structure with size smaller than ~16 nm or less in diameter, with a relative lack of pores larger than 20 nm in the whole meso and macropore range. This particular pore size distribution leads to considerable pore-blocking effect. The remarkable shift in chloride diffusion/migration coefficient is achieved for the GPC including 50% slag content. The high calcium content GPCs with more than 50% GGBFS content demonstrated chloride diffusion coefficients of up to several orders of magnitude lower than their fly ash based counterparts. The low permeability of calcium rich GPCs along with the high tortuosity of the pore structure measured through the water sorption test resulted in exceptional chloride diffusion resistance. Calcium plays prominent role in reducing the chloride diffusivity and increasing the durability of GPCs in marine environment.

Unlike Portland cement based systems, acid and water soluble chloride measurements and XRD analysis demonstrated no chloride binding capacity and crystalline chloride component formation (e.g. Friedel's salt) for geopolymer binders of low and high calcium content. Since it appears to be no chloride chemical binding capacity in GPCs, the chloride diffusion resistance in geopolymer binder system is only related to the pore structure, pore network tortuosity and physical binding and encapsulation of chloride ions.

The accelerated chloride migration and chloride penetrability tests were examined for various GPCs. The standard ASTM C1202 RCPT was unable to measure the charge passed through the low calcium content GPCs due to low resistivity of the pore solution. A modified version of RCPT using 10 V (as opposed to 60 V specified by standard ASTM C1202) successfully measured the charges passed through all GPC samples using a wide range of binders. A relatively good correlation was observed between modified ASTM C1202 and chloride diffusion coefficients measured according to ASTM C1556. The NT BUILD 492 standard chloride migration test appears to be a suitable method to evaluate chloride penetration in GPCs of various binders and demonstrated a good correlation with the chloride diffusion coefficient. However, the chloride concentration at the colour change boundary suggested in Nordtest method should be calibrated for the chemistry of the pore solution of geopolymer concrete.

The pH of hardened uncarbonated geopolymer concrete can range between 12.2 and 13.4. The pH is increasing by GGBFS addition to the mix. The pH of carbonated GPCs is ranging between 10.8 and 11.7. The pH of carbonated high calcium content GPCs is higher than that of low calcium content GPCs. All ambient cured GPCs of low and high calcium content provided a much higher carbonation rate as opposed to OPCC. However, the pH of the fully carbonated GPCs was always more than 10.8 that may still be high enough to sustain the passivity of steel reinforcement and avoid carbonation induced corrosion.

It appears that 6 weeks exposure at 1% CO₂ reproduces a similar carbonation penetration front as of natural carbonation for fly ash based GPCs with no GGBFS content. This is similar to fly ash based GPCs with 10% GGBFS content as reported by Khan et al. (2017b). For GPCs with 25% and 50% GGBFS content, 2 weeks accelerated carbonation reproduced 6 months natural carbonation. It is estimated that 1 week exposure at 1% CO₂ replicates 6 months natural carbonation for GPCs with more than 75% GGBFS content. However, the later requires validation through further experimental testing.

Performance-based recommendations are proposed for geopolymer concretes in marine environment. The modified ASTM C1202 chloride penetrability categorisation and chloride migration coefficients were calibrated to suit GPCs. The established criteria can be used for durability assessment of GPCs.

8.2 Future works

The following recommendations can be made towards future research;

A comparative study of various Australian fly ash sources linking their distinct chemical characteristic to durability and long term performance of the resulting GPC would be invaluable.

The chloride diffusion resistance of GPCs with moderate range of calcium content (i.e. GGBFS content between 25% and 75%) is not sufficiently studied in this dissertation and can be explored further.

The suitability of slag based GPCs for precast application and the effect of thermal curing on microstructure, mechanical performance and chloride diffusion resistance of high calcium content GPCs is of interest and remains to be explored.

The chloride concentration at the colour change boundary of the silver nitrate calorimetric measurement requires experimental investigations in order establish accurate C_d values to use for chloride migration coefficient calculation.

The correlation between accelerated chloride penetration/migration tests and chloride diffusion coefficients are established based on limited number of experimental data. A broader database is required to assess the validity of the proposed correlations and to further calibrated the relationships.

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