

Corrosion of reinforcement In alkali-activated materials

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CORROSION OF REINFORCEMENT IN ALKALI-ACTIVATED MATERIALS

by

Seyed Mahdi Babaee

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy



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

February 2018

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The increasing demand for sustainable concretes has promoted the development of a category of alternative binders called alkali-activated binders, including materials described as geopolymers, which are produced by the reaction of solid precursors such as fly ash, slag, and metakaolin with alkaline solutions. As buildings and infrastructures are ageing nowadays, the durability aspects of concrete have become more important than in the past, and despite the acceptable mechanical properties of alkali-activated concretes, there are some concerns over their durability and service life as they were brought into service very recently.

This dissertation aims to investigate various influential parameters involved in the initiation and propagation phases of corrosion of reinforcements in alkali-activated materials, as one of the main causes of deterioration of the concrete structures. Moisture transport, which influences several other corrosion-related properties such as the electrical resistivity and the oxygen diffusivity after depassivation of the reinforcement, is investigated for a range of representative samples. Water-vapour-sorption-isotherms were investigated and valuable insights into the pore structure of alkali-activated binders were obtained. The sorption kinetics was studied and the contribution of the non-Fickian sorption process was assessed for both aluminosilicate-dominated and calcium-rich binders. A systematic study of the effect of alkali, calcium, and silicate content on the apparent chloride diffusion coefficients and chloride threshold values of a wide range of alkali-activated mixes were conducted and the results were interpreted in light of the nano and microstructural properties. Applicability of the electrochemical test methods conventionally developed and used for Portland cement-based concretes was assessed for low calcium alkali-activated concretes, and the chloride-induced corrosion propagation phase was studied. The effect of alkali concentration in the activator, and the carbon dioxide concentration on the pH drop and passivity of the reinforcement were investigated by modeling the adsorption of carbon dioxide into an aqueous NaOH solution, as representative of the pore solution, and the results were validated against the experimental observations. Finally, the alkali cation leaching which can lead to the loss of alkalinity was also evaluated for a range of alkali-activated samples.

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Firstly, I wish to express my sincerest gratitude and appreciation to my supervisor, Associate Professor Arnaud Castel, for his supervision, strong supports and encouragements throughout this doctorate. His vast expertise in the field of concrete durability and his impeccable work ethics has been a continuous inspiration during my research. It has been a privilege studying under his supervision. I also would like to extend my gratitude to my co-supervisor, Dr Hamid Valipour, for his thoughtful guidance and unlimited supports.

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Above all, I would like to dedicate this dissertation to my beloved wife Zahra– without your supports, encouragements, constant optimism and belief in my abilities this dissertation would not have been accomplished- and also to my parents - I am forever

in debt for all the sacrifices you have made, without you I wouldn't be able to come this far.

ABSTRACT

The increasing demand for sustainable concretes has promoted the development of a category of alternative binders called alkali-activated binders, including materials described as geopolymers, which are produced by the reaction of solid precursors such as fly ash, slag, and metakaolin with alkaline solutions. As buildings and infrastructure are aging nowadays, the durability aspects of concrete have become more important than in the past, and despite the acceptable mechanical properties of alkali-activated concretes, there are some uncertainties about their durability and service life as they were brought into service very recently. This dissertation aims to investigate various influential parameters involved in the initiation and propagation phases of corrosion of reinforcement, as one of the main causes of deterioration of the concrete structures, in alkali-activated materials.

Analysis of Water-vapour-sorption-isotherms along with mercury intrusion porosimetry (MIP) test results revealed that the pore structure of low-calcium (aluminosilicatedominated) alkali-activated materials is comprised of a rather uniformly distributed volume of pores over the whole mesopore and macropore range. On the other hand, alkaliactivated slag binders have a significantly finer pore structure. Investigation of the sorption kinetics demonstrated a considerable contribution from non-Fickian (anomalous) sorption process, and the contribution factor was significantly higher for calcium-rich binders with finer pore structure, higher tortuosity and consequently lower permeability.

The effect of alkali, calcium, and silicate content on the apparent chloride diffusion coefficients and chloride threshold values were systematically studied. Increasing the slag content from 25% to 50% in blended fly ash and slag alkali-activated materials led to an

almost tenfold decrease in the apparent chloride diffusion coefficients, in agreement with the finer pore structure of calcium-rich binders. On the other hand, increasing the alkali content and silicate content led to higher chloride diffusivities, with the latter being more influential, in particular in aluminosilicate-dominated binders. Furthermore, chloride threshold of reinforced alkali-activated mortars were measured and values ranged between 0.19 (wt.% binder mass) for calcium-rich binders fabricated at low level of alkalinities (75% GGBS content, 3% Na₂O) and 0.69 for FA-dominated binders fabricated with highly alkaline activators (75% FA content, 8% Na₂O).

Applicability of the electrochemical test methods conventionally developed and used for Portland cement-based systems was assessed and the result suggested that some of the conventional classifications (e.g. half-cell potential or polarization resistance classifications) which commonly used to assess the severity/extent of corrosion might need some recalibration to be used for alkali-activated systems.

Effect of the alkali and carbon dioxide concentration on the pH drop and reinforcement passivity was investigated through experimental studies and analytical modelling and the results demonstrated the formation of bicarbonates over carbonates during the accelerated carbonation, leading to an increase in pH decline compared to natural condition. However, accelerated carbonation ($pCO_2=1\%$) did not lead to depassivation of reinforcement as pH of the carbonated low-calcium concrete remained at high levels.

Finally, the alkali cation leaching which can lead to the loss of alkalinity and efflorescence was evaluated. The prominent role of heat-curing in reducing the efflorescence was demonstrated. The sensitivity of the efflorescence severity to the mix composition was highlighted. The electrochemical investigations showed that alkali-leaching does not lead to depassivation of reinforcement as the presence of even low levels of alkalis is enough to provide a high pH and keep the reinforcements in passive condition.

PREFACE

This thesis is submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The University of New South Wales (UNSW), Sydney, Australia. The work described herein was performed by the candidate in the School of Civil and Environmental Engineering, UNSW. The candidate was supervised by Associate Professor Arnaud Castel during a period from August 2013 to August 2017. 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.

Journal publications

1- Babaee, M., and A. Castel, Water-vapour-sorption-isotherms, Pore Structure, and Moisture Transport Characteristics of Alkali-activated and Portland cement-based Binders, Cement and Concrete Research, accepted (Content of Chapter 3)

2- Babaee, M. and A. Castel, Chloride-induced corrosion of reinforcement in low-calcium fly ash-based geopolymer concrete. Cement and Concrete Research, 2016. 88:p. 96-107 (Content of Chapter 4)

3- Babaee, M. and A. Castel, Chloride Diffusivity, Chloride Threshold, and Corrosion Initiation in Reinforced Alkali-activated Mortars: Role of Calcium, Alkali, and Silicate Content, Cement and Concrete Research, accepted (Content of Chapter 5)

4- M. Babaee, M.S.H. Khan, A. Castel, Passivity of embedded reinforcement in carbonated low-calcium fly ash-based geopolymer concrete, Cem. Concr. Compos. 85 (2018) 32–43. (Content of Chapter 6)

5- A. Noushini, M. Babaee, A. Castel, Suitability of heat-cured low-calcium fly ashbased geopolymer concrete for precast applications, Mag. Concr. Res. (2015) 1–15.

Conference proceedings

1- Babaee, M. and Castel, A, The effect of alkali concentration and the binder composition on the alkali leaching in geopolymer binders, Concrete 2017 conference, Adelaide, Australia; accepted (Part of the content of Chapter 7)

2- Babaee, M. and Castel, A., Steel reinforcement corrosion in a low calcium fly ash geopolymer concrete, Key Engineering Materials, CONSEC 2016, Lecco, Italy, 12-14 September 2016, Volume 711, Pages 943-949.

3- M. Babaee, A. Castel (2015). Chloride induced corrosion of reinforcing bars in Geopolymer concrete, 27th biennial national conference of the concrete institute of Australia in Conjunction with the 69th RILEM week, Melbourne, Australia.

4- M. Babaee, A. Castel (2015). On the durability of steel reinforced geopolymer concrete in marine environments, International Conference on Geopolymers: the route to eliminate waste and emissions in ceramic and cement manufacturing; An ECI conference, Hernstein, Austria.

5- M. Babaee, A. Castel, Active steel corrosion in fly ash geopolymer concrete, 3rd
biennial conference of the Combined Australian Materials Societies (CAMS2014), 2628 November 2014, Sydney

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1.1. Introduction

Concrete is one of the most commonly used materials in the construction industry and the demand for it is increasing every day due to the need for new structures or ageing of existing structures. Although concrete is an attractive construction material in terms of structural performance, durability, and availability, the enormous amount of Ordinary Portland Cement (OPC) concrete used worldwide is one of the major sustainability concerns and contributes significantly to the environmental impacts of the construction and building industry; mainly due to the huge consumption of natural resources, energy and releasing as much as 6-7% of all greenhouse gases emitted worldwide during the production process [1-3].

As buildings and infrastructure are ageing nowadays, the durability aspects of concrete have become more important than in the past. Concrete structures can be prone to degradation and premature failure due to different durability issues such as corrosion of reinforcing bars which can lead to serious problems with millions of dollars spent for maintenance, repair or replacement of damaged structures. According to the ASCE 2013 Report Card, about \$3.6 trillion should be spent to maintain and rehabilitate the America's Infrastructure, which highlights the importance of durable concrete materials [4].

One of the main causes of shortening the service life of concrete structures is corrosion of the embedded reinforcement through either chloride contamination or carbonation. Chloride contamination usually takes place in tidal zones of marine environments or in highway bridges using the de-icing salts. Accumulation of chloride ions on the concrete-reinforcement interface leads to breaking down the passive layer formed around the reinforcement and eventually corrosion. In carbonation-induced corrosion, which is common in highly concentrated carbon dioxide environments such as in urban areas, carbonation of concrete provides an acidic environment leading to depassivation of reinforcement and consequently corrosion. Corrosion process is essentially an electrochemical process and its kinetic is highly dependent on the presence of moisture, oxygen and the electrical resistivity of the electrolyte (concrete here). Although there are some well-established electrochemical test methods to evaluate the corrosion rate which has been under development since almost 60 years ago, the inherent complexities associated with a multi-physics process in which different transfer mechanisms (Chloride, carbon dioxide, oxygen, moisture and charge transfer) are involved and interacting with each other has been a major obstacle to predict the service life of the structure based on experimental data or field observation.

While increasing the concrete durability is an effective way of decreasing the consumption of OPC and other required natural resources, replacement of OPC by other precursors to produce alternative binders can also reduce its consumption and associated environmental issues. Among all the available alternative binders, alkali-activated binders have a great development potential and are widely considered as a promising alternative for Portland cement binders from both scientific and commercial points of view [5,6]. Alkali-activated binders are produced by the reaction of solid precursors such as metakaolin, fly ash (FA), and ground granulated blast-furnace slag (GGBS) with an alkali metal hydroxide or silicate solution; and less carbon emission is attributed to their production [7]. Depending on the precursor used, the final products

can have considerably different nano/microstructures and properties. Alkali-activation of aluminosilicate sources such as metakaolin and FA results in an amorphous aluminosilicate network (also called geopolymer as first coined by Davidovits [8]). On the other hand, alkali activation of slag binders with a considerable amount of calcium in the matrix leads to the production of some form of calcium silicate hydrates with partial substitution of aluminium, also known as C-(A)-S-H [9–12]. Despite the considerable difference in the properties of the final product of materials fabricated of aluminosilicate sources or calcium-rich precursors, they are both called as alkaliactivated materials in this dissertation, and this nomenclature mostly refers to their production process where the application of an alkaline solution is an essential part. Having said that, whenever required during the detailed technical discussions in the main chapters, they are classified based on the properties of the final produced binder phase which can be a low-calcium aluminosilicate (or geopolymer-type¹) network in case of alkali activation of FA, or a calcium-rich gel (or C-(A)-S-H) in case of alkaliactivated slag binders².

While emitting up to nine times less carbon dioxide [13], alkali-activated concretes exhibit many of the engineering characteristics of traditional concretes, despite their vastly different chemical composition and reaction mechanisms [14–16]. Moreover, alkali-activated materials can display other benefits as well, such as higher stability when exposed to elevated temperature [17], higher resistance against chemical attacks [18–20] and better resistance to freeze-thaw cycles [21,22]. However, being a comparatively young engineering material, the quantity of available durability data

¹ Geopolymer-type materials are simply referred to as geopolymer material in some cases throughout the dissertation

² Formation of C-(A)-S-H is also highly dependent on the alkalinity level as will be discussed in the upcoming chapters. Some other secondary phases are also expected to form in alkali-activated slag binders.

(crucial for predicting the service life of reinforced GPC structures) such as chloride ingress properties or corrosion rate of embedded reinforcing steels is limited, and the long-term performance of GPC structures is yet to be determined [6,23].

1.2. Initial Questions

Predicting the service life of a concrete structure requires understanding different mechanisms during its service life: Moisture transport into the concrete, chloride transfer, carbonation, Oxygen transfer, and charge transfer which defines the rate of corrosion of reinforcement. All the mentioned mechanisms are involved during the process of corrosion of reinforcing bars; they are inherently complex and highly interacting with each other. Corrosion is composed of two main stages: the initiation phase which is the required time for aggressive agents (e.g. chloride ions) to reach the reinforcing bar and depassivate it, and the propagation phase which is the active phase of corrosion [24] (Figure 1-1).

As illustrated in Figure 1-1, during the initiation phase, moisture transport properties of concrete define the rate of moisture adsorption and consequently penetration of chloride ions through a convective process during wetting/drying cycles in non-saturated concrete. After saturation of the concrete, however, chloride diffusivity is the main controlling factor. When enough chloride ions reach the interface between concrete and reinforcement, the passive layer around the bars start to deteriorate, and the corrosion starts. Not all the penetrated chloride ions contribute in the depassivation process, as a percentage of them will be chemically bound to the matrix. The amount of chloride leading to breaking down the passive layer and the onset of corrosion is called chloride threshold, and it is highly dependent on the chemical composition of

the binder. After depassivation of the reinforcement, and during the propagation phase of corrosion, moisture adsorption and desorption play a significant role again, as the electrical resistivity of concert depends on the moisture content. Electrochemical parameters such as the corrosion potential and polarization resistance are other parameters defining the kinetic of corrosion during the propagation phase of corrosion. And finally, a lack of oxygen, which depends on the pore structure, can decrease the rate of corrosion as the corrosion process becomes concentration-controlled. The pore structure itself can be studied through water-vapour-sorption curves which are a major feature of moisture transport in any porous binder.



Figure 1-1. Corrosion phases and various transfer mechanisms involved in each phase

As explained previously, durability and long-term performance of concrete structures involve a wide range of influential material-related properties which interact with one another in a dynamic environment. Although the mentioned transfer mechanisms and the parameters defining them has been the subject of many types of research in the past for OPC concretes, the amount of literature for new and alternative binders such as alkali-activated binders is relatively small. In the initiation phase, the performance of alkali-activated binders to prevent ingress of aggressive agents such as chloride ions and the capability of these binders to passivate the reinforcement are topics which require further investigation. This means that moisture transport properties, carbon dioxide transfer, chloride transfer, and chloride binding, as well as chloride threshold values, need to be investigated. In the propagation phase, the rate of depassivation of the reinforcement by increasing the chloride content, and the corrosion rate when compared to their OPC counterparts remains to be explored through investigating parameters defining the charge transfer process, including the corrosion potential and polarization resistance.

1.3. Research objective and scope of work

The main obstacle for the widespread use of alkali-activated concretes for structural applications in the industry is the durability concerns, and the corrosion of embedded reinforcement remains one of the most controversial aspects of the durability of alkali-activated binders. To address this issue, this research aims to study the corrosion of reinforcement in alkali-activated materials in chloride contaminated, or carbon dioxide concentrated environments. The performance of both fly ash-dominated and slag-dominated alkali-activated materials is investigated.

Due to the very different chemistry of alkali-activated binders compared with traditional OPC binders, all governing parameters defining different mechanisms involved in the corrosion of reinforcement in alkali-activated binders are investigated. Water-vapour-sorption-isotherms and moisture diffusion coefficients are studied and determined for a range of low and high calcium binders. Through these studies, pore structure which plays a major role in all involved transfer mechanisms, including carbonation and chloride transfer, are studied. Chloride diffusion coefficients and binding capacity of a wide range of alkali-activated mortars are also systematically investigated. Chloride threshold values are determined as index values showing the stability of passive layer around the bars. Corrosion kinetic parameters are also studied for both passive (before corrosion) and active states of corrosion. Carbonation rates, the passivity of the reinforcement in carbonated geopolymer concretes, and the chemical adsorption of carbon dioxide into the pore solution of these systems are modeled and studied. Finally, the alkali cation leaching and its probable effects on the loss of alkalinity and stability of the passive layer are investigated.

1.4. Organization of dissertation

The contents of this thesis are divided into eight main chapters, with the first and last chapters being the introduction and conclusions, respectively. Other chapters are commenced with an introduction to present an overview of the contents of that particular chapter. In addition, the major and important conclusions corresponding to each particular chapter are summarised at the end of each chapter.

Chapter 2 present a review of the available literature on the topic of chloride and carbonation-induced corrosion of reinforcement in alkali-activated materials. It should be noted that although nano/microstructure of alkali-activated materials and their reaction mechanisms and kinetics have been a topic of interest in many types of

research studies recently, there is relatively a lack of literature on the durability aspects of these materials. Nonetheless, relevant previous studies on phenomena such as moisture transport, pore structure characteristics, chloride-induced corrosion, carbonation, and alkali leaching in alkali-activated materials are reviewed in Chapter 2.

Chapter 3 is devoted to the moisture transport in alkali-activated binders. Watervapour-sorption isotherms (WVSI) are established for a range of aluminosilicatedominated and calcium-rich systems. Through analyses of WVSIs, worthwhile insights into the pore structure, adsorption/desorption hysteresis, pore structure and pore blocking effects, and interlayer water binding mechanism of alkali-activated binders are obtained. Sorption kinetic curves are analysed to determine the contribution of Fickian and non-Fickian sorption processes, and to calculate the moisture diffusion coefficients. The valuable information about the nanoporosity of alkali-activated binders obtained in this chapter has been used in other chapters, in particular in chapter 5 to interpret the observed trends in chloride diffusivities in light of the pore structure of alkali-activated materials.

In Chapter 4, different electrochemical aspects of corrosion of reinforcement in low calcium geopolymer concretes are investigated. The traditional test protocols to measure the half-cell potential, polarization resistance (R_p), and Tafel coefficients are re-assessed and validated for alkali-activated materials. The rate of depassivation of reinforcement due to increase in chloride content in geopolymer concretes are compared with that of OPC concretes. The validated test protocols have been used in Chapter 5, Chapter 6, and Chapter 7 to perform all the electrochemical test measurements.

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Chapter 5 presents a systematic study of the chloride diffusivity, chloride binding, chloride threshold and the depassivation periods of a wide range of alkali-activated mortars. The effect of compositional variables such as the calcium content, alkali content and silicate content (adjusted by modifying the modulus ratio) on the pore structure development and hence the chloride diffusivity are systematically investigated. Chloride threshold values are measured and interpreted in light of the aforementioned compositional variables. The electrochemical aspects of alkali-activated systems in passive condition are also investigated. This chapter provides major durability implications for reinforced alkali-activated materials in chloride contaminated environments.

In Chapter 6 carbonation of low-calcium geopolymer concretes is investigated. An analytical chemisorption model is developed to predict the pH drop at various carbon dioxide pressures in a sodium hydroxide solution at different concentrations, as representative of the pore solution of low calcium alkali-activated binders. The pH drop under accelerated carbonation was experimentally measured and compared with the calculated pH drop. The passivity of the reinforcement in carbonated concrete was also assessed by long-term monitoring of the half-cell potential and R_p values.

Chapter 7 contains a brief investigation of alkali cation leaching in alkali-activated materials and its probable consequences on the efflorescence and loss of alkalinity which can lead to the depassivation of reinforcement. The effects of alkali type and content, calcium content and the curing regime on the efflorescence severity are investigated. The possibility of depassivation of reinforcement due to the pH drop caused by alkali leaching is also assessed by long-term monitoring of the electrochemical parameters of reinforced samples which have been submerged in water.

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Finally, in Chapter 8, a summary of the key outcomes of this study are presented and reviewed. The chapter and dissertation then conclude with some recommendations for further study.

2.1. Introduction

This chapter will present an overview of the previous research work and studies, which are relevant to the subject and objectives of this dissertation. It should be stressed that the required theoretical background for many investigated phenomena in this dissertation is provided in the corresponding chapters. Moreover, while a brief literature review is also presented in the introduction of each chapter, this chapter aims to further discuss the previous prominent research studies on the topics of interests.

2.2. Understanding the Alkali-activated materials

2.2.1. Reaction mechanisms and final products

Alkali-activated binders are produced by reaction of metakaolin or industrial byproduct materials such as fly ash (FA) and ground granulated blast-furnace slag (GGBS) with an alkali metal (usually Na or K) hydroxide or silicate solution, and a considerably lower carbon emission is attributed to their production compared with their Portland cement-based counterparts [13,25]. Depending on the precursor used, two different classes of binders are identified. Distinguishing between these two classes and their strikingly different properties with regard to the pore structure development and other durability-related characteristics is fundamental to understand the results and discussions provided throughout this dissertation. The main differentiating factor is the calcium content in the system. The final product of alkali activation of low-calcium precursors such as metakaolin or FA is a highly cross-linked aluminosilicate network (also referred to as geopolymer as coined by Davidovits for the first time [8]), whereas alkali activation of high-calcium precursors such as GGBS results in an aluminium and alkali substituted calcium silicate hydrate, also known as C-(A)-S-H, with a tobermorite-based structure similar to the structure of C-S-H gel in OPC systems, although, with some degree of cross-linking [9]. C-(A)-S-H gel is also accompanied by secondary aluminium- and/or magnesium-rich reaction products [9–12,26]. The alkali activation process and the primary reaction products are shown in Figure 2-1.

The effect of the alkalinity of the activator on the properties of the final product is also of interest. According to Figure 2-1 and a similar conceptual model proposed by Duxson et al. [27] for alkali activation of low-calcium precursors, higher alkalinity levels lead to a higher dissolution rate and consequently availability of more aluminate and silicate species to form the aluminosilicate network; a higher mechanical strength is expected as a result. For high-calcium precursors, however, high alkalinity levels can hinder the formation of the C-(A)-S-H gel and might reduce the mechanical strength as the diffusion of calcium ions out of the calcium source (e.g. slag particles) reduces at higher alkalinity levels [26,28].

Yip et al. [29] studied the effect of alkalinity and calcium content on the formation of C-S-H gel in blended metakaolin and GGBS 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 GGBS levels. On the other hand, at high alkalinity levels (>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 in particular their consequences on the pore structure and transport properties of blended alkali-activated binders requires further investigation, and are systematically studied in this dissertation.





2.2.2. Pore structure of alkali-activated binders

The pore structure which can be described by the total pore volume, pore size distribution, and connectivity of the pores [30] is one of the most important aspects of every porous binder, and correlates strongly with the mass transfer properties of the binder as a determining factor in designing durable materials. The aluminosilicate networks (geopolymers) and C-(A)-S-H gels show two distinctly different pore structures. The pore structure of aluminosilicate-dominated materials, as the end product of alkali activation of metakaolin or FA, has been studied in the past by employing gas adsorption/desorption, mercury intrusion porosimetry (MIP), or Wood's metal intrusion; and the general takeaway from these studies is the high porosity of these materials.

Ma et al. [31] studied the pore structure of alkali activated fly ash paste samples fabricated of sodium silicate solutions of various silica and alkali contents using MIP. Ordinary Portland cement (OPC) pastes were used for cross comparison. Similar to OPC systems, where two distinct main peaks for the gel pores and capillary pores was observed, the differential curves for alkali-activated FA samples demonstrated two main peaks: one peak in the range of several nm to 20 nm and another between 100 to 1000 nm (Figure 2-2). By further inspection of the micrographs obtained from environmental scanning electron microscopy (ESEM) of both alkali-activated and OPC paste samples, the authors argued that the second main peak in the pore structure of alkali-activated pastes is associated with a range of large pores which are fundamentally different from the capillary pores in OPC based materials. These large pores observed in the alkali-activated FA matrix were attributed to the cavities left by

the surface dissolution of fly ash particles or presence of hollow particles, and the inability of the aluminosilicate gel to fill these cavities.

Figure 2-2. Pore size distribution from MIP test for cement paste (W/C=0.45) (left), and fly ash activated by Ms=1.0 activator solution (right) at different ages (From [31]). (Figure has been removed due to copyright restrictions)

Rovnaník [32] investigated the effect of heat curing on the pore structure of Na-based metakaolin geopolymers using 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 was attributed to the rapid formation of the network which leads to a less ordered pore structure, while the ambient curing appeared to favour 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.

Despite the previous attempts to analyse the pore structure of alkali-activated (and OPC-based) materials using MIP test method, because of the pore structure of these materials in which a considerable volume of large pores are only accessible through

narrow constrictions, many large pores register as being small pores, leading to an underestimation of pore size distribution. In an attempt to obtain a visual insight into the pore distribution and pore connectivity in alkali-activated binders, Lloyd et al. [33] employed Wood's metal intrusion technique. A range of alkali–activated FA mixes with variable GGBS replacements was studied. A significant pore volume of well-reacted networks was observed in the cavities left by the dissolution of FA particles. The fact that majority of the observed large cavities were connected to one another through very fine pores, was suggested to mitigate the impact of such large pores on the mass transfer (This argument is not in agreement with the findings of this dissertation in Chapter 3).

Duxson et al. [34] studied the correlation between Si/Al ratio and the pore structure of a range of metakaolin-based geopolymers using nitrogen adsorption/desorption and transmission electron microscopy (TEM) technique. They reported an increase in the volume of inaccessible gel pores by increasing Si/Al ratio. The bulk of gel pores was reported to be in the order of 5-10 nm which is in line with the reported values by Ma et al. [31] and Rovnaník [32] for ambient-cured materials. They also argued that development of a high strength geopolymer inevitably requires an intrinsically porous microstructure, emphasising the high porosity of well-developed aluminosilicate networks reported by other researchers as well.

The pore structure of alkali-activated slag binders has been comparatively studied by fewer researchers, which might be due to the similarities between the reaction products of these binders and OPC binders which have been under investigation for decades. An inspection of the porosities reported by Lloyd et al. [33] for a range of FA and GGBS alkali-activated samples reveals the considerable lower porosity of GGBS-based samples compared to the alkali-activated FA samples, despite using noticeably higher

water contents in these samples. Provis et al. [35] used X-ray microtomography to investigate the pore structure of a range of blended FA and GGBS samples, aiming to visually observe the pore structure and the tortuosity; although, their findings were restricted to microscale pores due to the technical limitations. They found an increase in the pore network tortuosity and a decrease in total porosity by increasing the slag content which was attributed to the pore filling effect of C-(A)-S-H gel. 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.

All in all, it can be concluded that alkali-activated slag binders are considerably less porous and permeable compared to their FA-based counterparts. However, the possible consequences of the difference in the pore structure of FA-based and GGBS-based binders, in particular in blended systems, on various transport properties which can affect the durability of these materials are yet to be investigated. Assessing the effect of various compositional variables on the pore structure and hence transport of external agents such as water or chloride in alkali-activated binders is one of the main objectives of this dissertation.

2.3. Moisture transport and water vapour sorption isotherms in alkali –activated materials

Water vapour sorption isotherms (WVSI) establish the relationship between the moisture content and the environmental relative humidity at a fixed temperature [36].

They also provide valuable information regarding the structurally bound water, pore blocking effect, cavitation, and volume of pores involved during adsorption/desorption processes from dry/saturation conditions respectively. Correlation of many transport phenomena (e.g. chloride transport during wetting/drying cycles) with the moisture transport, and dependency of other parameters such as the bulk electrical resistivity and the oxygen diffusivity on the moisture content makes water/water vapour as the ideal probe to investigate the pore structure and permeability of porous binders [37]. The rate of attaining the gravimetric equilibrium from dry/saturated condition to a target relative humidity can also be studied to obtain some insight into the type of sorption process (Fickian or non-Fickian), and also to calculate the moisture diffusion coefficients which can be used to predict the moisture content of the binder in durability and Multiphysics modellings [36–39]. Moisture transport and WVSI in OPC binders have been a topic of interest for many years (see e.g. [40–42] and also more recent publications [36–39]); although, to the best knowledge of the author, only two relevant study of WVSI in alkali-activated binders can be found in the literature as follows.

Boher et al. [43] investigated the influence of water saturation level and pore size distribution on the diffusion of hydrogen in geopolymers and Vycor® glasses. As part of their studies, they established WVSIs for four metakaolin-based geopolymers fabricated of various alkaline solutions at different modulus ratios. A trend can be seen in all WVSIs where after an initial increase in the water saturation degree by increasing the relative humidity (RH) from 5% to 20%, water saturation degree remained rather constant up to 70% RH, and then a sharp increase in water saturation degree was observed For RH levels beyond 70% (and in particular beyond 95% for geopolymers with larger pore peak diameter). The sharp increase for RH>70~95% suggests the presence of a considerable volume of large pores which coexist with a large volume of
small pores (due to the small slope of WVSI between 20 and 70% RH). This behaviour is in line with the observations of De Burgh et al. [44] who studied the main features of the WVSI of two heat-cured alkali-activated blended FA and GGBS binders with GGBS contents of up to 35%. They reported a substantially different pore structure of aluminosilicate-dominated binders compared with OPC binders where instead of a network of connected capillary pores and smaller gel pores, a large quantity of small nanopores under 6-8 nm along with a quantity of substantially larger pores formed the pore structure. Also, a lack of low relative humidity hysteresis which was characteristic of a lack of water binding capacity was reported for the investigated mixes. The main features of experimentally obtained WVSIs were qualitatively discussed in their paper; although, due to the limited number of mixes studied, investigation of variables such as high calcium content, heat-curing, and alkali content was not possible. Chapter 3 of this dissertation aims to study the effect of aforementioned factors on the transport properties and WVSI of 4 alkali-activated mixes which are studied along with the results of De Burgh et al.'s work. Furthermore, the pore structure in the mesopore range (between 2 and 50 nm diameter [45]) will be mathematically studied using BJH method [46].

2.4. Chloride-induced corrosion of reinforcement in alkaliactivated materials

Regarding the corrosion of reinforcement in alkali-activated material, the literature is relatively limited; the performance of alkali-activated binders to prevent ingress of aggressive agents such as chloride ions, the capability of these binders to passivate the embedded reinforcement and then the rate of corrosion of depassivated reinforcement when compared to their OPC counterparts have been polarizing subjects so far.

Bastidas et al. [47] suggested that FA-based alkali-activated mortars are capable of passivating the reinforcement, and the stability of the passive layer depends on the type and concentration of the alkalis in the activator. However, it should be noted that the possible effects of alkali cation leaching which could lead to some degree of alkalinity loss could not be investigated in their study, as samples were kept in 95% relative humidity environment, and were not submerged in the water to be saturated.

Miranda et al. [48] studied the equilibrium half-cell potential and corrosion current of reinforcement embedded in OPC mortars and activated fly ash-based geopolymer-type mortars. They reported that activated fly ash mortars were capable of passivating embedded reinforcement as well as OPC mortars, and the initial pH level was even higher in the case of geopolymer mortars. They found equilibrium half-cell potential values for the passivated reinforcement in geopolymer mortar ranging between -100 to -200 mV (vs SCE) which is quite comparable to the OPC mortar results; however, after breaking the passivity down, potential values were more negative than those of OPC mortars (around -600 mV compared to ~-400 mV). Besides, the recorded corrosion current values were higher in geopolymer mortar than OPC mortar. Similar to [47], it can be deduced from the reported test protocol that samples have been stored in 95% RH during the testing period.

Reddy et al. [49] and Olivia and Nikraz [50] reported a superior performance of lowcalcium fly ash geopolymer concrete compared with OPC concrete in severe marine environments. They employed an accelerated corrosion test method to monitor the required time to corrosion cracking as a durability index in both sets of samples and the time to failure for geopolymer samples was reported to be much longer than their OPC counterparts. This was attributed to a lower permeability of geopolymer samples which delays depassivation of reinforcement, as well as the high electrical resistivity of samples which reduces the corrosion rate and hence extends the time to crack.

Kupwade-Patil and Allouche [51] and also Muntingh [52] reported high resistance to chloride penetration and low corrosion rates in geopolymer binders which is in agreement with the previously mentioned results. Kupwade-Patil and Allouche [51] also reported that the low calcium fly ash (Class F) geopolymer concrete has lower Chloride diffusion coefficients, Chloride content, porosity, equilibrium half-cell potential, and corrosion rate compared to Class C fly ash geopolymer concrete and OPC concrete which have higher calcium contents; on the other hand, Lloyd et al. [53] 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. [31] where a high water sorptivity rate which could be indicative of a high chloride diffusivity was reported for alkali-activated fly ash samples. Provis et al. [35] also emphasized the importance of the presence of slag in the matrix to reduce the porosity of alkali-activated blended FA and GGBS samples. The high porosity of aluminosilicate (geopolymer-type) networks which was discussed in Section 2.2.1 also suggests high mass transfer rates, and as a result, high chloride diffusivities in low-calcium alkali-activated binders, at least compared to OPC-based binders, which contradicts results of some of the aforementioned studies.

A review of previous studies on the chloride diffusivity and corrosion of low-calcium alkali-activated mortars and concretes reveal that in almost all cases, samples have been fabricated of very highly alkaline activators with low modulus ratios (= molar ratio of silicates to alkalis) which increases the safety concerns regarding the application of a caustic solution at very high pH levels during the manufacturing process. Variability of employed experimental techniques (e.g. accelerated corrosion vs. non-accelerated corrosion, natural chloride diffusion vs. built in chloride content, samples submerged in water vs. stored in environmental relative humidity chamber), and various sample compositions (e.g. different alkali concentration and modulus ratios, different chemical composition of the raw precursors, etc.) are also other factors which makes establishing a general trend difficult.

For alkali-activated slag binders, there is a better correlation between the reported pore structure observations and the chloride diffusivities. Roy et al. [54] showed that the chloride diffusion coefficient of alkali-activated slag based binders can be as low as half of that of OPC binders. Similarly, Ma et al. [55] reported lower chloride diffusivities in alkali-activated slag 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 2.2. A sensitivity of the recorded corrosion rates and chloride diffusivities to the alkali concentration and modulus ratio was reported in their study. An interesting electrochemical behaviour was also reported in their work where passive samples exhibited unusual negative half-cell potential values. This behaviour was attributed to the consumption of dissolved oxygen by sulphides in the pore solution. A similar phenomenon had been previously reported by Macphee and Cao [56] as well. Summarising, 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 diffusivities and electrochemical performance of alkali-activated binders are considered. In lieu of such an approach, and considering the often contradictory reported results in the literature, the performance of alkali-activated structural concretes in chloride contaminated environments can be still a source of ambiguity for both the research community and general practitioners.

2.5. Carbonation of alkali-activated materials

The capability of alkali-activated binders to passivate the reinforcement in lieu of aggressive agents such as chloride or carbon dioxide was discussed in the previous section; the effects of carbonation on the pore solution/structure of alkali-activated binders and the carbonation-induced corrosion of reinforcement will be discussed in this section. Unlike OPC binders where the hydration product portlandite (Ca(OH)₂) provides a buffer effect, low-calcium alkali-activated binders or calcium-rich alkali-activated binders which are fabricated of activators at low alkalinity levels do not have a substantial amount of portlandite, and it is important for the pore solution to contain enough concentration of OH^- ions to be neutralized during the carbonation [53,57].

Bernal et al. [57] investigated the carbonation of alkali-activated FA and GGBS samples. 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 binders. The structure of carbonated aluminosilicate network was remained rather unaltered based on nuclear magnetic resonance spectroscopy results. On the other hand, Puertas et al. [58] and Bernal et al. [59] reported substantial structural strength degradation and increase in porosity, particularly when the sodium silicate is used for the activation, in calcium-rich alkali-activated binders.

The artificial decline of the pH and alteration of the formed carbonation products were also further emphasised by Bernal et al. [60], and corroborated by the pH measurement of carbonated and uncarbonated FA-based geopolymers under various carbon dioxide concentration by Khan et al. [61]. Bernal et al. [60] developed a thermodynamic model which was capable of predicting the pH of alkaline solutions of various alkali concentrations after carbonation under different concentration 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. Having said that, no further experimental verification including pH measurements or electrochemical assessment of a reinforced system was provided to complement the theoretical results.

The effect of carbonation on the electrochemical performance of reinforced alkaliactivated systems was studied by Badar et al. [62] in which they concluded that the low calcium fly ash alkali-activated binders perform better than those containing higher amounts of Ca when it comes to the carbonation-induced corrosion of reinforcement. Besides, the high alkaline binder appeared to passivate the reinforcement for a considerable period of time of exposure to natural carbonation. However, after depassivation, fly ash-based alkali-activated samples with a higher amount of calcium experienced a steeper drop in recorded corrosion potential values. Interestingly, 5% carbon dioxide concentration was used in their studies to accelerate the carbonation, although, they claimed that due to the gradient of carbon dioxide concentration, the carbonation products at the level of the embedded reinforcement was not affected by accelerated carbonation. Aperador et al. [3] similarly reported the electrochemical performance of alkali-activated slag samples under both natural and accelerated (3% pCO₂) carbonation and compared the results with those of OPC concrete. They found an inferior electrochemical performance of alkali-activated slag samples under both natural and accelerated carbonation compared to their OPC counterparts.

All in all, 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 alkali-activated binders, the extent of pH drop due to the accelerated carbonation and whether or not the pH drop leads to depassivation of reinforcement under different carbon dioxide concentrations are less investigated in the literature.

2.6. Alkali leaching and efflorescence in alkali-activated materials

Alkali cation leaching which occurs through diffusion/leaching of free alkali ions in the pore solution of alkali-activated binders can be a serious durability and aesthetic concern. Alkali leaching can lead to loss of alkalinity which may/may not lead to depassivation of reinforcement; besides, the reaction of the leached out ions with the ambient carbon dioxide can lead to the formation of hydrous alkali carbonates [63] on the surface of samples, also known as efflorescence. The amount of literature on this topic is very limited and a few prominent studies on the alkali leaching or efflorescence in alkali-activated binders are reviewed below.

Lloyd et al. [53] studied the alkali leaching of a range of alkali-activated paste samples using high-pressure pore fluid expression. They emphasised the importance of the presence of calcium in the matrix to reduce permeability and retain the alkalis. It was also argued by the authors that due to the severe alkali leaching and loss of alkalinity in low calcium geopolymer-type binders, achieving a durable geopolymer concrete seems difficult. Interestingly, a systematic preference for incorporation of calcium over alkalis was observed in their results; increasing the free alkali content can be deduced as a result which is counterproductive. A curve fitting method was also employed through which the alkali diffusion coefficient and the initial free alkali content were determined for various mixes. By contrast, Škvara et al. [64] reported that the initial free alkali content is not important and almost all Na ions can leach out of the aluminosilicate network if the surrounding water is renewed constantly, without significant strength loss. They hypothesized that the negative charge of Al^{3+} in IV-fold coordination can be balanced by H_3O^+ ion.

Najafi Kani et al. [65] investigated the effect of hydrothermal curing at elevated temperatures as well as the presence of Al-rich mineral admixtures on mitigating the efflorescence in geopolymer binders. While hydrothermal curing at 65°C and higher reduced the efflorescence to some extent, addition of high-alumina cements proved to be a more efficient way of controlling the efflorescence in the natural pozzolan based geopolymers studied. They stated that the addition of alumina leads to a higher degree of crosslinking in the geopolymer structure and reduces the mobility of alkalis.

Zhang et al. [63] investigated the effect of composition and pore structure development on the amount and rate of the efflorescence of a range of alkali-activated binders. in agreement with the findings of Lloyd et al. [53], they found that addition of slag content will reduce the efflorescence rate through the development of a finer pore structure, although the total efflorescence products formed remained rather unchanged after a long-term exposure to the water. Heat curing was also proved to be very efficient in reducing the efflorescence. Furthermore, samples fabricated of activators of higher modulus ratio demonstrate less efflorescence. Designing an optimum alkali content level which minimizes the efflorescence while considering the reactivity of the fly ash used and the target compressive strength was emphasised as a challenging, yet necessary task during the mix composition design stage of alkali activated binders.

Investigating the alkali cation leaching in alkali-activated binders is still in its early research stages. While more systematic study of the phenomenon is required to establish solid trends between various compositional variables and the amount of leachable alkalis, the effect of alkali leaching on the passivity of the reinforcement yet to be explored.

CHAPTER 3: Water-vapour-sorption-isotherms, Pore Structure, and Moisture Transport Characteristics of Alkali-activated Binders

3.1. Introduction

The moisture content of concrete influences several other concrete properties such as the electrical resistivity and the oxygen diffusivity, both of which are of significant importance during the propagation phase of corrosion. Transport of moisture through a convective process during wetting/drying cycles also facilitates the penetration of aggressive agents such as chloride ions in marine environments that can lead to the eventual depassivation of reinforcement. Modeling moisture transport, as a result, is a fundamental component of any comprehensive durability model and requires some material-specific information regarding the rate of moisture adsorption/desorption, and the relationship between the moisture content and the environmental relative humidity which is established by water vapour sorption isotherms (WVSI) at a fixed temperature. WVSI were also proved to be strong tools providing a lot of information regarding the pore structure in nanoporous materials, the sorption transport rate, and water binding mechanism [36–39]. Besides, Pore structure and permeability implications from WVSI studies can correlate well with other phenomena such as carbon dioxide and chloride diffusion.

Although moisture transport and WVSIs in Portland cement-based binders have been studied by many researchers in the past (see e.g. [37,38,40,66]), there is a lack of

information for alternative binders such as alkali-activated binders in the literature. Regarding the study of WVSIs (and moisture transport) in alkali-activated binders, only two relevant study can be found in the open literature. Boher et al. [43] reported the WVSIs of four metakaolin-based geopolymers fabricated of various alkaline solutions at different modulus ratios. An almost constant slope of WVSIs for RH levels between 20% and 70% which was followed by a sharp increase in the slope of WVSIs for RH>70% was observed. This suggests the presence of a considerable volume of large pores which coexist with a large volume of small nanopores. This pattern that is considerably different from OPC binders, where a network of connected capillary pores and smaller gel pores form the pore structure, has been also reported by De Burgh et al. [44] who studied the main features of the WVSI of two heat-cured alkali-activated blended FA and GGBS binders with GGBS contents of up to 35%. Furthermore, a lack of low relative humidity hysteresis which was characteristic of a lack of water binding capacity was reported by De Burgh et al. [44] for the investigated mixes.

On the pore structure analysis front, however, more studies can be found (see e.g.[32– 35]) in the literature, majority of them investigated the pore structure of aluminosilicate networks fabricated of metakaolin or fly ash by employing gas adsorption/desorption, mercury intrusion porosimetry (MIP), or Wood's metal intrusion. The general agreement found in all these publications is that the aluminosilicate networks are highly porous with considerable pore blocking in the network. The effect of presence of calcium in the matrix of blended systems on the pore structure has attracted comparatively less attention. Provis et al. [35] employed X-ray microtomography technique that allowed direct assessment of the pore structure and tortuosity of blended FA and GGBS binders. They observed general improvement (i.e. finer pore development with higher tortuosity) in the pore structure as a consequence of GGBS addition, although their findings were restricted to microscale pores due to the technical limitations.

In this chapter, the WVSI of one heat-cured paste sample with 50% GGBS replacement and three ambient-cured blended FA and GGBS pastes with 25,50 and 75% GGBS replacement are evaluated using a sorption apparatus. The measured WVSIs along with the two WVSIs which were previously published by de Burgh et al. [44] are quantitatively analysed to have a better understanding of the nanopore structure of alkali-activated binders, in particular, to assess the effect of GGBS addition, alkali concentration, and curing regimes on the pore structure. Main features of the WVSI of alkali-activated binders are discussed and compared with those of Portland cementbased binders from the literature. The sorption kinetics of two ambient-cured alkaliactivated binders with low and high calcium contents are studied for the first time and compared with Portland cement-based binders. Major conclusions are made with regard to the type of sorption process (i.e. diffusive (Fickian) or anomalous (non-Fickian)) in light of the differences observed in the pore structures. The permeability of low-calcium geopolymer-type binders and calcium-rich binders are compared and key implications for durability design of alkali-activated binders are deduced.

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3.2. Experimental program

3.2.1. Materials and mix proportions

Three different Australian sourced low-calcium fly ashes are used to manufacture alkali-activated pastes in this study: Eraring fly ash obtained from Eraring power station in New South Wales, and Callide and Gladstone fly ashes from Callide and Gladstone power stations in Queensland, respectively. Ground granulated blast-furnace slag (GGBS) was supplied in two batches (namely A and B) by Australian Steel Mill Services (ASMS), Port Kembla, New South Wales. To prepare Portland cement-based control paste samples, Australian general-purpose cement (Type GP, SL and HE to AS 3972) manufactured at the Boral Berrima Cement Works (NSW, Australia) was used. To produce the cement, 7.5% limestone mineral addition had been used. The chemical compositions of the raw precursors as determined by x-ray fluorescence (XRF) analysis are shown in Table 3-1. The amorphous content of the raw materials used for alkaliactivated paste fabrication was also measured through the X-ray diffraction (XRD) test using the spike method (5 wt. % zinc oxide was used). The amorphous content of Eraring FA, Callide FA, Gladstone FA, GGBS A, and GGBS B was found to be 85.2%, 81.2%, 79.1%, 95.8% and 100%, respectively. The crystalline phases in fly ash samples consist of mullite (Al_{2.17}O_{4.89}Si_{0.78}), quartz (SiO₂), magnetite (Fe₃O₄) and hematite (Fe₂O₃) (in Callide and Gladstone FA). The crystalline phases in GGBS A were gypsum (CaH₄O₆S) and hatrurite (Ca₃O₅Si) with some traces of quartz, whereas GGBS B had some traces of quartz as the only crystalline phases.

Chemical composition and physical properties	General- purpose cement*	Eraring fly ash (wt.%)	Callide fly ash (wt.%)	Gladstone fly ash (wt.%)	GGBS (A) (wt.%)	GGBS (B) (wt.%)
SiO ₂	19.1	65.9	50.1	47.9	32.4	35.0
Al ₂ O ₃	5.8	22.10	26.72	25.7	13.1	14.1
Fe ₂ O ₃	2.68	3.44	12.66	14.7	0.41	0.36
CaO	62.2	1.65	3.52	4.11	41.5	40.9
MgO	1.31	0.69	1.52	1.36	4.99	5.51
Na ₂ O	0.02	0.59	0.60	0.81	0.30	0.29
K ₂ O	0.53	1.81	0.60	0.67	0.33	0.30
TiO ₂	0.28	0.90	1.45	1.39	0.60	0.59
P2O5	NA	0.11	1.19	1.21	0.02	0.02
Mn ₃ O ₄	NA	0.07	0.20	0.19	0.43	0.55
SO ₃	2.89	0.08	0.23	0.19	2.58	1.15
Loss on ignition (LOI)	4.5	1.36	0.62	0.69	2.17	NA

Table 3-1. Chemical compositions of Eraring, Callide, and Gladstone FA, and GGBSby x-ray fluorescence (XRF) analysis

* From [36] (NA: not available)

Particle size distribution of solid precursors was determined using the laser diffraction technique with a Malvern Mastersizer 2000 instrument (Figure 3-1). The powders were dispersed in water and ultrasonication at 20 kHz was used before the analysis. As it is shown, Callide FA and then Gladstone FA are the finest, followed by GGBS and Eraring FA. A considerable volume of Callide and Gladstone FA particles are about 5-6 μ m in diameter, as opposed to 30 μ m for Eraring FA particles.



Figure 3-1. Particle size distribution of Eraring, Callide, and Gladstone FA, and GGBS

A mixture of sodium hydroxide (NaOH) solution and grade D sodium silicate solution were used as the activator. The sodium hydroxide white pellets with a purity of at least 98% were supplied by Ajax Finechem under the commercial name of UNIVAR A-302. The sodium hydroxide solution used prepared by dissolving the technical grade NaOH pellets in tap water. These pellets have a specific gravity of 2.1 g/cm³ and a pH of approximately 14. Grade D sodium silicate, which was supplied by PQ Australia under the commercial name of Vistrol D–A53, has a chemical composition of Na₂O = 14.7%, SiO₂ = 29.4% and H₂O = 55.9% (by mass). The sodium silicate solution used is a thick adhesive liquid with a viscosity of 400 cps at 20°C, has a specific gravity of 1.53 g/cm³ and a pH of 12.9 (values provided by the supplier, PQ Australia). NaOH and sodium silicate solutions were mixed in proportions to form alkaline solutions at different concentrations and modulus ratios (M_s=molar ratio of SiO₂/Na₂O), according to Table 3-2. After mixing, the alkaline activator was allowed to cool to ambient temperature and equilibrate prior to preparation of the specimens.

Water-vapour-sorption-isotherms of HCP (hardened cement paste), AAP1, and AAP2 mixes were previously investigated by de Burgh & Foster [36] and de Burgh et al. [44], and their different aspects are further analysed here in comparison with the other mixes. To perform complementary tests required to study material-specific properties, these mixes are refabricated and cured according to the conditions mentioned in Table 3-2.

Mix	FA+Slag (%)	M_{s}	Na ₂ O%	Water/binder	¹⁾ Curing method
HCP ⁽²⁾	-	-	-	0.45	Ambient cured (sealed)
AAP1 ⁽³⁾	70% Er FA+20% Cal FA+10% GGBS(A)	1.17	9.25	0.28	Heat cured (18h@75°c)
AAP2 ⁽⁴⁾	65% Gl FA+35% GGBS(B)	1.5	7.7	0.3	Heat cured (18h@75°c)
AAP3	50% Gl FA+50% GGBS(B)	1.5	8	0.3	Heat cured (18h@75°c)
AAP3A	50% Gl FA+50% GGBS(B)	1.5	8	0.3	Ambient cured (sealed)
AAP4	75% Gl FA+25% GGBS(B)	1.5	8	0.35	Ambient cured (sealed)
AAP5	25% Gl FA+75% GGBS(B)	1.5	4	0.45	Ambient cured (sealed)

Table 3-2. Mix proportions for alkali-activated and hardened cement pastes (kg/m^3)

⁽¹⁾ Calculated considering the total water and the total solids (precursors+anhydrous activator)

^{(2) (3) (4)} Mix proportions are from [36], [67], [44] respectively

Note: Er FA: Eraring FA, Cal FA: Callide fly ash, Gl FA: Gladstone fly ash

Mix AAP3 is solely designed and manufactured to investigate the effect of GGBS addition on the WVSI and the pore structure, in conjunction with AAP1 and AAP2 mixes. For this purpose, the water to binder ratio was kept almost at the same level as those of AAP1 and AAP2. The alkalinity of the activator, represented by the percentage of sodium oxide (by mass of FA+GGBS), is also not very different among AAP1, AAP2, and AAP3 which further facilitates drawing a conclusion on the effect of the presence of more calcium ions in the structure.

To investigate the effect of curing regime on WVSI and pore structure, AAP3A samples were fabricated from the same paste batch as AAP3 samples and were cured in a sealed condition at ambient temperature instead.

Finally, ambient-cured AAP4 and AAP5 mixes were designed at higher water to binder ratio levels to provide reasonably workable concretes; they were used to manufacture large volume of concretes in a parallel study and provided average spread diameters of 525 and 450 mm on a flow table test apparatus (test protocols according to [68]), respectively. A minimum of 25% GGBS was considered for the AAP4 mix to enhance the early-age strength development in ambient condition. AAP4 has twice as much sodium oxide and silicates in the alkaline solution as what can be found for AAP5. This is mainly due to the different reaction mechanisms in geopolymer-type binders (with a little amount of GGBS and hence calcium) and calcium-rich binders. Higher levels of alkalinity are required for geopolymer-type binders (with a dominant aluminosilicate network) to achieve acceptable early-age and long-term strength as opposed to calcium-rich binders where C-S-H gel formation plays a major role in strength development [69]. Less alkalinity in blended calcium-rich binders can also promote formation of C-S-H over the incorporation of calcium in the aluminosilicate binder [12,29].

3.2.2. Sample fabrication and curing condition

Alkali-activated pastes were manufactured in a Hobart planetary type mixer. FA and GGBS were first introduced into the bowl and dry mixed to achieve a uniform dispersion. Then the activator solution was added and the pastes were mixed for two minutes at low speed. Mixing then stopped to scrape down the bowl and the blade, followed by another two minute of mixing at medium speed. The pastes were then poured into cylindrical moulds (\emptyset 100×200 mm) in two layers and vibrated on a vibration table. Ambient-cured samples were kept sealed in the moulds in a controlled room at a constant temperature of 23°C ± 2° until the preparation day which has been about five months after the casting date for all mixes to ensure a minimal influence of chemical reactions during the sorption experiments. Heat-cured samples were kept sealed in their moulds in the oven for 18 hours at 75°c, after which they were stored in

the controlled room until the preparation dates. For control cement paste samples that were used for complementary tests, a different mixing procedure was used to be consistent with the work of de Burgh & Foster [36] whose WVSI result for HCP samples are used in this paper. To follow their procedure, pastes were mixed for 60s in the mixer at low speed, followed by 90s at medium speed and then 60s at high speed after a short stopping to scrape the bowl. In general, longer mixing periods were chosen for alkali-activated pastes to ensure a proper exposure of solid precursors to the alkaline solution. This leads to a better dissolution and availability of more aluminate and silicate species for later phase reactions to develop the aluminosilicate network [27]³.

3.2.3. Preparation of sorption samples

At least five months after the casting date, samples were demoulded and wet sawn into $\emptyset 100 \times 3-6$ mm thick slices. Discs were then stored in water for not more than seven days, during which succeeding measurements were conducted to assess the level of saturation. After saturation, Thickness of samples was measured by Vernier calipers at multiple points around the discs, and the average of these measurements was used to study the sorption kinetics (Section 3-3). Finally, saturated surface dry (SSD) weights of the discs were measured by removing the excess surface water with a paper towel. For desorption tests, immediately after SSD weight measurements, discs were transferred to the appropriate WVSI test chamber, and the weight measurements started. For adsorption tests, following the same desiccating procedure used by de Burgh & Foster [36], discs were stored in a desiccator for drying under controlled

³ Since all samples are fabricated of blends of FA and GGBS, the aluminosilicate network along with the C-A-S-H gel forms the main structure; although, the contribution percentages of each sub-structure will be highly dependent on the calcium content and the alkalinity level of the activator.

temperature of $23^{\circ}C \pm 2^{\circ}$ in laboratory condition. About 3 kg of conditioned 2-3 mm size spherical beads of 4Å molecular sieves were used to dry eight to ten samples at a time (equilibrium RH over 4Å molecular sieves was less than 0.1%). The desiccator was also equipped with a 120 mm fan to ensure uniform drying of the samples. Drying state of the samples was monitored by opening the port at the top of the desiccator and suspending two discs inside the desiccator from an analytical scale. The mass loss rate was less than 0.00015 g/g per day after at least 75 days of desiccating, even for the thickest discs (about 6 mm thick). Discs were considered dry at this stage, were individually weighed, and then immediately transferred to appropriate WVSI test chamber. After completion of desorption or adsorption tests, samples were confirmed by subsequent measurements until the mass change was less than 0.025% of the lesser value obtained from two successive measurements. The measured oven dried masses are fundamental to calculate evaporable water contents (Section 3-3-2).

3.2.4. Sorption apparatus

The sorption apparatus used in this study was originally designed and developed by de Burgh & Foster [36]. The sorption apparatus comprised of eight environmental chambers, 13.75 dm³ each, where the temperature is regulated at 23°C by circulating water jacket around and below the individual chambers. Chambers were covered by insulation panels to minimize heat exchange with the ambient environment. Relative humidity inside individual enclosed chambers was adjusted by placing a glass dish containing appropriate saturated salt solutions according to Table 3-3. For desorption to dry condition, Potassium sulfate salt solution was replaced by 4Å molecular sieves. To prepare the saturated salt solutions, reagent grade salts and deionized water were used.

All chambers were equipped with a small internal fan to minimize the external mass transfer limitation through the air boundary layer which can delay the initial mass change within a few hours after starting the tests. As it can be seen in Figure 3-2, each chamber has a removable tempered glass with a port in the middle, through which a single sample is suspended on a hanger and a hook with an integral stopper. A precision scientific balance (±0.001 g) was placed above each chamber on a levelled weighing rail (not shown in Figure 3-2) for gravimetric measurements. During the short period of weight measurements (several seconds), no significant RH perturbation through the very small gap between the integrated stopper and the port was observed. This was corroborated by the constant monitoring of the internal relative humidity and temperature using combined temperature and humidity sensors placed inside the chambers.

Saturated salt solutions	Formula	Regulated relative humidity at 23°C	
Lithium chloride	LiCl	11%	
Magnesium chloride	MgCl ₂	33%	
Potassium carbonate	K ₂ CO ₃	43%	
Sodium bromide	NaBr	58%	
Sodium nitrate	NaNO ₃	75%	
Potassium chloride	KCl	85%	
Ammonium dihydrogen orthophosphate	NH ₄ H ₂ PO ₄	93%	
Potassium sulfate	K_2SO_4	97%	

Table 3-3. Saturated salts used to regulate relative humidity inside individual chambers

Notes:

Relative humidity estimated using chamber humidity sensors and available references [70]



Figure 3-2. Test chamber details (the top insulation panel is removed)

3.2.5. SEM and EDS analysis

To perform microstructure analysis, thin slices were cut from bulk paste with precise diamond-bladed saw. Samples had been kept in sealed condition for 90 days prior to the preparation date. Samples were embedded in Huntsman RENLAM M-1 C1/REN HY 956 cold setting epoxy resin, then degassed by vacuuming for 10 mins and given 24 hours for curing the resin. The mounted samples were then ground and polished on Struers Labopol-5 machines using a set of 120, 320, 600 and 1200 grit emery papers. The resulting surfaces were then polished using 3 μ m and finally 1 μ m polishing pads. The polished samples were gold or carbon coated for SEM and EDS analysis respectively. A Hitachi S-3400N scanning electron microscope, operated at 20 kV was used to analyse the surface morphology of gold-coated samples. To analyse the elemental compositions, Energy Dispersive Spectroscopy (EDS) analysis was also conducted by a Quantax 400

spectrometer and Espirit 1.9 software. The microscope parameters that were used for the EDS analysis were as follows; accelerating voltage: 15 kV, probe current number: 50 (producing around 1nA probe current), working distance: 10 mm, Input counts: 1000 ± 300 cps.

A series of point analysis was performed to study the elemental composition of the binder phase in paste samples. Since the interaction volume of the electron beam has a radius of approximately 1-2 μ m at 15 kV accelerating voltage [71], spots were chosen far enough (usually more than 4 μ m away) from each other to avoid overlapping of the interaction volumes. During the analyses, unreacted fly ash and GGBS samples were avoided to make sure that the measured values are representative of the binder phase. Having said that, and considering the interaction volume of the electron beam, partial interference of underlying unreacted particles is possible. This interference, however, is inevitable, due to inherent limitations of EDS technique as a surface analysis method. The probable interfering effect of the invisible unreacted particles was (at least partially) rectified by eliminating the outlier data points when calculating the average of ion ratios (results are presented in Table 3-4).

After element identification, the weight percent of the elements present in the samples were calculated by Espirit 1.9 software by comparing the characteristic X-rays with the standard data available in its internal library. Although this method may lead to some inaccuracies, compared to standardization by standard reference materials, it is accurate enough for comparative studies and investigating various trends observed in the present study as it is plausible to assume a consistent level of (probable) inaccuracy for all measurements.

3.3. Results and discussion

3.3.1. SEM + EDS results

Figure 3-3 shows SEM micrographs of alkali-activated pastes (AAP2 excluded) and the control cement paste. Different surface morphologies are observed, depending on GGBS content, alkali level, and curing regime. AAP1, AAP3, and AAP4 show a more homogeneous binding matrix compared with AAP5, which is due to the higher concentration of the alkaline solution and consequently higher extent of dissolution of the solid precursors. On the other hand, many unreacted/undissolved GGBS (and FA) particles are observed in the AAP5 binding matrix. Elemental analyses of the binding matrices are also conducted through point analysis, and the average values are presented in Table 3-4. One sample per each mix has been studied extensively: between 30 to 45 spot analyses were conducted on the sample. 30 data points were chosen after eliminating the outliers, and the average of point analysis values along with the associated standard deviations was calculated and reported (Table 3-4). In general, samples fabricated of activators containing lower alkali contents showed more outliers. As mentioned previously in Section 3.2.5, this behaviour appears to be due to the interference of underlying unreacted particles. Another sample per each mix was also studied briefly through EDS analysis of a limited number of points (between 10 to 15 points) to assess the consistency of the obtained results through comparing the average values. In all cases, results were quite comparable, although the result of the second sample is not presented here due to the limited number of investigated points.

As it can be seen, samples fabricated with concentrated alkaline solutions (8% Na₂O and more), show higher Si/Al ratios, suggesting a higher rate of dissolution of

aluminate and silicate species and incorporation of them in the matrix [27]. In particular, AAP1 has the highest Si/Al ratio due to its highest alkali level (9.25% Na₂O according to Table 3-2), the chemical composition of Eraring FA which contains more silicate than the other fly ashes (Table 3-1), and the heat curing.

Interpreting the effect of slag addition requires an understanding of the differences in reaction mechanisms between calcium-rich and aluminosilicate binders. As explained in Chapter 2, 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, also called geopolymer [8,72]. The primary reaction product of calcium-rich GGBS, on the other hand, is an alkali charge-balanced aluminiumsubstituted calcium silicate hydrate gel, aka 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 [9–12]. In blended FA and GGBS 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, between 25% and 50% slag content according to [35], 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, which as will be discussed further in this chapter, is 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 are 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 [12,29,73].

The average Ca/Si ratios are presented in Table 3-4. The general trend, in accordance with the explanations provided above, is increasing the Ca/Si ratios 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 AAP3 with AAP5. While the slag content has been increased by 50%, Ca/Si has increased by more than 88%. This non-proportional growth is attributed to the lower alkalinity of the activator that promotes the formation of silicate hydrates, as discussed before. Of interest is the Ca/Si of Portland cement paste sample, which is considerably higher than all the alkali-activated pastes. The Ca/Si ratio of mix AAP5 with 75% GGBS is still far below that of HCP, suggesting a different nature of the calcium silicate hydrate gel in alkali-activated slag binders which is also consistent with the lack of interlayer space water in AAP3 and AAP5 as will be discussed in detail in section 3-2-2. Lower Ca/Si ratio of alkali-activated binders, even in calcium-rich matrices, was also previously reported by Yip & Van Deventer [12] through the microanalysis of blends of metakaolin and slag at different alkali levels.



Figure 3-3. SEM micrographs of alkali-activated and cement paste samples (magnification level is the same for all micrographs)

Mix	FA/Slag	M_{s}	Na ₂ O (wt. %)	Number of points	Si/Al (molar ratio) ± SD	Ca/Si (molar ratio) ± SD
AAP1	90/10	1.17	9.25	30	3.55±0.31	0.10±0.02
AAP3	50/50	1.5	8	30	2.58±0.25	0.67±0.15
AAP4	75/25	1.5	8	30	2.17±0.25	0.53±0.06
AAP5	25/75	1.5	4	30	2.05±0.32	1.26±0.22
НСР	-	-	-	30	3.09±0.42	2.07±0.08

 Table 3-4. Elemental composition ratios

Upon closer look at micrographs of Figure 3-3, an interesting difference in the macropore structure of alkali-activated and cement pastes is evident. HCP sample shows a network of large capillary pores that form from the space left by water and not filled up by the growth of C-S-H gel around the cement particles. As discussed previously for fly ash-based geopolymer-type binders by Ma et al. [31], the large macropores found in alkali-activated samples with a little amount of calcium (such as AAP1 and AAP4 in this study) are mainly large cavities left by the dissolution of fly ash particles or surface dissolution of hollow fly ash particles. These spaces are not filled by the growth of 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 [31,34]. The influence of rapid setting on the pore volume can get intensified for heat-cured samples where the reactions are accelerated, and as it will be discussed in the following sections, it can be as important for the small nano-scale sized gel/network pores as it is for larger pores. As it can be seen in Figure 3-3, no large pores (larger than 1 µm) were observed for AAP3 and AAP5 samples. The lack of large macropores for calcium-rich binders containing more than 50% GGBS is supported by the results of sorption and MIP tests and is discussed more in detail in the subsequent sections.

3.3.2. Water vapour sorption isotherms and pore structure of alkaliactivated binders

Water vapour adsorption and desorption isotherms describe the relationship between the environmental relative humidity and the retained evaporable moisture at a fixed temperature [36,44]. In a nanoporous material, a combination of different phenomena such as pore filling, pore condensation, pore blocking during evaporation (due to the presence of ink-bottle pores), and cavitation creates a hysteresis behaviour which introduces considerable difficulties for the interpretation of water vapour adsorption and desorption isotherms. Despite these complications and if carefully interpreted, WVSIs provide an insight into the pore structure and remain as an essential tool in Multiphysics modeling of phenomena influenced by the moisture transport such as the chloride ingress, and corrosion of reinforcement [30,38,74].

Figure 3-4 demonstrates the WVSIs of the alkali-activated paste (AAP) samples fabricated from blends of FA and GGBS. WVSI of an HCP with a water to cement ratio of 0.45 is also presented for comparison. All the measurements were carried out at a fixed temperature of 23±0.1°C. The isotherms are comprised of several individual points across the whole range of relative humidities; these points are calculated from the time-dependent mass changes in each environment, according to Equation (3-1).

$$EWC = \frac{W_{RH} - W_D}{W_D}$$
(3-1)

where EWC is evaporable water content, W_{RH} is the final stabilized weight of the disc sample in a chamber with internal relative humidity of RH according to Table 3-3, and W_D is the oven-dried mass of the disc. To form the isotherms by connecting the discrete points, the 'Akima' spline method [75] was used to avoid wobbly curve segments around any outlier point.



Figure 3-4. Water vapour sorption isotherms of heat and ambient-cured alkali-activated pasts, and the ambient cured hardened cement paste (EWC: Evaporable Water Content). WVSIs of AAP1 and AAP2 are from [44], and HCP from [36]

After establishing the relationship between the pore radius and the condensation pressure, and also calculation of the pre-adsorbed water layer in section 3-3-2-1 which

are fundamental to pore volume distribution calculations, a thorough discussion on the WVSIs along with the pore volume distributions which are calculated from WVSIs and MIP tests are presented in section 3-3-2-2. The time-dependent mass change graphs are used later to investigate the sorption kinetics and are presented in section 3-3-3.

3.3.2.1. Specific surface area, t-curve, and relationship between the pore radius and the condensation pressure

For cylindrical and slit-like pores with uniform shape and width, the pore condensation pressure can be described as a function of the pore radius by using the (modified) Kelvin equation [76]:

$$\ln \frac{p}{p_0} = \frac{-2\gamma V_m}{r_k RT}$$
(3-2)

where p/p_0 is equal to the relative humidity (divided by 100) at thermodynamic equilibrium over a curve liquid surface of radius $r_k=r_p-t_c$, r_p is the pore radius, t_c is the thickness of the multilayer adsorbate film attached to the surface of the absorbent which is formed prior to condensation and varies at different relative humidities, γ is the surface tension of the liquid ($\gamma = 235.8(1-T/647.096)^{1.256}[1-0.625(1-T/647.096)]mN/m$ [77]), V_m is the molar volume of the liquid (18.015×10^{-6} m³/mol), *R* is the universal gas constant (8.31446 J.mol⁻¹.K⁻¹), and *T* is the absolute temperature [46,78,79]. Replacing all these values in Equation (3-2) for the experimental temperature of 23°C (296.15 K) provides the relationship between the variable relative humidity and the core pore radius (r_k) as shown below:

$$\ln\left(\frac{RH}{100}\right) = \frac{-10.576}{r_k\,(\text{\AA})} \tag{3-3}$$

In order to calculate the pore radius (r_p) at a given relative humidity from the above equation, the thickness of the pre-adsorbed multilayer film (t_c) should be known beforehand. t_c can be taken from standard isotherms, or t-curves, which describe the average thickness of an adsorbed film on the surface of a non-porous solid as a function of relative humidity [79]. Various isotherms/t-curves can be found in the literature for both nitrogen and water adsorptive [80–83]; majority of t-curves are based on the calculation of the average thickness of the pre-adsorbed film (t(h)) from the total volume of the adsorbate at a given relative pressure h ($V_{ads}(h)$), divided by the pore specific surface area ($S=S_{sBET}$) according to Equation (3-4) [38,82].

$$t(h) = \frac{V_{ads}(h)}{S_{sBET}}$$
(3-4)

The specific surface area (S_{sBET}) is conventionally driven by the Brunauer-Emmett-Teller (BET) method [84] where the monolayer capacity (v_m) and the constant (C) is calculated from the BET plot which is obtained from the adsorption isotherm for $0.05 < p/p_0 < 0.35$. v_m is the volume of adsorbate required to cover the adsorbent with a unimolecular layer.

After obtaining v_m , S_{sBET} can be calculated by multiplying the number of molecules required to form a unimolecular layer by the average area occupied by each molecule [84]:

$$S_{sBET} = v_m N \sigma / V_m \tag{3-5}$$

here *N* is the Avogadro constant (6.0221×10²³ mol⁻¹), σ is the cross-sectional area of a single molecule (10.6 Å² [85], other values are also reported [81,82]), and *V_m* is the

molar volume of water ($18.015 \times 10^{-6} \text{ m}^3/\text{mol}$). Substituting these values into Equation (3-5) results in:

$$S_{sBET} = v_m / 2.82 \text{ Å}$$
 (3-6)

This conversion factor which reflects the thickness of a monolayer of the adsorbed water is in agreement with the available published data in the literature: Hagymassy et al. [82] 'tentatively' suggested 3Å, a similar value was recommended by Harkins and Jura [81].

 υ_m and S_{sBET} constants are calculated from the adsorption branch of WVSIs in the lowhumidity range for all the mixes, according to BET method [84], and the results are presented in Table **3-5**.

Mix	AAP1	AAP2	AAP3	AAP3A	AAP4	AAP5	НСР
$v_m \times 10^{-6} (m^{3/g})$	0.037	0.042	0.056	0.062	0.055	0.045	0.036
S_{sBET} (m ² /g)	132	149	194	221	194	160	128

Table 3-5. Specific surface area (S_{sBET}) of mixes (m² per gram of dry paste)

As noted in Table 3-5, the specific surface areas range between 128 and 221 m²/g which is in the range of the reported values for Portland cement-based binders in the literature: Baroghel-Bouny [38] reported values of 80 to 143 m²/g for cement pastes with degree of hydrations ranging from 0.48 to 0.92. In particular, the specific surface area of a cement paste referenced as CN with water to binder ratio of 0.45 and degree of hydration of 0.85 was reported to be around 118 which is close to the calculated value of 128 for the HCP in this study. Other researchers have reported values ranging between 100 and 200 m²/g for hardened cement pastes obtained through water vapour adsorption measurements [86,87]. Comparing the alkali-activated mixes with (almost) similar water to binder ratios in Table 3-5 (AAP1 to AAP3), it is evident that the addition of slag has increased the specific surface area. An increased surface area is indicative of the development of finer pores as fine pores have larger surface area. The correlation of the specific surface area with the slag content and hence the amount of C-(A)-S-H gel, is consistent with the reported correlation between the specific surface area of Portland cement-based binders with variable degrees of hydration [38,39]. Furthermore, a direct comparison between AAP5 and HCP mixes with 0.45 water to binder ratios reveals that the slag-based mix has a higher volume of fine pores compared with HCP. In addition, comparison of the specific surface area of AAP3 and AAP3A reveals formation of finer pores due to ambient curing. These observations are further corroborated by the pore volume distribution calculations in the following sections.

Having determined the specific surface areas, it is possible to calculate and draw the tcurves for individual mixes according to Equation (3-4) (Figure 3-5). These t-curves will be used to determine the pore volume distribution in the following section. For comparison, a t-curve from Hagymassy et al. [82] with a similar BET constant (C) (i.e. similar molar heat of adsorption of water molecules on the solid surface) as the pastes in this study is presented. For relative humidities below ~33%, all graphs are closely matching each other, in spite of different curing regimes, precursors and reaction mechanisms. A rather good match can also be seen for relative humidities ranging between ~33 and ~65%. A small deviation is visible for relative humidities less than 11%, which is due to the lack of a third data point between RH=~0 and RH=11% for AAP3 to 5, according to Figure 3-4. For RH values larger than ~65% in Figure 3-5, it is apparent that increasing the slag content and ambient curing increases the capacity of adsorbing several layers of water on the internal surface of pores; the average thickness of the adsorbed multi-molecular water layer for the ambient cured AAP5 is the highest among all the mixes and equals to almost eight monolayers of water (i.e. eight water molecule) at RH=100%. Considering that the thickness of a monolayer of water was calculated as 2.82 Å, it can be seen from Figure 3-5 that the adsorbed surface water can be removed in very low relative humidities of less than ~10-17%, depending on the mix composition.



Figure 3-5. t-curves of alkali-activated and hardened cement pastes. t-curve proposed by Hagymassy et al. [82] for nonporous materials with similar BET constant (C>50) is also presented for comparison

Recalling Equation (3-3) and $r_k=r_p-t_c$ where t_c can be taken from Figure 3-5, the relation between the pore radius (r_p) and the condensation pressure can be established for different mixes as it is illustrated in Figure 3-6. Since filling up the core of the pores depend only on the properties of the adsorbate according to Equation (3-2), the pore cores are filled up at the same condensation pressure, regardless of the differences in the properties of adsorbents. As a result, any difference observed in the curves presented in Figure 3-6 is caused by the differences in the average thickness of the preadsorbed water layer (Figure 3-5): For RH<~40%, the average thickness values are very close to each other, hence RH- r_p curves almost match for all mixes. For RH>~40%, the pore core radii (r_k) are considerably larger than the average thickness of the adsorbed surface water which means that the differences in the average thickness of adsorbed surface water layer are comparatively insignificant, and RH- r_p curves are very similar consequently. In fact, all curves are lying in such a narrow range which are hardly distinguishable; this similarity encourages using average representative values at different relative humidities to interpret WVSIs; however, the actual calculated r_p at each RH for individual mixes is used in the following section for pore volume distribution calculations. The average representative points are labelled in Figure 3-6.



Figure 3-6. The relationship between the pore radius and condensation pressure

3.3.2.2. Analysis of WVSIs

Water vapour adsorption and desorption isotherms for the three heat-cured and the two ambient cured alkali-activated pastes were previously presented in Figure 3-4. WVSIs for a control HCP sample with a water to cement ratio of 0.45 is also presented (from [36]) for comparison. In order to study the effect of different mix variables on the pore structure and pore size distribution of the pastes, main features of WVSIs can be identified as: 1- Evaporable water content and chemically bound water, 2- General pore size distribution in mesopore range, 3- Cavitation (i.e. the tensile strength effect), 4- The pore blocking effect and general hysteresis between the adsorption and desorption branches, and 5- Pore volume in macropore range. All the features mentioned above are discussed in detail for all the mixes subsequently.

a) Low relative humidity hysteresis (RH<33%): role of interlayer water

Figure 3-7 illustrates the maximum evaporable water content of the mixes which is indicative of the total porosity, excluding the closed pore. The maximum evaporable water content (EWC) is calculated as follows:

$$EWC_{\max} = \frac{W_{SSD} - W_D}{W_D}$$
(3-7)

where W_{SSD} denotes the saturated-surface-dry mass of the paste sample, and W_D is the desiccator-dried mass. Water-to-dry binder (W/b) ratios are also depicted in Figure 3-7(a). To calculate W/b ratios for alkali-activated mixes, the water content of sodium silicate solution, as well as sodium hydroxide pellets, are included. The anhydrous part of the activator is also considered as part of the dry binder. Comparison of W/b ratios
and EWCs is of interest as the difference between these two values is roughly indicative of the amount of water that is bound into the structure, disregarding the amount of water trapped in the closed pores.

As it is illustrated in Figure 3-7(a), increasing W/b ratio has generally increased the total porosity and the EWC trend of alkali-activated samples follows the W/b trend; besides, increasing the calcium content seems to have increased the difference between W/b and EWC values, and hence the bound water. The smallest retained water amount has recorded for AAP1, where the structurally bound water is almost non-existent and all the introduced water can get evaporated at very low relative humidities⁴. On the other hand, HCP sample with the same W/b ratio as AAP5 mix shows considerably higher amount of bound water. The main hydration product of Portland cement is calcium silicate hydrate (C-S-H) with a mostly amorphous colloidal structure [39,88]. The exact nano-structure of C-S-H gel in hydrated Portland cement is still a subject of controversy and different nano-structural units have been proposed so far [88,89]. Traditionally, a layered structure at the scale of tens of nanometers is considered with the ability to hold 'interlayer' water molecules in the spaces within the layers. Since the typical basal spacing of tobermorites⁵, as crystalline C-S-H minerals with similar composition to C-S-H gel, is around 11 or 14 Å, no more than one or two water molecules could be probably accommodated in the interlayer spaces [9,39,90,91]. A similar tobermorite-based structure, although, with some degree of cross-linking, was

⁴ The lack of structurally bound water for geopolymer-type binders was already addressed in [44] for mixes AAP1 and AAP2, and will be discussed here more in detail along with other high-calcium content mixes.

⁵ Tobermorite is usually considered as representative of C-S-H of low Ca/Si ratio, whereas jennite structure is a more valid analogy to describe the structure of C-S-H of high Ca/Si ratio [90]

proposed for alkali-activated slag systems [9], and a similar water-holding mechanism in the interlayer spaces can be expected for these binders as a result.

Recalling that the thickness of a monolayer of water is 2.82 Å, and considering the tcurves depicted in Figure 3-5, the average relative humidity corresponding to the thickness of one and two water molecules is around 11.3% and 53% respectively. Historically, the observed hysteresis below ~35% is associated with desorption of part of the interlayer layer water in OPC-based binders which can lead to a mostly reversible interlayer space reduction in C-S-H gel [40,86]. All the retained water for RH<11.3% can be regarded as the interlayer water (characteristic of evaporation of one water molecule), while the retained water within 11.3%<RH<~33% can be due to the structural binding of one or two water molecules, or the pore blocking effect, or a combination of both. Nevertheless, the low relative humidity hysteresis in WVSIs of Figure 3-4 can be regarded as a qualitative index representing the retained interlayer water.

To have a better understanding of the low relative humidity hysteresis behaviour of mixes, the area enclosed by the adsorption and desorption branches of WVSIs (with the exception of AAP3A) in Figure 3-4 are calculated and shown in Figure 3-7(b). Two curves are presented: one for the hysteresis area within RH<11.3%, and another for RH<33%. Increasing the calcium content (see Ca/Si ratios in Table 3-4) has increased the hysteresis area marginally, with a sharper increase recorded between RH=11.3% and 33% than RH<11.3% for the ambient cured mixes. The results depicted in Figure 3-7(b) are also in agreement with the trends observed in Figure 3-7(a) where increasing the calcium content develops more interlayer spaces to retain water, and geopolymertype binders (with insignificant calcium content) do not preserve the water in their

structure due to their vastly different structural system compared with the calcium-rich matrixes.

The more notable growth for ambient-cured mixes within the range 11.3%<RH<~33% can be attributed to more nanostructural units with more than one water molecule held in the interlayer space, or a formation of finer pores which amplifies the pore-blocking effects in these mixes. The pore blocking occurs if a pore has a restricted access to the external gas phase via narrow constrictions. These type of pores are often called ink-bottle pores in the literature [30,45]. This limited access means that the capillary condensate in the pore cannot empty during desorption until the liquid in the neck empties at lower relative humidities. Thus, the evaporation of capillary condensate in ink-bottle pores depends on the size of the constrictions and the network connectivity [30].

Unlike the ambient-cured samples, heat-cured samples contained less structurally bound water and showed considerably lower hysteresis behaviour within the lowhumidity range. Apart from AAP1 with minuscule amount of calcium in the mix (Ca/Si=0.10 according to Table 3-4), the lack of hysteresis behaviour for AAP2 and AAP3 with 35% and 50% slag content could stem from heat-curing effects, sufficiency of the calcium content (or insufficiency thereof), higher concentration of the activator, and comparatively lower W/b ratio. As it will be discussed in the following sections, heat-curing mainly affects the kinetic of C-(A)-S-H gel and/or aluminosilicate network formation which leads to a less ordered pore structure with larger pores [32]. Larger pores and wider constrictions reduce the possibility of formation of ink-bottle pores; as a result, less pore blocking effects and hysteresis behaviour is expected for heat-cured samples. Availability of enough calcium sources in blended systems is also important in the formation of C-S-H gels: below a certain threshold, calcium ions will be absorbed into the aluminosilicate network via a charge balancing mechanism. Based on the macrostructure study of a range of blended fly ash and slag samples using X-ray microtomography, Provis et al. [35] has reported a threshold of 25 to 50% where the C-S-H formation starts to dominate the binder, and beyond 50% slag replacement, the pore filling effect of C-S-H gel becomes highly effective. These reported numbers are similar to the findings of this paper based on nanostructural studies as opposed to the macro-scale investigations in [35]: AAP1, AAP2, and AAP4 appear not to have enough calcium to have significant C-S-H components. This brings back the issue of uncertainty about the source of hysteresis within the range 11.3<RH<33 for AAP4 mix which seems to be rooted in the physical pore blocking effect, as explained above, rather than the chemical water implementation in the structure due to lack of enough calcium source. For mix AAP3 with 50% slag, there should exist sufficient calcium source in the matrix to develop considerable C-(A)-S-H matrix; although, the small hysteresis observed for RH<11.3% is against this assumption. This contradiction can be explained by the high concentration of NaOH in the mix which promoted formation of calcium hydroxide and inhibited formation of C-(A)-S-H [29]. For comparison, AAP5 with almost half sodium concentration shows more hysteresis behaviour and consequently water binding.

All in all, it seems that the interlayer water plays a more prominent role in OPC-based binders, even AAP5 mix with 75% slag does not show considerable hysteresis within RH<11.3% as opposed to the remarkable hysteresis of HCP mix. This difference can be in part due to a different nanostructure of the C-(A)-S-H gel in the alkali-activated binders than the C-S-H gel formed in OPC-based binders, consistent with considerably lower Ca/Si ratios (Table 3-4) even for AAP5 with 75% GGBS. In view of the complexity of the phenomenon and the lack of data in the literature, further

investigation is required regarding the adsorption/desorption of the evaporable water which is structurally bound in alkali-activated systems, particularly for the calciumrich binders.



Figure 3-7. Evaporable water contents and water-to-binder ratios (a), and Hysteresis area enclosed by desorption and adsorption branches of WVSIs (b)

b) Pore size distribution in mesopore range, cavitation, and general hysteresis behaviour

To have a quantitative insight into the pore size distribution (PSD) of samples, the wellknown BJH method [46] based on the original work published in 1951 is used to analyse the pore structure in mesopore range⁶ (2 nm<d_p<50 nm, i.e. *RH*<94.5% from the average curve in Figure 3-6). BJH procedure was developed on the basis of Kelvin equation (Equation (3-2)) and provides a numerical algorithm to calculate pore size distribution based on the emptying of the cylindrical pores following a step-wise reduction of p/p_0 (= RH/100) [92]. The retained water is assumed to be either physically adsorbed to the pore walls, or in form of condensate water in pore cores. Reduction of p/p_0 generates desorbed vapour by emptying $r_p(p/p_0)$ radius pores of their condensate

⁶ According to IUPAC's recommendation [92], micropore range is less then 2nm, mesopores have radii between 2 and 50 nm, and macropores are larger than 50nm in radius

water and by reducing their pre-adsorbed water layer thickness. In addition to these two contributing gas volumes, part of the total desorbed gas also comes from the reduction of the thickness of the pre-adsorbed water layer in pores larger than $r_p(p/p_0)$ which were already emptied [46]. This assumed desorption sequence is the backbone of BJH algorithm. The accuracy of BJH method has been extensively studied in the past and the general consensus among the researchers is that the BJH method underestimates the pores size, and that the underestimation is larger for smaller pores [30,93]. Despite the inaccuracies, BJH method is capable of capturing the main features of PSDs [93], and still remains as a powerful tool to study the pore size distribution in mesopore range by non-destructive test methods such as adsorption/desorption of nitrogen gas or water. The underestimation of pores size, however, is probably of subordinate importance in this study since PSD graphs are only used for comparison purposes; besides, the underestimation will be assessed by comparing the calculated PSDs with the MIP test results.

Figure 3-8 depicts the pore size distributions for heat and ambient-cured alkaliactivated samples as well as the OPC paste. PSDs are presented in groups for cross comparison (see Figure 3-8(a) for heat-cured and (b) for ambient cured samples), and also individually presented with their main peaks annotated on each graph. The desorption branch of WVSIs are used to calculate PSDs. WVSI of HCP sample presented in Figure 3-4 is analysed to compare against PSD of alkali-activated pastes. Also, the cumulative pore volume for all the mixes is calculated and presented in Figure 3-9. The main peak at around ~3.00-3.10 nm is identifiable for all PSDs, regardless of the binder type (alkali-activated or OPC-based), with the exception of AAP1 which shows two peaks at 2.73 and 3.41 nm. As discussed by other researchers [30,36], the high intensity of this peak is not necessarily indicative of pore water evaporation from the pores in this range, it can be in part due to the artificial amplification associated with the characteristic step-down in the desorption branch within the RH range 33% to 43%. The characteristic step-down in the desorption branch, which is evident in Figure 3-4 for some mixes, is attributed to the spontaneous nucleation and evolution of gas bubbles in the metastable condensed water in ink-bottle shaped pores. This phenomenon is called 'cavitation' or 'tensile strength effect' and occurs in ink-bottle shaped pores with constrictions smaller than a critical width (~6 nm according to [30]). For the neck sizes above the critical width, the usual pore-blocking governs the desorption process at higher RH levels [30]. Nevertheless, increasing the intensity of the main peak can be regarded as developing a finer pore structure that partly increases the volume of pores around the location of the main peak, and partly enhances the cavitation leading to a higher intensity of the main peak.

Upon a closer look at WVSIs of Figure 3-4, it can be seen that the characteristic stepdown is more distinguishable for AAP2, AAP3, AAP3A and AAP4, while AAP1, AAP5 and HCP samples do not demonstrate such a prominent step down as in other cases. This observation is also consistent with the PSDs presented in Figure 3-8 where AAP2, AAP3, AAP3A and AAP4 show narrower main peaks, as opposed to the broader main peaks of AAP1, AAP5 and HCP. This difference seems to suggest that cavitation plays a more prominent role in increasing the intensity of the main peak in samples with medium levels (i.e. between 25 and 50%) of GGBS content.

As it is illustrated in Figure 3-8 for heat-cured AAPs with almost the same amount of water to binder ratio (AAP1 to AAP3), the intensity of the main peak increases by increasing the slag content. Development of finer pores as well as narrower constrictions in mesopore range which can also amplify the cavitation can be inferred as a result of increasing the calcium content (also see Table 3-4 For Ca/Si ratios).

Moreover, HCP sample shows a smaller main peak (and less cavitation) compared with all alkali-activated pastes, with the exception of the AAP1 mix with the least amount of calcium in the matrix (Ca/Si=0.10 according to Table 3-4).

AAP1 has three main peaks closely located between 1.68 and 3.41 nm, and the intensity of these main peaks is comparatively slightly larger than the next major peak at 11.4 nm. The smaller intensity of the main peaks is also reflected in Figure 3-4 by the lack of the typical step-down which leads to less cavitation, and almost a linear desorption path for RH<93%. AAP1 also has the least hysteresis between the adsorption and desorption branches (Figure 3-4) throughout the whole mesopore range from which a uniform pore size distribution is inferred; this is in agreement with its PSD in Figure 3-8(c). The pore structure of AAP1, which can be considered as representative of geopolymer-type binders, is comprised of a rather uniformly distributed volume of pores in the mesopore range as it can be seen in the cumulative pore volume curve of Figure 3-9. On the other hand, AAP2 mix with 35% slag replacement shows considerably finer pores (Figure 3-8(d)) and a more prominent main peak: The main peak is shifted to 3.06 nm (as opposed to 3.41 nm for AAP1), and while both graphs show a peak at around 11.4-11.5, a new peak is generated at 5.15nm in PSD of AAP2. Furthermore, the main peak at 3.06 nm has a considerably higher intensity due to the amplification of cavitation. Increasing the slag content to 50% (mix AAP3, and AAP3A), helps to develop a finer pore structure further as it is evident from disappearing of the peak at 11.5, shifting the cumulative pore volume graphs toward smaller pores, and a higher peak intensity at around 3.1 nm.

These result again confirm findings of Provis et al. [35] where formation of the pore filling C-(A)-S-H gel in blended systems with less than 25% slag content was found

unlikely; below this threshold, calcium ions get adsorbed into the aluminosilicate network without chemically binding the water, leading to less pore filling effect.

A similar trend can be seen for ambient-cured mixes with regard to the increase in the intensity of the main peak, characteristic of the development of finer pores and amplification of cavitation. In addition, of interest is the finer pore structure of the ambient-cured samples compared to the heat-cured samples with similar or even higher slag content. AAP4 mix with 25% slag evidently shows finer pores than the heat-cured AAP2 with 35% slag; the peak at 11.5 nm is disappeared and a considerable volume of pores can be seen at 6.18 nm instead. The intensity of the main peak at 3.10 nm is also higher than that of AAP2 and it is very close to the heat-cured AAP3 with 50% slag content (compare Figure 3-8(f) with (d) and (e)).

A similar difference can be found by direct comparison of AAP3 and AAP3A samples that were fabricated from the same batch but cured differently. The ambient-cured AAP3A demonstrated a higher main peak and finer pores than its heat-cured counterpart; the pore volume associated with the peak at 5.13 nm is shifted toward finer pores, and a considerable volume of pores smaller than 2.5 nm can be spotted in the PSD graph. This pore volume is consistently appearing in the PSD of all ambient-cured mixes and is insignificant for heat-cured samples. This trend is consistent with the higher pore blocking effect observed for 11.3%<RH<33% in the WVSIs of ambient-cured mixes presented previously. These results are in agreement with the findings of Rovnaník [32] where heat curing increased the pore sizes of metakaolin-based geopolymers. Increasing the pore sizes and hence shifting the cumulative pore volume graphs toward larger pores in mesopore range for heat-cured mixes, as explained earlier, is a consequence of a faster hardening/development of the aluminosilicate

network (in case of fly ash-based systems) or C-S-H gel (for calcium-rich systems) which results in a less ordered pore structure with more pores.

According to Figure 3-9, the ambient-cured AAP5 mix with the highest slag content among all mixes and an average Ca/Si ratio of 1.26 (Table 3-4) has the finest pore structure in the mesopore range, along with AAP3 and AAP3A, both with 50% slag content. By contrast, all the other mixes, including HCP, have larger pores distributed throughout the whole mesopore range (i.e. pores up to 50 nm in diameter; although, only pores smaller than 20 nm are presented in the graphs, due to the negligible volume of pores larger than 20 nm). For AAP5, the shift toward smaller pore sizes is apparent where bulk of the pores are less than ~15 nm in diameter (Figure 3-9) and the volume associated with this pore range is considerably higher than all the other mixes, due to a higher water to binder ratio, and consequently a higher overall porosity. This particular pore structure shows the importance of the addition of slag in blended alkali-activated systems; the very fine porosity of C-(A)-S-H gel produced by alkali-activation of slag can drastically decrease the total porosity. The slag addition is obviously more efficient when the C-(A)-S-H gel dominates the binder, which occurs when the slag replacement is 50% or more. It seems plausible to assume that in calcium-rich alkali-activated binders, the volume of macropores (i.e. pores larger than 50 nm in diameter) reduces significantly as well. Although, due to the limitations of the BJH calculation method, evaluating the macropores from WVSIs is not possible, unless qualitatively, as will be explained subsequently (Figure 3-12). It should be also noted that, the analysis and discussion presented in this section are all based on the analysis of the desorption branch of WVSIs. Analysing the adsorption branch, can lead to overall higher volume of pores, in particular in porous materials with considerable pore blocking in the network.



Figure 3-8. BJH pore size distribution for alkali-activated and cement paste samples



Figure 3-9. Cumulative pore volume of all mixes (BJH method)

Explaining the observed substantial hysteresis between the desorption and adsorption branches of AAP5 samples (Figure 3-4) requires more information regarding connectivity of the pores which can result in a pore blocking effect. This will be discussed more in detail in the next section, based on MIP test results which provide an insight into the macroporosity of the samples. Further inspection of Figure 3-8 reveals some differences in the PSDs of OPC paste and alkali-activated pastes. HCP sample shows less intensity of the cavitation-associated peak which is also corroborated by a less prominent characteristic step-down in desorption branch of WVSI (Figure 3-4). This behaviour can be attributed either to a larger pore content with a width larger than the critical width necessary for cavitation, or larger pores in general. The cumulative pore volume graph of HCP sample interestingly shows a rather high volume of pores compared to the alkali-activated pastes with the exception of AAP1 with negligible calcium content in the mix. As it is noted in Figure 3-8, the PSD graphs of HCP sample shows a more uniform distribution of pores within the whole mesopore range. This uniformity can also be deduced from the rather linear desorption branch of WVSI in Figure 3-4 for RH>~33%.

c) MIP test results, evaluation of large mesopores and small macropores

In order to investigate the pore structure of samples in the whole porosity range more in detail, Mercury Intrusion Porosimetry (MIP) test was performed for all samples (except AAP3A), and the results are presented in Figure 3-10 and Figure 3-11. Caution needs to be exercised while interpreting the results of MIP test in binders with a considerable amount of ink-bottle 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 [33]. The pore blocking associated error could also be identified by the presence of pores larger than 1 μ m in AAP1 and AAP4 SEM micrographs in Figure 3-3, whereas only an insignificant volume of pores larger than 1 μ m (1000 nm) could be seen in MIP incremental pore volume graphs. Furthermore, MIP does not provide any information in micropore range (pores smaller than 2 nm according to [45], 3 nm in this study), and the discussions in this section are limited to meso-to-macropore range. Despite all inaccuracies, MIP has provided some valuable information regarding the pore volume distributions, particularly for pores larger than 50 nm and up to 1000 nm that could not be assessed by BJH method. The consistency of the main features of the pore structures in the mesopore range between the BJH calculated PSDs and the MIP results, as will be discussed in this section, further suggests the reliability of the MIP results for mesopores as well as small macropores.

The pore sizes associated with the main peaks are annotated in Figure 3-10 on individual PSDs, and the peaks associated with bulk of fine and large pores are marked with arrows. Several interesting features can be found as follows. Two main pore modes are distinguishable for samples with less than 50% GGBS content: one

associated with the bulk of fine mesopores, ranging from 3 nm to ~15 nm. There are three main peaks in this range at 4.30, 6.60 and 11.40 nm. The second pore mode is associated with the larger mesopores and small macropores ranging from 15 nm to 130 nm with a prominent peak at 46 nm. Comparison of the above-mentioned peaks with the small mesopore peaks (smaller than 7 nm) calculated from WVSIs by using BJH method (Figure 3-8) shows a systematic underestimation of the peak locations in PSDs calculated by BJH method; although, the main features of the PSDs, including the general shape and number of main peaks, are generally preserved. Peaks associated with pores larger than 7 nm show less underestimation, in particular the peak at 11.4-11.5 nm which is present in both calculated and measured PSDs.

In accordance with the BJH calculated PSD, AAP1 sample shows a very porous structure with an almost constant volume of pores across the whole meso-to-macropore range. The addition of 25 or 35% GGBS (Figure 3-10 (d) and (f)), has led to the formation of two distinct pore modes as discussed before. The coincidence of the main peak associated with the second pore mode at 46 nm in alkali-activated AAP2 and AAP4 with HCP samples, suggests some level of similarities in the pore networks. For HCP, the second pore mode is associated with the capillary network, in which a connected network of small and large pores forms the main pore structure. Given the very fine porosity of alkali-activated slag, the addition of a small-to-medium level of GGBS (between 25 to 50%) to the porous aluminosilicate network appears to be able to generate a similar network by filling some of the larger pores within the considered range. The presence of two distinct pore modes in AAP2 and AAP4 confirms the possibility of connection of pores of different sizes, leading to pore blocking effect which was reflected in the observed amplified cavitation. AAP3 also shows the largest step-down in its WVSI, although only one main pore mode is evident in Figure 3-10

(e). Although AAP3 demonstrates the finest pore structure (Figure 3-11), as it is demonstrated in Figure 3-12 and will be discussed accordingly, it seems that a volume of large mesopores/small macropores in AAP3 have been submitted as finer pores during the MIP test.

AAP5 shows only one main pore mode, similarly to AAP3, with the largest peak at 9.6 nm. Lack of a second main peak is considered reasonable for AAP5 due to the presence of 75% GGBS which dominates the binder. The relative lack of large mesopores/macropores in AAP5 is also consistent with the findings of the previous section where no significant volume of large mesopores could be found in the PSD of AAP5.

Similar to the findings of the previous section, heat curing has increased the pore sizes. The disappearance of the peak at 11.40 nm in AAP4 PSD curve when compared with AAP2 PSD curve, and shifting the location of the main peak from 4.30 to 3.40 nm demonstrates the development of a finer pore structure for the ambient-cured AAP2 with less calcium in the binder.



Figure 3-10. Pore size distribution for alkali-activated and cement paste samples (MIP result)



Figure 3-11. Cumulative pore volume of all mixes (MIP result)

The relative absence/presence of large mesopores/small macropores in AAP3 and AAP5 samples (and other samples as well) can be further investigated by interpreting WVSIs in Figure 3-4. According to Figure 3-6, the moisture content gain by increasing RH from 93% to 97% is associated with the volume of pores between 30 and 84 nm. Further increasing RH from 97% to 100% fills up all the pores larger than 84 nm; although MIP provides some information on the pores in this range (unlike BJH method), any probable ink-bottle pore effect may lead to underestimation of the pore sizes. The mass gains from 93% to 97%, and from 97% to 100% are calculated from WVSIs and presented in Figure 3-12. As it is shown, AAP5 has the smallest volume of pores larger than 84 nm, consistent with the relative lack of pores in this range from MIP test and BJH calculated PSD. On the other hand, the volume of pores larger than 84 nm is almost three times as large for AAP3, increasing the skepticism over the accuracy of MIP result for large macropores in AAP3. By contrast, AAP5 has more pores between 30 and 84nm than AAP3, this is reflected in the cumulative pore volume graphs of Figure 3-11. The very large volume of pores larger than 84 nm in AAP1 and

AAP2 samples are also of interest, these volumes might not be completely reflected in MIP PSDs, due to pore blocking effects, in particular for AAP2.

Considering the marginal quantity of large mesopores and macropores in the pore structure of AAP5 which was confirmed qualitatively, the large hysteresis observed in Figure 3-4 for AAP5 can be attributed to hysteresis in individual pore level, rather than in network level due to pore blocking, as uniformity of pore sizes minimizes the possibility of pore blocking. In fine pores, the adsorbed multi-molecular water layer contributes more in the total water filling the pores, compared with larger pores where condensation of the water in the pore cores plays a significantly more important role. Because of the strong surface and intermolecular forces [30], desorption of the whole water only takes places at lower relative humidities than the relative humidity associated with the adsorption process. This hypothesis can explain the wide hysteresis observed in AAP5's WVSI throughout the whole relative humidity range in the absence of significant pore size differences.



Figure 3-12. Qualitative estimation of the volume of large mesopores as well as macropores

To summarize, reviewing Figure 3-4, Figure 3-8 and Figure 3-10 reveal the prominent effect of calcium content on the pore size distribution of alkali-activated blended paste samples. Achieving a very fine pore structure is certainly possible by adjusting the slag content; although, a fine pore structure does not necessarily translate into less permeability as connectivity of the pores is also an important parameter which will be discussed later in light of the observed sorption rate data. Geopolymer-type binders with a little amount of calcium are highly porous, and consequently, their WVSI has less hysteresis due to insignificant pore-blocking effect and less cavitation as well. The high porosity of geopolymer-type binders was previously reported by Ma et al. [31] for alkali activated fly ash paste samples fabricated of sodium silicate solutions of various silica and alkali contents.

Alkali-activated slag binders, on the other hand, show a very fine pore structure, with a relatively small volume of large mesopores/macropores. This particular pore size distribution leads to considerable pore-blocking effect which is reflected in the observed prominent hysteresis in the WVSI. For blended fly ash and slag binders, the main features of WVSI and the pore structure are highly dependent on the availability of enough calcium content to form C-(A)-S-H gel which leads to considerably finer pore structure than the aluminosilicate matrices. Increasing the slag content in blended alkali-activated binders (with less than 50% GGBS) also appears to lead to more cavitation and pore-blocking effect, due to co-existence of the C-(A)-S-H gel with a very fine pore structure and the aluminosilicate network with larger pores.

3.3.3. Sorption kinetics, and moisture diffusion coefficients

3.3.3.1. Fickian and non-Fickian processes

In this section, the time-dependent mass loss/gain of the specimens (sorption kinetics) are analysed to calculate the moisture diffusion coefficient of two alkali-activated pastes and one hardened OPC paste, and to assess the probable anomalies in the sorption process. Saturated (desorption) or dry (adsorption) samples have been exposed to various environmental water vapour pressures in which the variability of the vapour flux density with time resembled a non-steady state diffusion condition [37].

Moisture transport in unsaturated porous media is a multi-phase mechanism involving both gas and liquid phases. It occurs in partially saturated pores via adsorption/desorption of the multi-molecular water layer adsorbed into the pore walls, and the condensate water which is in equilibrium with a mixture of water vapour in the gas phase and the dry air. By averaging the flow equations for liquid and gaseous phases at the microscopic level over a representative volume of the element, it was shown that moisture transport due to both the liquid and vapour phases can be expressed by Richards' equation [94–97]:

$$\frac{\partial}{\partial x}(D_w \frac{\partial w_l}{\partial x}) = \frac{\partial w_l}{\partial t}$$
(3-8)

where W_l denotes the retained evaporable moisture (in grams of water per gram of dry material), x is a distance coordinate, and D_w is called the total moisture diffusion coefficient which is comprised of both liquid and vapour components. Equation (3-8) expresses transport of the total moisture (both vapour and liquid water) in terms of the

liquid water content as the variable. Using the liquid water (w_l) as the state variable, instead of relative humidity is also beneficial in modeling the moisture transport through advection which can be used to estimate the concentration of transported ions, such as chloride ions, during wetting-drying cycles [97].

Considering the dimensions of the paste slices used for adsorption tests in this study, a one-dimensional adsorption process is assumed to solve the non-steady state diffusion equation. For a membrane of thickness 2l, with a uniform initial concentration, and equal surface concentrations, the total amount of diffusing adsorptive at time $t(M_{t},F)$ can be calculated from the solution of Equation (3-8) [98]:

$$M_{t \cdot F} = M_{\infty, F} \left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-D_w (2n+1)^2 \pi^2 t / 4l^2\right) \right]$$
(3-9)

 $M_{\infty,F}$ is the total amount of diffusing substance after infinite time, and D_w is the moisture diffusion coefficient. Equation (3-9) provides a convenient solution for moderate to large values of $D_w t/l^2$, but for small $D_w t/l^2$ values the series become slowly convergent which makes the numerical evaluation difficult. Equation (3-10) was suggested by Crank [99] to circumvent this difficulty, provided that the volume of adsorptive is infinite:

$$M_{t \cdot F} = M_{\infty, F} \left[\frac{2}{\sqrt{\pi}} (D_{w} t / l^{2})^{1/2} \right]$$
(3-10)

The threshold value of $D_w t/l^2$ which determines the applicability of equations 3-9 or 3-10 can be found by equating these equations and solving the equation for $D_w t/l^2$. When the transport process follows Equation (3-8), it is called a 'Fickian' process; however, anomalies leading to 'non-Fickian' or 'anomalous' behaviour are reported in the literature for cementitious materials [36,100,101]. The sources of anomalies, particularly in cementitious materials, are still debated. In a recent study, de Burgh and Foster [36] assessed the non-Fickian sorption process in hardened cement pastes, including the HCP which is used as a control sample in this study, and it was found that the non-Fickian process plays a major role in long-term equilibrium kinetics. After reviewing a range of probable causes for the observed anomalies, it was argued that the time-dependent microstructural changes are the main reason for the non-Fickian sorption phenomenon. Other reasons are also suggested for the non-Fickian sorption behaviour by other researchers, foremost among which are the delayed diffusion from the constrictions [101], non-instantaneous equilibrium of the surface concentration [102], Internal relaxation of the adsorbent [101,103,104], uptake of water by ongoing hydration of cement or slag particles and/or slowly reversible changes to the C-S-H microstructure upon drying and consequent wetting [105], and history-dependency of the diffusion process [102]. It should be noted that, a detailed investigation of sources of the anomalies in the sorption process is out of the scope of the present study, and readers are referred to previously published research studies in the literature for more information (see e.g. [36,101–103,106]).

In a non-Fickian process, water sorption proceeds through two sub-processes. One contributing process is a macroscopic diffusive (Fickian) process which follows Equation (3-8), and is responsible for short-term gravimetric equilibrium. This means that, if plotted against the square root of time (\sqrt{t}) , the initial part of the sorption curve should be linear [98,103,107], followed by a knee where a rapid rate change occurs leading to a plateau. The mass change becomes almost negligible at around twice the time associated with the knee point; thus, the Fickian-associated part of the sorption process can be considered as a constant after this point [36,103]. The second sorption

process which is responsible for longer term mass changes generally attains the equilibrium at a slower rate. This non-Fickian component has been commonly presented as an exponential type decay function [1,38,43], according to Equation (3-11):

$$M_{t,nF} = M_{\infty,nF} \left[1 - \exp(-kt) \right]$$
(3-11)

where $M_{t,nF}$ is the time-dependent mass change associated with the non-Fickian process, $M_{\infty,nF}$ is the ultimate amount of sorption due to the non-Fickian behaviour, and k is an exponential decay constant.

The complete sorption process (Equation 3-12) can be presented by linear superimposition of the Fickian (Equations (3-9) or (3-10)) and non-Fickian contributing parts (Equation (3-11)), provided that the diffusive process takes place adequately rapidly to precede the independent secondary non-Fickian component [104].

$$M_{t} = M_{t,F} + M_{t,nF}$$
(3-12)

Superimposition of the contributing sorption processes was originally proposed by Berens and Hopfenberg [104] for glassy polymers, and the non-Fickian process was attributed to stress relaxation during the adsorption process. The superimposition method is fundamentally different from the previously suggested analysis methods (see e.g. [102]) where a Fickian (diffusion) sorption process was assumed as the sole mechanism, and some modifications, such as a time-dependent surface concentration relaxation, was introduced into the model to take into account the effects of anomalies [104]. The superimposition principle, stated by Equation 3-12, underlies the deconvolution method used here, and also used by some other researchers to study the sorption processs in cementitious materials [36,101,108]. de Burgh and Foster [36] used the concept of superimposition to calculate the decay constant and non-Fickian associated mass change for a range of hardened cement pastes exposed to different temperatures during adsorption/desorption processes. To minimize the effect of the Fickian process, only part of the sorption curve which was sufficiently far from the knee point was considered in their study. This means that, as previously mentioned, $M_{t,F}$ in Equation (3-12) becomes a constant in that region. In the present study, however, a curve fitting method by using Equation (3-12) is employed to assess not only the non-Fickian contributing component of the sorption process but also the Fickian component. Assessing the Fickian part enables calculating the moisture diffusion coefficients and Fickian/non-Fickian contribution factors in alkali-activated binders for the first time ever.

3.3.3.2. Assessment of the sorption kinetics

Adsorption and desorption kinetics are shown in Figure 3-13 for AAP4 and AAP5. In addition, the sorption kinetic curves for the HCP sample are presented (from [36]). Each curve in Figure 3-13 corresponds to the mass change of a single dry/saturated sample exposed to a target relative humidity in an environmental chamber. Only AAP4 and AAP5 are analysed and further implications for heat-cured mixes are possible in light of the observed higher porosity of their pore structure (refer to the previous section). The adsorption kinetics are analysed more in detail to avoid the complications due to the network effects during the desorption process.

a) Adsorption kinetics

According to Equations (3-9) and (3-10), the square root of time to equilibrium in a Fickian sorption process is proportional to the sample thickness and inversely proportional to the square root of the moisture diffusion coefficient. The moisture diffusion coefficients of the different mixes can be qualitatively assessed considering the thickness of the samples, which are provided next to each curve, and the knee location as the point where the rate of mass change start to plateau. The knee locations are schematically identified and connected by a solid line as a visual guide. As it is shown, AAP4 has the shortest time to the knee location, followed by HCP and then AAP5. To eliminate the effect of thickness differences on the initial rate of stabilization, the time to knee locations are divided by the average thickness of samples of each mix (average thicknesses are presented in each graph in Figure 3-13). By applying this reduction factor, AAP4 samples started to equilibrate after 0.25-0.195 $day^{0.5}$ (from dry condition to 11% and 97% respectively), as opposed to 0.48-0.65 $day^{0.5}$ for AAP5 samples, and 0.35-0.4 day^{0.5} for HCPs. These values are indicative of significantly higher permeability for AAP4: the time required for AAP4 samples to achieve the short-term equilibrium is 3.7-11 and 2-4.2 times shorter than the AAP5 and HCP counterparts. Since the observed sorption processes are not 100% Fickian, as it will be discussed, these figures are not to be regarded as representatives of the moisture diffusion coefficients, and rather they are important parameters showing the total (Fickian and non-Fickian) sorption rate which is indeed very crucial in durability design.

As discussed before, one of the main characteristics of Fickian sorption processes is the relatively rapid rate of approaching the gravimetric equilibrium. Accordingly, the mass changes become almost negligible shortly after the point of rapid rate change (i.e. the knee point). This behaviour appears not to be followed in a number of adsorption kinetic curves, and depending on the humidity, the initial gain in evaporable moisture content is followed by a gradual mass loss or gain through a secondary sorption process. To quantify the non-Fickian adsorption contributions, deconvolution of the adsorption kinetic curves is performed through non-linear regression analysis to determine the best fit between the theoretical adsorption curve according to Equation (3-12) and the experimental data. The best fit was found by minimizing the mean of the squared residual errors. Results of the regression analysis are presented in Table 3-6 to Table 3-8 for AAP4, AAP5 and the HCP samples respectively. The correlation coefficients (\mathbf{R}^2) values are also calculated and presented in the tables. As noted in the tables, the very low mean squared error values (and very high correlation coefficients) are suggesting the suitability of the superimposition concept used for deconvolution of Fickian and non-Fickian processes in alkali-activated and OPC pastes investigated. Another notable trend is the calculated lower error values, i.e. a better fit, for the lower relative humidity domains. The increasing trend in error values can be attributed to a slight dependency of the diffusion coefficients on the moisture content; although, since the calculated error values and correlation coefficients for the adsorption in the widest RH range (from 0 to 97%) are still suggesting reasonably good fits, this probable dependency is considered negligible. Upon further inspection of Figure 3-13 and Table 3-6 to Table 3-8, several interesting features can be observed regarding the sorption kinetics of different mixes.

A secondary long-term mass loss can be observed in the adsorption kinetic curves of alkali-activated materials, especially in the moderate range of humidities, up to 75%, that is indicative of contribution from a non-Fickian process; this secondary mass loss is reflected in Table 3-6 and Table 3-7 by a negative ultimate non-Fickian sorption

mass ($M_{\infty,nF}$). This secondary mass loss is, however, absent at higher RH levels; and particularly in case of AAP5 is replaced with a slow-rate, secondary mass gain. A similar behaviour has been reported by Powers and Brownyard [40] for equilibrating fine granular cement-based samples toward intermediate RH levels, but was not seen at higher humidites. This behaviour is also consistent with the observations of de Burgh and Foster [36] for HCP samples (the HCP kinetic curves are analysed and results of regression analysis is presented in Table 3-8).

While further investigation is strongly recommended to assess sources of the observed anomalies, and in light of the lack of data and consensus in the literature in this regard, the spinodal time-dependent microstructural change theory as suggested by de Burgh and Foster [36] is used here to explain the observed anomalies. According to [36], during the desorption process from saturation, saturated spaces tend to contract and move together under consolidation forces. At humidities below the cavitation point, increasing the surface energy and disjoining pressure, in addition to the loss of water from the interlayer spaces (of CSH gel for HCP samples) are the main consolidation forces. At higher humidity levels, capillary forces mainly drive the microstructural rearangements. During the rearrangement process, smaller pores (mainly in mesopore range) tend to get smaller, and larger pores tend to get larger. Due to the delayed mechanical response of the adsorbent, the aformentioned microstructural changes lead to a time-dependent, secondary reduction in the mesopore volume and the retained water volume. This hypothesis is also in agreement with the study of Maruyama et al. [109] in which a reduction in mesopore volume was reported after long-term conditioning of samples at various RH levels.

The mass gain and then loss for the moderate range of relative humidities during the adsorption process was atributed by de Burgh and Foster [36] to the effect of the perior

dessication process used to bring the sample to the dry state before starting the adsorption tests. It can be speculated that for moderate range of humidities the residual consolidation forces are still strong to cause a similar microstructural rearangement to those observed during the desorption process, leading the secondary long-term mass loss. For higher humidities, however, a relaxation process offsets the consolidation pressure which now sources from the capillary tensions. The relaxation results in increasing the volume of mesopores which leads to long-term non-Fickian mass gains.

As it can be seen, the long-term mass gain associated with the relaxation process is more notable in AAP5, consistent with the pore size distribution of this mix (Figure 3-8 to Figure 3-11) where the bulk of the pores are very fine, in the range of less than 15-20 nm in diameter. The higher volume of mesopores, and relative lack of macropores amplifies the relaxation, and also may increases the shrinkage during the desorption process from a saturated condition down to 40% RH [109]. Further to this, as it is reflected in the Fickian ratios in Table 3-7, an increasing trend can be seen in the mass gain associated with the relaxation-induced, non-Fickian sorption process. The Fickian ratios in Table 3-6 to Table 3-8 are calculated as:

Fickian ratio =
$$\frac{\left|M_{\infty,F}\right|}{\left|M_{\infty,F}\right| + \left|M_{\infty,nF}\right|}$$
(3-13)

The increasing contribution of anomalous behaviour for AAP5 can be explained by the fact that by increasing the relative humidity up to the saturation, the consolidation forces (i.e. capillary pressures) decrease while the relaxation due to the swelling of the fine pores increases. Since AAP5 has the finest pore structure compared with AAP4 and HCP, the increasing anomalous behaviour is more prominent in AAP5 samples to

the extent that only about 20% of the total moisture transfer takes place through a diffusive (Fickian) process for the adsorption in 0-97% RH range.

Unlike AAP5, AAP4 samples show a very Fickian behaviour, even more than HCP samples, especially for the higher relative humidities of 85%, 93%, and 97%, which are 100% Fickian according to Table 3-6. The comparatively rapid rate of gravimetric equilibrium at higher humidities can be attributed to less swelling which can be due to the presence of larger pores especially in macropore range, or less susceptibility of the geopolymer network to swelling in general, or a higher pressure from consolidation forces acting on the structure which offsets the pore expansions, or a combination of these factors. Less shrinkage in desorption to dry condition might also be inferred from the observed behaviour for geopolymer-type binders compared to calcium-rich binders, although additional experimental testing is required to provide further validation.

Of interest is also the increasing trend of the moisture diffusion coefficients in Table 3-6 and 3-7 by increasing the target relative humidities. As noted by Xi et al., and Bažant & Najjar [42,66], the sharp rise in the moisture diffusivity values near 100% RH can be either due to a very porous microstructure (i.e. very large pores in macropore range), or presence of microcracks due to previous shrinkage. The moisture diffusivity of AAP4 samples have experienced a steady growth (and not a sharp rise) by increasing target humidities, characteristic of the presence of a considerable volume of pores distributed in the whole mesopore and macropore range in accordance with Figure 3-8 and Figure 3-10. By contrast, AAP5 shows a remarkable sharp rise at the highest humidity level. Recalling the pore size distribution of AAP5 in which the absence of large pores was apparent, the author speculates that the observed sharp rise could probably be attributed to the shrinkage-induced microcracks that had been developed during the conditioning of the samples in a desiccator prior to the adsorption tests. This

observation further supports the susceptibility of the investigated alkali-activated slag paste sample to drying shrinkage; however, its magnitude also highly depends on the water to binder ratio, and this remains to be explored in detail.

Compared to AAP4 and AAP5 samples, HCP samples demonstrate a rather uniform moisture diffusion coefficient profile throughout the whole humidity ranges. Lack of a sharp rise in the diffusivity of samples equilibrating at 97% RH indicates no significant shrinkage-induced microcracks in HCP samples. Moreover, the sorption process in HCP samples is more Fickian than the AAP5 samples which is consistent with the presence of larger mesopores as well as macropores in the gel (Figure 3-8 and Figure 3-10).

Overall, it is apparent that prediction of the evaporable moisture content by using the classic moisture diffusion equation can lead to invalid results, particularly for the alkaliactivated slag binders that show the most non-Fickian behaviour. Given the notable non-Fickian nature of the sorption process, the calculated moisture diffusion coefficients are not to be used exclusively as durability indexes reflecting the moisture transfer rate. Nonetheless, the geopolymer-type AAP4 samples show the highest rate of achieving gravimetric equilibrium, which is indicative of the highest permeability, followed by HCP and then the alkali-activated slag samples.

b) Desorption kinetics

In general, desorption kinetics are indicative of more non-Fickian behaviour compared with the adsorption kinetics. This is in particular very noticeable for AAP4 samples, where unlike its very Fickian adsorption behaviour, a long-term gravimetric equilibrium at all humidities is evident. Similar to adsorption kinetics, AAP5 samples have the slowest rate of achieving the equilibrium, followed by HCP and AAP4 samples.

After eliminating the thickness effect by dividing the time to knee locations by the average thickness of each mix (reflected in Figure 3-13), the time required for a 1 mm thick sample to start achieving equilibrium is 0.08-0.26 day^{0.5} for the AAP4 mix, as opposed to 0.08-0.59 day^{0.5} for AAP5, and 0.09-0.39 day^{0.5} for HCP mix. These numbers can be used as a rough indication of the permeability of the different mixes where AAP4 samples have attained the short-term equilibrium in a period approximately 1-5 and 1-2 times shorter than AAP5 and HCP samples respectively, depending on the target humidity (rate of achieving short-term equilibrium becomes more comparable when equilibrating at higher humidities). It should be noted that similar to the adsorption kinetics, attaining the equilibrium takes place through a combination of Fickian and non-Fickian contributing processes, and the moisture diffusion coefficients cannot be directly deduced from the calculated times.

Another interesting point is the very small time to knee locations for AAP5 samples desorbing to relative humidities above 75%, followed by a major jump by decreasing the relative humidity to 58%. This behaviour can be explained by the negligible volume of pores larger than 15-20 nm in diameter in the AAP5 gel matrix (Figure 3-8 and Figure 3-9). In this particular pore structure, desorption from saturated condition to around 85%, which corresponds to emptying pores larger than 15 nm in size according to Figure 3-6, will be comparatively very quick.



Figure 3-13. Adsorption (left) and Desorption kinetics (right) for AAP4 and AAP5 along with the control HCP from [36]

RH domain	Thickness (mm)	D_w (10 ⁻¹¹ m ² /s)	$M_{\infty,nF}$ (mgr)	k (10 ⁻⁶)	Fickian ratio	Mean squared error	R ² (Correlation coefficient)
0-11	5.99	3.655	-3.47	1.56	92.6	4.92E-09	0.9999
0-33	6.00	5.092	-12.11	1.36	87.2	1.09E-08	0.9999
0-43	5.59	5.316	-20.12	0.95	85.3	7.97E-09	0.9999
0-58	5.65	6.158	-18.13	1.00	90.2	2.12E-07	0.9992
0-75	6.08	6.885	-9.47	2.40	95.2	5.11E-07	0.9992
0-85	5.80	8.90	0	-	100	1.37E-06	0.9978
0-93	5.88	9.25	0	-	100	3.20E-06	0.9951
0-97	6.00	8.05	0	-	100	4.83E-06	0.9946

Table 3-6. Parameters defining the Fickian and non-Fickian adsorption process for

 AAP4 samples

Table 3-7. Parameters defining the Fickian and non-Fickian adsorption process for

 AAP5 samples

RH domain	Thickness (mm)	D_w (10 ⁻¹¹ m ² /s)	$M_{\infty,nF}$ (mgr)	k (10 ⁻⁶)	Fickian ratio	Mean squared error	R ² (Correlation coefficient)
0-11	4.20	0.544	0.00	0.00	100.0	4.52E-08	0.9995
0-33	4.15	0.878	-9.51	2.49	87.4	6.47E-08	0.9999
0-43	4.07	1.028	-7.49	0.28	95.0	8.69E-09	0.9999
0-58	4.18	1.017	-24.73	5.46	83.3	1.62E-07	0.9996
0-75	4.13	4.017	90.60	4.72	39.6	1.57E-07	0.9998
0-85	4.16	2.479	93.98	3.00	54.3	5.27E-07	0.9997
0-93	4.14	3.315	191.48	2.89	36.8	7.21E-07	0.9998
0-97	4.17	9.363	269.32	3.94	19.9	2.66E-06	0.9996

Table 3-8. Parameters defining the Fickian and non-Fickian adsorption process for HCP samples

RH domain	Thickness (mm)	D_w (10 ⁻¹¹ m ² /s)	$M_{\infty,nF}$ (mgr)	k (10 ⁻⁶)	Fickian ratio	Mean squared error	R ² (Correlation coefficient)
0-11	4.26	1.387	17.63	0.02	95.4	6.93E-09	0.9997
0-33	4.46	2.167	-3.72	2.21	92.6	9.09E-09	0.9997
0-43	4.08	3.183	-4.65	1.42	92.5	2.45E-08	0.9991
0-58	3.81	3.225	2.21	1.94	97.0	7.05E-08	0.9985
0-75	4.88	3.751	19.61	2.45	81.5	3.67E-08	0.9998
0-85	4.09	2.739	14.25	2.45	89.0	8.32E-08	0.9996
0-93	4.44	2.419	11.05	1.24	93.2	6.46E-08	0.9998
0-97	4.30	1.929	9.58	0.83	95.2	3.68E-07	0.9997

3.4. Conclusion

Water vapour adsorption and desorption of a range of alkali-activated pastes and a control cement paste were investigated in this chapter. Several valuable outcomes regarding the sorption process and nanopore structure of the investigated samples were deduced, many of which are reported for the first time, contributing to a better understanding of moisture transport in alkali-activated binders. The main outcomes are summarized as follows:

- Water vapour sorption isotherm (WVSI) of alkali-activated binders fabricated of blends of fly ash (FA) and Ground granulated blast-furnace slag (GGBS) are reported, thus a database is available for durability design of alkali-activated binders with similar mix compositions. Analysis of WVSIs shows that water is not structurally bound in alkali-activated binders or the bound water is negligible compared to Portland cement-based binders where a considerable hysteresis is evident for relative humidities less than 11% (characteristic of holding water in interlayer spaces of C-S-H gel). Water-binding capacity did not change by increasing GGBS content up to 75% which has led to the formation of some form of C-S-H, suggesting a different nature/structure of C-S-H gel in slag-based binders which is consistent with the considerably lower Ca/Si ratios for these binders than their Portland cement-based counterparts.
- Through analyzing WVSIs by BJH method, and along with the MIP test results, two vastly different pore structures can be inferred for geopolymer-type and calcium-rich binders. The pore structure of geopolymer-type binders is comprised of a rather uniformly distributed volume of pores over the whole

mesopore and macropore range. On the other hand, alkali-activated slag binders have a considerably finer pore structure. For blended FA and GGBS systems, GGBS content of up to 50% helps to develop a finer pore structure, with two main distinguishable pore modes: one between 0-15 nm with a peak between 3 to 7 nm, and the other between 15 and 100 nm with the main peak at around 45 nm. Formation of different sized pore groups in blended binders amplifies the pore blocking effect and to a larger extent, cavitation.

- Ambient curing (as opposed to heat curing) develops a finer pore structure, also intensifies pore blocking effect and cavitation consequently (in blended FA and GGBS materials).
- The sorption kinetics of two ambient-cured blended alkali-activated mixes, one with 25% and another with 75% GGBS content, were studied and compared with that of a Portland cement paste. Several interesting features were observed: sorption process took place via a combination of Fickian (diffusive) and non-Fickian (anomalous) sorption processes. Successful deconvolution of Fickian and non-Fickian processes revealed that the sample with 75% GGBS-25% FA had the highest contribution of non-Fickian sorption component, perhaps due to a very fine pore structure which is more prone to time-dependent microstructural changes. By contrast, FA dominated sample showed the most Fickian behaviour. The moisture diffusion coefficients were also calculated for the first time for alkali-activated binders.
- The time required for the dry alkali-activated paste sample fabricated of 25% GGBS-75%FA to achieve the short-term gravimetric equilibrium at different relative humidities was 3.7-11 and 2-4.2 times shorter than the alkali-activated

sample with 75% GGBS-25%FA and a Portland cement sample respectively. This considerable difference in the rate of gravimetric equilibrium (i.e. sorption rate) highlights the importance of the presence of enough calcium in the alkaliactivated binder mix for durability purposes.
CHAPTER 4: Electrochemical Aspects of Chloride-Induced Corrosion of Reinforcement in Fly Ash-based Geopolymer Concretes

4.1. Introduction

This chapter is focused on the electrochemical aspects of corrosion of reinforcement in low calcium alkali-activated (geopolymer) concretes fabricated of mainly fly ash. Previous studies report that the performance of fly ash-based geopolymer concretes (GPC) is similar to Portlanad cement concrete (PCC) in passive state (i.e. in the absence of chloride ions) [48,110], an (at least) equivalent performance of low-calcium fly ashbased GPC compared with PCC in severe marine environments during the propagation phase of corrosion is emphasized [49,50,110]. The capability of the alkali-activated binders to keep the reinforcement in passive condition during the chloride contamination or carbonation, and other relevent parameters involved in the initiation phase of chloride-induced or carbonation-induced corrosions will be addressed in Chapter 5 and 6 respectively. Regarding the active phase of corrosion, also known as propagation phase of corrosion, none of the previous works have extensively studied the electrochemical aspects of corrosion of reinforcement in alkali-activated binders, and the electrochemical test protocols employed are those developed for Portland cement-based systems. Considering the limited literature available related to the electrochemical aspects of chloride-induced corrosion of reinforcement in geopolymer concretes, this chapter aims to:

- Assess the performance of low-calcium fly ash-based geopolymer concretes during the propagation phase of corrosion process through a long-term monitoring of corrosion parameters such as open circuit corrosion potential, polarization resistance and Tafel coefficients. The results are compared with the reported values for Portland cement concretes. Direct mass loss measurement is carried out as a way to validate results of the corrosion tests.

- Find out if the existing electrochemical test methods calibrated and validated for reinforced Portland cement concrete are suitable for geopolymer concrete.

4.2. Experimental program

4.2.1. Materials and mix proportions

An experimental investigation is conducted to assess the corrosion of reinforced GPC fabricated from a blend of Class F fly ash and ground granulated blast-furnace slag (GGBS) stockpiles. Similar to AAP1 mix tested in Chapter 3, three different sources of aluminosilicate precursors have been used: 1- Eraring Fly ash (FA), 2- Callide FA, and 3- Ground granulated blast-furnace slag (GGBS). Eraring FA and Callide FA are from the same batch as the materials in Chapter 3, although their chemical composition were retested by x-ray fluorescence (XRF) analysis and are listed in Table 4-1. GGBS used is from a different batch (but from the same supplier) compared to the slag sources tested in Chapter 3, and its chemical composition is also presented in Table 4-1. The amorphous content and the crystalline phases of the raw precursors have been previously presented in Section 3.2.1. Particle size distribution of solid precursors can also be found in Figure 3-1.

Oxide	Eraring FA [wt. %]	Callide FA [wt. %]	GGBS [wt. %]
Silicon dioxide (SiO ₂)	66.56	45.14	31.52
Aluminium oxide (Al ₂ O ₃)	22.47	33.32	12.22
Iron oxide (Fe ₂ O ₃)	3.54	11.99	1.14
Calcium oxide (CaO)	1.64	4.13	44.53
Potassium oxide (K2O)	1.75	0.13	0.33
Sodium oxide (Na ₂ O)	0.58	0.07	0.21
Magnesium oxide (MgO)	0.65	1.37	4.62
Manganese oxide (MnO)	0.06	0.23	0.36
Phosphorus oxide (P2O5)	0.11	0.56	0.02
Titanium oxide (TiO ₂)	0.88	2.19	1.03
Sulphur trioxide (SO ₃)	0.10	0.48	3.24

Table 4-1. Chemical compositions of Eraring FA, Callide FA and GGBS by x-rayfluorescence (XRF) analysis

Similar to the activator preparation method explained in Chapter 3, a mixture of sodium hydroxide (NaOH) solution and grade D sodium silicate solution were used as the activator. The technical specification of these materials can be found in Section 3.2.1 (Chapter 3). NaOH and sodium silicate solutions were mixed in proportions according to Table 4-2 to form the alkaline solution. The paste composition closely resembles the AAP1 mix tested in Chapter 3, although with a higher water to binder ratio to increase the workability of concrete. After mixing, the alkaline activator was allowed to cool to ambient temperature and equilibrate prior to preparation of the specimens. As it is noted in Table 4-2, about 85% of the blend is composed of low-calcium class F fly ash (Eraring and Callide). Sydney sand was used as fine aggregate, and the coarse aggregate was 10 mm nominal size crushed basalt. The aggregate's mass shown in Table 4-2 is in the saturated surface dry (SSD) condition.

Material	Kg/m ³
Coarse aggregate	1138
Fine aggregate	730
Eraring FA	200
Callide FA	55
GGBS	45
NaOH pellet	16.5
Sodium silicate solution	114.3
Free water	60.1
Total binder (Eraring FA, Callide FA, GGBS)	300
Water/binder ¹	0.35
Modulus (SiO ₂ /Na ₂ O)	1.17
Na ₂ O/ binder (%wt)	9.86

Table 4-2. GPC mix proportions

¹ Water means: free water + water from sodium hydroxide, as well as sodium silicate solutions, and binder means: Eraring FA+Callide FA+GGBS+ solid part of sodium hydroxide+ sodium silicate solutions.

4.2.2. Sample fabrication, curing, and conditioning

To prohibit any external corrosion, a specific method of fabrication has been adopted (Figure 4-1), similar to the approaches employed in some previous studies to assess the steel corrosion in traditional PCC [111,112]. Normal ductility standard Australian deformed bars of 12 mm diameter (N12's) with 500 MPa yield strength were embedded in the concrete. All embedded bars were 50 mm long and were machined at both ends. Rebars were gently wire-brushed to eliminate any pre-formed rusts which could affect the gravimetric mass loss calculations. All steel bars were then weighed and tagged for gravimetric mass loss measurements at the end of the testing period (after doing the destructive Tafel test on each sample). One acrylic tube was attached at each end. The internal diameter of the acrylic tubes was almost equal to the external diameter of the machined part of the steel bars, so the steel bar could easily fit in the tube, although a thin layer of silicone sealant was used as an adhesive and also to avoid any corrosion

on the machined parts of the steel bars. Acrylic tubes were then filled with Silicone sealant to block the access for chloride ions to the steel bar (Figure 4-1). An electrical wire was welded on each steel bar to perform as a working electrode during the electrochemical measurements. Both top and bottom sides of samples were coated with an anti-chloride resin (supplied by the Australian supplier "Parchem" under the commercial name of Emer-Stop S100N), to enforce peripheral penetration of chloride ions.



Figure 4-1. GPC Specimen configuration

After casting, moulds were sealed with either a proper lid or a plastic sheet to prevent excessive loss of moisture and were stored in a chamber at 40°C for 24 hours. The specimens were then demoulded, sealed again and placed in a hot water bath at 80°C for another 24 hours. After that, samples were stored in a room with a fixed temperature of 23 ± 2 °C and relative humidity (RH) of 50% until the testing dates. The average compressive strength (average of 3 standard cylindrical Ø200×100 (H×D) mm samples without reinforcement) at 28th day was 54.5 MPa with a standard deviation of 1.10 MPa. Also, the average elastic modulus (average of 3 samples) at 28th day was 23.8 GPa with a standard deviation of 0.61 GPa.

The initiation period of the chloride-induced corrosion process (i.e. chloride penetration through the concrete cover) was accelerated as the study focuses on the steel corrosion during the propagation phase of corrosion. 28 days after casting, 11 specimens were dried in an oven at 50°C to enhance capillary suction before the first immersion in a 35 g/l sodium chloride solution, which is similar to the concentration of the seawater. This method has been already used for Portland cement concretes successfully to accelerate the initiation phase of corrosion [112]. After that, specimens were subjected to alternating wetting/drying cycles during the whole testing period (almost 11 months), immersed in the sodium chloride solution for one week, followed by at least two weeks of air exposure under a fixed temperature of 23 ± 2 °C and RH of 50%. Alongside with the samples whose initiation phase of corrosion was accelerated, six samples were submerged in tap water for almost seven weeks to be saturated and used for passive condition corrosion assessment.

4.2.3. Electrochemical experiments

All tests have been carried out in a room with a fixed temperature of 23°C. Corrosion parameters such as the corrosion potential (E_{corr}), polarization resistance (R_p) and Tafel constants have been measured and the obtained results were verified by comparing the gravimetric and electrochemical mass losses. Also, Gravimetric measurements were beneficial to calibrate R_p measurements regarding finding an appropriate potential sweep rate range [113,114]. pH of the samples was measured as the passivity of steel bar depends on the pH of the concrete. Chloride content measurements were carried out as well using the ion chromatography (IC) technique. To carry out all the electrochemical tests, a three-electrode system was used comprising of a Saturated Calomel Electrode (SCE) as the reference electrode (RE), a titanium mesh as the counter electrode (CE) and the reinforcing bar as the working electrode (WE). During the LPR tests samples have been placed partially in water, they were not completely submerged to avoid concentration polarization due to the lack of oxygen. RE and CE were also put in the water next to the sample. E_{corr} was determined by open circuit measurement of the potential difference between the WE and RE while the stability of the half-cell potential was controlled beforehand (E_{corr} was monitored but not recorded until the deviation was lower than 1 mV during a 60s period) [115].

The most widespread technique to evaluate the corrosion current (I_{corr}) is the Linear Polarization Resistance (LPR) method which allows calculation of the corrosion rate via the Stern-Geary equation [116,117]:

$$I_{corr} = \frac{\beta_a \beta_c}{2.3 R_p (\beta_a + \beta_c)} = \frac{B}{R_p}$$
(4-1)

where β_a and β_c are anodic and cathodic Tafel slopes (= $\frac{d\eta}{d \log i}$, and *i*=corrosion current density in μ A/cm²), respectively. Measuring the corrosion potential (*E*_{corr}) beforehand, R_p can be obtained from the slope of the polarization curve in the vicinity of *E*_{corr} [117]:

$$R_{p} = \left(\frac{\Delta E}{\Delta I}\right)_{\Delta E \to 0} \tag{4-2}$$

In a potentiodynamic test, ΔE is the potential step applied within a limited range of overpotentials ($\eta = E \cdot E_{corr} = -20$ to +20 mV in the current study) to polarize the corrosion system and ΔI is the system response to the potential excitation.

Values of B=26 and 52 mV are suggested for the active and passive state, respectively and widely used in the corrosion rate estimation of reinforced PCC [117]. However, in the present study, they are obtained from the slope of the anodic and cathodic branch of Tafel plots at large overpotentials (E- E_{corr} = -200 to +200 mV). A Tafel plot, which is a plot of log I vs. overpotential (E- E_{corr}), can be utilized to obtain both Tafel slopes and I_{corr} simultaneously by extrapolating the anodic and cathodic linear segments to an intercept of log I_{corr} through a curve-fitting analysis [118,119]. However, the Tafel test is considered as a destructive test, since the strong level of polarization can trigger some irreversible changes in the WE [120]. Due to this drawback, Tafel tests have been conducted only five and three times for active and passive samples respectively within the whole period of the experimental program (about 48 weeks). E_{corr} and R_p have been monitored on a regular basis at the end of wetting cycles for active samples and after seven weeks of immersion in water for passive samples.

A VMP3 Multi-channel potentiostat was employed to perform all the electrochemical tests. It was capable of compensating the ohmic (IR) drop due to the electrolyte resistance by either Current Interruption (CI) method or ZIR method. ZIR technique is very similar to the Potentiostatic Electrochemical Impedance Spectroscopy (PEIS) technique, except that it is performed at a single frequency. Only 85% of the measured ohmic drop was compensated to avoid oscillation of the instrument [114,121]. IR compensation was always implemented before other electrochemical tests to take into account the effect of uncompensated electrolyte resistance (R_e) on the shape of polarization curves (or Tafel plots) and hence revising R_p , Tafel constants and I_{corr} .

The effect of sweep rate on the polarization behavior and R_p of reinforced PCC systems during potentiodynamic polarization tests has been discussed in detail in [113] and then the same concept was adapted for steel/concrete corrosion systems by González et al. [120] and Martínez and Andrade [114]. González et al. [113] investigated the response of a modified Randles circuit (Figure 4-2) to an applied potential sweep, and they found out that the range of sweep rates in which R_{p+} R_e achieves a constant value, is appropriate to do a potentiodynamic polarization test. Faster sweep rates overestimate the corrosion current (and hence underestimate R_p) as the current bypasses R_p through the capacitor, and the transient component of the intensity is still considerable and cannot be ignored. In this case, the apparent resistance (R_{app}) is equal to the electrolyte resistance (R_e) which is less than the actual resistance of R_{p+} R_e . On the other hand, if the sweep rate is too slow, the concentration of ions in the solution layer around the electrode will change which can lead to underestimating the corrosion current due to the altering of the electrode equilibrium conditions [113,120]. A too long recovering time for the electrode equilibrium potential to return to the initial E_{corr} is a sign of electrode altering which is more common in the case of passive systems and also in diffusion controlled systems.



Figure 4-2. The modified Randles circuit used by González et al. [113]; R_e is the electrolyte resistance, R_p is the polarization resistance and C is the capacitance of the double layer

After determining the apparent resistance $R_{app} = R_{p+} R_e$ by applying an appropriate sweep rate, R_p can be directly determined from this value if either R_e is known beforehand or $R_{e<<}R_p$. To find the suitable sweep rate and to calculate R_e as a way to calibrate the results of IR drop compensation techniques, a similar methodology was adopted in the current study. A set of cyclic voltammetry (CV) tests in a range of ±10 mV away from E_{corr} and in a wide range of sweep rates from 1 to 500 mV/min was performed to establish the relation between the R_p values and the sweep rates. Then R_e was estimated from the measured resistance at very fast sweep rates (sweep rates which are larger than 100-200 mV/min), while the proper sweep rate was chosen within the range where $R_{p+}R_e$ attained a constant value.

To validate the results of electrochemical tests, gravimetric mass loss measurements were conducted [117] on samples which had been already used for Tafel tests based on the ASTM G1-03 protocol [122]. After splitting the samples, reinforcing bars were taken out and lightly brushed with a non-metallic bristle. Then they were immersed for about 20 minutes in a chemical solution composed of 1000 mL hydrochloric acid (HCL, sp g 1.19), 20 g antimony trioxide (Sb₂O₃) and 50 g stannous chloride (SnCl₂). During the immersion, the cleaning solution was vigorously agitated, and the bars were removed from it alternatively, and lightly brushed to ease removing the solidly adhered corrosion products. Only reagent grade chemicals were used to prepare the cleaning solution. After treatment, all the bars were brushed again, rinsed and dried and their masses were measured consequently. This process was repeated several times to obtain a plotted function of mass loss vs. number of cycles for each bar; where the mass loss corresponds to the point where the graph begins to plateau. Also to measure the mass of the available oxide layer around the bars, applying the same treatment to 3 replicate un-corroded control reinforcing bars resulted in a mass loss of 0.083 g in average with a standard deviation (SD) of 0.0078. This mean value was then deducted from the total measured mass loss to get the actual mass loss due to the chloride-induced corrosion.

4.2.4. Chloride content

To obtain the total chloride content of concrete (% per binder mass), powder samples were extracted along the cover depth at 1 mm increments using a German Instrument profile grinder (PF-1100). The test protocol of "ASTM C1152: *Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete*" [123] is followed and adapted for the ion chromatography (IC) method: five grams of the extracted powder was weighed to the nearest 0.01 g and dispersed with 75 mL water in a beaker. 25 mL (1+1) diluted reagent grade Nitric acid was gradually added to the solution afterward, and the final solution was stirred using a magnetic stirrer for 20 minutes. The solution was rapidly brought to a boil on a hot plate and after cooling down was filtered through a Millex-GS syringe membrane filter (0.22 μ m pore size) to remove fine particles. The filtered solution was then diluted to an appropriate mark and analyzed by an ICS-3000 ion chromatography system supplied by Dionex (Sunnyvale, CA, USA).

4.2.5. pH of Geopolymer concrete

The pH of concrete is critical for protecting the reinforcement against corrosion, and it is about 12.5-13 for uncarbonated Portland cement binders [124]. The pH was measured for a GPC sample and compared to the pH of Portland cement concretes to explain the differences observed in the corrosion potential of passive samples. A pH profile was obtained by combining the powder suspension method and pore solution extraction method. pH profile of an uncarbonated GPC sample was measured using the suspension method proposed by Räsänen & Penttala [125]. For pH profile measurement, concrete powder samples were taken along the cover depth using the German Instrument profile grinder, 28 days after the heat curing. The sample has been in ambient condition during that period. A suspension mixture was made which was comprised of 50% concrete powder and 50% de-ionised water. Then, the suspensions were stirred for 5 minutes on a magnetic stirrer and finally the pH values were measured using a pH meter. To validate the results, the pore solution from a paste sample (with the same mix design as Table 4-2 but without aggregates and also with the same curing condition as the geopolymer concrete samples in this study) was extracted and its pH was measured [126]. The maximum applied pressure on the extraction apparatus was 500 MPa and the load rate was 1 MPa/s. As it has already been observed for PCCs [125], the pH value measured by pore solution extraction method was less than the pH values measured using the water suspension method. The difference was about 0.67 which was subtracted from each data point along the profile to obtain the calibrated profile. The higher pH measured by suspension method has been previously reported by Räsänen & Penttala [125] and was attributed to the separation of structurally bound OH⁻ ions during the stirring phase which leads to overestimation of pH level in the suspension. Results are presented in the following sections.

4.3. Results and Discussion

4.3.1. Chloride Content

Chloride content at the level of the reinforcement was measured for two samples at different ages: after the first day of immersion in NaCl solution, and after six drying/wetting cycles. A chloride content of 0.45% by mass of binder (The mass of binder comprises the mass of fly ashes and GGBS) is measured after only one day of

immersion in NaCl solution. It is worth reminding that achieving this high level of chloride content within a very short time is due to the high capillary suction induced by oven-drying. Although there is not a consensus among the researchers regarding the chloride threshold (the chloride concentration required to depassivate reinforcement) values in Portland cement concrete yet, the recorded chloride content after one day is higher than the chloride threshold levels of 0.2% and 0.4% by mass of cement suggested by ACI [127] and RILEM [128] respectively. The chloride content after 132 days (after six drying/wetting cycles) has increased by about 29% compared to the value measured after one day which is possibly due to the combined effects of longer exposure time to chloride ions and the wetting/drying cycles. A comprehensive study of chloride threshold values and various parameters affecting it in alkali-activated binders is presented in the next chapter.

4.3.2. Sweep Rate effects

As it is previously discussed in section 4-2-3, potentiodynamic tests should be performed at sweep rates which are slow enough to ensure a steady-state condition and are also fast enough to avoid altering the electrode due to the change in the concentration of ions around the electrode [129]. Although the proper sweep rate ranges for PCC systems are already suggested in the literature [114,120], like any other unknown corroding system, preliminary tests for geopolymer concrete-based corroding system are required to establish an appropriate sweep rate range.

To investigate the effect of variation of sweep rate (SR) on polarization behavior of reinforced GPC samples, a set of Cyclic Voltammetry (CV) tests has been carried out on both passive and active samples. A potential excitation in the form of a triangular

cycle of amplitude 20 mV was applied on two passive, and two active samples with different sweep rates and the results are summarized in Figure 4-3. Figure 4-3(a) is the result of a set of CV tests on a saturated passive sample which has been submerged in water for six months. By increasing the SR, response amplitudes increase and an increase in the slope of the cycles is also noticeable which results in smaller R_p values. A similar trend was also observed for the active samples. Higher sweep rates also increase ΔI , the distance between the recorded responses at zero overpotential. This behavior has been already captured successfully and explicitly formulated by studying a modified Randles circuit [113]. Variation of R_p in a broad range of sweep rates from 1 to 500 mV/min is depicted in Figure 4-3(b). The measured R_p of both passive and active samples at very fast sweep rates (sweep rates larger than 100-200 mV/min) approaches a constant value which compares well against the compensated ohmic (IR) drop measured using either ZIR or CI method (Table 4-3).



Figure 4-3. (a) Response of a passive sample to a triangular wave of potential applied at different sweep rates in a CV test. (b) Variation of R_p with increasing the sweep rates for two passive and two active samples (responses are uncompensated for IR-drop)

Sample	$R_e (k\Omega.cm^2)$ IR drop compensation	$\frac{R_{e} (k\Omega.cm^{2})}{CV}$
Passive sample 1	204	189
Passive sample 2	132	125
Active sample 1	51	51
Active sample 2	139	142

Table 4-3. Comparison of Re measured by IR-drop compensation and CV tests at fastSR

Another noteworthy trend is the difference between the R_p values measured at both ends of the sweep rate spectrum. While the difference can be of two orders of magnitudes for passive samples, active samples experience minor changes with the SR variations. Similar behavior is reported for reinforced Portland cement concretes [114,120]. Figure 4-3(b) is also used to determine the range of appropriate sweep rates at which all the potentiodynamic tests on active and passive GPC samples are conducted throughout this study. The appropriate range, i.e. the range in which the measured resistance values achieve a constant value, is from 5 to 10 mV/min for active samples. Although the graphs do not show an apparent plateau in the case of passive samples in Figure 4-3(b), sweep rates from 2.5 to 10 mV/min seem to be suitable. These ranges are quite comparable with the ranges already suggested for the reinforced PCC [114].

Considering these results, the sweep rate in all the LPR tests have been set as 5 and 10 mV/min for passive and active samples respectively. The necessity of having low sweep rates while doing a potentiodynamic test on passive PCC samples has been discussed in [113,120].

4.3.3. Corrosion Potential and pH of geopolymer concrete

Corrosion potential (E_{corr}) is the most general used corrosion index, due to the convenience of measurement either on site or in the laboratories using widely available, well-developed instruments. However, unlike all the other measured variables, E_{corr} is rather a qualitative parameter, and there is no direct correlation between E_{corr} and the corrosion current (I_{corr}), which describes the rate of dissolution of steel [48,50,114,130].

Figure 4-4 shows the average value of E_{corr} for six passive samples after seven weeks of immersion in tap water (data point at day 0), along with the evolution of E_{corr} of 11 already-depassivated (active) samples after almost 11 months of monitoring. The reference values commonly used to evaluate the severity of corrosion in reinforced PCC [130] are presented on the same graph for comparison purposes. Since the active samples were also used to carry out the destructive Tafel test throughout the monitoring period, the average values are representative of only 2 data points at the end of the testing period. To assess the potentials which were measured versus SCE, the reference values in ASTM C876-09 [130] which are versus a Copper-Copper Sulfate Reference Electrode (CSE) are increased by 60 mV, based on the recommendations of ASTM G3-14 [131].



Figure 4-4. Evolution of the average open circuit corrosion potential (E_{corr}) along with the standard deviations of each data point and the suggested reference values for PCC [130]. E_{corr} values during the initiation phase are not included, as the initiation phase is accelerated

The average value of the measured open circuit corrosion potentials decreases significantly (hundreds of millivolts) with the chloride contamination; this behavior is similar to what have frequently been reported for PCC corroding systems. However, the absolute value of the average corrosion potential of passive specimens is more negative than the range in which reinforced Portland cement concretes considered passive (i.e. $E_{corr} > -140$ mV vs. SCE). The more negative values observed in passive samples are not necessarily indicative of a higher risk of corrosion; this can be attributed to a combination of factors such as a lower pH level [132] in geopolymeric binders compared to Portland cement binders (Figure 4-5). Another reason might be the high porosity of fly ash binder (Chapter 3) which facilitates saturation of the sample and provides a less alkaline environment which leads to more negative corrosion potential values [47,133–135]. For calcium-rich binders, as it is reported by other researchers(see e.g. [55,56]), the unusual negative potential values of passive samples

can be attributed to the consumption of dissolved oxygen by sulphides in the pore solution. Alkali leaching and loss of alkalinity can be another factor, although as it will be discussed in Chapter 7, it appears to be negligible⁷.

To investigate the pH level of the geopolymer binder in this research, the pH profile of an uncarbonated GPC sample (Figure 4-5) is measured using the suspension method [125] and calibrated by direct measurement of the extracted pore solution. Figure 4-5 shows that the pH of the geopolymeric binder is around 11.5 at the level of the reinforcing bar compared to the widely accepted pH of about 12.5-13 for uncarbonated Portland cement binder systems. As a result, it can be concluded that the lower initial alkalinity of GPC is one of the factors leading to more negative corrosion potential values compared to the reference values which have been calibrated for PCC corroding systems.



Figure 4-5. The calibrated measured pH profile of an uncarbonated GPC vs. the pH value for uncarbonated Portland cement concrete

⁷ A more extensive study of the half-cell potential of alkali-activated samples is presented in Chapter 5

For further investigation of the corrosion susceptibility, two passive samples were tested to measure the corrosion current. In addition to the very low measured corrosion currents, the general shape of the polarization curves around the corrosion potential helped to check that the reinforcement in passive samples were still passivated (passive samples have very high R_p values which means the slope of the polarization curve around the corrosion potential is very small compared to active samples). Inconsistency between the results of half-cell potential measurements and corrosion current densities has been already reported for GPC [50,51].

For active specimens, due to the low initial corrosion potential and the high chloride content (Section 4-3-1), corrosion potentials fall rapidly into the active corrosion zone after only seven days of immersion in NaCl solution. The observed 200 mV drop in the average values after the second wetting cycle is comparable to the potential drop criterion which is used to distinguish between the passive and active steel reinforcement in PCC [136,137]. After 28 days and throughout the testing period, corrosion potential figures fluctuate between -550 and -650 mV vs. SCE, which are slightly more negative than the reported figures for PCC in the literature.

These results draw attention to the intrinsic qualitative nature of the half-cell potential measurements and justify conducting more time-consuming quantitative techniques such as LPR method to assess the state of corrosion reliably. Furthermore, using the conventional reference values of corrosion potential commonly used for PCC increases the possibility of misinterpreting the data while evaluating the passivity of the samples.

4.3.4. Polarization Resistance

Polarizing the working electrode (reinforcement) around the free corrosion potential (E_{corr}) to obtain the slope of the polarization curve at E_{corr} is a reasonably reliable, yet relatively fast and non-destructive technique to assess the corrosion state. Performing the test within a limited range of potentials, an appropriate sweep rate to achieve a stationary value within a not too long testing time, and the inherent characteristics of steel-concrete systems in which the polarized corrosion system returns to the previous state after only a few hours, are three main factors assuring the system is not undergoing any irreversible alterations. As a result, LPR tests can be repeated on the same sample to monitor corrosion evolving.

Figure 4-6 compares the Polarization Resistance (R_p) values of the same specimens of the previous section which are measured at the same time intervals. Reference values of R_p which are widely used to classify the state of corrosion of reinforced Portland cement concretes [138] are also presented in Figure 4-6. The reference values are derived by employing Stern-Geary equation (4-1); a "B" coefficient equal to 25 is divided by the reference values of corrosion current density suggested by Andrade & Alonso [117]. B=25 is very close to the recommendation of Andrade & Gonzalez [139] in which they suggested a B value equal to 26 for PCC samples experiencing corrosion. Although "B" might be of a different value when dealing with Geopolymer concretes (section 3-5), R_p values are expected to stay within the high corrosion rate range regardless of the further modification of "B" coefficient. Also, results of a set of tests on PCC samples [112] with a similar fabrication method and almost the same exposure condition as the current study is presented in Figure 4-6. The values reported here from Zhang et al. [112] for PCC samples are average of the results obtained from four specimens.



Figure 4-6. Evolution of the Polarization Resistance (R_p) along with the standard deviations of each data point and the suggested reference values for PCC. R_p values during the initiation phase are not included, as the initiation phase is accelerated

The average R_p trend is comparable to the corrosion potential trend; the average values reduce significantly (up to 15 times) and fall into the high corrosion rate range after just two cycles of exposure to NaCl solution (samples had been partially dried before the first immersion). The downward trend tends to stabilize toward the end of the testing period, with the average R_p values approaching 2 k Ω .cm². Also, the standard deviations and coefficient of variations change from 25.2 and 0.84 respectively after the first wetting cycle to 0.8 and 0.33 at the end. The average polarization resistance trends for GPC and PCC samples exhibit a remarkably good match. As a result, a similar electrochemical performance of Portland cement binders and geopolymer binders in chloride-contaminated environments during the propagation phase of corrosion (after depassivation of reinforcing bars) can be inferred. R_p values measured on passive GPC specimens are slightly lower than the expected values (i.e. $R_p > 250$ k Ω .cm² for passive samples). The lower polarization resistance of the passive samples means that to achieve the same anodic or cathodic current level, a smaller overpotential is required. This finding suggests that the PCC classifications might need some recalibration for GPC samples in the passive state.

4.3.5. Tafel Constants

To evaluate the corrosion current density by employing LPR technique and according to Equation (4-2), besides R_p measurement, two more unknowns should be determined: the anodic Tafel constant (β_a) and the cathodic Tafel constant (β_c). These constants can be calculated from the slopes of the anodic and cathodic branches of the polarization curve which are extrapolated to E_{corr} . This method is known as the "intersection" method [117] or "Tafel extrapolation" method, has also been beneficial to determine the corrosion current density (i_{corr}). Although plotting the polarization curve is worthwhile to get some of the most critical parameters defining the kinetic of corrosion, it demands to polarize the sample over a large overpotential range which can introduce some irreversible changes into the system. This justifies the past efforts to figure out some prescribed values for "B" coefficient to be used in the Stern-Geary equation and hence employing an LPR test in the vicinity of E_{corr} instead of doing the destructive Tafel test. Theoretically; an error factor of less than two is expectable using the Stern-Geary equation to estimate the corrosion current [140].

Corrosion of the reinforcement in concrete can be simulated by its oxidation/reduction reactions in representative solutions. The Tafel slope for oxidation of iron in a basic solution with pH>13 at 20 °C is about 30-39 mV ($30 < \beta_a < 39$). Assuming that reduction

of oxygen is the main cathodic reaction at the surface of the reinforcement; the cathodic Tafel slope is highly dependent on the pH of the electrolyte solution and could vary from 48 to 120 mV (48< β_c <120). As a result, when the concentration of chloride ions is considerably higher than the chloride threshold, and there is no lack of oxygen (concentration polarization is not rate-determining), B constant for active samples is in the range 8-13.5 (8<B<13.5). For passive samples, the anodic Tafel slope approaches infinity ($\beta_a \rightarrow \infty$). Assuming the supply of oxygen is enough, cathodic Tafel slopes are in the same ranges as the active samples (48< β_c <120). B constant values in this case range from 21 to 52 (21<B<52) [141]. The lower conductivity of concrete compared to the solution electrolytes, reduces the rate of transfer of ions into and from the electrolyte (concrete here). A slower charge transfer rate means that a larger potential perturbation is required to achieve the same corrosion rate. Therefore, the Tafel slopes ($d\eta/d \log i$) in concrete are expected to be larger than the values mentioned above for the solution electrolytes.

In a prominent paper, Andrade & Gonzalez (1978) reported results of gravimetric and polarization resistance measurements on mortar samples with embedded reinforcement, manufactured by different types of cement: Portland cement, slag cement, and pozzolanic cement. By contrasting the gravimetric losses with the electrochemical mass losses, B values of 26 and 52 for the active and passive state respectively were proposed by Andrade & Gonzalez [139]. Using Equation 1, B=26 corresponds to β_a and β_c values of 120 mV/decade and B=52 could be obtained if β_c to be 120 mV/decade and the β_a infinity [119]. Andrade & Gonzalez' suggested figures have been extensively used in practice for reinforced concrete corroding systems, although a wide range of experimentally measured β_a , β_c and B values can be found in the literature. Locke and Siman [142] investigated the effect of sodium chloride concentration on corrosion rate and Tafel constants of reinforced concrete samples. Average B constants were ranging from 82 to 278 depending on the sodium chloride content of the concrete, which are much higher than the proposed 52 and 26 for passive and active samples respectively [139]. Locke and Siman argued that the higher observed Tafel slopes are in part due to IR-drop, which was not compensated [142]. The amplifying effect of uncompensated IR-drop on the Tafel slopes of the polarization curve is theoretically discussed in detail in [143]; Although, it is of course insignificant for very low electrolyte resistances [144]. Alonso et al. [145] reported the corrosion current density and Tafel slopes of macrocell beams composed of one chloride containing concrete segment as an anode in the middle and two chloride-free concrete segments as cathodes on both sides of the anode. Macrocell specimens have been in the dry atmosphere for six years, after which they were dampened. The measured anodic Tafel constants (β_n) were approaching infinity while the cathodic Tafel constants were 441 and 289 mV/decade for the dry and damp beams respectively.

Overall, there is an apparent discrepancy in the reported values of Tafel slopes and B constant for OPC based concrete in the literature which comes from a large number of parameters that can affect the Tafel slope figures. These parameters can be listed as: the conductivity of the electrolyte [144] which depends on the moisture content and presence of various ions in the electrolyte, the presence and concentration of chloride ions [142], pH of the electrolyte that can be affected by the carbonation or chemical composition of the electrolyte [146], the polarization mechanism (i.e. activation polarization or concentration polarization) which depends on the availability of the ions involved in redox reactions [141,147], dependency of the Tafel constants on the corrosion potential which varies with time [118,148], the presence of surface films or

the mill scale covering the surface of the reinforcement and the surface preparation method [142,149], and pore structure of the concrete which influences the transport properties of different species within the concrete medium. Although chemical composition of the binder (electrolyte) is only one of the many parameters which affect the corrosion kinetic, the polarization curve, and hence the Tafel slopes, given the distinct lack of data on Geopolymer-based corroding systems, measuring the Tafel constants seems to be a necessary step toward developing a database which can be used further in the non-destructive LPR test method.

Figure 4-7(a) and (b) show the evolution of the average "B" coefficient for passive and active state samples up to 336 days of immersion in tap water and NaCl solution respectively. The anodic and cathodic Tafel constants for each data point are also presented in Table 4-4. To obtain both Tafel constants and the corrosion rate at the same time, the commercial software EC-LAB is used to perform a curve-fitting method. Goodness of the fit is assessed by the Chi-squared (χ^2) test procedure in which χ^2 values are minimized [119].



Figure 4-7.	Variation of	of the avera	ge "B"	' coefficients	with time	for (a)	Passive	samples
		(left) and	l (b) A	ctive sample	s (right)			

Sample	Time after first immersion (day)	β_{a} (mV)	β_{c} (mV)	<i>B</i> (mV)
Passive samples: 1	42	∞	38	17
2	42	∞	45	20
3	112	∞	40	17
4	112	∞	37	16
5	336	∞	30	13
6	336	∞	32	14
Active samples: 1	7	514	213	65
2	7	536	153	52
3	49	574	221	69
4	49	570	175	58
5	49	430	130	43
6	112	530	153	52
7	112	1107	135	52
8	288	∞	120	52
9	288	œ	133	58
10	336	00	110	48
11	336	x	106	45

Table 4-4. Cathodic and anodic Tafel constants for passive and active samples

For passive samples, anodic Tafel slopes approach infinity which is an indication of the passivity of the samples. Also, the cathodic Tafel slopes range between 30 to 45 which results in B coefficients varying from 13 to 20 (as opposed to the conventional B=52 for PCC samples in the passive state). For active specimens, anodic Tafel constants range between 430 and infinity, while the cathodic Tafel constants range from 106 to 221. These figures result in B coefficients starting at 59 and achieving an average value of 46 after 336 days of immersion in NaCl solution.

The evolution of the polarization curve from the passive state to moderately and then highly active state is depicted in Figure 4-8. As it can be seen in Figure 4-8 and also Table 4-4, the anodic Tafel slopes of the active samples show an increasing trend and ultimately approach infinity. The infinite anodic Tafel slopes for corroding samples is also reported in [145]. The very high anodic Tafel slopes in the present study can be attributed to the formation of iron oxide layers around the reinforcing bar. This accumulation of corrosion products slows down the rate of charge transfer and hence the average corrosion rate, as the rate of diffusion of ions involved in the redox reactions into and from the concrete-reinforcement interface reduces. A slower charge transfer rate means higher anodic Tafel slopes, as only a fraction of the applied anodic over-potential is effective to reduce the energy barrier for oxidation of iron.

The presence of an iron oxide layer which is uniformly formed around the reinforcing bars is illustrated in Figure 4-11 (Section 4-3-7). Also, the effect of the formed iron oxide layer on the reduction of the increasing trend of the average corrosion current density with time is discussed in the following section.



Figure 4-8. Polarization curves for passive and active samples

4.3.6. Corrosion current density and mass loss measurement

Figure 4-9 depicts the corrosion current densities of GPC samples which are calculated using two different techniques: 1- The intersection (Tafel extrapolation) method, and

2- The LPR method (the Stern-Geary equation) using B value of 26 which is commonly used to calculate the corrosion rate of PCC corroding systems, along with the average R_p values of all samples at each data point. For comparison purposes, the corrosion current densities of a set of PCC samples from Zhang et al.'s study [112] are calculated from the reported R_p values (Figure 4-6), using the Stern-Geary equation and a B coefficient of 26, and the results are also presented in the same figure. All the presented corrosion current density graphs are an upper bound for the actual corrosion current densities, as the measurements have been taken place at the end of wetting cycles. As it is shown, the corrosion current density values plateaued with time which is consistent with the high measured anodic Tafel slopes. This behavior can be attributed to the formation of iron oxide layers around the reinforcing bars; more explanations are provided in the previous section.

The corrosion current densities of GPC samples calculated using B=26 are as low as one-third of the corrosion current densities calculated using the Tafel extrapolation method. This dissimilarity is in part due to the difference in the number of samples used in the calculation of the corrosion current in each method which results in different average R_p values at each data point. The mean R_p value of the two samples tested at each data point for the Tafel slope measurement is not representative of the average R_p of all the samples (refer to Figure 4-6 to see the standard deviations of R_p values at each data point). If the same number of samples were used for both methods, the observed difference in the corrosion current density values would be only due to the difference between the measured B values (Table 4-4) and the prescribed B value of 26 mV. Either way, it is apparent that using the prescribed value of B constant instead of the measured value might introduce a considerable error factor into the system (assuming that the gravimetric and electrochemical mass losses are reasonably close to each other, i.e. electrochemical results are accurate enough). Considering the significant variability of the B constant (Section 3-5), and given all the economic and safety issues associated with an inaccurate estimation of the corrosion rate, having more experimental results to build up a reliable database of B constants to be used in the Stern-Geary equation for low calcium fly ash geopolymer-based corroding systems is strongly recommended.

Another source of error that affects the accuracy of the calculated corrosion current densities, irrespective of the measurement method, is the presence of localized attacks (pitting) which is common in the case of chloride-induced corrosion. In pitting corrosion, the actual area which is being actively corroded is smaller than the total area of the electrode. This means that using the total area of the electrode to calculate the intensity of the corrosion current leads to underestimation of the corrosion current density [117]. This remains a general difficulty in the study of the chloride-induced corrosion using the conventional electrochemical techniques; especially when both localized and general corrosions are available (like in the present study, Section 4-3-7) and distinguishing between their associated contributions in the total corrosion current density is impossible.

Despite all the inaccuracies associated with measuring the minuscule amount of rust products, measuring the mass difference of the embedded reinforcement before and after submitting the sample to the corrosive conditions is still the most reliable technique to assess the corrosion rate and to validate the results of electrochemical measurements. This mass loss can be directly compared to the mass loss calculated from corrosion current densities using Faraday's law. Figure 4-10 compares the gravimetric and electrochemical mass losses of 8 GPC samples (each data point is the average of two measurements). Mass loss measurements were conducted after each Tafel test in which the corrosion current density had been measured.



Figure 4-9. Average corrosion current density of GPC and PCC samples during the propagation phase of corrosion. (The initiation phase is accelerated and not presented here)



Figure 4-10. Gravimetric mass loss vs. electrochemical mass loss for GPC and PCC

To calculate the electrochemical mass loss using Faraday's law, the area under the average corrosion current density curve vs. time has been integrated and used. During the drying cycles, only a fraction of the area is used (for instance 62.5% for two-weeks-

long drying cycles), to take the effect of decreasing corrosion current during the drying cycles into account. To calculate this modification factor for drying cycles, two samples were polarized over a rather limited range of overpotentials ($E-E_{corr}=-120$ to +120 mV) at the end of their wetting cycles and then over the normal range ($E-E_{corr}=-200$ to +200 mV) at the end of their two-weeks drying cycle. The former limited polarization range enables measuring the corrosion current values using the Tafel plot method while minimizing the introduced irreversible changes into the system [119]. Corrosion current densities at the end of the drying cycles were almost 25% of the values recorded at the end of the wetting cycles which means an average decline of about: [1-(1+0.25)/2]×100=37.5% within two weeks of drying.

Results of a comparison between the gravimetric and electrochemical mass losses of bare steel bars embedded in hardened mortar from Andrade & Gonzalez [139] is also presented in Figure 4-10 as a benchmark. Andrade & Gonzalez's reported results show a general tendency for the gravimetric mass losses to be larger than the electrochemical mass losses. The authors have claimed that this behavior can be improved by eliminating the effect of uncompensated IR-drop. Nonetheless, the IR-drop is automatically compensated by the potentiostat in the current study (Section 4-2-3). Two dashed lines which are parallel to the line of equality are representative of the acceptable scattering range for PCC samples, due to an intrinsic error factor of 2 when the Stern-Geary equation is employed to assess the corrosion current density [117,140]. While all the GPC data points in Figure 4-10 scatter in a range which is comparable to the reported acceptable results for Portland cement concrete, they are all lying around the line where the gravimetric mass loss is equal to the electrochemical mass loss. This implies that the employed conventional electrochemical test methods predicted the corrosion rate of the geopolymer-based corroding system with an acceptable level of

accuracy. Also, these results confirm the suitability of the selected sweep rates to perform the potentiodynamic tests, as too slow or too fast sweep rates could lead to an underestimation or overestimation of the corrosion current density and hence the calculated electrochemical mass losses.

4.3.7. Corrosion pattern

Figure 4-11 shows the corrosion pattern for a sample after experiencing 15 wetting/drying cycles (336 days) in NaCl solution and ambient condition respectively. No corrosion induced crack was observed around the steel bar. The steel bar is gently brushed with a non-metallic bristle to remove loose and bulky corrosion products as well as the loose adherent concrete particles before taking the photo. As it can be seen, a combination of uniform (microcell) and localized (pitting) corrosion is observed, and the pitting attack is concentrated on the lower surface of the reinforcing bar which has the least amount of concrete cover against the chloride penetration. Formation of macrocells between the anodic parts (pits) and the rest of the steel surface (as cathode) increases the corrosion current and decreases the corrosion potential [117]. The employed electrochemical test methods are not capable of quantifying the contribution of the pitting or uniform corrosion in the total measured corrosion parameters. As a result, the measured corrosion parameters such as open circuit corrosion potential and corrosion current densities are representative of the whole electrode surface. The corrosion pattern observed in Figure 4-11 is similar to the corrosion pattern observed in Portland cement based concrete beams corroded in natural condition combining uniform and localized (pitting) corrosion [150,151].



Figure 4-11. Corrosion pattern for a sample after 15 wetting/drying cycles (336 days).

4.4. Conclusion

To investigate different aspects of corrosion of reinforcement in low-calcium fly ashbased geopolymer concretes during the propagation phase of corrosion, a set of electrochemical tests are conducted, and parameters such as corrosion potential, polarization resistance, Tafel constants and corrosion current density are investigated. Gravimetric mass loss measurements are utilized as a tool to validate the electrochemical results. The test results led to the following conclusions:

• By conducting a set of cyclic voltammetry tests, sweep rates of 5 and 10 mV/min for passive and active samples are established and used throughout the experimental investigations (i.e. in potentiodynamic tests). These sweep rates are slow enough to ensure a steady-state condition which is required to avoid overestimation of the corrosion current density. They are also fast enough to avoid altering the electrode equilibrium due to the change in the

concentration of ions around the electrode which consequently leads to underestimation of the corrosion current density.

- Corrosion potential and polarization resistance values after depassivation of the reinforcement fall in the same zone of corrosion risk as expected for Portland cement-based corroding systems. On the other hand, based on the reference classifications commonly used to evaluate the severity of corrosion in reinforced Portland cement concretes, open circuit corrosion potential of passive samples fell in the uncertain to high corrosion risk zones, as opposed to passive/low corrosion risk zone. The lower pH level of the geopolymer binder is considered as the main reasons for the observed low corrosion potential values, although further investigation of the phenomenon is required. Similar behavior was observed for the polarization resistance of the passive samples, where the polarization resistance values were in the low to moderate corrosion risk zones. This finding suggests that the traditional classifications which have been developed for Portland cement-based corroding systems might need some recalibrations to be used for geopolymer-based corroding systems while assessing the passivity of samples.
- The measured proportionality constants (B), showed a substantial divergence from the conventional values established for Portland cement-based corroding systems (for passive samples: 13<B<20 vs. 52 for PCC, for active specimens after 112 days of wetting-drying in NaCL solution: 45<B<58 vs. 26 for PCC). Using the traditional value of B=26 may lead to underestimation of the corrosion current density of geopolymer-based corroding systems.

Although, the approximate inherent of "B" constant which has resulted in evident discrepancies in the reported values for Portland cement-based corroding systems on the literature, suggests that not all the difference should be attributed to the application of a different binder type. While the values of B=52 and 26 for passive and active Portland-cement based corroding systems are widely accepted as approximate values which provide an accurate enough estimation of the corrosion current density, more experimental results are required for geopolymer-based corroding systems to build up a database of B constants to be used in the Stern-Geary equation.

 Under the experimental conditions of this study, reinforced low-calcium fly ash-based geopolymer concrete samples exhibit polarization resistance values comparable to Portland cement-based corroding systems. This behavior can be interpreted as a similar electrochemical performance of both binders when used in chloride-contaminated environments.

CHAPTER 5: Chloride Diffusivity, Chloride Threshold, and Corrosion Initiation in Reinforced Alkali-activated Mortars

5.1. Introduction

The electrochemical performance of low calcium alkali-activated (geopolymer-type) binders during the propagation phase of corrosion was investigated in the previous chapter, and this chapter will be focused on the initiation phase and various factors involved in this phase. To perform the electrochemical experiments, the test protocols used and validated in the previous chapter will be employed.

While the reinforced concrete members can still sustain the applied loads during the initial stages of the propagation phase [152], it is 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 (i.e. the service life), including the rate of diffusion of chloride ions which is influenced by the permeability of the concrete/mortar (physical absorption) and the chloride binding capacity of the matrix, as well as the stability of the passive film around the reinforcement which is indirectly measured by the concentration of chloride ions required to break it down (chloride threshold). While a considerable amount of research has been conducted in the past to study various factors involved in the initiation phase of corrosion of ordinary Portland cement (OPC) binders, there is still some uncertainty regarding topics such as the chloride threshold,
passivation/depassivation mechanism and the effect of chloride binding in these binders (see e.g. [153,154]). For alkali-activated binders, there is more concern and comparatively only few data available regarding their durability in marine environments, as these materials have recently gained momentum as viable alternative construction materials [23,69].

Apart from relatively limited previous research studies on the corrosion initiation of alkali-activated binders, variabilities of these binders in terms of both precursors and the properties of the final product are other factors widening the consensus gap among researchers with regards to the durability performance. Depending on the precursor used, the final products can have considerably different nano/microstructures with different transport properties. Alkali-activation of aluminosilicate sources such as metakaolin and FA results in an amorphous aluminosilicate network with a porous nano/microstructure, as discussed in Chapter 3. On the other hand, alkali activation of slag binders with a considerable amount of calcium in the matrix leads to the production of some form of calcium silicate hydrates with partial substitution of alkalis and aluminium [9–12] with a considerably finer pore structure than those of aluminosilicate networks (Chapter 3). The type and concentration of the activator and the ratio of silicates to alkalis play an important role in developing the pore structure and stability of the passive layer as it is reported in a number of previous research studies [47,55,155,156]. Involvement of all the variables mentioned above can explain the (sometimes contradictory) results reported on the corrosion performance and transport properties of alkali-activated and geopolymer-type materials in the literature.

With regards to the chloride penetration in geopolymer-type binders, only a limited number of studies are available in the literature, and a higher resistance to chloride penetration and lower rate of corrosion of reinforced samples are reported by some researchers (see e.g. [51,52]). However, as it was mentioned in Chapter 2, a quick review of the samples compositions in those studies reveals that in almost all cases samples have been synthesized using very highly alkaline solutions with low modulus ratios (= molar ratio of silicates to alkalis), increasing the risk of efflorescence [63] (also refer to Chapter 7), and safety concerns regarding the application of a caustic solution at very high pH levels during the manufacturing process. On the other hand, necessity of presence of calcium in the matrix to form a finer gel structure to reduce the rate of chloride penetration was observed and emphasised in Chapter 3, and is also suggested in a number of previous studies, based on the observed superior performance of alkali-activated slag binders, or blended fly ash and slag binders, compared with geopolymer-type or even OPC binders in chloride contaminated environments [35,53,55,69,157–159].

Although previous studies provide valuable information regarding various aspects of durability performance of alkali-activated materials during the initiation phase of corrosion, they lack a systematic approach which incorporates all the different influential parameters and investigates their correlations. Variabilities of sources of the raw precursors as well as the experimental techniques used in the previous studies also add another layer of difficulty while interpreting the available results in the literature. Thus, the current study aims to systematically investigate the effect of binder composition, including FA/GGBS ratio, alkali concentration and modulus ratio on the chloride diffusivity and chloride threshold values of a wide range of alkali-activated mortar samples. Results are discussed in light of the pore structure development in various compositional conditions. Chloride binding is also studied through assessment of free and total chloride content of chloride contaminated mortar samples. The electrochemical

aspects of samples before depassivation are studied and the results are discussed accordingly.

5.2. Experimental program

5.2.1. Materials and mix proportions

Gladstone fly ash and ground granulated blast-furnace slag (Gladstone FA and GGBS (B) as presented in Chapter 3) were used as solid precursors to fabricate alkali-activated samples. The chemical composition, amorphous content and the crystalline phases of the raw precursors have been previously presented in Section 3.2.1. Particle size distribution of solid precursors can also be found in Figure 3-1.

A mixture of sodium hydroxide (NaOH), or sodium hydroxide (NaOH) + potassium hydroxide (KOH) solution, and grade D sodium silicate solution were used as the activator. The sodium hydroxide and grade D sodium silicate solution are same as the ones used and described previously in Chapter 3 (Section 3.2.1). The technical grade NaOH pellets supplied were dissolved in tap water to prepare NaOH solution. KOH flakes were supplied by Recochem Inc. and dissolved in tap water as partial replacement of NaOH in some mixes. NaOH or NaOH + KOH and sodium silicate solutions were mixed in proportions to form alkaline solutions at different concentrations and modulus ratios ($M_s = molar ratio of SiO_2/M_2O$, M = Na or Na+K), according to Table 5-1. After mixing, the alkaline activator was allowed to cool to ambient temperature and equilibrate for 24 hr prior to fabrication of the specimens.

To prepare Portland cement-based control samples, Australian general-purpose cement manufactured at the Boral Berrima Cement Works (NSW, Australia) was used. To produce the cement, 7.5% limestone mineral addition had been used. Four OPC mortars with water to cement ratios similar to the water to binder ratios of alkali-activated mixes were fabricated to be able to compare the chloride diffusivities and electrochemical performance of alkali-activated samples with those of OPC samples.

precursor	Na/(Na+K) (molar)	SiO ₂ /M ₂ O (molar)	Na ₂ O%	Water/binder
75% FA/25% GGBS	1.0	1.0	5,8	0.35
		1.5	5,6,8	
	0.5	1.0	8	
50% FA/50% GGBS	1.0	1.0	3,5,8	0.375
		1.5	3,4,5,8	
25% FA/75% GGBS	1.0	1.0	3 ,8	0.4
		1.5	3,4,5, 8	
	0.5	1.0	3	
100% OPC	-	-	-	0.35-0.375-0.4-0.45

Table 5-1. Mix proportions of the alkali-activated and Portland cement mortars

Note 1: M= Na or K and M₂O%=M₂O/ (FA+GGBS) (%)

Note 2: Water/binder ratios are calculated considering the total water and the total solids (precursors+anhydrous activator)

Note 5: All samples are ambient-cured at $23^{\circ}C \pm 2^{\circ}$ in sealed condition

Note 6: For samples containing KOH, Na₂O% represents the equivalent Na₂O concentration that has the same molar concentration of alkalis as in Na,K-based activator

For FA-dominated samples (75% FA – 25% GGBS) a minimum alkali content of 5% was used to enhance the early-age strength development which is mainly through formation of aluminosilicate network. By increasing the GGBS content to 50% or more, lower alkali

Note 3: Superplasticiser of 0.6 %, 0.5%, and 0.4% by mass of cement was used for OPC mixes with W/C of 0.35, 0375, and 0.4 respectively

Note 4: Sand to binder ratio is 2.0 for all mixes

contents could be used as in these binders a combination of the aluminosilicate network and some form of calcium silicate hydrate gel (with a higher probability of formation at lower alkalinity levels [12,29]) is responsible for strength development and provide higher early-age strength as a result.

5.2.2. Manufacturing mortar samples and curing condition

Alkali-activated mortars were manufactured in a Hobart planetary type mixer. FA and GGBS were first introduced into the bowl and dry mixed to achieve a uniform dispersion. Then the activator solution was added and the pastes were mixed for two minutes at low speed. Mixing then stopped to scrape down the bowl and the blade, followed by another two minute of mixing at medium speed. Then the mixer stopped and switched to low speed, the entire quantity of sand slowly introduced into the mixer over a 30 s period, while still mixing at low speed, and then followed by 30 s mixing at medium speed. The mixer stopped and let the mortar stand for 30 s, to scrape down the blade and the bowl again. Finally the mixing continued for another 90 s at medium speed. For control cement paste samples, a different mixing periods were chosen for alkali-activated pastes to ensure a proper exposure of solid precursors to the alkaline solution, leading to a better dissolution and availability of more aluminate and silicate species to develop the aluminosilicate network [27].

After finishing the mixing, mortars were transferred into $\emptyset 100 \times 200$ mm cylindrical moulds to be cut in 75 mm slices for bulk diffusion test. Corrosion samples ($\emptyset 50 \times 100$ mm cylinders with assembled reinforcement, refer to Figure 5-1) were also filled.

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Mortar pouring was conducted in two layers accompanied by proper vibrating on the vibration table. For SEM/EDS tests, select paste samples with the same mix proportions as the investigated mortars were prepared following the same mixing procedure mentioned above for fabrication of paste. All samples were kept sealed in the moulds in a controlled room at a constant temperature of $23^{\circ}C \pm 2^{\circ}$ until the preparation/test days which was 90 days after the casting date to make sure of a negligible microstructural change due to the polymerization or hydration at later ages.

5.2.3. Fabrication of corrosion samples

A specific method of fabrication similar to that of Chapter 4 was employed to avoid any external exposure of the embedded reinforcement to the chloride ions. A normal ductility 12 mm deformed bar with 500 MPa yield strength was embedded according to the details in Figure 5-1. All reinforcing bars were gently wire-brushed before assembling them inside the mould to remove loose pre-formed rusts. Both ends of the bar were machined to the proper diameter to help fitting into the acrylic tubes. The exposed length of the bar was 50 mm. A copper wire was soldered to the bar to perform as working electrode during electrochemical measurements. A thin layer of silicon sealant was applied around the machined parts before fitting the bar inside the tubes to avoid any probable corrosion through accumulation of chloride ions at the connection spots. After attaching the tubes, they were filled by silicon sealant to block the access to the core reinforcement. Both top and bottom sides of samples were coated with an anti-chloride resin (supplied by the Australian supplier "Parchem" under the commercial name of Emer-Stop S100 N), to enforce peripheral penetration of chloride ions. Another layer of silicon sealant was also applied on top of the resined surface as an additional layer of protection.



Figure 5-1. Reinforced mortar samples details

5.2.4. SEM and EDS analysis

The employed SEM and EDS methodology and details are similar to what mentioned in Chapter 3. Please refer to Section 3.2.5 for more information.

5.2.5. XRD analysis

X-ray diffractograms of specimens were collected on a PANalytical Powder X-Ray diffractometer with Co as anode at 45 kV and 40 mA X-Ray generation condition, using BBHD optics with ¹/₂° Div. slit and 1° Anti Scatter slit, 10 mm beam mask and 0.04 rad soller slit. The scan results were interpreted using the software HighScore Plus (Supplier: PANalytical); ICDD database was used to search candidate pattern of possible crystalline phases in the samples.

5.2.6. Bulk diffusion test

To calculate the diffusion coefficients by measuring the total (acid soluble) chloride contents as well as to estimate the chloride binding capacity of select samples through free (water soluble) chloride content measurements, $\emptyset 100 \times 75$ mm slices were cut from standard $\emptyset 100 \times 200$ mm cylinders. Two samples were tested per each mix-design to obtain an average diffusion coefficient. ASTM C1556 [161] was followed to determine the apparent chloride diffusion coefficients, with the exception that samples kept submerged in 16.5% NaCl solution for 45 days (as opposed to the recommended 35 days), which was due to the very low permeability of the GGBS-dominated mortars as will be discussed subsequently. A German Instrument profile grinder (PF-1100) was used to obtain the powder samples at 1 mm increments along the depth. The total and free chloride content of samples were determined according to the test protocols of ASTM C1152 [123] and ASTM C1218 [162] respectively. The apparent chloride diffusion coefficients were measured by fitting Equation (5-1) to the total (acid soluble) chloride profiles:

$$C(x,t) = C_s - (C_s - C_i) \operatorname{erf}\left(\frac{x}{\sqrt{4.D_a t}}\right)$$
(5-1)

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 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 m²/s and *erf* denotes the error function described in Equation (5-2) as follows.

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-u^2) du$$
(5-2)

5.2.7. Electrochemical tests

All corrosion samples were stored in 3.5% NaCl solution and tested on a weekly basis throughout the testing period of up to 9 months. Half-cell potential and polarization resistance (R_p) were measured to monitor evolution of the electrochemical equilibrium of the samples. To carry out the electrochemical tests, a three-electrode system was used comprised of the reinforcment as the working electrode (WE), a titanium mesh as counter electrode (CE), and Saturated Calomel Electrode (SCE) as reference electrode (RE). During the testing, samples were partially submerged in water to avoid concentration polarization due to the lack of oxygen. CE was placed inside the water container and around the samples as it is shown in Figure 5-2. RE was also placed in the water and next to the sample. The half-cell potential was measured by open-circuit measurement of the potential difference between the RE and WE after stabilising the potential difference which was not recorded until its fluctuations was smaller than 1 mV during a 60 s period. All the electrochemical tests were carried out using a VMP3 Multi-channel potentiostat which was capable of compensating the ohmic (IR) drop. Other test protocols such as the sweep rate, percentage of the ohmic drop compensation, the potential excitation range for LPR test, etc. were similar to those mentioned in Chapter 4. The half-cell potentials and R_p values are presented in the following sections.



Figure 5-2. Half-cell potential and LPR test setup

5.3. Results and discussion

5.3.1. Surface morphology observations and elemental analysis

Figure 5-3 depicts the surface morphology of a representative set of samples. Depending on the slag/fly ash content, alkali content, and modulus ratio, various morphologies can be observed. In general, the higher alkali content of the activator has led to the development of more homogeneous binders (compare 3 or 5% alkali containing samples with 8% samples), due to the higher rate of dissolution of solid precursors. A higher dissolution rate, as previously discussed, suggests the availability of more aluminate and silicate species which can be incorporated into the matrix and ultimately can lead to higher Si/Al ratios [27]. This is further corroborated by the elemental analysis of the binding matrices; the averages of point analysis values along with the associated standard deviations are presented in Table 5-2.

One sample per each mix has been studied extensively: between 30 and 45 spot analyses were conducted on the sample. 30 data points were chosen after eliminating the outliers, and the average of point analysis values along with the associated standard deviations was calculated and reported (Table 5-2). In general, samples fabricated of activators containing lower alkali contents showed more outliers. As mentioned previously, this behaviour appears to be due to the interference of underlying unreacted particles. Even after elimination of the outlier points, samples fabricated of activators containing 3 or 5% alkalis show larger standard deviations (particularly in case of Ca/Si ratios at Ms=1.5), suggesting some interferences from unreacted/partially reacted particles. Another sample per each mix was also studied briefly through EDS analysis of a limited number of points (between 10 to 15 points) to assess the consistency of the obtained results through comparing the average values. In all cases, results were quite comparable, although the result of the second sample is not presented here due to the limited number of investigated points.

As it can be seen, samples fabricated of activators containing 3 or 5% alkalis show systematically lower Si/Al ratios compared with those fabricated of higher alkali content of 8%, consistent with the SEM observations. Another increasing trend in Si/Al ratios can be seen by increasing the silicate content of the activator (i.e. increasing the modulus ratio), and this is in agreement with the work of Sindhunata et al. [156] in which a higher reaction rate and polymerization was observed by increasing the modulus ratio from 0.79 to 1.4 in Na-silicate activated Gladstone fly ash. 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 formation of more porous geopolymer gel in low-calcium binders (see the high porosity of FA-dominated samples in Chapter 3); as a result, increasing the alkali content or the soluble silicate content leads to increasing the mesopore volume [34,156]. Si/Al ratios can also be influenced by the ratio of GGBS/FA as it can be seen in Table 5-2; a higher Si/Al ratio

is expected for C-(A)-S-H gels compared to aluminosilicate networks due to a limited uptake of aluminium in the tobermorite-like structure of these systems [26].

Apart from affecting the pore structure development of aluminosilicate networks, the alkalinity of activator can also hinder/promote the formation of calcium silicate hydrates when there is calcium (sourced from GGBS here) in the matrix. According to previous research studies [9–12], some form of calcium silicate hydrate with partial substitution of aluminium, also known as C-(A)-S-H gel, is the main reaction product of alkali activation of slag binders. Depending on the alkalinity level, some degree of aluminosilicate network formation can also be expected in slag binders. In blended FA and GGBS systems, formation of C-(A)-S-H over aluminosilicate network is promoted in less alkaline environments and at higher calcium contents. Presence of excessive amount of hydroxide ions is suggested to hinder the formation of calcium silicate hydrates by developing a calcium hydroxide layer around the slag particles which prevents the diffusion of calcium ions from the particle into the binder phase [12,29,73].

Availability of enough calcium sources in the matrix is also vital for the formation of C-(A)-S-H gel. Below a certain GGBS content, recommended between 25% and 50% in blended fly ash and slag systems by Provis et al. [35] and also in accordance with the observed high permeability of sample AAP4 in Chapter 3 with 25% GGBS, majority of the calcium ions appear to be adsorbed into the coexisting aluminosilicate network through a charge balancing mechanism, decreasing the likelihood of calcium silicate hydrate formation. C-(A)-S-H gel has a lower porosity than the aluminosilicate (geopolymer-type) networks as it can incorporates the water into its crystalline structure during the hydration process which grows and play a pore filling role as a result [69]. The importance of presence of enough calcium in the matrix to reduce the

permeability was also discussed in Chapter 3 by studying the sorption kinetics. Thus, investigation of the effect of alkalinity and calcium availability on C-(A)-S-H gel formation which reduces the chloride diffusivity is one of the key goals of this chapter: in lieu of effective chemical binding (as will be discussed in the following section), reducing the porosity and permeability of the matrix in alkali-activated materials appears to be the only viable method of reducing the chloride diffusion rate which can be achieved by formation of C-(A)-S-H gel along the aluminosilicate network (refer to MIP and BJH derived pore structures, and also sorption kinetics of blended FA and GGBS binders in Chapter 3 for more information).

As an indication of the diffusion rate of calcium ions out of the slag particle which is essential to C-(A)-S-H gel formation, Ca/Si ratios are calculated and presented in Table 5-2. In accordance with the previous explanations and published research studies, Ca/Si ratios show a good correlation with the alkali content as well as the GGBS contents: decreasing the alkali content from 8 to 5% has increased the Ca/Si ratios by at least 60%, regardless of the GGBS content and modulus ratio. Furthermore, increasing the GGBS content from 25% (5% Na₂O) to 75% (3% Na₂O) has led to almost 40% Ca/Si growth at the same modulus ratio (Ms=1.5), suggesting formation of even more C-(A)-S-H gel. These findings will be used in the following sections to analyse the diffusion coefficient results, and consequently, the corrosion initiation times, which as will be discussed, correlate rather well with the amount of calcium in the matrix (as an indication of the fraction of C-(A)-S-H gel in the binder matrix) as well as Si/Al ratios.



Figure 5-3. SEM micrographs of representative alkali-activated paste samples

FA/Slag	Ms	Na ₂ O (wt. %)	Number of points	Si/Al (molar ratio) ± SD	Ca/Si (molar ratio) ± SD
75/25	1.0	5	30	1.62±0.37	0.79±0.20
75/25	1.0	8	30	2.01±0.26	0.49±0.19
75/25	1.5	5	30	1.73±0.13	1.04±0.25
75/25	1.5	8	30	2.17±0.25	0.53±0.06
25/75	1.5	3	30	1.70±0.22	1.47±0.56
25/75	1.5	8	30	2.53±0.24	0.89±0.09

Table 5-2. Elemental composition ratios of representative alkali-activated pastes

5.3.2. Chloride binding in alkali-activated and OPC mortars

Figure 5-4 compares the total chloride and free chloride profiles of three select alkaliactivated mortar samples as well as one OPC control mortar sample (W/C=0.35). The alkali-activated samples are representative of: FA-dominated samples fabricated of sodium silicate activator at high alkalinity level and with aluminosilicate-dominated matrix (Figure 5-4(a)), GGBS-dominated samples fabricated of sodium silicate activator at low alkalinity level to promote formation of C-(A)-S-H gel (Figure 5-4(b)), FA-dominated samples fabricated of sodium silicate activator with partial potassium replacement at high alkalinity level and with aluminosilicate-dominated matrix (Figure 5-4(c)). As it can be seen for all alkali-activated samples, there is a remarkably good match between the total and free chloride profiles, revealing insignificant chloride binding capacity through chemical reactions. OPC mortar, on the other hand, shows a clear chloride binding capacity in Figure 5-4(d) where the contribution of chemical binding is variable between 20 to 40% of the total chloride, increasing by depth as the total chloride decreases.



Figure 5-4. Comparison of total and free chloride profiles (wt. % by sample mass) in select alkali-activated and OPC mortars after 45 days of immersion in 16.5% NaCl solution

The formation of new crystalline phases was also investigated by X-ray diffraction; paste samples were fabricated with the same composition as the mortars in Figure 5-4, and after crushing were stored in 16.5% NaCl solution (1 to 100 weight ratio) for 45 days. The intact (uncontaminated) and chloride contaminated crushed paste particles were then powdered and analysed by XRD. The diffraction patterns along with the identified phases are presented in Figure 5-5. In both FA-dominated and GGBSdominated samples (Figure 5-5(a) and (b) respectively) no new crystalline phases is observed, except some crystalline NaCl (halite). Unlike alkali-activated samples, OPC samples show Friedel's salt (calcium chloroaluminate hydrate crystals (Ca₂Al(OH)₆(Cl, OH).2 H₂O)) formation, consistent with the observed difference between the total and free chloride profiles in Figure 5-5(d).

While a lack of chemical binding capacity for aluminosilicate-dominated (geopolymertype) materials has been previously reported in the literature (see e.g. [163]), there are indications that pure slag-based alkali-activated materials are capable of binding chloride ions through surface adsorption and inter-layer ion-exchange in Mg-Al hydrotalcite-like and AFm structures respectively, with the former having a more prominent role [164,165]. The apparent lack of chemical binding in the slag-dominated alkali-activated samples of the present study can be mostly attributed to the absence of hydrotalcite-like (and also AFm) reaction products; the GGBS studied here has a lower Mg content compared to the samples studied in [164,165], presence of FA in the mix can also have some hindering effects on the formation of hydrotalcite-like and AFm structures. Further investigation is required to assess the dependency of formation of hydrotalcite-like and AFm phases on the Mg content and FA content in blended alkali-activated materials.

Based on these results and in the following sections, the observed differences in the measured chloride diffusion coefficients of alkali-activated samples will be discussed solely in light of the differences in the pore structure and tortuosity, and various parameters that can affect them.







Figure 5-5. XRD patterns of select alkali-activated and OPC pastes before and after exposure to NaCl solution. M: mullite, Q: quartz, A: aragonite, C: calcite, Ma: magnetite, He: hematite, H: halite (NaCl), V: vaterite, P: portlandite, E: ettringite, F: Friedel's salt

5.3.3. Chloride diffusion coefficients

The apparent chloride diffusion coefficients for a range of mixes were determined according to ASTM C1556 [161] by employing a non-linear regression analysis and minimizing the sum of the squared residual errors (SSRE). Two typical chloride profiles and the associated fitted curves are presented in Figure 5-6. Due to its lowest Ca/Si ratio according to Table 5-2, Figure 5-6(a) depicts the chloride profile of a sample which can be considered as representative of aluminosilicate dominated matrices. Figure 5-6(b), on the other hand, presents the chloride profile of a sample with the highest Ca/Si ratio in Table 5-2, representative of calcium-rich matrices. As it is shown, increasing the GGBS content from 25% of binder content to 75% has led to an almost tenfold decrease in the diffusion coefficient values, highlighting the critical role of presence of calcium in the matrix to decrease the porosity and increase tortuosity.



Figure 5-6. Typical total chloride (*Ct*) profiles of (a) a sample representative of lowcalcium mixes (Ca/Si=0.49), and (b) a sample representative of high-calcium mixes (Ca/Si=1.47)

Results of the analysis for the representative alkali-activated mixes are summarized in Figure 5-7(a). Each result is the average of two measured diffusion coefficients. Error bars are indicative of standard deviations. The mix specifications, including the water to binder ratios are also presented on the same figure. Only the mixes with minimum and maximum alkali oxide concentrations for each modulus ratio (1.0 or 1.5) are analysed (refer to Table 5-1 for mix details); further implications for medium levels of alkali concentration is possible considering the lower and upper bound values. In general it appears that for FA-dominated samples, 5 to 8% alkali oxide content at Ms=1.0 delivers the lowest chloride diffusion coefficients, while the best performance for calcium-rich (75% GGBS) samples are obtained with the lowest alkali content of 3% (or 4% although not presented here) and at either Ms=1.0 or Ms=1.5. The main features observed in Figure 5-7(a) can be discussed in light of the differences in: calcium content, alkali concentration, and modulus ratio, and their influences on porosity as well as tortuosity of the binders as follows.





Figure 5-7. Chloride diffusion coefficients of: (a) Alkali-activated mortars, (b) OPC mortars

5.3.3.1. Effect of calcium content on the apparent chloride diffusion coefficients

Analysis of Figure 5-7(a) reveals that the presence of calcium has the most prominent effects among the other influential parameters on the diffusion coefficients. 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 affect the chloride diffusion in a major way in most cases. This is consistent with the findings of Provis et al. [35] where the pore filling effect of calcium silicate hydrate gel, formed due to the presence of slag in the blended matrix, started to become notable when the slag dominated the binder (minimum 50% slag). Similarly in this study and according to Figure 5-7(a), the apparent diffusion coefficients have declined sharply when the calcium-rich binder becomes dominant. This is indicative of a finer pore structure with higher tortuosity of the slag-based binders, compared to that of aluminosilicate binders as the end result of alkali-activation of fly ash, and is in agreement with the previous research studies [35,166,167], and the pore structure characteristics discussed in Chapter 3.

Lloyd et al. [33] argued that due to the especial pore structure of geopolymer binders, where large pore/cavities are only accessible through smaller mesopores, the effect of presence of large pores on mass transfer might be mitigated. Inspection of Figure 5-7(a) reveals that, however, in general fly ash-rich binders are considerably permeable, and this becomes even more clear by direct comparison with the control OPC-based sample with the similar water to binder ratio of 0.35 (Figure 5-7(b)). Having said that, the permeability, which depends on both porosity and pore connectivity, shows a high sensitivity to the alkali and silicate content of the activator solution as well; and this will be discussed in the next section. Except the samples manufactured with 50% FA and 50% GGBS at modulus ratio of 1.5 and with 8% Na₂O, the difference between the diffusion coefficients of samples fabricated of 50% or 75% slag is not comparatively significant, suggesting close fineness of the pore structures and high tortuosity of both binders as the binder is dominated by GGBS.

The apparent chloride diffusion coefficients of OPC-based mortars manufactured at different water to cement ratios are also presented in Figure 5-7(b). The general trend, as expected, is increasing the diffusion coefficients by increasing the water to cement ratios. Comparison of the diffusion coefficients of OPC-based mortars (Figure 5-7(b)) and alkali-activated mortars (Figure 5-7(a)) fabricated with the same water to binder ratios reveals an interesting trend: Alkali-activated mortars with 50% slag content or more, have considerably lower diffusion coefficients than that of OPC counterparts, and the difference can be up to an order of magnitude, or more in some cases. This can be attributed to the finer porosity, and higher tortuosity of the C-(A)-S-H gel in the alkali-activated slag binders than that of C-S-H in OPC-based binders, despite comparable water amounts in both mixes and rather low Ca/Si ratios of the alkali-

activated matrices (compared with OPC based binders as discussed by [29], and also can be seen in Table 5-2).

The lower chloride diffusivity of alkali-activated slag binders compared with OPC binders was also previously reported by Ma et al. [55] and was speculated to be the result of a better pore structure and chloride binding of alkali-activated slag samples; although as discussed previously in this paper, chloride binding is very negligible in alkali-activated slag rich binders studied here and the fine porosity (as well as high tortuosity) appears to be the main reason for the better performance of these binders against chloride ingress.

5.3.3.2. Effect of alkali and silicate content of the activator on the apparent chloride diffusion coefficients

Effect of alkali content and silicate content on the development of the aluminosilicate network and C-(A)-S-H gel was discussed previously in Section 5-3-1; their effects on the chloride diffusion coefficients are discussed more in detail herein. As it can be seen in Figure 5-7(a), increasing the alkali content has led to increasing the chloride diffusivities, regardless of the modulus ratios. This consistent trend can be explained by the fact that according to Table 5-2 and previous explanations, increasing the alkali content leads to formation and development of more nano-porous aluminosilicate network which is reflected in higher Si/Al ratios. Besides, highly alkaline environments hinder diffusion of calcium ions from the slag particles and thus formation of the less porous and pore-filling C-(A)-S-H gel which can be confirmed by lower Ca/Si ratios at higher alkalinities in Table 5-2. As a result, increasing the alkali content leads in a more porous matrix which facilitates transportation of external ions. It should be noted

that the maximum alkali oxide content is limited to 8% in this study, to avoid the undesirable efflorescence observed in alkali-activated binders (see Chapter 7 for more detail) with a lot of free alkali ions in the pore solution; as a results, the effect of higher alkali content levels is not addressed in this study.

The effect of silicate content on the diffusion coefficients is also of interest. Increasing the silicate content (i.e. increasing the modulus ratio) generally has increased the diffusion coefficients, suggesting development of more porous and permeable matrices. Interpretation of the observed behaviour is not as straightforward as the effect of alkali content on the diffusion coefficients, as increasing the modulus ratio leads to an increase of the Si/Al ratio and advancement of the porous aluminosilicate gel, and at the same time, it promotes formation of C-(A)-S-H gel (reflected in higher Ca/Si ratios in Table 5-2) by reducing the pH level.

To have a better understanding of the role of modulus ratio, its effects should be studied for FA-dominated and GGBS-dominated samples separately. For FA-dominated samples (75% FA) with an aluminosilicate-dominated network, there is a little amount of GGBS in the mix and majority of calcium ions most probably get adsorbed into the aluminosilicate network, and as a result, the role of silicate content in the formation of more aluminosilicate gel becomes more important. This explains the strikingly large difference between the diffusion coefficients of these samples at Ms=1.0 and Ms=1.5 (for e.g. the diffusion coefficient of samples with 5% alkali oxide content is around 7 times larger at Ms=1.5 than at Ms=1.0). On the other hand, in GGBS-dominated samples where the C-(A)-S-H gel becomes dominant, the porosity decreases by increasing the Ca/Si ratios, partially compensating the growth in the pore volume caused by the development of the coexisting aluminosilicate matrix at higher silicate content levels. For comparison, the diffusion coefficients of samples containing 3% alkali content at Ms=1.5 is only 2.8 times larger than that of Ms=1.0, a considerably smaller difference compared with 75% FA samples as mentioned above.

5.3.3.3. Effect of type of alkali on the apparent chloride diffusion coefficients

Figure 5-8 depicts the effect of partial replacement of NaOH with KOH on the chloride diffusion coefficients. All samples were fabricated of activators of M_s =1.0. Evidently, the sodium activated samples with 75%FA and 25% GGBS show a lower diffusion coefficient, while not much of difference can be observed in the diffusion coefficients when GGBS content increases to 75%. The higher porosity of potassium activated fly ash-based geopolymers at low modulus ratios was also reported by Sindhunata et al [156] based on Mercury Intrusion Porosimetry (MIP) measurements, and it was suggested to be due to the higher efficiency of the K-based geopolymers in the dissolution step, as well as the larger K⁺ cation size which might increase the number of Al—O—Si bonds due to its association with larger aluminosilicate anions. Given the limited number of Na/K-based samples investigated in this study, establishing a general trend is not possible and the effect of presence of potassium in the activator remains to be explored further in the literature, in particular in conjunction with sodium and for the calcium rich binders.



Figure 5-8. Effect of addition of KOH on the chloride diffusion coefficients

5.3.4. Corrosion initiation

Figure 5-9 shows the half-cell potential and polarization resistance (R_p) of a range of reinforced alkali-activated mortar samples fabricated of activators with a constant modulus ratio of 1.5 and containing different alkali oxide concentration levels. Results are also categorized based on the blending ratio of fly ash and slag. Samples have been tested on a weekly basis; as soon as a sharp decline was observed in the half-cell and polarization resistance values, the samples were split in half and investigated for any crevice corrosion around the connections at both ends of the embedded reinforcement. If any crevice corrosion was observed, sample was discarded, and result is not presented in Figure 5-9 to 12. As it is illustrated in Figure 5-9, the general trend is the remarkably better performance of samples containing more slag in the binder. All samples fabricated of 75% FA and 25% slag were depassivated in less than 80 days (more than half of them in less than 50 days), as opposed to the samples with 50% slag content where majority of samples were depassivated after approximately 100 to 200 days of immersion in 3.5% sodium chloride solution.

On the other hand, no sign of corrosion was observed in majority of samples containing 75% slag, and only three samples were depassivated after around 200 days. The corrosion initiation periods are consistent with the measured chloride diffusion coefficients in Figure 5-7 (a) where samples containing 25% slag showed the highest diffusion coefficients, followed by a remarkable decline by increasing the slag content to 50% and then a less prominent, yet significant decrease by increasing the slag content further to 75%. As it was discussed previously, this behaviour suggests that when slag starts dominating the binder (i.e. at 50% slag content), there is enough calcium content to form a considerable volume of the C-(A)-S-H gel with intrinsically finer pore structure than the aluminosilicate network , leading to substantially less permeability. It appears that due to the combined effect of adsorption of the calcium ions into the aluminosilicate network and lack of enough calcium sources to form considerable amount of the pore filling C-(A)-S-H gel, 25% slag content has not improved the permeability noticeably.



Figure 5-9. Half-cell potential and the polarization resistance of alkali-activated mortars, M_s =1.5. All the potential values are vs. saturated calomel electrode (SCE)

Although there is a general consistency between the corrosion initiation periods and the chloride diffusion coefficients when the addition of the slag is taken into the account, investigation of the behaviour of individual samples in light of their alkali content is more case-sensitive because the effect of alkali content on the diffusion coefficients is not as significant as the effect of calcium content, and in this case, the chloride threshold value might become a more influential factor to be considered and cannot be omitted. The chloride threshold values are investigated and discussed in the next section. The fact that only a limited number of samples depassivated during the long exposure time of up to nine months, in addition to availability of a limited number of samples at each alkali content level means that establishing a solid trend between the initiation periods and the alkali contents was not possible.

To study the effect of silicate content, a limited number of samples were fabricated of activators of modulus 1.0 (M_s =1.0), and their half-cell potential and polarization resistance (R_p) are depicted in Figure 5-10. Of interest was the performance of FAdominated samples, which generally require higher alkalinity levels compared with the calcium-rich samples; as a result, more samples with 75% FA and 25% GGBS were fabricated. Furthermore, the effect of addition of potassium hydroxide in the alkaline solution is investigated by fabricating some samples using alkaline solutions of modulus 1.0 and with the molar ratio of sodium to the total alkali content of 0.5 (as opposed to 1.0 for Na-based samples⁸). As it can be seen, in general, all samples have shown a better performance (i.e. remained passive for longer times) compared with their Ms=1.5 counterparts (Figure 5-9), consistent with considerably lower diffusion coefficients as reflected in Figure 5-7(a). While samples manufactured with 50% slag or more did not show any sign of corrosion, an improvement in the corrosion initiation time of samples with 75% FA and 25% GGBS is observed, particularly for samples fabricated at lower alkali content (5% Na₂O). This is also in agreement with the higher reduction of the chloride diffusion coefficients at lower alkali levels by moving from $M_s=1.5$ to $M_s=1.0$ (Figure 5-7(a)). There is also not a considerable difference in the

⁸ Throughout this chapter, the molar ratio of sodium to the total alkalis are equal to one, unless explicitly mentioned otherwise

depassivation behaviour of samples containing potassium hydroxide, although as it will be discussed further, the electrochemical aspects are interestingly different. According to Figure 5-7(a), the largest reduction of the diffusion coefficients is observed for 50% FA- 50% SI samples with 8% alkali content which is reflected in the early depassivation of these samples in Figure 5-9(c)/(d), while the single 8% alkali containing sample of Figure 5-10(c)/(d) has remained passive throughout the test period.

Figure 5-11 shows the half-cell potential and R_P values for a range of OPC reinforced mortar samples manufactured at different water to cement ratios. The water to cement (W/C) ratios of 0.35, 0.375 and 0.4 are similar to the water to binder ratios used to fabricate the alkali-activated mortar samples. The chloride diffusion coefficients were previously presented in Figure 5-7(b). The corrosion initiation periods correlate rather well with the diffusion coefficients and water to cement ratios, with the exception of the sample with W/C=0.4 where it has been depassivated later than the samples with W/C=0.375 which have considerably lower diffusion coefficients. Another notable trend is the generally better performance of alkali-activated samples manufactured with at least 50% slag compared with the OPC-based samples. Except 50% FA – 50 % S1 samples with M_s=1.5 and Na₂O=8% (Figure 5-9(c)/(d)), all the other samples with 50% or 75% slag has performed better than the best OPC mortar sample with W/C=0.35, regardless of the alkali content and the modulus ratio values. Considering that W/C ratio of 0.35 is very low, the results show the potential for alkali-activated slag-dominated samples in chloride contaminated environments.



Figure 5-10. Half-cell corrosion potential and the polarization resistance of alkaliactivated mortars, Ms=1.0. All the potential values are vs. saturated calomel electrode (SCE)



Figure 5-11. Half-cell corrosion potential and the polarization resistance of OPC mortars. All the potential values are vs. saturated calomel electrode (SCE)

5.3.5. Cl thresholds of reinforced alkali-activated mortar samples

After observing signs of depassivation, i.e. a considerable drop in the half-cell and polarization resistance values (Figure 5-9 and 10), the depassivated samples were split, powders obtained from the interface between the concrete and reinforcement, and their chloride content was measured following ASTM 1152 test protocol. The threshold values of all the depassivated alkali-activated samples are presented in Table 5-3, categorised based on the FA/GGBS content, modulus ratio and the alkali content.

Before discussing the results, it should be stressed that owning to the fact that various measurement techniques, definitions, and testing conditions have been used in the past, and also due to the inherent complexities of the depassivation process, there is a considerable scattering in the reported chloride threshold values for the OPC-based mortars and concretes in the literature; despite being under investigation for a comparatively long time. After a comprehensive review of the reported chloride threshold values in the literature, Angst et al. [153] concluded that establishing a reliable range of chloride threshold values for OPC systems based on the available published data is not possible as different testing procedures and conditions were used

which in some cases do not provide realistic results. As a result, the chloride threshold for OPC-based binders currently used in the service life design and in condition assessment procedures is conservatively chosen to provide some safety margins: it is suggested as 0.2% and 0.4% by weight of cement by CEB [168] and RILEM [128] respectively⁹.

For alkali-activated and geopolymer-type binders, however, there is an absolute lack of data in the literature, and the current study is the first systematic study of the chloride threshold in these binders. Yu et al. [155] recently studied the effect of alkali content on the chloride threshold of alkali-activated slag materials. Their work is, however, different compared with the current research in two fundamental aspects: Firstly, they used simulated pore solution, and secondly, they were focused on the alkali-activated slag samples fabricated of activators of fixed modulus ratio; thus, the effects of presence of fly ash or variability of the modulus ratio were not investigated.

Table 5-3 shows some correlation with variables such as the slag content as well as the alkali content. The presented threshold values in the last column are total chloride content of the powders, although as discussed previously, the lack of binding capacity of alkali-activated binders means that there is not a meaningful difference between the total and the free chloride contents. As it can be seen, in general, results demonstrate a high degree of reproducibility which suggests the reliability of the employed methodology and techniques. The trends observed in Table 5-3 can be summarised and discussed as follows.

 $^{^{9}}$ A review of the total chloride threshold values from previously published data in [153] (Table 4) reveals that almost all the reported values are larger than 0.2%, and also majority are larger than 0.4% (by weight of binder).

- The chloride threshold values range between 0.19 and 0.69 which are in line with the recommendations for OPC-based binders [128,168], particularly for FA-dominated samples. For slag-dominated samples fabricated with activators of low-alkali content, on the other hand, it appears that the suggested thresholds of 0.4% and even 0.2% are not conservative enough. Further investigations and more experimental data are required to build up a statistically large data base to establish the threshold values to be used in the durability design as well as condition assessment of structures fabricated of alkali-activated materials.
- By increasing the slag content, chloride threshold values decreased markedly, regardless of the alkali content or modulus ratios. The lower chloride threshold of slag rich binders could indicate a less developed passive film in these binders which can be broken down (comparatively) easily. The lower stability of the passive layer can be attributed to the oxidation of sulphide anions which prevents or slows down oxidation of iron, impeding the formation of iron oxide layer around the reinforcement during the early stages of matrix development [55,56,169]. This behaviour has further consequences on the redox potential and the corrosion rate (and hence polarization resistance) which will be discussed in the next section.
- The chloride threshold values show a tendency to increase by increasing the alkali content, although due to the availability of a limited number of samples, a clear trend cannot be identified. The possibly higher chloride threshold of samples fabricated of activators of higher alkalinities can be attributed to a better dissolution of the precursors which generates a more homogeneous binder, and as a result, a less permeable passive layer forming around the bars which takes a longer time to break down. Also it appears that the availability of more hydroxide

ions which react with the iron cations to form the iron hydroxide layer around the bars could be another influential factor. This is also consistent with the previous observations for Portland cement-based materials where the chloride threshold is often represented as Cl^{-}/OH^{-} ratios [153].

• Modulus ratio and alkali replacement (partial replacement of sodium with potassium) seems not to be an influential as the slag content or the alkali content, however, it should be noted that only a few samples with Ms=1.0 or with potassium hydroxide in the activator have been fabricated and tested in this study, and further experimental investigation of the effect of silicate content or the alkali replacement is strongly recommended.

precursor	Na/(Na+K) (molar)	SiO ₂ /M ₂ O (molar)	M ₂ O%	Cl (wt.% by binder mass ¹)
75% FA/25% GGBS	1.0	1.0	5	0.341, 0.521
			8	0.519, 0.328
	1.0	1.5	5	0.488
			6	0.626, 0.638
			8	0.623, 0.50, 0.563, 0.501, 0.513, 0.692
	0.5	1.0	8	0.548, 0.511
50% FA/50% GGBS	1.0	1.5	4	0.335
			8	0.436, 0.403
25% FA/75% GGBS	1.0	1.0	8	0.219
	1.0	1.5	3	0.190, 0.221
			4	0.274
			5	0.30

 Table 5-3. Chloride threshold values for alkali-activated mortar samples

 $^{(1)}$ Binder = FA + GGBS + anhydrous activator

5.3.6. Electrochemical assessment of the passive condition

The electrochemical characteristics of passive (i.e. before onset of corrosion) alkaliactivated systems is a subject of interest; they provide helpful information on electrochemical parameters that are used as index values to distinguish actively corroding systems from passive systems. The electrochemical aspects of fly ash-based geopolymer concretes during the propagation phase of corrosion (i.e. after depassivation) was studied in Chapter 4, the electrochemical behaviour of alkaliactivated and geopolymer-type reinforced systems before depassivation is less paid attention to in the literature and requires further study as follows.

5.3.6.1. Half-cell potential

Half-cell potential values of alkali-activated mortars in Figure 5-9 and Figure 5-10 are in general more negative than the OPC mortars in Figure 5-11. For alkali-activated samples, the potential values range between -100 and -300 mV (vs. SCE), while OPC samples showed potential values of more positive than -150 mV. This difference can be misleading if one tries to interpret the potential values based on the commonly used reference values developed for OPC concretes. As it was mentioned in Chapter 4, according to ASTM C876 [130], if potentials are larger than -200 mV vs. CSE¹⁰ (=-140 mV vs. SCE if converted according to ASTM G3-14 [131]), there is greater than 90% probability that the reinforcement is in passive condition. It should be stressed that, the sample surface preparation in ASTM C876 is more suitable for the onsite measurements.

¹⁰ SCE: Saturated Calomel Electrode, and CSE: Copper-Copper Sulphate Reference Electrode
As it was mentioned previously in Chapter 4, more negative potential values of alkaliactivated samples can be attributed to various influential factors. For 75% FA samples with an aluminosilicate dominated matrix, it was speculated that the high porosity of the binder (compared with OPC and slag-based binders) which facilitates water penetration and provides a less alkaline environment can be one of the factors. The lower pH of geopolymer-type binders [170] and alkali cation leaching [53] which consequently leads to lower pH levels may be other factors to be considered (more details about the alkali leaching effects on electrochemical parameters can be found in Chapter 7). For slag-rich binders, as it is reported by other researchers(see e.g. [55,56]), the unusual negative potential values of passive samples can be attributed to the consumption of dissolved oxygen by sulphides in the pore solution. In addition, the very low porosity of slag-based binders appears to cause difficulties for renewal of the oxygen which can lead to more negative potential values. An interesting exception can be seen in the half-cell potential of Na,K-based slag-dominated samples in Figure 5-10 (e) where these samples show considerably higher potential values, more in line with the potential values observed in OPC mortars. Due to the availability of a limited number of Na,K-based samples, further experimental testing is suggested to provide explanation for the observed behaviour.

5.3.6.2. Polarization resistance

Similar to half-cell potential values, Polarization resistance (R_p) of alkali-activated samples are lower than those of OPC mortars, although the difference is not as strikingly large. Traditionally, samples with R_p values larger than 250 k Ω .cm² are considered passive [170], and as can be seen in Figure 5-11, majority of OPC samples have R_p values larger than this threshold. On the other hand, the alkali-activated samples have R_p values of larger than 125-200 k Ω .cm² which decline to 100 k Ω .cm² or less by increasing the GGBS content (Compare Figure 5-9(b) with Figure 5-9(f)). As discussed in the chloride threshold result section, increasing the slag content and thus sulphides in the matrix leads to formation of a less stable and less developed passive layer around the bars by hindering the oxidation of iron [55,56,169]; as a result, it is possible to assume lower polarization resistance for the passive interface layer in slag-rich binders.

Decreasing the silicate content (i.e. decreasing the modulus ratio) seemingly has increased the R_p values (see Figure 5-10), consistent with the lower porosity of these samples that could have helped a better formation of the passive layer around the bars and hence resulted in higher R_p values in general. Of interest is also the polarization resistance value of Na,K-based samples in Figure 5-10(f) which are similar to their Nabased counterparts, unlike their potential values. These result suggest that the presence of potassium in the activator does not affect the formation or stability of the passive layer and hence the R_p values. A similar indifference was observed in the chloride threshold values of samples fabricated of Na,K-based and Na-based activators in Table 5-3. All in all, in agreement with the findings in Chapter 4, it seems that until availability of a large database of half-cell potential values for passive reinforced alkaliactivated concrete/mortars which enables calculating statistically reliable threshold values, using LPR technique provides a better insight into the passive/active status of these systems than half-cell potential.

5.4. Conclusion

Under the experimental conditions of this study, the main outcomes are summarised as follows.

- An insignificant chloride binding capacity was observed in the investigated alkaliactivated materials in this study. As a result, it appears that only physical binding and encapsulation of chloride ions in the pore network determined the rate of diffusion and amount of chloride bound.
- Increasing the calcium content appears to be the most efficient method of decreasing the permeability and the chloride diffusivity by formation of C-(A)-S-H gel. Increasing the GGBS from 25% of binder content to 75% led to an almost tenfold decrease in the diffusion coefficient values, highlighting the critical role of presence of calcium in the matrix to design durable alkali-activated concretes in marine environments.
- Higher alkali contents (8% Na₂O (wt.% of FA+GGBS mass)) as opposed to lower levels (3% to 5%) led to an increase in the dissolution rates and consequently higher Si/Al ratios. Higher Si/Al ratios are indicative of a larger volume of aluminosilicate network and higher mesoporosity; thus, increasing the alkali content led to a systematic increase in the diffusion coefficients of both aluminosilicate-dominated and calcium-rich binders.
- Similar to the alkali content, increasing the silicate content (modulus ratio) led to the enhancement of the aluminosilicate matrix and increased the mesoporosity. On the other hand, increasing the modulus ratio had a secondary effect on reducing the porosity by promoting the formation of C-(A)-S-H gel which can be attributed to a higher of calcium leaching from the GGBS particles under lower alkalinity levels.

Interaction of the mentioned opposing effects means that while decreasing the modulus ratios reduced the porosity and hence diffusion coefficients for all mixes, the reduction was strikingly larger for samples containing less GGBS and more FA

- Partial replacement of NaOH with KOH led to slightly larger diffusion coefficients for FA-dominated samples, while the difference was less noticeable for GGBSdominated samples.
- The chloride threshold of a wide range of depassivated alkali-activated samples was investigated as the first systematic attempt at developing a chloride threshold database for alkali-activated materials. Result showed that the chloride threshold values range between 0.19 (wt.% binder mass) for calcium-rich binders fabricated at low level of alkalinities (75% GGBS content, 3% Na₂O) and 0.69 for FA-dominated binders fabricated with highly alkaline activators (75% FA content, 8% Na₂O). It appears that the suggested threshold values of 0.2% and 0.4% for OPC based binders are suitable for FA-dominated alkali-activated samples, but it is not conservative enough to be used for alkali-activated slag binders fabricated at low alkalinity levels. Furthermore, modulus ratio and potassium replacement seems not to be as influential as the calcium content or alkali concentration, although further research is strongly recommended to solidify this finding
- A comparison between the half-cell potential of alkali-activated and OPC mortars in passive condition revealed that the alkali-activated samples have more negative half-cell potential values in general. Their half-cell potential was in average between -100 and -300 mV (vs. SCE), while OPC samples showed potential values of more positive than -150 mV. For geopolymer-type samples, the lower half-cell potential values can be stemming from the higher porosity which leads to higher moisture content, the lower pH of binder in general, and the alkali cation leaching. For calcium-rich binders

on the other hand, the more negative potential values can be attributed to consumption of dissolved oxygen by sulphides in the pore solution. The different equilibrium potential of alkali-activated passive systems compared with the OPC-based systems can be misleading if one tries to interpret the potential values based on the commonly used OPC reference values to detect corrosion activities.

• The polarization resistance (R_p) of alkali-activated samples were also lower than their OPC counterparts, majority of the recorded R_p values were larger then 125-200 k Ω .cm² which declined even further to 100 k Ω .cm² (as the lower bound) for samples containing 75% GGBS. For comparison, majority of OPC samples had R_p values larger than 200-250 k Ω .cm². The reducing effect of the slag addition was attributed to the presence of sulphides which hinders oxidation of iron and leads to formation of a less stable and less developed passive film with lower resistance around the bars. Lower modulus ratios also provided slightly higher polarization resistances, consistent with the lower porosity of the binder, which could have led in a better integration of the reinforcement with the surrounding matrix and a better protection against polarization accordingly. Furthermore, no considerable difference was observed in the depassivation behaviour of samples containing potassium hydroxide as opposed to Na-based samples.

CHAPTER 6: Passivity of Embedded Reinforcement in Carbonated Low-Calcium Fly Ash-Based Geopolymer Concrete

6.1. Introduction

Carbonation, as one of the main durability threats, plays a detrimental role to concrete by reducing the alkalinity of the pore solution at the vicinity of reinforcing steel. This may lead to the depassivation of reinforcement, leaving them prone to corrosion [171,172]. For the ordinary Portland cement (OPC) concrete, the hydration product portlandite $(Ca(OH)_2)$ provides a buffer effect in which the continuous dissolution of portlandite maintains the high pH level of the pore solution in case of neutralization of the OH⁻ ions during the carbonation process. Unlike the OPC binders, low-calcium fly ash-based geopolymer-type binders 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 [53]. During the Carbonation of fly ash-based geopolymers, the main process is carbonation of the highly alkaline pore solution in which the alkali carbonate/bicarbonate salts precipitate from the pore solution. No significant change in the aluminosilicate gel nanostructure has been reported [57], yet some minor strength degradation is observed which intensifies by increasing the calcium content of the fly ash (i.e. by using high calcium fly ash) [173]. On the other hand, the alkali-activated slag binders experience carbonation of the pore solution, followed by carbonation of secondary products and decalcification of calcium aluminosilicate hydrate (C-(A)-S-

H) gel which can lead to considerable structural strength degradation and increasing the porosity particularly when the waterglass is used for the activation [58,59]. 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 [57]. Therefore, the pore solution alkalinity and composition plays a major role during the carbonation process of calcium-rich alkali-activated and low-calcium geopolymer-type binders: 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.

Apart from the alkalinity of the pore solution which directly depends on the alkali concentration level and type of the alkaline solution, the partial concentration of the carbon dioxide used in accelerated carbonation test is another important factor affecting the carbonation rate and the pH drop [59]. Criado et al. [174] have reported formation of nahcolite (sodium bicarbonate) during the exposure of fly ash-based geopolymers to the ambient carbon dioxide while Bernal et al. [57] stated that the sodium carbonate/bicarbonate phase equilibria are a function of the geopolymer binders. The accelerated CO₂ concentration strongly influences the pore structure and the composition of the pore solution, and therefore, it is not recommended to carry out accelerated carbonation testing of geopolymer binders at high CO₂ concentration levels [60,172]. Khan et al. [61] observed considerably lower pH values in carbonated fly ash-based geopolymer concrete under 3% accelerated carbonation compared with 1% accelerated carbonation or natural carbonation (in ambient condition).

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Carbonation of the pore solution might or might not lead to the depassivation of reinforcement which depends on the extent of carbonation and the pH drop level. Depassivation is imminent in ordinary Portland cement (OPC) concrete when the pH of the carbonated binder falls below ~9 [175]. In low-calcium fly ash-based geopolymer concrete, the pH value was reported to remain around 10 in the carbonated zone during the carbonation of the pore solution [61], and therefore, the pH drop in the carbonated zone may not be sufficient to destroy the passive film and initiate the corrosion during the service life of the structure. Monitoring the evolution of the electrochemical properties of the reinforcement (electrode)-concrete (electrolyte) system is the most practical method to assess the extent of the pH drop which leads to depassivation of the reinforcement. It was shown in Chapter 4 that the electrochemical performance of the reinforced low-calcium fly ash-based corrosion systems can be comparable to their OPC counterparts after depassivation of the reinforcement; although, the pH drop due to the carbonation can be vastly different from the OPCbased systems, depending on the precursors and the type and concentration of the alkaline solution.

Previous studies emphasized the capability of the fly ash geopolymer-based binders to keep the reinforcement bar passivated due to the high alkalinity of the activating solution [48,176], and this was confirmed by the rather high chloride threshold of embeded reinforcement in these binders (Chapter 5); although, the stability of the passive film is highly dependent on the concentration of the alkaline solution as it can lead to formation of a denser matrix around the reinforcement beside having higher alkalinity, or vice versa. (Chapter 5). The alkaline solution concentration can change the pore size as well as the pore size distribution of the binder as discussed in Chapters 3 and 5, and defines the rate of diffusion of the aggressive agents into the concrete.

In conclusion, with regard to the carbonation of fly ash-based geopolymer-type binders, the capability of the binders fabricated at different levels of alkaline solution concentration to keep the reinforcement in a passive condition, the pH of the carbonated binder, and finally, the pH drop that could lead to depassivation of reinforcement are yet to be investigated. To investigate these subjects, this chapter reports the carbonation-induced pH drop of two low-calcium fly ash-based geopolymer concretes (blended with less than 15% slag) fabricated of alkaline solutions at different concentrations. An analytical model is used to study the equilibrium of carbonate species in a carbonated aqueous sodium hydroxide solution to replicate the carbonation of pore solution in low-calcium fly ash geopolymer binders. Moreover, the corrosion potential and polarization resistance of both concretes subjected to accelerated carbonation is investigated to assess the stability of the passive film during the long-term exposure to the carbon dioxide.

6.2. Experimental program

6.2.1. Materials and mix proportions

Similar to AAP1 paste samples tested in Chapter 3 and the concrete samples tested in Chapter 4, a blend of Eraring fly ash (FA), Callide FA, and GGBS (A) was used to fabricate the samples. The elemental composition of the precursors has been previously presented in Table 3-1. Particle size distributions can also be found in Figure 3-1.

A mixture of sodium hydroxide (NaOH) solution and grade D sodium silicate solution were used as the activator (readers are reffered to Section 3.2.1 for technical specification of NaOH pellets and sodium silicate solution). The geopolymer concrete mix composition is presented in Table 6-1. GPC_50 mix proportion is similar to AAP1 samples in Chapter 3, and the mix proportion used in Chapter 4 for concrete fabrication, although with slightly different water to binder ratio. GPC_30 has a lower binder content, a higher water to binder ratio and a lower alkali content to produce a lower strength concrete.

Materials	GPC_50	GPC_30
Coarse aggregate	1221.2	963
Fine aggregate	620.8	852.1
Eraring FA	271.6	227.5
Callide FA	77.6	70
GGBS	38.8	52.5
NaOH pellet	19.96	14.44
Sodium silicate solution	138.7	100
Water	66.5	91
FA+HPA+GGBS	388	350
Water/binder*	0.32	0.37
Ms=[SiO ₂]/[Na ₂ O]	1.17	1.17
Na ₂ O/ (FA+GGBS) (%)	9.24	7.40

Table 6-1. Mix proportions for geopolymer concretes (kg/m³)

* Calculated considering the total water and the total solids (precursors+anhydrous activator).

6.2.2. Sample fabrication, curing and conditioning

Two sets of samples were cast, standard cylinders which were cut in slices for grinding and measuring the pH profile at different carbon dioxide exposure periods, and corrosion samples for electrochemical monitoring of the effect of carbonation-induced pH drop on the passivity of reinforcement. Details of preparation of corrosion samples have been already presented in Chapter 4 (Figure 4-1), except the anti-chloride resin was replaced by aluminium foils to prevent penetration of carbon dioxide (as opposed to chloride). After casting, both cylinders and the corrosion samples were sealed and heat-cured in an oven at 75° C for 18 hours [67], and then were demoulded. After demoulding, 25 mm thick slices were removed from top and bottom of each cylinder; the remaining part was cut into 50 mm slices which were then stored in a controlled room at a constant temperature of $23^{\circ} \pm 2$ C and 55% relative humidity, along with the corrosion samples. Carbonation tests started after two weeks of conditioning of the samples in the controlled room. After conditioning, 50 mm discs were sealed using aluminum tapes along the perimeter, leaving top and bottom sides exposed for onedimensional CO₂ diffusion. Both top and bottom sides of the corrosion samples were sealed as well by aluminum foils to enforce peripheral penetration of the carbon dioxide.

6.2.3. CO₂ exposure conditions

For natural carbonation, the specimens were kept in a controlled environmental room. For accelerated carbonation, the specimens were placed in a carbonation chamber with a CO_2 concentration of 1%. The exposure temperature and relative humidity, in all cases, were 23°C and 55% respectively.

6.2.4. SEM analysis

Microstructural analysis was performed using a Hitachi S-3400N scanning electron microscope (SEM). Paste samples were fabricated according to the mix proportions in Table 6-1 but without the aggregates, and then heat-cured in an oven at 75° C for 18 hours. All micrographs were obtained on the gold coated fractured surfaces of paste samples using a secondary electron detector and 20 kV accelerating voltage.

6.2.5. Identification of the carbonation products

X-ray diffraction (XRD) was carried out in this study to identify the carbonation products. 50 mm cube specimens were cast with geopolymer paste having the same mix design and curing conditions as the concrete samples. Samples were collected from the surface of the cubes for the XRD analysis. The paste samples were ground to powder, and the powder was analyzed using X-ray diffractometer Phillips X'Pert Pro Multi-purpose (MPD) system housed at the Mark Wainwright Analytical Centre at the University of New South Wales, Australia. This used Cu-K α radiation with a wavelength of 0.15418 nm, and operated at 45 kV and 40 mA, scan range 5-65° and 0.026° 20 step size. The scan results were interpreted using the software package HighScore Plus.

6.2.6. Mechanical properties

The compressive strength and the elastic modulus were measured after 28 days on standard concrete cylinders (height = 200mm, diameter = 100mm) in accordance with AS 1012.9 [177].

6.2.7. pH profile and carbonation depth

pH profiles were obtained and calibrated based on the methodology previously explained in Chapter 4 (Section 4.2.5). Phenolphthalein indicator spraying was also done as a quick test to get an idea of the pH range and carbonation front of the carbonated samples; each specimen was split, and 1% phenolphthalein was sprayed on the fractured surface.

6.2.8. Electrochemical measurements

The same test protocols as what used in Chapter 4 were employed to perform the electrochemical tests. All tests have been carried out in a room with a fixed temperature of 23°C. Specimens were used only once for the electrochemical measurements after which they were split for visual inspections and also phenolphthalein spraying. Corrosion parameters such as the half-cell potential (E_{corr}), and polarization resistance (R_p) have been measured and the results are reported in the following sections.

6.3. Results and discussions

6.3.1. Mechanical properties and SEM micrographs

Table 6-2 presents the 28-day compressive strength of the geopolymer concretes. The compressive strength of GPC_50 was 55.7 MPa compared to 28.9 MPa for GPC_30. The higher compressive strength of GPC_50 is attributed to the greater degree of

geopolymerisation achieved due to its higher alkaline solution concentration and binder contents than that of GPC_30.

Concrete type	Compressive strength (MPa)	
GPC_50	55.7	
GPC_30	28.9	

 Table 6-2. Compressive strength of concretes at 28 days

SEM micrographs of GPC_30 and GPC_50 paste samples are presented in Figure 6-1. In general, GPC_50 displays a more homogeneous binding matrix compared to GPC_30, which is due to a better-developed aluminosilicate matrix in a highly alkaline environment. Remnant of fly ash particles are present in both samples but more in GPC_30, as it can be inferred by the traces of unreacted particles which have been pulled out of the matrix during the sample preparation. Also, the unreacted fly ash particles have experienced a more advanced surface dissolution in GPC_50. The higher dissolution rate of aluminosilicate source in GPC_50 leads to a higher Si/Al ratio; Si—O—Si bonds have a higher strength compared to Al—O—Al and Si—O—Al bonds [34], and as a result, a higher Si/Al ratio leads to a higher matrix strength as reflected in Table 6-2.



Figure 6-1. SEM micrographs of GPC_30 (left), and GPC_50 (right)

6.3.2. Identification of carbonation products by using XRD

Figure 6-2 shows the XRD patterns of GPC_30 pastes exposed to 1% accelerated carbonation. The figure shows that both natron (Na₂CO₃.10H₂O) and nahcolite (NaHCO₃) were identified as carbonation products after two weeks of exposure and their intensity peaks increased with the exposure duration. The formed phases are in agreement with those reported in the literature [57]. Phases identified including natron and nahcolite for GPC_50 paste for natural carbonation, 1% and 3% accelerated carbonation are reported and discussed in Khan et al [61].



Figure 6-2. XRD traces of GPC_30 pastes exposed to 1% accelerated carbonation

6.3.3. Carbonation and pH drop in low-calcium fly ash-based geopolymer concretes

6.3.3.1. Understanding the carbonation of pore solution of low-calcium geopolymer binders

As it was mentioned previously, the formation of alkali carbonate/bicarbonates is the primary reaction during the carbonation of the pore solution of low-calcium fly ash based geopolymer binders. The ratio of bicarbonate to carbonates then defines the pH of the carbonated alkali solution [178]. The chemical adsorption of carbon dioxide into an aqueous sodium hydroxide solution, as representative of the pore solution for NaOH+Na₂SiO₃ activated binders, can be studied based on the fundamental principles and the equilibrium of the different species which coexist in the carbonated solution and interact with each other. The method used in this study, although not as advanced as thermodynamic models (see e.g. [60]), provides a noteworthy insight into the carbonation of low-calcium fly ash based geopolymer binders and is capable of explaining some of the main features of these systems. To simplify the calculations, the effect of the presence of silicate and aluminate species is neglected as it is recognized that they do not have any significant influence on the pore solution chemistry or carbonate phases formed [60]. An open carbonation system is considered to replicate the pore solution carbonation, in which a constant renewal of carbon dioxide in the gaseous phase is assumed. Full details of the calculation method are presented in Appendix A, while the results are presented and discussed in this section.

Figure 6-3(a) illustrates the percentage of natron at different carbon dioxide partial pressures and for several NaOH solutions with different Na concentrations. As it is

noted, increasing the carbon dioxide concentration reduces the natron formation dramatically. Under natural carbonation in ambient air $(pCO_2=0.03-0.04\%)$, carbonation products comprise of around 85% natron and 15% nahcolite for a solution 1N (=1 mol/l) with respect to total sodium. These ratios change to 45% and 55% respectively at 1% carbon dioxide concentration, and further altered to 23% and 77% at 4% carbon dioxide concentration. This substantial difference in the composition of carbonate phases emphasizes the high sensitivity of the carbonate/bicarbonate phase formation to the partial pressure of carbon dioxide. Unlike the accelerated carbonation of OPC-based concretes, which is usually carried out at 4% carbon dioxide concentration, using too high levels of carbon dioxide to accelerate carbonation of lowcalcium FA-based geopolymers can lead to unrealistic formation of bicarbonates; this behaviour does not reflect the carbonation in natural condition (i.e. ambient air) and can lead to considerable pH drop as it is discussed subsequently. The formation of bicarbonates during the accelerated carbonation of geopolymer binders is consistent with the previous published experimental observations [57] as well as thermodynamic simulation results [60].

Further Inspection of Figure 6-3(a) reveals the prominent influence of the alkali concentration level on the carbonate phase composition, particularly at lower carbon dioxide concentrations. To facilitate comparison, formed natron percentage as a function of the alkali concentrations of up to 2N is presented in Figure 6-3(b) for three carbon dioxide concentration levels. As it can be seen, in general, the quantity of formed natron increases by increasing the sodium content of the solution; however, as it is illustrated in Figure 6-3(b), natron formation decreases by increasing the sodium content; this trend is more notable for lower carbon dioxide concentrations where a tenfold increase in the sodium concentration of naturally carbonated pore solution (from

0.2 to 2N), increases the quantity of natron by only 37%. Also it is apparent from Figure 6-3(b) that under natural carbonation, for all sodium concentrations beyond $0.5N^{11}$ with respect to total sodium, natron accounts for more than 80% of the total carbonate phases; although, this figure declines sharply for 1% and 4% carbon dioxide concentrations.



Figure 6-3. Percentage of natron for different alkali concentrations and CO₂ levels

pH of the investigated open carbonation systems are also presented in Figure 6-4(a) and (b). On the same graphs, color change chart of the phenolphthalein indicator over the considered range of pH values is schematically presented. Phenolphthalein is almost colorless for pH values less than 9.0^{12} , and starts turning pink for pH values larger than 9.0. The gradual smooth transition from colorless region to an intense

¹² The theoretical colourless pH level is 8.3, it corresponds to the point where all CO_3^{2-} has been

¹¹ The sodium concentration in the pore solution of a fly-ash based alkali-activated paste prepared with an activator containing 7% Na₂O and 7% SiO₂ was reported as 0.61 mol/l [53]. Considering the limited available experimental data in open literature and the Na₂O% of the alkaline solutions in this paper (around 7.4 and 9.2% for GPC_30 and GPC_50 respectively, as reflected in Table 6-1), values between 0.6 and 1.0 N (= mol/l) are thus considered as reasonable estimations representative of the sodium concentration in the pore solution of GPC_30 and GPC_50 samples.

converted to HCO_3^- in a titration system which resembles closed carbonation systems [178] with no considerable amount of CO_2 entering or leaving the aqueous solution. Regarding the practical application of phenolphthalein on carbonated concrete surfaces as opposed to titration solutions, it is widely accepted that the colourless region corresponds to pH<9.0, as the very faint pink colour for 8.3<pH<9.0 zone is hardly noticeable by the naked eye.

pink/fuchsia color is complete at around pH=10. Since depassivation of reinforcement occurs at pH<~9.0, having a colorless concrete surface after spraying phenolphthalein is traditionally considered as a sign of carbonation of the (OPC-based) concrete which consequently leads to the onset of corrosion.

For geopolymer-type binders with a negligible amount of calcium, the main carbonation mechanism is carbonation of the pore solution which is highly alkaline. Depending on the partial pressure of the carbon dioxide in the gaseous phase and the alkali concentration level, formation and equilibrium of carbonate/bicarbonates in the carbonated pore solution might not reduce the pH to a level which is required for depassivation of the reinforcement. This concept is illuminated in Figure 6-4(a) and (b). Inspection of these figures reveals that the pH levels decreases by increasing the carbon dioxide concentration which is consistent with the formation of more bicarbonate (nahcolite) as discussed earlier. Also, a significant higher pH level of naturally carbonated solutions ($pCO_2 \sim 0.03\%$) compared to the accelerated carbonated solutions (pCO₂=1% and 4%) is noticeable. Although the higher pH drop of solutions under accelerated carbonation is not representative of the natural carbonation in ambient air, the pH values for all the solution with Na concentration larger than 0.5N interestingly lies in the range of 8.7-10.25 for 0.03% < pCO₂ < 4% (Figure 6-4(b)). pH values between 9.0- ~9.5 will give a faintly discernible pink color as it is shown in Figure 6-4. This is of great importance with regards to the interpretation of the results of phenolphthalein indicator spraying test on carbonated low-calcium fly ash-based concretes, where the carbonated concrete is not colorless; unlike the carbonated OPC concretes (Also see Figure 6-7).

Another noteworthy subject is the concentration of the alkaline solution which is required to maintain the pH level high enough to keep the reinforcement in a passive condition during the natural carbonation. As it is shown, even a 0.2 N solution can keep the pH at rather high level (pH=10.0) during the natural carbonation which provides enough protection for the passive layer. Similar findings is reported in the literature [60].

In accordance with the trend for natron formation in Figure 6-3, increasing the alkali concentration beyond 0.5 N seems not to be an efficient way of increasing the pH level, as it is reflected in Figure 6-4(b). This is very important with regards to the durability design of fly ash-based geopolymers, where increasing the alkali content of the activator beyond a certain level does not provide a sensibly improved performance against carbonation, and even might increase the risk of efflorescence [63]. On the other hand, reduction of the alkali concentration below 0.2 N in the pore solution will increase the risk of depassivation by natural carbonation significantly.



Figure 6-4. pH of the aqueous alkali solution at different alkali concentrations and CO₂ levels for an open carbonation system

6.3.3.2. pH profile of carbonated geopolymer concretes

Figure 6-5 shows the pH profiles of GPC_30 specimens exposed to natural carbonation. The lower bound of pH of the uncarbonated concrete is also marked on the graph. The pH of uncarbonated GPC samples was measured and was around 11.5-11.8 which is in line with the pH of the sample measured in Chapter 4. Although, it should be noted that if the pore solution is represented by an ideal 0.6-1.0 N sodium hydroxide solution, the theoretical pH level should be higher than 13. This suggests that the measured pH values, particularly for uncarbonated concrete, should be treated cautiously as various factors can affect the reliability of the measurements, besides the errors associated with idealisation of the pore solution as an aqueous sodium hydroxide solution. As it will be seen subsequently, however, the measured and calculated pH values have shown a remarkably better agreement for carbonated samples.

As it is shown, the pH values gradually declined with the exposure time. The profile is linear along the depth which suggests that the carbonation front had reached beyond 25mm thickness after eight months of natural carbonation. This is in particular intriguing considering the low concentration of carbon dioxide in the ambient air and the somewhat short exposure time of eight months. The high rate of carbon dioxide diffusion compared to OPC-based binders is due to the high porosity of geopolymertype binders, as it was observed in Chapter 3. Despite the high rate of carbon dioxide adsorption, pH values along the depth remained at rather high levels: they are ranging between 10.6 at the surface and 11 at 25 mm depth. pH value at the surface is comparable to the theoretical value of ~10.2 (Figure 6-4(b), [Na]=~0.6N, $pCO_2=~0.03\%$). It must be kept in mind that the theoretical discussions in the previous section are strictly about the pore solution chemistry and distribution of carbonate

phases in an ideal aqueous sodium hydroxide solution representative of the pore solution of low-calcium fly-ash based geopolymers. For a concrete sample, a gradient of carbon dioxide concentration within the depth is expected which results in higher quantity of natron and less pH drop compared to the surface layers. This gradient is evident from the pH profiles having a slope in Figure 6-5. As a result, the theoretical values from Figure 6-4 should be compared against the measured pH of the layers close to the surface (i.e. 10.2 vs 10.6), as it is reasonable to assume that they have been exposed to the same concentration of carbon dioxide as in the surrounding environment. There are other factors as well that contribute into the observed difference between the experimental results of carbonated concrete and the theoretical calculated values for carbonated pore solution, such as existence of condensate and adsorbed water in the pores which can block the gas adsorption, presence of powdered aggregate in the suspension used for pH measurement, dissolution of carbonates during the preparation of the suspension which leads to releasing more OH⁻ ions in the suspension, heterogeneity of the concrete, and availability of other species in the pore solution. In spite of all these different parameters which interact in the system, the theoretical calculations are still capable of providing reasonably accurate estimations.



Figure 6-5. pH profiles of GPC_30 concrete exposed to natural carbonation

Figure 6-6 shows pH profiles of GPC_30 concrete samples exposed to 1% accelerated carbonation. After four weeks of exposure, the pH decline was steeper than the naturally carbonated samples, due to the higher concentration of the carbon dioxide. The measured pH of the layers close to the surface is 9.5 after eight weeks of carbonation, which is again closely predicted at 9.25 (Figure 6-4(b), [Na]=~0.6N) for 1% concentrated carbonation. These results are also in partial agreement with the phenolphthalein indicator spraying test (Figure 6-7), where the concrete cover is fully carbonated at some point between seven and ten weeks. According to phenolphthalein indicator results, the colour of the carbonated concrete cover to the steel bar changes from faint pink after two weeks, to very faint pink after ten weeks. Based on the explanations provided in section 6.3.3.1 and color change chart of the phenolphthalein indicator in Figure 6-4, pH values should be between 9.0-~9.5 for the aforementioned colors which are consistent with the predicted and measure pH values explained above for surface layers; however, it is still lower than the measured pH values by suspension method at the depth of reinforcing bar (between 10.1 and 10.25 in Figure 6-6).

After a long exposure period of 12 months, pH profiles remained rather unchanged for depths>16mm compared to four and eight weeks profiles, although an unexpected increase in the pH of surface layers is evident in Figure 6-6. This re-alkalinisation is due to the dissolution of carbonation products in water: while pH profiles up to 8 weeks were measured by using the powder sampled from 50mm slices, the powder samples for 12 month pH profile was obtained by grinding the surface of a corrosion sample after finishing the corrosion test. As it was mentioned previously in section 6.2.8, during the half-cell potential measurements and LPR test, the corrosion samples have been submerged in water; thus, a surface dissolution of carbonation products are expected. Indeed, sodium carbonates and bicarbonates are highly soluble compared to

the calcium carbonates forming in OPC concrete or GGBFS alkali-activated concrete. A similar behaviour can be seen in Figure 6-8 for GPC_50 concrete, where a corrosion sample was used for long-term (eight month) pH profile measurement, and the same re-alkalization was occurred, although owing to a lower permeability, the affected depth is smaller.



Figure 6-6. pH profiles of GPC_30 concrete exposed to 1% concentrated carbon dioxide



Figure 6-7. phenolphthalein indicator test on GPC_30 samples under 1% accelerated carbonation after two weeks (a), seven weeks (b), ten weeks (c).

Figure 6-8 illustrates the measured pH profiles for GPC_50 samples exposed to 1% accelerated carbonation. As it is shown, the pH at the depth of reinforcement remained almost unchanged between six weeks and eight months of exposure. pH of the surface layers after six weeks of exposure is around 9.70, as opposed to the calculated value of 9.4 in Figure 6-4 (b) ([Na]=~1N, pCO₂=1%). Although the eight-week pH profile for GPC_50 is not available to be able to directly compare it against GPC_30 samples, it is realistic to assume a slightly lower pH for the surface layers after eight weeks of exposure. This brings the pH level closer to the predicted pH value of 9.4, and pH of GPC_30 which was 9.5. The small difference in the pH of carbonated GPC_30 and GPC_50 samples further confirms the trend observed in Figure 6-4(b) where beyond 0.5N sodium content, pH of carbonated pore solution remains almost constant.

From Figures 6-8 and 6-10, it is evident that pH of both GPC_30 and GPC_50 is higher than 10 at the depth of reinforcement (15 mm) and will probably not lead to depassivation of the reinforcing bars; although, further electrochemical experiments were carried out for both carbonated low-calcium fly ash-based concretes in the following section to investigate the passivity of the reinforcement.



Figure 6-8. pH profiles of GPC_50 exposed to 1% concentrated carbon dioxide

6.3.4. Assessing the capability of carbonated binder to keep the passivity: electrochemical test results

Figure 6-9(a) illustrates the evolution of the half-cell potential (E_{corr}) values for GPC_30 and GPC_50 samples exposed to accelerated carbonation for more than 500 days. Each data point corresponds to the average of half-cell potential of two samples. Although the half-cell potential value is a qualitative parameter, it is the most commonly used corrosion index due to the vast availability of the measurement tools and well-established assessment techniques [48,114]. Along with the measured E_{corr} values, the classification commonly used to assess the severity of corrosion for OPC concretes [130] is also presented for comparison. As illustrated, both GPC_30 and

GPC_50 samples show very high half-cell potentials of more positive than -200mV. This is indicative of the capability of the binder to keep the reinforcement passivated, even after the long exposure time of 508 days.

Figure 6-9(b) depicts the polarization resistance (R_p) values for both GPC_30 and GPC_50 samples. The R_p values lie within the low-to-moderate corrosion rate range initially; however, after an early-age increase, both trends approach the passive condition zone. A similar behavior can be seen for E_{corr} trends, where GPC_50 samples experience a more notable growth compared to GPC_30 samples. This behavior can be attributed to the stabilization and ongoing development of the passive film due to the progressive polymerization reactions which are expected for highly alkaline geopolymer binders [173]. The high R_p values attained after the initial stabilization of the passive film confirms the passivity of samples which was inferred from the half-cell potential measurements.

Despite having a lower polarization resistance and lower activator alkalinity, GPC_30 samples showed more positive half-cell potential values. This can be explained by the fact that the half-cell potential is intrinsically a semi-quantitative parameter. Although a lower pH leads to a more negative half-cell potential, the measured potential values can also be influenced by other parameters such as lack of oxygen in the concrete-reinforcement interface, and the internal moisture content [133–135], both of which depend on the pore size distribution and porosity of the binder. GPC_30 mix has a higher slag content compared to GPC_50 mix (15 wt.% vs 10 wt.%), and the presence of slag has proved to improve the pore size distribution and reduce the total porosity by the formation of pore filling C-(A)-S-H gel [35]. The lower alkalinity of the GPC-30 mix also favors formation of calcium silicate hydrate over the calcium aluminosilicate [12]. On the other hand, slag replacement of less than 25% (wt.% of

binder) has reported to not provide the same extent of pore filling compared to the higher replacements [35]. It seems that not all the observed difference in half-cell potential values can be attributed to the role of C-(A)-S-H gel, and the pore size distribution, as well as the porosity of the aluminosilicate network, could be important factors that need to be further investigated.

 E_{corr} and R_p trends confirm that both binders have been capable of keeping the reinforcement in passive condition even with the low pH condition caused by the accelerated carbonation. Evaluating the performance during the accelerated carbonation is in particular very crucial from a durability point of view where the naturally carbonated geopolymer concretes will not even experience the same level of pH drop as the accelerated carbonated samples; and hence, will certainly not suffer from the reinforcement corrosion as one of the main factors threatening the service life. This is very promising regarding the application of low-calcium fly ash-based geopolymer concrete in areas where a high-strength concrete is not required. On the other hand, the conclusion made in this section are not applicable to alkali-activated slag binders in which involvement of different carbonation products (i.e. calcium carbonates) and carbonation of hydration products after exhaustion of the OH⁻ ions in the pore solution can lead to different outcomes and even strength degradations [58,59].



Figure 6-9. Electrochemical test results, a) half-cell potential and b) the polarization resistance

6.4. Conclusion

Carbonation of two reinforced fly ash-based geopolymer concretes fabricated with alkaline solutions at different alkali concentrations was investigated. 1% concentrated carbon dioxide was employed to accelerate the carbonation process. pH drop and the carbonate phase distributions were predicted based on the equilibrium of different coexisting species in an aqueous sodium hydroxide solution at various alkali concentrations and partial pressure of the carbon dioxide in the gaseous phase. The pH drop development with time was assessed under both accelerated exposure condition and natural carbonation in ambient condition. The evolution of the half-cell potential and the polarization resistance of the samples were monitored to investigate the probability of depassivation of the reinforcement due to the carbonation-induced pH drop. The results show that:

- Accelerated carbonation promotes the formation of bicarbonates over carbonates leading to an increase in pH decline compared to natural condition.
- pH of the carbonated surface layers was around 9.5 and 10.6 for accelerated and natural carbonation, respectively, and was predicted successfully within a reasonable range by analysing the adsorption of carbon dioxide into an aqueous sodium hydroxide solution representing the pore solution of fly ash-based geopolymer binders. After 8 to 12 months of exposure to 1% CO₂, pH values of fully carbonated concrete were higher at the depth of reinforcement (between 10-11), due to the gradient of carbon dioxide concentration in concrete which results in formation of more natron and less pH drop compared to the surface layers.
- Although the pH of carbonated concrete is artificially lower in accelerated carbonation (pCO₂=1%) than natural carbonation, it still does not lead to depassivation of reinforcement.
- Low level of alkali concentrations in the pore solution ([Na]~0.2mol/l) can provide enough protection for the reinforcement during natural carbonation, and increasing the alkali concentration beyond 0.5mol/l does not significantly contribute to increase the pH level, and then the level of protection against steel corrosion in low-calcium fly ash-based carbonated geopolymer concrete. On the

other hand, very low alkali concentration in the pore solution ([Na]<0.2mol/l) will increase the risk of depassivation considerably.

• Dissolution of sodium bicarbonates/carbonates can lead to re-alkalinisation of the carbonated pore solution, this is important for structures where there is the coupled effect of carbonation and high relative humidity transportation.

The findings of this study bring more confidence in the industrial application of lowcalcium fly ash-based geopolymer concretes where carbonation-induced steel corrosion is a concern, typically reinforced concrete members exposed to wetting and drying cycles (i.e. outdoor exposure). Indeed, the pH of carbonated low-calcium fly ash-based geopolymer concrete remains at high levels. Consequently, there is not the risk of corrosion due to natural carbonation.

CHAPTER 7: Alkali Cation Leaching in Alkaliactivated Binders

7.1. Introduction

Consumption of highly concentrated alkaline solution to achieve high mechanical strengths can lead to the availability of free and mobile alkali ions in the pore solution of alkali-activated materials which cannot be incorporated into the matrix. Moreover, various degrees of reactivity of the solid precursors, in particular fly ash, may lead to overestimation of the absorbable alkalis and a partial incorporation of the designated alkali content. As a result, a fraction of alkalis will be not structurally bound and can diffuse out of the matrix. Alkali leaching may lead to serious problems such as efflorescence or loss of alkalinity of the binder phase, especially in Na-silicate based binders [26,53]. The literature remains limited on these issues, and the capability of alkali-activated binders to protect the reinforcement from the corrosion which can be affected by a loss of alkalinity due to the alkali leaching requires further investigation.

In previous studies published so far, parameters such as the alkali content, the presence of calcium in the binder, curing regime (ambient cured or heat cured), alkali type (Na or K), and the silicate content have been found to affect the alkali leaching and the efflorescence substantially [53,63,179]. Among those variables, the alkali content is of a great importance: reducing the alkali content to minimize the efflorescence and the alkali leaching will lead to strength loss; also, determination of optimum alkali content depends on the reactivity of the aluminosilicate precursors. The presence of calcium-rich precursors in the binder is also another source of complexity in establishing the

relationship between the alkali content and the amount of leachable ions as the calcium ions can be incorporated into the aluminosilicate network and/or C-A-S-H gel which leads to the release of more alkalis [26,53]. In addition, the type of alkali (Na or K) and the curing regime can be other influential factors to be considered. In this context, this chapter aims to investigate the effect of the alkali content, calcium content, silicate content, the alkali type and the curing regime on the alkali leaching and the formation of efflorescence products.

7.2. Experimental program

7.2.1. Materials and mix proportions

Gladstone fly ash and GGBS (A) was used to manufacture the alkali-activated paste samples. The chemical composition, amorphous content and the crystalline phases of the raw precursors have been previously presented in Section 3.2.1. Particle size distribution of solid precursors can also be found in Figure 3-1.

Table 7-1 presents the details of the alkali-activated paste mixes, along with the activator constituents. Similar to the activator used in previous chapters, a mixture of sodium hydroxide solution and grade D sodium silicate solution (provided by PQ Australia) were used for mixes 1 to 5 (reffer to Section 3.2.1 for technical specifications of NaOH pellets and sodium silicate solution). For mix 6, a mixture of KOH flakes (supplied by Recochem Inc.) and potassium silicate (purchased from PQ Australia) was used. Potassium silicate supplied under the commercial name of KASIL 1552 with a chemical composition of K₂O = 21.2%, SiO₂ = 32.0% and H₂O = 46.8% (by mass). The NaOH/KOH and the sodium/potassium silicate solutions were mixed in

proportions to provide M_s (molar ratio of SiO₂ to Na₂O/K₂O) according to Table 7-1, and allowed to cool down for 24 hours before use. The water content of NaOH pellets or KOH flakes and the silicate solutions was considered in the formulation of the solutions and calculation of the water to binder ratios.

Paste samples were fabricated following the mixing procedure explained in Chapter 3 (Section 3.2.2). After casting, all samples except for Mix 4 were cured in sealed moulds and were stored in a room with a fixed temperature of 23 ± 2 °C until the testing dates. Mix 4 samples were stored in on oven at 75°C for 18 hr in a sealed condition, after which transferred to the controlled room.

Mix	FA/GGBS	Na/(Na+K) (molar)	Ms	Na ₂ O(wt.%)	Water/binder ¹	Curing regime
Mix 1	25%/75%	1.0 (Na-based)	1.5	4	0.40	Ambient-cured
Mix 2	75%/25%	1.0	1.5	8	0.35	Ambient-cured
Mix 3	75%/25%	1.0	1.5	4	0.35	Ambient-cured
Mix 4	75%/25%	1.0	1.5	8	0.35	Heat-cured
Mix 5	75%/25%	1.0	1.0	8	0.35	Ambient-cured
Mix 6	75%/25%	0.0 (K-based)	1.0	5 ²	0.35	Ambient-cured

 Table 7-1. mix designs details

Note 1: Calculated considering the total water and the total solids (precursors+anhydrous activator)

Note 2: For Mix 6, Na₂O% represents the equivalent Na₂O concentration that has the same molar concentration of alkalis as in K-based activator

7.2.2. SEM-EDS analysis

SEM and EDS methodology and details have been previously mentioned in Chapter 3. Please refer to Section 3.2.5 for in-depth information.

7.2.3. Ion leaching and ICP analysis

Small paste cylinders (50(H) x 25(D) mm) were fabricated for ion leaching analysis (Figure 7-1). Samples were submerged in Milli-Q deionized water, and the concentration of the leached out ions were analyzed for Na/K content by inductively coupled plasma-optical emission spectrometer (ICP-OES), using Optima7300DV-ICP-OES (Perkin Elmer, US). The top and bottom surfaces of each sample were sealed using a silicon sealant to eliminate the end effects. The ratio of the total exposed side surface area to the exposure water volume was 100 cm²/L for all samples.



Figure 7-1. ion leaching test

7.2.4. Efflorescence tests

To investigate the efflorescence due to the leaching of the sodium ions and their reaction with the carbon dioxide in the ambient air, paste cylinders (100(H) x 50(D) mm) were fabricated and were kept in contact with the Milli-Q deionized water at the bottom. The water depth was maintained at 1 to 3 mm constantly. This method has been successfully used previously to accelerate the efflorescence rate [63]. Samples were stored in ambient condition at a controlled temperature of 23 ± 2 °C and the formation of the efflorescence products was photographed at the desired ages.

7.2.5. Electrochemical tests

Reinforced mortar samples have been fabricated in accordance with the fabrication method explained in Chapter 5 (Figure 5-1). The cover to the reinforcement is 20 mm. To investigate the effect of loss of alkalinity due to the alkali leaching on the passivity of the reinforcement, samples have been stored in deionized water up to 100 days (the water was renewed every month), and the half-cell potential and polarization resistance values were recorded. The test protocols are the same as those of Chapters 4 and 5.

7.3. Results and discussion

7.3.1. SEM/EDS results

Fly ash-based geopolymer binders are X-ray amorphous alkali aluminosilicate networks [27] with a similar alkali binding properties as metakaolin-based
geopolymers; i.e. the alkali cations incorporation in the geopolymeric network is only via a charge balancing role to offset the charge imbalance of Al^{3+} in IV-fold coordination [8,180]. On the other hand, as it has been addressed in Chapter 3, slag-based (calcium-rich) systems, are mainly comprised of calcium silicate hydrate (C-S-H) gel [10,11,181] . For blended fly ash and slag binders, the co-existence of the aluminosilicate (geopolymeric) gel and the C-S-H gel is assumed; although, the formation of C-S-H or the aluminosilicate gel depends on the alkalinity of the alkaline solution and the amount of slag available in the structure [12], and this was discussed in detail in chapters 3 and 5.

Figure 7-2 illustrates the SEM micrographs of the mixes mentioned in Table 7-1. Table 7-2 presents the elemental composition of the samples obtained from EDS analysis. Table 7-3 shows the 90 day compressive strength of the mortar samples measured using 50 mm cubic specimens. As it can be seen Figure 7-2, Mixes 2, 4, 5, and 6 display a rather homogeneous binding matrices compared to the other two mixes, which is due to a well-developed matrix in a highly alkaline environment. On the other hand, Mix 1 and Mix 3 contain more undissolved/unreacted FA and slag particles and a more heterogeneous structure. This can be explained by the lower alkalinity of the solution which leads to lower dissolution of the solid precursors and releases fewer aluminate and silicate species [27]. Furthermore, the lowest Si/Al ratio among Na-based alkaliactivated samples was recorded for Mix 3 which is consistent with the compressive strength results (Table 7-3); Si—O—Si bonds have a higher strength compared to Al— O—Al and Si—O—Al bonds [34], and a lower Si/Al ratio leads to a lower matrix strength. Mix 6 also shows a rather low Si/Al ratio, consistent with the low alkali concentration (5%) used to fabricated the samples. Low alkalinity levels has led to generally lower Ca/Si ratios which is in agreement with the discussions on the effect of alkalinity on the Ca/Si ratio presented in previous chapters; Mix 5 has slightly lower Ca/Si ratio compared with those of Mix 2 and Mix 4 due to a lower modulus ratio (Table 7-2). Ca/Si ratios for Mixes 2 and 4 are almost the same which is expectable as these mixes have the same composition and only the curing regime is different. Ca/Si ratio for Mix 1 is the highest, in agreement with its highest GGBS content among all the mixes.Also, the K-based Mix 6 samples show rather high Ca/Si ratios which is consistent with Na-based samples containing 5% alkali content in Table 5-2 (Chapter 5); although, further investigation with regards to the role of potassium in development of CSH gel in alkali-activated materials is strongly recommended.





Figure 7-2. SEM micrographs of alkali-activated paste samples

Mix	Number of points	Si/Al (molar ratio) ±SD	M/Al (molar ratio) ±SD	Ca/Si (molar ratio) ±SD
1	30	2.05±0.32	0.7±0.26	1.26±0.22
2	30	2.17±0.25	0.97±0.15	0.53±0.06
3	30	1.64±0.49	0.48±0.18	0.25±0.11
4	30	2.36±0.52	0.85±0.16	0.50±0.13
5	30	2.01±0.26	0.97±0.19	0.49±0.19
6	30	1.55±0.20	1.28±0.36	0.96±0.21

Table 7-2.	EDS	analysis	results
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Note: M denotes Na or K

		(55 1111 64	ore sun	iipies)	
Mix	FA/Slag	Sand/binder	Ms	Na ₂ O (wt. %)	Compressive strength ±SD (MPa)
1	25/75	2.75	1.5	4	68.8±0.56
2	75/25	2.75	1.5	8	70.8±0.26
3	75/25	2.75	1.5	4	27.4±1.30
5	75/25	2.75	1.0	8	65±0.05

 Table 7-3. 90-day Compressive strength of corresponding mortar mixes

 (50 mm cubic samples)

7.3.2. ICP analysis and efflorescence results

Previous XRD studies of the efflorescence products show that the efflorescence products are hydrous alkali carbonates [63] and provided that the efflorescence products form on the surface of the sample rather than inside the pores, the efflorescence test provides a rapid and basic tool to study the ion leaching. However, the efflorescence test is more of a qualitative method; by contrast, the leaching test yields more quantitative results under a more controlled experimental condition.

Table 7-4 presents the absolute value of the concentration of the leached out Na/K ions, as well as the relative percentage of the alkali ions which have diffused out of the specimens. The absolute values are essential to assess the severity of efflorescence of the different mixes, while the percentage of the leached out ions provides valuable information on the relation between the binder composition and the leaching potential of individual mixes. The percentage of the leached out ions is calculated as follows:

Leached out Na ion (%)=
$$[Na/K]_L / [Na/K]_0 \times 100$$
 (%) (7-1)

Where $[Na/K]_L$ denotes the amount of the leached out sodium or potassium ions, and $[Na/K]_0$ is the total Na or K content (in the alkaline solution and the amorphous phase of FA and slag). Mixes 5 and then 2 have the highest concentration of leached out Na ions which is consistent with the efflorescence observations (Figure 7-3). The remaining mixes have almost the same absolute values of leached out ion, although the relative values are not proportional to the amount of alkali oxides introduced to the mixes. The higher than expected ion leaching of Mix 1 is in part due to the lower Al content of GGBS compared to FA (Table 3-1, Chapter 3), as well as the limited uptake of aluminium in the tobermorite-like structure of C-(A)-S-H gels compared to

aluminosilicate networks [26]. Tetrahedral aluminum will incorporate the alkali cations in the matrix via a charge balancing mechanism. Reduction of the aluminum content of the binder, as it is reflected in Na/Al ratio presented in Table 7-2, will increase the availability of the alkali cations in the pore solution. Furthermore, a systematic preference for incorporation of calcium over monovalent cations into the aluminosilicate gel is reported [53] by analyzing the extracted pore solution of a range of mixes with variable FA/GGBS ratios. This preference can be another reason for the rather high concentration of leached out alkalis in slag-rich mixes.

Mix	FA/Slag	Ms	Na ₂ O%	Leached out [Na] or [K] mM (ppm)	Percentage of leached out [Na]/[K] ions (%) (theory)
1	25/75	1.5	4	31.1 (715)	25.0
2	75/25	1.5	8	40.3 (927)	17.9
3	75/25	1.5	4	31.6 (726)	24.3
4	75/25	1.5	8	30.7 (706)	13.6
5	75/25	1.0	8	50.04 (1150)	21.1
6	75/25	1.0	5	30.5 (1223)	18.9

Table 7-4. Leached out Na ion concentration after 77-days of immersion

Despite having a comparable amount of leached out sodium ions, Mix 3 did not show any noticeable sign of efflorescence (Figure 7-3); this behavior is consistent with the lower Na/Al ratio of Mix 3 (Table 3). The authors hypothesize that although the Na ions are less available to leach out due to the lower Na/Al ratio of the gel and lower Ca content compared to Mix 1 (for instance), they are more mobile in Mix 3 due to a weak bond; that is, they can easily be dissolved in the water (during the ion leaching test), or they can eventually leach out of the matrix if the efflorescence test would have continued for a longer time. It is worth mentioning that the ions can leach out into the solution via two different mechanisms: diffusion due to a concentration gradient and surface dissolution (wash-off). In the case of Mix 3, it seems that the surface dissolution mechanism is the key factor to the unexpectedly high level of the leached out ions.

Mix 4 shows the smallest percentage of leached out ions which highlights the critical role of heat-curing in mitigating the alkali leaching. Heat curing has increased the Si/Al ratio (Table 7-2) which is indicative of a higher aluminosilicate network development leading to adsoprion of more alkalis via charge balancing mechanism as explained previously. This becomes more clear when compared with the ambient-cured Mix 2 with the same mix composition.

Of interest is also the effect of alkali type on the ion leaching. As it is noted in Table 7-4, Mix 6 has the lowest absolute molar concentration of leached out alkalis which is consistent with the efflorecence test results in Figure 7-3 (with the exception of Mix 3 which discussed above). Having said that, the percentage of leached out ions is comparatively higher than Na-based samples with 8% alkali content and not proportional to the amount of available alkalis in the system; for comparison, the percentage of leached out ions for mix 6 (18.9 %) is considerably higher than 5/8 of the calculated values for Mix 5 ($5/8 \times 21.1 = 13.18$ %). Both of these mixes have the same modulus ratios. The effect of alkali type on the ion leaching requires further investigation and a larger experimental database to validate these findings.



Figure 7-3. Efflorescence of paste samples after 77 days of partial immersion



Figure 7-4. Efflorescence of concrete samples (Mix 1 and 2) after 150 days of partial immersion

Figure 7-4 depicts the efflorescence in concrete samples with the same binder composition as Mix 1 and 2. Assessing the effect of ion leaching and efflorescence on concrete samples, rather than paste samples, is of high importance as it gives a more realistic estimation of the amount of efflorescence products formed on the surface of the concrete structures. As it can be seen, the efflorescence products are considerably less noticeable, due to a smaller portion of paste present in the matrix, and perhaps differences in the pore structure and the permeability of the concrete and paste samples. As a result, it is plausible to assume that Mixes 3, 4, and 6 will have an acceptable/insignificant level of efflorescence if used to fabricate concrete samples.

7.3.3. Electrochemical test results

Figure 7-5 presents the half-cell potential and polarization resistance of samples of representative mixes which have been immersed in the deionized water for more than three months. As it is illustrated, no visible drop in the corrosion potential and R_p curves can be observed, suggesting that the long-term alkali leaching does not affect the passivity of reinforcement with 20 mm cover in conditions where there is not a flow of water (similar to the condition of the tests in this study). This behaviour is also consistent with the result of the analytical model developed in Chapter 6 (Appendix A), where a rather low level of alkalinity of the pore solution was enough to keep the pH at rather high levels, enough to keep the bars in passive condition (Figure 6-4 and its discussion).



Figure 7-5. Half-cell potential and R_p of reinforced mortar samples immersed in deionized water

7.4. Conclusion

Alkali ion leaching and the efflorescence of alkali-activated pastes fabricated from blends of fly ash and slag at different alkali contents, modulus ratios and with different alkali type and curing regimes were investigated. The results show that:

 Although the alkali content is the most important parameter influencing the ion leaching and the efflorescence, the amount of leached-out alkalis and consequently efflorescence severity is not proportional to the alkali content introduced into the mixes. The presence of calcium ions leads to the availability of more alkalis; also, the degree of matrix development and hence incorporation of alkalis into the matrix which depends on the initial alkalinity of the solution is another important factor to be considered.

- Heat curing result in less efflorescence. Heat curing increases the matrix development leading to incorporation of more alkalis and availability of less free alkalis, and as a result, less efflorescence.
- K-based samples showed a slightly lower degree of efflorescence, although the percentage of leached out ions were almost equal, or higher than the Na-based samples.
- Higher modulus ratios appear to lead to a better development of the aluminosilicate network and appear to slightly increase the alkali incorporation into the network, and thus, reduce the alkali leaching and the efflorescence.
- No significant change in the long-term trends of half-cell potential and polarization resistance of samples immersed in deionized water was observed, suggesting the negligible effect of loss of alkalinity due to ion leaching on the passivity of reinforcement under the experimental conditions of this study.

8.1. Concluding remarks

This thesis investigates one of the main durability threats concrete structures have been facing for decades, i.e. corrosion of reinforcement, with a focus on alkali-activated materials as the alternative binders which have been in the forefront of academic research and have also appealed to the concrete industry recently. Various phenomena are involved and interact with each other to transform a passive reinforced concrete/mortar system to a corroding system, as well as during the active phase of corrosion. Evaluation of these phenomena is more challenging in case of alkaliactivated materials than ordinary Portland cement (OPC) materials, due to the high dependency of properties of the final product on various compositional parameters controlling the reaction mechanisms and kinetics in these binders. To circumvent this difficulty, different aspects of corrosion of reinforcement in alkali-activated materials and their interactions have been systematically investigated in this dissertation, and the results are discussed in light of nano/microstructural properties which depend on the mix compositions.

In Chapter 3, moisture transport in a range of aluminosilicate-dominated (geopolymertype) and calcium rich alkali-activated paste samples was investigated. Water vapour sorption isotherms (WVSI) were established for the investigated mixes; hence a database is available for the future numerical studies of phenomena such as moisture adsorption/desorption, chloride adsorption/desorption through convective processes, electrical resistivity during the propagation phase of corrosion, oxygen diffusion, etc. Analysis of WVSIs revealed that water is not structurally bound in alkali-activated binders to the same extent as in OPC binders; and the low Ca/Si C-S-H gel developed in alkali-activated slag binders did not improve the water binding mechanism, suggesting a different nature/structure of C-S-H gel in slag-based binders. The desorption branches of WVSIs were analysed using the BJH method and the results were cross-compared against MIP test results to obtain an insight into the nanoporosity of alkali-activated binders. Result showed totally different pore structures for aluminosilicate-dominated and calcium-rich binders. The pore structure of an aluminosilicate-dominated sample (90%FA-10%GGBS) was comprised of an almost uniformly distributed volume of pores over the whole mesopore (2 nm< pore dimeter <50 nm) and macropore (pore dimeter> 50 nm) ranges. For a calcium-rich binder (75% GGBS-25% FA), on the other hand, a considerably finer pore structure was observed where the bulk of pores were smaller than 15 nm with a relative lack of larger pores. The different pore structure of aluminosilicate-dominated binders and calcium-rich binders means that in blended FA and GGBS binders with less than 50% GGBS, a considerable cavitation and network effect is expected due to the presence of some large pores which are accessible only through narrow constrictions. Heat-cured samples also appeared to have higher porosities compared to the ambient-cured samples.

The time dependent sorption kinetics was also studied for one FA-dominated (75% FA), one GGBS-dominated (75% GGBS) and one OPC sample to analyse the type of sorption process, i.e. Fickian (diffusion-controlled) or non-Fickian (anomalous), and to calculate the moisture diffusion coefficients through nonlinear regression analysis. Successful deconvolution of Fickian and non-Fickian sorption components revealed that the slag-dominated sample had the highest contribution of non-Fickian sorption component, followed by the OPC and then the FA-dominated samples. The high

anomalies observed in the sorption process of GGBS-dominated sample could be attributed to its very fine pore structure which is more susceptible to the time-dependent microstructural changes as the probable source of anomaly. Further investigation of the sorption kinetic curves also demonstrated a considerable lower permeability of GGBSdominated sample, and highlighted the importance of presence of calcium to develop a fine pore structure with high tortuosity which is critical to develop durable engineering binders. The pore structure implications deduced from the results of Chapter 3 is critical to understand many durability and transport-related properties of alkali-activated binders such as chloride diffusivity and stability of the passive layer around the bars (investigated in Chapter 5), gas (including CO₂) diffusivity (investigated in Chapter 6), and alkali leaching (investigated in Chapter 7).

Chapter 4 contains a comprehensive study of the electrochemical aspects of reinforced fly ash-based alkali-activated concretes in both passive (no chloride contamination and no corrosion as a result), and active phases of corrosion. Electrochemical test protocols for ohmic drop, half-cell potential, and polarization resistance (R_p) measurements were re-validated for alkali-activated binders. These test protocols were used to perform all the electrochemical tests in Chapters 5, 6, and 7. New proportionality constants (B) were reported for low-calcium alkali-activated binders which enables estimation of the corrosion rate by using the results of the non-destructive linear polarization resistance (LPR) test. Aiming to simulate the natural conditions as closely as possible, the samples were subjected to the wetting-drying cycles in 3.5% sodium chloride solution, the depassivation of samples was studied and compared with those of OPC samples reported in the literature. Result showed a similar rate of decline of the polarization resistance values by increasing the chloride content in both fly ash-based alkali-activated and OPC samples. Another interesting trend observed was the lower (more

negative) half-cell potential and smaller recorded R_p values for the investigated fly ashbased alkali-activated samples compared with the values reported for reinforced OPC concretes, suggesting that the traditional classifications which have been developed for OPC corroding systems might need some recalibration to be used for this type of alkaliactivated systems while assessing the passivity of samples.

Chapter 5 was devoted to a systematic investigation of the initiation phase of chlorideinduced corrosion in alkali-activated materials. All the influential parameters such as the chloride diffusivity, chloride binding, chloride threshold and electrochemical aspects (during the initiation phase) were studied for a wide range of mortar samples and the results were interpreted in light of the effects of variables such as the calcium content, alkali content, and the silicate content on the pore structure and chemical composition of the investigated binders. Comparison of acid and water soluble chloride contents showed no bound chloride in the aluminosilicate-dominated and calcium-rich alkali-activated paste samples submerged in sodium chloride solution, characteristic of a lack chemical binding in the materials studied here. As a result, any discussion regarding the chloride diffusivity in the alkali-activated binders have been focused on the role of the pore structure in physical chloride binding and encapsulation; this highlights the importance of the pore structure studies performed in Chapter 3. Among all the compositional variables investigated, and in agreement with the content of Chapter 3, calcium played the most prominent role in reducing the chloride diffusivities, emphasizing the critical role of presence of calcium in the matrix to design durable alkali-activated binders in marine environments. On the other hand, increasing the alkali content and silicate content led to higher chloride diffusivities, with the latter being more influential, in particular in aluminosilicate-dominated binders. Effect of partial replacement of sodium hydroxide with potassium hydroxide was also

investigated, and it appeared that the presence of potassium increases the chloride diffusion values.

Chloride threshold results, which were obtained by chloride content measurement of the powder sampled from the concrete-reinforcement interface of depassivated samples, ranged between 0.19 (wt. % binder mass) for calcium-rich binders fabricated at low alkalinity levels (3% Na₂O) and 0.69 for FA-dominated samples manufactured with highly alkaline activators (8% Na₂O). It seems that the suggested threshold values of 0.2% or 0.4% (wt. % binder mass) commonly used for OPC binders are suitable for aluminosilicate-dominated materials which require high alkalinity levels to provide acceptable mechanical strengths; although, they are not conservative enough for calcium-rich binders fabricated at low (to medium) levels of alkalinities.

Finally, the long-term monitoring of half-cell potential and the polarization resistance values of a wide range of reinforced alkali-activated mortars submerged in 3.5% sodium chloride solution revealed that, in general, the potential values and R_p values in alkali-activated mortars are smaller (i.e. more negative in case of the potential values) than those of OPC mortars, which was in agreement with the findings of Chapter 4. The difference becomes more notable for slag-rich binders which according to the literature, can be attributed to the presence of sulphides in the pore solution consuming oxygen and hindering the formation of iron oxide layers around the bars.

The carbonation-induced corrosion of reinforcement in low-calcium alkali-activated concretes was investigated in Chapter 6. The study focused on the effect of carbonation-induced pH drop on the passivity of reinforcement in these materials. An analytical chemisorption model was developed to predict the pH drop and carbonate phase distributions based on the equilibrium of different coexisting species in an aqueous sodium hydroxide solution (as representative of the pore solution of low calcium alkali-activated materials) at various alkali contents and partial pressure of the ambient carbon dioxide. Result demonstrated that the accelerated carbonation tests in laboratory conditions using high carbon dioxide concentration promotes formation of bicarbonates over carbonates leading to an artificial pH decline compared with natural carbonation. Nevertheless, the artificially decreased pH level (pCO₂=1% accelerated carbonation in this study) did not lead to the depassivation of reinforcement as the pH remained at rather high levels after carbonation. Furthermore, based on the developed model, even low level of alkali concentrations in the pore solution ([Na]~0.2 mol/l) appear to provide enough protection for the reinforcement during natural carbonation, and increasing the alkali concentration beyond 0.5mol/l does not significantly contribute to increase the pH level, and then the level of protection against steel corrosion in low-calcium fly ash-based carbonated geopolymer concrete. On the other hand, very low alkali concentration in the pore solution ([Na]<0.2 mol/l) will increase the risk of depassivation considerably. The findings of this chapter bring more confidence in the industrial application of low-calcium fly ash-based alkali-activated concretes where carbonation-induced steel corrosion is a concern, as these binders were shown to be capable of providing the required passivity for the reinforcement.

In Chapter 7, alkali cation leaching in alkali-activated binders was investigated. Both aluminosilicate-dominated and calcium-rich binders were studied. The results of Inductivity Coupled Plasma (ICP) tests coupled with an accelerated efflorescence test method used in this chapter revealed that although the alkali content is the most important parameter influencing the ion leaching and the efflorescence, the amount of leached-out sodium ions and consequently efflorescence severity is not proportional to the alkali content introduced into the mixes. The presence of calcium ions, the degree of matrix development which depends on the initial alkalinity of the activator solution, and the curing regime (heat curing or ambient curing) can affect the amount of the leaching ions. In general, higher calcium and alkali content, lower silicate content, and ambient curing, increased the ion leaching and risk of efflorescence. The loss of alkalinity, however, did not lead to depassivation of reinforcement, which was studied through long-term monitoring of the electrochemical parameters of reinforced mortar samples immersed in deionized water. This finding is also consistent with the results of the chemisorption model in Chapter 6, where considerably low level of alkali concentration in the pore solution was enough to keep the pH at rather high levels, enough for protecting the reinforcement.

To summarise, this dissertation contributes to develop a better understanding of the corrosion of reinforcement in alkali-activated binders and the various phenomena involved in both the initiation phase of corrosion, and propagation phase, i.e. after depassivation of reinforcement. One of the main outcomes of the work is the strong dependency of the investigated phenomena/parameters to the mix composition and chemistry of the binders. All the investigated materials are generally called alkali-activated binders (or geopolymers when there is a little amount of calcium in the mix); however, they are rather a diverse family of materials that can present vastly different properties depending on their mix composition. Although this variability introduces some difficulties for general practitioners and the commercial application of these materials as developing durable materials requires a proper understanding of the nano/microstructure and its dependency on various factors, it presents interesting opportunities to produce alkali-activated materials which can be tailor-made for particular engineering applications.

8.2. Recommendations for future research

From the outcomes of this study, a number of recommendations can be made towards future research as follows.

- Further experimental study of WVSIs is required to develop a more comprehensive database for future durability design studies to include the effect of modulus ratio and alkali type along with the results of the current study.
- The insignificant bound water in the interlayer spaces observed in the alkaliactivated slag binders in this study suggests that the C-(A)-S-H gel formed in these binders and its structure can be different from the C-S-H gel in OPC binders and it requires further research.
- Effect of potassium replacement on the chloride diffusivity and the observed electrochemical properties requires further investigation.
- Macrocell (galvanic) corrosion in reinforced alkali-activated materials is not investigated in this dissertation and can be a topic of interest for future research.
- As can be found in the literature, carbonation products formed in the calciumrich binders can be different from those of aluminosilicate-dominated binders investigated in this dissertation. The consequences of such a difference on the pH drop and depassivation of reinforcement is of interest and remains to be explored.
- Alkali binding mechanism and the effect of curing regime, or the preference of matrix to incorporate various cations is not fully comprehended in the literature.

Furthermore, establishing an empirical relationship between the risk of efflorescence and the influential parameters such as the alkali, calcium, and silicate content as well as the alkali type and the curing regime requires a systematic study of a wide range of alkali-activated mix compositions which is a necessary step toward mitigating the efflorescence risk in alkali-activated materials, and requires further studies.

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Appendix A: Estimation of the pH and carbonate species in an open aqueous alkaline carbonate system

The reaction mechanisms of the chemical adsorption of carbon dioxide in an aqueous sodium hydroxide solution are well understood and are as follows [182–184]:

$$CO_{2}(g) \rightarrow CO_{2}(aq) \tag{a}$$

$$CO_{2}(aq) + OH^{-} \leftrightarrow HCO_{2}^{-} \tag{b}$$

$$HCO_{3}^{-} + OH^{-} \leftrightarrow CO_{3}^{2^{-}} + H_{2}O$$
(c)

Both reactions (*b*) and (*c*) are reversible and exothermic in the forward direction; also, they are very fast in highly alkaline environments [182]. The concentration of the dissolved carbon dioxide, $CO_2(aq)$, can be calculated by using Henry's law:

$$CO_2(aq) = pCO_2 \times H_{CO_2,0} \tag{d}$$

where pCO_2 is the partial pressure of the carbon dioxide in the gas phase and $H_{CO_2,0}$ is Henry's law coefficient at the considered absolute temperature $(T)^1$ [185]:

$$H_{co_{2},0} = 3.54 \times 10^{-7} \exp(2044/T) \ mol.m^{-3}.Pa^{-1}$$
 (e)

The presence of alkali ions has been shown to affect the solubility of carbon dioxide [186]. The equation proposed by Weisenberger and Schumpe [187] is used to calculate the modified solubility coefficient H_{CO_2} (notations are changed for consistency):

$$\log(H_{CO_{2},0}/H_{CO_{2}}) = \Sigma(h_{i} + h_{G})c_{i}$$
(f)

where h_i and h_g are ion and gas specific parameters, suggested as 0.1143 and -0.0172 m³.kmol⁻¹ for Na⁺ and CO₂ respectively, and c_i is the concentration of (alkali) ions

¹ All the calculations were done for T=298.15K

(kmol/m³). H_{CO_2} is then replaced in equation (*d*) to determine the concentration of the dissolved carbon dioxide ($CO_2(aq)$). The equilibrium constants for reactions (*b*) and (*c*), K_1 and K_2 , can be defined as:

$$K_{1} = \frac{[HCO_{3}^{-}]}{[CO_{2}(aq)][OH^{-}]}$$
(g)

$$K_2 = \frac{[CO_3^-]}{[HCO_3^-][OH^-]}$$
(h)

 K_1 and K_2 were chosen from Greenwood and Earnshaw's work [188] and are 6.18×10^7 and 6.72×10^3 respectively; although, other different values can be found in the literature too [183,186,189].

The concentration of sodium as NaHCO₃ and Na₂CO₃ (denoted as *B* and *C* respectively) is equal to the total concentration of sodium in the solution (*A*) according to equation (*i*):

$$A = B + C \tag{i}$$

The carbonate and bicarbonate ion concentrations can be expressed in terms of sodium carbonate or sodium bicarbonates, if the degree of dissociation of NaHCO₃ and Na₂CO₃ is defined as α_1 and α_2 , respectively [184]:

$$[HCO_3^-] = \alpha_1 B \tag{j}$$

$$[CO_3^{2^-}] = \frac{\alpha_2}{2}C = \frac{\alpha_2}{2}(A - B)$$
(k)

Concentration of [Na] as NaHCO₃ can be found by combining equations (*d*), (*g*), (*h*), (*i*), (*j*) and (k) to form the following quadratic equation:

$$\frac{B^2}{A-B} = \frac{K_1}{K_2} [pCO_2 \times H_{CO_2}] \times \frac{\alpha_2}{2\alpha_1^2}$$
(*l*)

For a given value of A, B can be calculated from equation (*l*). The value of C, $[HCO_3^-]$, and $[CO_3^{2^-}]$ can also be determined by employing equations (*i*), (*j*) and (*k*) accordingly.

Moreover, having the carbonate-bicarbonate ion concentrations, equation (h) can be used to calculate the concentration of hydroxide ions, and then pH can be calculated as below:

$$pH = -\log_{10}[H^+] = -\log_{10}[\frac{K_w}{OH^-}]$$
(m)

where $K_w = [H^+][OH^-] = 10^{-(5839.5/T+22.4773\log(T)-61.2062)}$ [190]. Equations (*l*) and (*m*) are the basis of all the calculations and results presented previously in section 3.3.1.