A Conceptual Model of Geopolymerisation

by

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Bachelor of Engineering (Hons)

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For Mom and Dad

For Your tireless dedication, unconditional love and support
God does not play dice…..

Albert Einstein
ABSTRACT

The discovery of geopolymers is a breakthrough which provides a cleaner and environmentally-friendlier alternative to Ordinary Portland Cement (OPC). Since the pioneering days, the understanding of the chemistry, synthesis, and practical application of geopolymers has improved to the extent that commercialisation of geopolymers on a large scale is possible in the near future. However, the fundamental breakthroughs and understanding to date are based on investigations of ‘pure’ raw materials, like metakaolinite. The utilisation of metakaolinite has been useful in a research setting, but will be impractical for widespread application. Therefore, the thesis attempts to do a more detailed study on geopolymers synthesised from waste materials, such as fly ash. The motivation for using fly ash as the main raw material is driven by various factors: (1) it is cheap and available in bulk quantities, (2) it is currently under-utilised, except for its use as an additive in OPC, (3) it has high workability, and (4) it requires less water (or solution) for activation.

Previous workers utilised extreme experimental conditions, such as high alkali concentration and high water content to analyse various reaction steps, which occur during fly ash-based geopolymerisation. While the earlier results might provide important insight into the reaction mechanisms, the conditions used did not represent those normally chosen for synthesising geopolymers. With this in mind, the experiments reported in the thesis have been conducted under controlled conditions typically used for geopolymerisation, thus leading to findings, which should improve our understanding of reaction steps. In order to do this, the various influencing parameters will be considered and investigated accordingly, namely the concentration of reactants (silicate concentration, alkalinity, and water content) and the curing conditions (temperature, time, humidity). Based on the results obtained, a conceptual model of geopolymerisation is developed by incorporating the above mentioned factors, with the purpose of providing a better understanding of the mechanism and kinetics of geopolymerisation.
At least three key areas are believed to be novel from the work undertaken in the thesis. Firstly, an investigation on the development of pore structure in geopolymers. Secondly, an investigation on the competition between dissolution, polymerisation, and crystallisation of aluminosilicate gels during geopolymerisation. The occurrence of these reaction steps is influenced by the alkali-silicate concentration and the type of alkali metal cation used. Finally, an investigation on the ageing of geopolymers in alkali and carbonate solutions, which provides insight into the reaction mechanisms of late geopolymerisation (i.e. after geopolymers set). These key findings will also be incorporated into the conceptual model presented in the conclusion of the thesis.
PREFACE

I hereby declare that, to the best of my knowledge, the content of the thesis is original in its entirety and contains no material which has been previously published by another person, except where due reference is stated. In addition, no part of this work has been submitted for the award of any other degree or diploma in any university.

I certify that the work has been undertaken solely by the candidate, except where due acknowledgement is given. The text of the thesis, exclusive of tables, figures and bibliography, does not exceed 100,000 words.

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CHAPTER 1
INTRODUCTION

The term ‘geopolymer’ was used for the first time by Davidovits (1991) to describe his findings of a new breed of aluminosilicate binders, synthesised by activating calcined kaolinitic clay (metakaolinite) with sodium silicate solution at low temperature. Geopolymer is an aluminosilicate gel, whereby the silicon and aluminium are tetrahedrally-bonded through sharing oxygen atoms. The basic monomer unit is called a sialate \((\text{O-Si-O}^{\cdot}\text{-Al-O})\), which carries excess negative charge due to the substitution of \(\text{Si}^{4+}\) with \(\text{Al}^{3+}\). The polysialate structure is charge-balanced by alkali metal cations \((\text{K}^+ \text{ or Na}^+)\). The research of geopolymers has been closely associated with cement and concrete technology, particularly that of alkali-activated cement (AAC) because of the alternative applications and superior properties that traditional OPC materials cannot offer (Krivenko, 1994; 2002; Krivenko and Kovalchuk, 2002; Palomo et al., 1999b; Roy, 1999). Recent understanding, however, has tied geopolymers (particularly those synthesised from ‘pure’ raw materials, such as metakaolinite) closely to the chemistry of aluminosilicate gels (Duxson et al., 2005a; Kriven et al., 2003) and/or zeolites (Provis et al., 2005c). Despite the resemblance of geopolymers to these traditional materials, the chemistry and application of geopolymers are unique and should be treated as such.

The objective of the thesis is to provide original research of waste-based geopolymers; thus the majority of work presented is novel in terms of its approach and methodologies and makes a significant contribution, filling the current knowledge gap in understanding the chemistry of geopolymerisation, particularly fly ash-based geopolymerisation. There are four main areas of research presented, which include: 1) the effect of curing conditions on the properties of geopolymers, 2) the development of pore structure of fly ash-based geopolymers, 3) the reaction mechanism of early fly ash-based geopolymerisation, and 4) the reaction mechanism of late fly ash-based geopolymerisation (i.e. after geopolymer materials set). In the thesis, the four areas are investigated progressively, gradually developed to provide readers with new and fundamental understanding of geopolymerisation.
An overview of the chemistry and properties of cement, porous gels, zeolites, and geopolymers will be presented in chapter 2. The aim of the review is to provide a comparison for the different materials, and to describe the fundamental chemistry of each material, from which a description and understanding of the chemistry and synthesis of the geopolymers can be obtained.

Chapter 3 discusses the various novel methodologies applied in order to appropriately understand the physico-chemical properties of geopolymers, and the mechanism and kinetics of geopolymerisation process. The experimental methodologies can be divided into two main parts: (1) the synthesis and (2) the characterisation of geopolymer materials. The synthesis of geopolymers can be classified into the sol-gel methodology, which is commonly used to synthesise silica gels and glasses (Brinker and Scherer, 1990). The characterisation of geopolymers can be categorised into two main areas, chemical and physical characterisation. In the chemical analysis, the progress of reaction is monitored starting from a fresh mix to a hardened material. The physical characterisation can be further divided into two aspects: (1) micro, and (2) macro. The micro-physical characterisation includes gel morphologies, gel compositions, chemical bonding, and porosity. The macro-physical characterisation includes compressive strength testing and permeability measurement.

Chapter 4 provides a preliminary understanding of the physico-chemical properties of geopolymers derived from metakaolinite (MK), granulated blast furnace slag (GBFS), and fly ash (FA). This chapter highlights the complexities involved in studying geopolymers prepared from different raw materials. The reactivity, chemical structure, and strength of geopolymers are significantly different due to the variations in the composition of raw materials, the particle reactivity and kinetics, and the chemistry of phases (or mineralogy). In the following chapters, a large volume of work will be devoted to understand further the chemistry of fly ash-based geopolymerisation. Class F fly ash is used because: 1) it is a waste-based material thus it adds value, reduces cost, and enhances the environment, 2) its potential application in cement and/or geopolymer technology is under-utilised, 3) it possesses slower kinetics, making it suitable to study the mechanism and kinetics in real-time, and 4) it is highly workable.
Very few authors (Bakharev, 2005; Barbosa et al., 2000; Criado et al., 2005; Van Jaarsveld et al., 2002) have investigated the effect of curing parameters on geopolymers. This is in contrast to the large amount of work conducted in understanding the effect of curing on pozzolanic blended cements, such as on MK- (Bai et al., 2002; Curcio et al., 1998; Dunster et al., 1993; Poon et al., 2001; Rojas and Cabrera, 2002; Rojas and Sanchez de Rojas, 2003; Wild et al., 1996); GBFS- (Aldea et al., 2000; Bakharev et al., 1999; Ma et al., 1994; Shi, 1996); and FA-blended cement (Bleszynski and Thomas, 1998; Brough et al., 2001; Lee et al., 1997; Li et al., 2000; Pietersen and Bijen, 1994). Consequently, the lack of systematic studies has led to the differences in the physical and chemical properties reported. The aim of the study presented in Chapter 5 is to investigate systematically the effect of changing curing parameters (e.g. temperature, humidity, and time) on the physico-chemical properties of geopolymers (e.g. strength, permeability, and gel structure).

As a progressive study of the curing effect on geopolymerisation, Chapter 6 correlates the rate and extent of reaction with the development of porosity and gel composition of fly ash-based geopolymers. The rate and extent of reaction are manipulated by varying reaction parameters, e.g. temperature, alkali concentration, silicate concentration, and reaction time. Provided that the chemistry of geopolymers resembles that of porous aluminosilicate gels and glasses, then it is reasonable that the pore structure of geopolymers would resemble that of porous gels. Therefore, the porosity of geopolymers can also be tailored to produce specific material properties, such as mechanical strength, flexibility, durability and fluid permeability. For the first time, the development of pore structure of fly ash-based geopolymers is determined using MIP (Mercury Intrusion Porosimetry), N₂ adsorption and high resolution-electron microscopy (FESEM and TEM).

Having understood the correlation between reactivity, pore structure, and gel formation, it is therefore essential to investigate the reaction mechanisms of early fly ash-based geopolymerisation. In Chapter 7, the heat of reaction from fly ash-based geopolymerisation at different silicate concentrations (expressed in SiO₂/M₂O ratios, M = Na or K) is measured in-situ using a JAF Isothermal Conduction Calorimeter. In this
study, a novel method of mixing solid and liquid raw materials in the calorimeter will be used. The activating solutions are directly injected to solid after the temperature stabilisation required by the calorimeter is completed. It eliminates the delay time during which all information on the early reaction might be neglected. Due to the absence of preliminary mixing, inhomogeneity in the mixture is an issue, but its effect has been reduced by using a higher liquid to binder (fly ash) ratio. The heat released is correlated with the dissolution, polymerisation, and crystallisation of aluminosilicate gel. The conditions in which polymerisation and/or crystallisation of aluminosilicate species take place, are established.

Chapters 4-7 will primarily focus on the mechanism, kinetics, and properties of geopolymers from the early reaction steps. However, it is known that once geopolymers set, the extent of reaction is minimal because the effects of influencing parameters, namely silicate concentration, alkali concentration, curing temperature, and humidity are not very significant. Instead, a further reaction will be controlled by the rate of diffusion of remaining soluble species in the pore solution onto the fly ash particles or a growing gel network. By manipulating the concentration of ions in the pore solutions, the equilibrium of ionic precursors can be altered as well, which means that the later reaction steps might not be diffusion-limited anymore. To prove this, Chapter 8 investigates the transport behaviour of precursors, the change in the pore structure, and the morphologies of geopolymers with respect to time of ageing by immersing fly ash-based geopolymers in various alkali and carbonate solutions.

Based on the results obtained from Chapters 4-8, a conceptual model of geopolymerisation is developed in Chapter 9. The model incorporates the effect of aluminosilicate solids, activating solutions, curing conditions, ageing conditions on the reaction steps in geopolymerisation (e.g. dissolution, polymerisation, and crystallisation of aluminosilicate). The alteration in each reaction step determines the types of product phases formed, which in turn affects the physico-chemical properties of geopolymers (e.g. porosity, strength, gel composition, and chemical bonding) as well.
CHAPTER 2

THE CHEMISTRY OF CEMENT, POROUS SILICA, ZEOLITES, AND GEOPOLYMERs

This chapter provides an overview of the chemistry of cement, porous silica, aluminosilicates, and zeolites. The similarities and differences between these materials and geopolymers will be highlighted through a discussion of physico-chemical properties, synthesis, and chemistry of materials. The effect of processing conditions, such as temperature, ageing time, and reactant concentration will also be presented, with major emphasis on the development of various phases and pore microstructure.

In Section 2.1, the hydration chemistry of various calcium silicate phases in Portland Cement (OPC) is discussed. In addition, the effect of curing temperature and methods of cement hydration and properties are presented. The most recent understanding on the physico-chemical properties and pore structure of OPC paste and pozzolanic-blended cement using fly ash, slag, and metakaolinite are also reviewed. It is significant to understand the chemistry of both OPC and geopolymers because of the potential application of geopolymers as construction materials.

Recent investigations have found that the microstructure of geopolymers resembles that of porous aluminosilicate gels. Section 2.2, will therefore cover the synthesis and physico-chemical properties of porous silica and aluminosilicate gels. The aim of this review is to provide the fundamental knowledge of sol-gel methodology, which is commonly used in the synthesis of amorphous gels, glasses, and geopolymers. The three steps of sol-gel methodology, which include the hydrolysis and condensation of gel, the ageing of gel, and the post-treatment of gel are discussed in detail.

The chemistry of zeolite synthesis has been revolutionised with the successful preparation of synthetic zeolites at hydrothermal conditions. It is believed that geopolymers (aluminosilicate gels) are essentially amorphous precursors to zeolitic
crystals. In the thesis, the formation of zeolites during geopolymerisation is an indication of the close connection between the chemistry of zeolites and geopolymers. Therefore, a review of the synthesis, mechanism, kinetics, and other factors that influence the nucleation and crystallisation of synthetic zeolites is presented in Section 2.3.

Finally, a review of geopolymer literature is presented. It covers past to recent understanding of synthesis, chemistry, and properties of geopolymers. Based on the literature review, it is found that there are still knowledge gaps in the current understanding of geopolymerisation, particularly fly ash-based geopolymerisation. The work conducted in the thesis attempts to fill these gaps by investigating four areas: (1) the effect of curing conditions on the properties of geopolymers, (2) the development of pore structure of fly ash-based geopolymers, (3) the reaction mechanism of early fly ash-based geopolymerisation, and (4) the reaction mechanism of late fly ash-based geopolymerisation (i.e. after geopolymers set). The overall research theme is to describe a conceptual model that better explains geopolymerisation based on the key results obtained from the four studied areas.

2.1 Cement and concrete

An overview of chemistry of cement and concrete is essential for the research and development of geopolymer technology because of the following reasons:

1. Waste-based geopolymers, namely fly ash and slag-based geopolymers have potential application as construction materials. Currently, cement and concrete have been the major construction materials, which are used widely for more than a century. Therefore, in order to understand the advantages, disadvantages, superiority and inferiority of geopolymers over cement, one needs to understand the physico-chemical properties of both materials, and the chemistry of materials that leads to such properties as well.

2. In cement terminology, geopolymers are commonly referred as Alkali-Activated Cement (AAC). Although there is a close connection between geopolymers and AAC, they are slightly different in synthesis, chemistry, and properties. The close
The connection between the two types of materials lies in the use of fly ash and other pozzolans, such as slags, metakaolinite, and fused silica; and the use of alkali-based solution as activating solution.

### 2.1.1 The chemistry of cement hydration

The chemistry of geopolymers is dependent on the content of amorphous aluminosilicate phases in the solid, the concentration of alkali-silicate solution, and the solid to liquid ratio. However, the chemistry of cement hydration is mainly dependent on the composition of calcium silicate phases and the content of water. Ordinary Portland Cement (OPC) consists of four types of phases, i.e. alite (C₃S), belite (C₂S), tricalcium aluminate (C₃A) and calcium alumino ferrite (C₄AF). The equivalent chemical names and formulae are listed in Table 2.1. The composition of these four phases can be varied by changing raw materials and clinkering process conditions, thus resulting in cement with various physico-chemical properties (Mindess and Young, 1981).

<table>
<thead>
<tr>
<th>Product phases</th>
<th>Chemical name (abbreviated)</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite (dicalcium silicate)</td>
<td>C₃S</td>
<td>3CaO. SiO₂</td>
</tr>
<tr>
<td>Belite (tricalcium silicate)</td>
<td>C₂S</td>
<td>2CaO. SiO₂</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>C₃A</td>
<td>3CaO. Al₂O₃</td>
</tr>
<tr>
<td>Calcium alumino ferrite</td>
<td>C₄AF</td>
<td>4CaO. Al₂O₃.Fe₂O₃</td>
</tr>
</tbody>
</table>

Table 2.1 The summary of products from cement clinkering process.

From 0-3h, the C₃S phase initially reacts with water to form crystalline Ca(OH)₂ (is commonly abbreviated as CH) and a gel of hydrated CaO-SiO₂. The hydration of C₃S phase is shown in Equation (2.1) (Jawed et al., 1983). From 3-24 h, C₂S starts to hydrate and form hydrated calcium silicate (CSH) very slowly. The slow rate of reaction is reflected in the low heat of hydration of C₂S (Table 2.2). The hydration of the alite (C₃S) and belite (C₂S) phases may continue even long after the cement phase sets, and only ceases when no more water remains (Powers, 1958). The third phase, C₃A hydrates well with the presence of gypsum, CaSO₄.2H₂O. The hydration of C₃A leads to the
formation of two phases, ettringite (C₆A(SO₃)₃H₃₂ or AFt), and monosulphoaluminate hydrate (3C₄A(SO₃)H₁₂ or AFm) (Equations (2.2) and (2.3)). In the absence of gypsum, C₃A reacts very rapidly with water to form metastable hexagonal hydrates, C₂AH₈ (Equation (2.4)) then converts to a more stable phase, hydrogarnet (C₃AH₆) with the liberation of large amount of heat (ΔH= -340 kJ/mol, Table 2.2). The hydration of C₄AF proceeds in a similar manner to C₃A, i.e. it can be accelerated with the addition of gypsum to form crystalline phases, C₃(AF).6H. However, C₃A and C₄AF are minor constituents, thus the effect of their hydration to the physical expansion of cement gel is significantly low.

Table 2.2 The depth of hydration product in OPC (microns) and its heat of hydration on 30-55 micron grains (Lea, 1970; Mindess, 1983).

<table>
<thead>
<tr>
<th>Phases</th>
<th>3 days</th>
<th>7 days</th>
<th>28 days</th>
<th>6 months</th>
<th>Heat of hydration (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>3.5</td>
<td>4.7</td>
<td>7.9</td>
<td>15.0</td>
<td>-114</td>
</tr>
<tr>
<td>C₂S</td>
<td>0.6</td>
<td>0.9</td>
<td>1.0</td>
<td>2.7</td>
<td>-43</td>
</tr>
<tr>
<td>C₃A</td>
<td>10.7</td>
<td>10.4</td>
<td>11.2</td>
<td>15.0</td>
<td>-362 (with gypsum)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-340 (without gypsum)</td>
</tr>
<tr>
<td>C₄AF</td>
<td>7.7</td>
<td>8.0</td>
<td>8.4</td>
<td>13.2</td>
<td>-203</td>
</tr>
</tbody>
</table>

2C₃S + 7H → C₅S₂H₄ + 3 CH  \hspace{1cm} (2.1)

C₃A + 3C(SO₃)H₂ + 26H → C₆A(SO₃)₃H₃₂ ettringite (AFt) \hspace{1cm} (2.2)

C₆A(SO₃)₃H₃₂ + 2C₃A + 4H
→ 3C₄A(SO₃)H₁₂ monosulphoaluminate hydrate (AFm) \hspace{1cm} (2.3)

2C₃A + 21H → C₄AH₁₃ + C₂AH₈ hexagonal hydrates \hspace{1cm} (2.4)

2.1.2 The microstructure and porosity of hydrated cement paste

The microstructure of hydrated cement consists of large solid-appearing grains embedded in a porous matrix (Diamond and Bonen, 1993). The solid grains are called
'Inner products' (Ips) (Richardson, 2000; Taylor, 1990), while the more porous matrix is called ‘Outer products’, Ops. The ‘Ips’ are generally non- or partly-hydrated C₃S, which is surrounded by a porous structure, also known as gel pores. Other Ip phases include agglomerates of CH, and insoluble additive materials (limestone, dolomite, and quartz). The ‘Ops’ are the hydrated products, such as CSH, CH, AFm, and ettringite (AFt). In term of structures, Ops contain skeletal, amorphic solid, and pore space. The skeletal solid consists of fibrillar (CSH), needle (AFt) and hexagonal crystal structure (AFm). The amorphic solid is a ‘fuzzy’ phase, which cannot be classified distinctively.

The microstructures of geopolymers are as complex as cement due to the presence of non-reactive phases. For example, in fly ash-based geopolymers, the microstructure comprises of non-reacted impurities, partly-reacted fly ash particles, amorphous aluminosilicate gel (geopolymer gel), alkaline precipitates, and calcium or iron-based precipitates (Fernandez-Jimenez et al., 2005a; Sindhunata et al., 2004). However, in metakaolinite-based geopolymers, the microstructure contains less partly-reacted phases with more homogeneous gel composition and structure observed (Duxson et al., 2005a).

In OPC there are two types of pore space; one is called the capillary pore, which is a residual water-filled space (only in fresh pastes). The average diameter of capillary pores is 1.3 µm. The other is an interstitial void, which exists within the gel itself, and is called a gel pore. The average diameter of gel pores is about 3 nm (Neville, 1995). During hydration, the size of capillary pores is reduced, which shows that capillary porosity depends on the degree of hydration and water/cement ratio of the mix. Furthermore, the capillary pores are open and inter-connected. The inter-connectivity of these pores is primarily responsible for the fluid permeability, the vulnerability to any freezing and thawing cycles, and the resistance to chemical attack.

Unlike capillary porosity, the gel porosity is independent of the progress of hydration and water/cement mixture. This means that cement gel has similar properties from one hydration step to another. However, as the volume of gel increases along with the progress of hydration, the volume of gel pores also increases due to the formation of the more porous CSH phases (Neville, 1995). Gel pores contain two types of molecular
water, i.e. chemically and physically adsorbed water (Tritthart and Haussler, 2003). Unlike the capillary pores, gel pores are not necessarily open or inter-connected.

For geopolymer materials, when reactivity is low, pores are large and filled with residual activating solution. The type of pores formed is similar to the type defined as ‘capillary pores’ in fresh OPC paste. However, when reactivity is high, ‘capillary pores’ in geopolymers are filled with more gel. As a result, pores become smaller and pore surface area increases. The type of pores formed is similar to the type defined as ‘gel pores’ in hardened OPC paste. The characteristics of ‘capillary’ and ‘gel’ pores in geopolymer gel will be investigated in the work conducted for the thesis.

2.1.3 The effect of curing temperature on the properties of cement
Figure 2.1 shows the effect of curing temperature at different curing time on the compressive strength of OPC paste. A rise in curing temperature usually accelerates the hydration and thus increases the early strength of cement and concrete. Although a higher temperature increases the early strength, it may adversely affects the strength from 7 days onward (Neville, 1995). The reason for this behaviour is that prolonged curing at higher temperature results in the formation of porous cement structure. Verbeck and Helmuth (1968) suggested that at higher curing temperature, the diffusion of the products of hydration away from the cement particle is slower. As a result, there is a non-uniform precipitation in the interstitial space. This leads to a porous structure, which causes a reduction in long-term reactivity and strength (Jennings, 2000; Kjellsen et al., 1990).

The other methods of curing cement and concrete are steam and autoclave curing. The objective of steam curing is to obtain a high early strength soon after casting so that moulds can be removed. This is very significant from a practical point of view because it requires less time and space storage (Neville and Brooks, 1990). In practice, an optimal temperature is sought for generating both high early strength and late strength. When cement or concrete is cured at high temperature curing (> 85 °C) under steam environment, a regression in strength is usually observed. This can be seen from the surface cracking, caused by the expansion of air bubbles in the cement paste. The
expansion of air bubbles creates tensile stress in the surrounding paste, and results in the crack propagation (Neville, 1995). The detrimental effects of steam curing can be avoided by prolonging the pre-steaming period (increases the tensile strength of the paste) or by lowering the rate of temperature rise.

**Figure 2.1** The relationship between curing temperature, curing time, and compressive strength of OPC (Neville, 1995).

Unfortunately, while there have been many investigations conducted to study the effect of curing temperature, time, and methodologies on the properties of cement and concrete, there is little investigation of the effect of curing conditions on the properties of geopolymer materials. As a result, there is little knowledge of the effect of curing on the chemistry of geopolymerisation. Therefore, curing temperature and time will be some of the many curing parameters to be studied in the thesis.
2.1.4 Pozzolanic-blended cement

Pozzolans were originally defined as volcanic ashes that react with lime to form hardened materials, which in turn can be used as binders. However, the terminology of pozzolans has been broadened when it is found that non-natural resources, such as fly ashes, blast furnace slags, and silica have similar chemical properties to original pozzolanic ashes, and can be incorporated into OPC as well. The addition of pozzolans into OPC has reduced the volume of cement usage and greenhouse gas emission, associated with the cement manufacturing processes. Pozzolanic-blended cements are also found to have better physico-chemical properties than OPC, namely reduction in permeability, expansion, heat of hydration, micro-cracking, and freeze-thaw damage. Additional benefits include an increase in compressive strength, protection of steel reinforcement from corrosion, protection from sulphate attack and alkali-silica reaction, and lower water requirement. Understanding how fly ash and other pozzolans intimately react with various phases in OPC under different alkali concentrations, may provide insight to understand the chemistry of geopolymers derived from the same pozzolanic materials.

There are three main research areas for pozzolanic-blended cements:

1. *The mechanism, kinetics, and microstructure of pozzolanic-blended OPC.*

2. *The reaction of pozzolanic materials with Ca(OH)$_2$.* The Ca(OH)$_2$ in hydrated cement and concrete reacts intimately with pozzolanic materials because pozzolanic particles are believed to serve as seeds for the precipitation of Ca(OH)$_2$ in the hardened paste.

3. *Alkali-activated cement (AAC).* In AAC, slags, fly ashes, and metakaolinites are reacted with alkali-containing solutions, e.g. NaOH, KOH, Na$_2$CO$_3$, silicate solution. At high pH, the activation of amorphous aluminosilicate phases in pozzolans is greatly induced. To some extent, the AAC research intersects with geopolymer research, therefore, a further discussion of AAC will be included in the review of geopolymers (Section 2.4).
2.1.4.1 The chemistry of granulated blast furnace slag-blended cement

The incorporation of blast furnace slags (BFS) into OPC has been studied in a more thorough and fundamental fashion than for any other pozzolans, which is driven by the economic (waste-based material) and technical advantages (high Ca content in GBFS). Prior to being blended into OPC, BFS is rapidly cooled to form amorphous granules. The cooled slag granules are commercially named granulated blast furnace slag (GBFS). The mixing ratio of cement to GBFS ranges from 25-75 weight %.

The hydration mechanism of cement-slag mixture and the microstructure of phases formed have been investigated by a number of workers (Pietersen and Bijen, 1994; Richardson, 1999; Richardson et al., 1993; Richardson and Groves, 1993; 1997). In summary, the ‘Inner Products’ (Ips) from a slag-blended cement consist of CSH phases, which are formed from the hydration of alite, belite, and slag grains. The CSH phases originating from hydration of alite and belite generally display fine homogeneous texture. The ‘Outer products’ (Ops) present in a mature slag-blended OPC are similar to those in non-blended OPC. The phases that are present include CSH, Ca(OH)\textsubscript{2}, AFm, with additional Mg- and Al-rich phases (hydrotalcite-like, HT, M\textsubscript{4/6}AH\textsubscript{10-13}). In OPC, the CSH phase has a fibrillar, directional morphology. However, in the slag-blended cement, the morphology changes from a fibrillar to foil-like, which results in a less interconnected capillary porosity (Richardson, 2000). This accounts for the lower permeabilities and so enhanced durability.

2.1.4.2 The chemistry of fly ash-blended cement

There are two main classes of fly ash, i.e. Class C and Class F fly ash. Class C fly ash contains a high composition of CaO (25-30 weight %), while Class F fly ash contains 2-5 weight % CaO. Although both types of fly ashes are used equally in OPC, there has been much interest in Class F fly ash lately due to the higher amorphous aluminosilicate content. Furthermore, the low calcium content in Class F fly ash delays the hydration process, which provides a better workability. In general, fly ash is added up to 30% by weight into a cement paste. It has been found that fly ash blended cement has a reduced permeability, and is more resistant to sulphate attack (Dhir and Byars, 1993).
In OPC, fly ash reacts with lime and water to produce CSH phase. The CSH structure from fly ash-blended cement is similar to the one produced from OPC, but usually contains minor elements that are derived from fly ash particles, such as Mg, Al and Fe. In the initial incubation period, fly ash serves as a precipitation nucleus for Ca(OH)$_2$ and CSH gel, which originates from cement hydration (Fraay et al., 1989). After the incubation period, the porous CSH will precipitate very quickly near the vicinity of fly ash particles. Rodger and Groves (1988) observed that after some months of hardening, these pores in CSH are filled and a finer pore structure is thus obtained. At a longer period of hydration, more dense clusters of hydrogarnet-like crystals are also found, along with other phases including AFt, AFm, and Stralingite (Pietersen and Bijen, 1994).

2.1.4.3 The chemistry of metakaolinite-blended cement

Clay-related minerals that are used as pozzolans contain a significant amount of kaolinite (Al$_2$O$_3$·2SiO$_2$·2H$_2$O). When kaolinite is calcined at high temperature (600-800°C), it is converted to metakaolinite (MK). MK contains reactive, amorphous SiO$_2$ and Al$_2$O$_3$. Dunster et al. (1993) concluded that the hydration products of OPC-MK-water pastes are derived from two distinct processes: the hydration of OPC and the pozzolanic reactions between Ca(OH)$_2$ and metakaolinite. In the earlier stages of hydration, OPC is hydrated and immediately forms Ca(OH)$_2$, which is later consumed by MK to form aluminosilicate gel, CSH and faujasite-type zeolites (Alonso and Palomo, 2001b; Palomo et al., 1999a). In the later stages (180-360 days), calcium aluminium hydrate (C$_3$AH$_6$, C$_4$AH$_13$), and gehlenite (C$_2$ASH$_8$) are also formed. The high content of Al from MK becomes more reactive in later stages, to form observable crystalline products (Frias and Cabrera, 2001).

The optimum quantity if MK to be added into a cement mix ranges from 10-40 weight % (Curcio et al., 1998; Poon et al., 2001). It has been found that for replacement below 10 weight %, MK does not change the properties of OPC paste. However, if the content of MK in the mix is more than OPC, the amorphous aluminosilicate in MK causes an incomplete hydration of OPC due to an early consumption of alkali, i.e. from Ca(OH)$_2$. This has been proven to be detrimental to the structural integrity of cement paste.
2.2 Porous silica

Recent understanding of the synthesis and physico-chemical nature of geopolymer materials has led researchers to believe that geopolymers closely resemble aluminosilicate gels in many aspects (Kriven et al., 2003). Firstly, geopolymers can be synthesised at relatively low temperatures (25-100 °C) using sol-gel methodology. The two main reaction steps in geopolymerisation are the hydrolysis and condensation reactions in sol-gel chemistry (Brinker and Scherer, 1990). Secondly, the pore structure of a geopolymer gel resembles that of an aluminosilicate gel, whereby the mesopore (2-50 nm) is the typically observed pore region (Sindhunata et al., 2006). Therefore, a review on the synthesis and chemistry of silica and aluminosilicate solids is necessary, with an aim to provide background knowledge in explaining various findings from the work conducted in the thesis.

2.2.1 Amorphous silicas

Synthetic amorphous silicas can be divided into four general classes: colloidal silicas, silica gels, precipitated silicas, and fumed silicas (Iler, 1979; Setzer et al., 2002). Figure 2.2 illustrates the process for the formation of silica gels and solids (Iler, 1979).

2.2.1.1 Colloidal silicas

Colloidal silicas are suspensions of fine-sized silica particles in a liquid phase. Colloidal silicas are highly polymerised species or particles with sizes larger than 5 nm. The colloidal particles are typically non-porous and spherical in shape and are electrostatically stabilised to prevent coagulation to larger aggregates.

2.2.1.2 Precipitated silicas

In the course of the precipitation, the silica particles are so densely cross-linked that they settle out of suspension. The structure is distinct from the structure of a gel in that it does not fill space, but the internal structure still consists of continuous liquid and solid materials of colloidal dimensions (Scherer, 1999). Silica precipitates have pore sizes that can be classified into mesopore (2-50 nm) and macropore regimes (>50 nm).
2.2.1.3 Silica gels

In brief, silica gels can be defined as irregular aggregation of silica particles that continue to react on their surface upon contact with alkali and/or acid media (Setzer et al., 2002).

2.2.1.4 Xerogels and aerogels

The different methods of drying lead to the synthesis of two well-known silica gels, xerogels and aerogels. Xerogel is a type of silica gel that is dried normally at a temperature a little over 100 °C, where all adsorbed water is removed. During the drying, the gel shrinks because of the surface tension created in the pores. The final gel, therefore will depend on the structure of the original gel, however it will be a distorted version of the original gel. An aerogel is a type of silica gel which is dried such that the pore structure is closely maintained to the original structure. These can be achieved by replacing pore water with solvent (Kistler, 1932), and/or with supercritical drying using CO₂ (Setzer et al., 2002).

Looking from the perspective of formation mechanism, geopolymer gels are essentially an aluminosilicate gel and/or precipitate. The pore structure of geopolymer gels is constituted from an array of aluminosilicate particles in a complex gel network. The
dried geopolymer gels have been found to behave like xerogels, whereby the shrinkage of gel is observed during ageing or drying. However, the effect of prolonged ageing and drying on the pore structure of geopolymers has not been investigated previously. In the thesis, studies on ageing and drying of geopolymers will be conducted to fill the current lack of understanding in the research field.

2.2.2 Sol-gel synthesis

In sol-gel methodology, the synthesis of amorphous solids is carried out by containing a liquid sol in an acid or alkali medium, after which the sol is converted to a gel through the surface reaction between the sol particles and bulk solution. The pore microstructure can be controlled by manipulating the processes of ageing, drying and sintering. The advantages of sol-gel synthesis are the ease of steps, low temperature application, and the ability to tailor-make the desired pore structure prior to drying or sintering at high temperature. It is important to understand the fundamental chemistry of sol-gel synthesis, particularly on the synthesis of silica gels and glasses because the synthesis of geopolymers also utilises sol-gel methodology.

In the sol-gel synthesis of silica gels and glasses, the following routes must be followed:
1. The hydrolysis and condensation of silicates species.
2. The ageing of gel

The manipulation of each step has been found to modify the final pore structure and physical performance of silica materials. For example, the pore structure can be controlled during the hydrolysis and condensation (Brinker, 1988; Iler, 1979), or by ageing and drying at various temperatures and pressures (Einarsrud et al., 2001; Nakanishi et al., 2000; Scherer, 1999; Titulaer et al., 1994a; b), or by impregnating the formed gel in different alkali media (Goworek et al., 1999; Janowski and Enke, 2002; Vendange et al., 1996). Figure 2.3 depicts the effect of ageing, pH, time, and temperature on the BET surface area and total pore volume of silica gels. The pore volume increases, while the surface area decreases with increasing ageing time, pH, and temperature.
2.2.2.1 Hydrolysis and condensation

Hydrolysis is the attachment of OH⁻ on the surface of silica particles, which results in the dissolution of silica species into the solution to become silicic acid, i.e., Si(OH)₄. Equation (2.5) shows the simplified chemical reaction that occurs on silicon alkoxide species. As the concentration of Si(OH)₄ increases, the polymerisation of Si(OH)₄ occurs easily by forming siloxane bonds (-O-Si-O-), which produces H₂O as its by-product (Equations (2.6) and (2.7)). According to Iler (1979), the siloxane bonds grow to become ring structures, which turn into nuclei. These nuclei are linked together into branched chains, which finally become a gel during polymerisation process (Figure 2.4).

$$≡\text{Si-O-R} + \text{H}_2\text{O} \leftrightarrow ≡\text{SiOH} + \text{ROH} \quad (2.5)$$

$$≡\text{SiOH} + \text{OHSi≡} \leftrightarrow ≡\text{Si-O-Si≡} + \text{ROH} \quad (2.6)$$

$$≡\text{SiOH} + \text{OHSi≡} \leftrightarrow ≡\text{Si-O-Si≡} + \text{H}_2\text{O} \quad (2.7)$$
Geopolymerisation is the sum of several heterogeneous reactions, which take place simultaneously (Provis et al., 2005b), with hydrolysis and condensation are the main mechanistic steps (Xu and Van Deventer, 2000b; 2002a). The dissolution (or hydrolysis) of Si$^{4+}$ and Al$^{3+}$ precursors starts immediately upon contact of raw materials with alkali-silicate solutions. The polymerisation (polycondensation) of aluminosilicate gel occurs immediately after the dissolution step. It is known that high alkali concentration and high solid to liquid ratio usually complicate the mechanistic study of geopolymerisation.

From Equations (2.5) to (2.7), it can be seen that polymerisation of silica is dependent on the pH of the solution. In an acidic condition, hydrolysis occurs by rapid attack on alkoxy group (O-R) or OH-substitution that is attached to Si (Brinker, 1988), while polymerisation primarily occurs between a more and less highly condensed phase. However, in a basic condition, hydrolysis occurs when hydroxyl or silanolate anions attack Si directly (Brinker, 1988). In this condition, the Si(OH)$_4^-$ species are abundant.
due to a greater hydrolysis. At high pH, the aggregation of particles is less due to the stability of Si(OH)$_4^-$ in the solution. Therefore, the growth of particles continues not through the formation of new nuclei, but follows the “Ostwald’s ripening” mechanism, whereby the smaller, more soluble particles dissolve and re-precipitate on the surface of the larger particles (Iler, 1979). This mechanism generates bulkier polymers consisting of highly cross-linked large silica particles, larger than the ones formed in acidic condition. At ambient temperature or lower, the main particles of silica could grow to a size of 5-10 nm diameter. The growth mechanism of aluminosilicate particles in geopolymers is likely to follow the mechanism of base-catalysed polymerisation because of the high alkali concentration used during geopolymerisation. In the thesis, the correlation between changing alkali-silicate concentration and the formation of aluminosilicate particles with critical sizes will be investigated.

2.2.2.2 Ageing of gel

A prolonged ageing time affects the properties of silica gel in three ways:

1. The growth of nuclei and gel network. In a base-catalysed polymerisation, more nuclei are likely to be formed when the ageing time is prolonged. However, the growth of nuclei or particles is limited to a certain critical size, which is dependent on pH, temperature, alkali, and silicate concentration. Furthermore, the growth of silica gel usually occurs through a coarsening method (Ostwald’s ripening). Therefore, prolonged ageing time leads to a finer pore structure due to an enhanced nucleation, but the process is slowed down when nuclei reach a certain critical size.

2. The syneresis phenomenon. Syneresis is an autogenous shrinkage of silica gel, and is usually caused by the tension force exerted when water is expelled during the polycondensation process. Syneresis leads to an apparent shrinkage of gel network and narrowing in porosity as well. When condensation takes place, less space is required to accommodate the gel network due to the transformation from a liquid to solid state (Setzer et al., 2002). The extent and rate of shrinkage have been found to be influenced by the solid content in the gel, temperature of ageing, permeability of gel network, and the viscosity of pore liquid.
3. *The formation of new phases.* Prolonged ageing may also lead to the formation of crystalline products, e.g. in the preparation of zirconia from titania gels (Setzer *et al.*, 2002).

2.2.2.3 *The washing, liquid impregnation, and drying of gel*

In the thesis, fly ash-based geopolymers will be subjected to various post-treatments, which include ageing, drying, and immersion in alkali and carbonate solutions. Therefore, understanding the effect of post-treatments on the properties of silica gel, particularly on the porosity is essential. The further treatments and their effects on the pore structure of the gel can be classified into three categories:

1. *Washing.* Washing silica gels in pure water at a pH close to 7 usually results in a gel with higher pore volume and lower surface area than if they are washed in alkali-based solutions. The washing of gels in water also leads to a significant increase in the permeability of gel due to the re-occurrence of dissolution-precipitation reactions (Einarsrud *et al.*, 2001; Setzer *et al.*, 2002).

2. *Impregnating gel with alkaline and salt solutions.* Janowski and Enke (2002) suggested that impregnating porous silica gels with various alkali-based solutions leads to the formation of hierarchical pore structure in the gel. The treatment using alkali media removes both colloidal and network SiO₂ (spongy structure), which constitute the microporosity in the gel. As a result, the mesoporosity and macroporosity can be obtained with ease.

3. *Drying.* When it is applied appropriately, pore structure can be tailored directly by different drying methods alone, e.g. xerogels and aerogels (Titulaer *et al.*, 1994a).

2.2.3 *Porous aluminosilicate gel*

The synthesis of porous aluminosilicate gel can be done in acid or base-catalysed reactions. In a sol-gel synthesis of aluminosilicate gel, an alkoxy-derived silica (TMOS, TEOS) is mixed with aqueous Al-containing solution, namely Al-salts. The physical properties of wet and dry aluminosilicate gels are dependent on pH of reaction, temperature and initial Al concentration. De Witte *et al.* (1996) showed that addition of small amount of Al (10 molar %) results in an increase of surface area and a decrease of pore volume. The finer pore is attributed to a higher condensation activity of Al-
containing solution (McCormick and Bell, 1989). However, as the concentration of Al is increased (up to 25 molar %), pore volume and surface area decrease, suggesting that there is a stronger coagulation between the sol particles as a result of Al\(^{IV}\) incorporation. In general, a system of low water, low aluminium content, and high solvent content results in aluminosilicate gels that have microporous characteristics. The mesoporous gels are formed in the converse conditions (Jones et al., 1995).

The chemistry of geopolymer gel closely resembles the chemistry of aluminosilicate gel. It is found that with the inclusion of more aluminium, there is an increase in the rate and extent of gel formation, shown by the increase in pore volume and surface area (Sindhunata et al., 2006). However, the synthesis of geopolymers is different from aluminosilicate gels in terms of the raw materials and concentration of activating solution used. The incorporation of aluminium into the silicate structure is complex in geopolymerisation because of the different rates of dissolution of Si\(^{4+}\) and Al\(^{3+}\) from aluminosilicate solids. The reactions therefore are typically heterogeneous, with a low reactivity. In this case, the microstructure of geopolymers can be a mixture of geopolymer gels and aluminosilicate solids residue.

### 2.3 Zeolites

It has been suggested that geopolymer gels are the amorphous precursors of zeolitic crystals (Davidovits, 1991; 1999). Although geopolymers are aluminosilicate gels by definition, the macro-molecular structure of geopolymers resembles the the crystal lattice of various zeolites, e.g. hydroxysodalite, kalsilite, and analcime (Davidovits, 1999). The co-formation of zeolites and aluminosilicate gels (geopolymer gels) has also been reported in metakaolinite-based geopolymers (Palomo and Glasser, 1992; Palomo et al., 1999a) and fly ash-based geopolymers (Bakharev, 2005; Palomo et al., 1999b). There is a lack of understanding about the conditions which will yield crystallisation of zeolites. As a result, the correlation between polymerisation and crystallisation of aluminosilicate during geopolymerisation has never been established. In this section, the synthesis, mechanism, and kinetics of zeolites are reviewed to provide an understanding of the fundamental chemistry of zeolites. In addition, a brief review of fly ash utilisation for synthesising zeolites as industrial adsorbents is also presented.
2.3.1 The synthesis of zeolites

The synthesis of different types of zeolites is influenced by various factors, namely the reaction temperature, the composition of reactants, the pre-treatment of aluminosilicate precursors, and the presence of chemical impurities as seeds for nucleation. These factors may control the reaction kinetics by inducing or retarding nucleation and crystal growth. In 1950s, Milton (1959a; b) employed lower pressure and temperature condition (i.e. close to the boiling point of water) to make hydroxysodalite and zeolite Y (a type of faujasite). The process is more well-known as the hydrothermal synthesis of zeolites. In this process, silicate and aluminate solutions are mixed together and stirred at relatively low temperatures, from 25 to 50 °C for a period of time (Equation (2.8)). The synthesis methodology can also used in the synthesis of geopolymers, except that geopolymerisation implements a lower liquid to solid ratio.

\[
\text{NaOH (aq) + NaAl(OH)₄ (aq) + Na}_2\text{SiO}_{₃} \text{ (aq)} \\
\rightarrow [\text{Na}_a(\text{AlO}_2)_b(\text{SiO}_2)_c\cdot\text{NaOH.H}_2\text{O}] \text{ gel} \\
T_1 = 25-50 °\text{C} \quad (2.8)
\]

\[
[\text{Na}_a(\text{AlO}_2)_b(\text{SiO}_2)_c\cdot\text{NaOH.H}_2\text{O}] \text{ gel} \\
\rightarrow \text{Na}_x[(\text{AlO}_2)_x(\text{SiO}_2)_y]\cdot m\text{H}_2\text{O zeolite crystal + solution} \\
T_2 = 25 \text{ to } 175 °\text{C} \quad (2.9)
\]

The mixture containing aluminosilicate precursors is stirred and heated at a temperature ranging from 25 °C to 170 °C in an autogenous pressure, generated by water vapour pressure for a few hours or days (Equation 2.9). The amorphous precursors start to form nuclei, which grow to form zeolitic crystals. Slurry containing zeolites is filtered, washed, and dried. Zeolites A, X, Y, T, and P can be synthesised in hydrothermal conditions, with a percentage yield reaching up to 100% depending on the conditions and reactants used. As it has been mentioned earlier, the formation of zeolites is likely possible, even if the synthesis is implemented in more constrained conditions, such as the conditions used to synthesise geopolymers (Bakharev, 2005; Palomo and Glasser, 1992; Palomo et al., 1999a; b).
2.3.2 Zeolites from fly ashes

Waste based materials, such as fly ash have been used to synthesise zeolites because of the technological and economical benefits. The application of fly ash derived zeolites is directed toward the immobilisation of toxic metals (Lin and Hsi, 1995) and the manufacturing of molecular sieves (Chang and Shih, 1998; Li et al., 2006; Querol et al., 1997a). The use of Class F fly ash is preferred in the synthesis of zeolites because of higher amorphous aluminosilicate phases, and low Ca content. With higher Al and Si, but lower Ca the supersaturation period is achieved at a longer time, which allows a better workability and greater reactivity. The types of zeolite formed from the activation of fly ash with alkali solutions include Na-P1, analcime, hydroxysodalite, faujasite, phillipsite, cancrinite, chabazite and bayerite (Larosa et al., 1992; Querol et al., 1995; 1997a). The formation of these zeolites are determined by the compositional ratio of silicon to aluminium in glassy phases of fly ash, the alkali concentration, and temperature of reaction (Catalfamo et al., 1993; Murayama et al., 2002; Querol et al., 1997a).

Currently, there are three different methods employed to synthesise zeolites from fly ash:

1. The hydrothermal hot pressing method (Sato et al., 1997; Wu, 2002). In this technique, a high mechanical pressure (up to 20 MPa) at hydrothermal temperature (up to 120 °C) is used not only to synthesise zeolites, but also to solidify waste materials. The technology is useful to solidify waste slurry for easier handling and disposal, and also to encapsulate toxic metal wastes.

2. The hydrothermal synthesis of zeolites. The synthesis of zeolitic materials from fly ash by alkali-hydroxide at hydrothermal reaction has been widely investigated (Lin and Hsi, 1995; Murayama et al., 2002; Querol et al., 1997a; b). Similar to the synthesis of molecular sieve zeolites, fly ash is mixed with solutions containing alkali-hydroxide and stirred at hydrothermal conditions (80-200 °C). The solid is separated from the liquid, washed, and filtered. However, the efficiency of this method reaches only up to 75% because the crystalline aluminosilicate phases in fly ashes, e.g. mullite and quartz, remain inert.
3. The fusion of fly ash and alkali. In this method, fly ash and alkali solid are pre-treated (fused) in a furnace at 500-650 °C for a few hours. The fused solid is dissolved in water to form amorphous precursors at ambient temperature before being further treated at hydrothermal temperatures (Chang and Shih, 1998; Shigemoto and Hayashi, 1993). It is found that the fusion of fly ash with alkali-hydroxide at very high temperatures causes the solid-state reaction to take place. The product yield from the fusion can be as high as 100%. Some of the crystalline phases, such as mullite and quartz are fully reacted at very high alkali concentration.

In the thesis, the formation of zeolites during fly ash-based geopolymerisation will be investigated. Furthermore, zeolites will be synthesised from fly ash by combining the fusion and hydrothermal methodologies.

2.3.3 Kinetics and mechanisms

It is generally agreed that there are two main mechanisms in the crystallisation of zeolites, i.e. nucleation and subsequent growth of crystals. Prior to nucleation, there is an ‘induction period’, a period when aluminate and silicate anions rearrange themselves in order to form a polymeric network that later nucleates. During the induction period, the heat of reaction is minimal (near to zero). Typically, the gel network will grow to become nuclei of critical size. These nuclei usually exist in two states: 1) a single large nuclei and 2) group of small nuclei forming short-range ordering gel network. Smaller nuclei will dissolve and serve as reservoir for larger nuclei, which grow to become a more ordered crystalline structure (Ciric, 1968; Kerr, 1966b). Then, crystallisation proceeds through the mass transfer of dissolved species to the crystal surface. After the initial rapid growth, continued crystal growth is difficult to maintain and the yield of reaction will be depleted due to the exhaustion of aluminosilicate anions available in the solution.

There are two types of nucleation in zeolite synthesis, i.e. homogenous and heterogeneous types. In a homogeneous nucleation, nucleation takes place only in a solution-based system. However, in a heterogeneous nucleation, the extraneous surface is introduced in order to facilitate nucleation (Randolph and Larson, 1988). In a more
recent investigation, heterogeneous nucleation is believed to take place more than homogeneous nucleation (Serrano and Van Grieken, 2001). Subotic and Sekanovic (1986) proposed the ‘autocatalytic mechanism’ to describe the heterogeneous nucleation in solution-mediated reaction. During early stages of reaction, small microcrystallites remain dormant in the gel phase. The increasing surface area of growing crystals leads to more consumption of solute, which in turn results in the increase of the rate of gel dissolution. The increasing rate of gel dissolution auto-induces the rate of activation of those dormant microcrystallites. In some cases, soluble species do not participate at all, so that the reorganisation of the amorphous or pseudo-crystalline is only through solid-solid transformation (Serrano and Van Grieken, 2001).

The mechanism and kinetics of nucleation and growth of crystals during the synthesis of zeolites can be affected by many factors, such as:

1. **Temperature.** Elevated temperature increases the solubility of nutrients in the solution. As a result, the nucleation and crystal growth may be accelerated if the temperature of reaction is increased.

2. **Ageing time.** Prolonged ageing time usually leads to an early formation of small nuclei (small particles). However, the longer the ageing time applied, the more heterogeneous will the nuclei formed be (Koroglu et al., 2002). It is also found that the crystallisation process is accelerated in aged solutions. In some cases, different types of zeolites may also be formed.

3. **The presence of impurities or ‘seeds’**. Nishi and Thompson (2002) have shown that adding seeds into the aluminosilicate precursors leads to an increase in surface area of crystals, increase in the consumption of reagents, and reduction in the degree of supersaturation.

### 2.3.4 The chemistry of the incorporation of aluminium into silicate solution

A review of aluminium chemistry in silicate solutions is presented because it is closely connected to the chemistry of zeolite and/or geopolymer gel formation. The chemistry of aluminosilicate solution has been extensively studied and published in the literature (Dent Glasser, 1984; Dent Glasser and Harvey, 1984; Harvey and Dent Glasser, 1989;
Harris et al., 1996; 1997; McCormick and Bell, 1989; McCormick et al., 1989b; North and Swaddle, 2000; North et al., 2001; Samadi-Maybodi et al., 2001; Swaddle, 2001). The studies can be divided into 3 main areas: 1) The structure of silicate anions in the silicate solution; 2) The incorporation of aluminium into the structure of silicate anions; and 3) The effect of cations on the chemistry of aluminosilicate solutions.

2.3.4.1 The structure of silicate anions
At low pH and high silica concentration, the dissolution of silicate species is low. Thus, the colloidal silica particles are formed easily. However, at high pH and low silicate concentration, silicate anions are more stable than colloidal silicas (Iler, 1979). The synthesis of porous gels and glasses, particularly geopolymers is usually carried out in a basic condition. Thus, soluble silicate anions are readily available in the solution. The structure of dissolved silicate is dependent on the pH, silicate ratio (is usually expressed as SiO$_2$/M$_2$O or m, with M = alkali metal cations), and alkali cation size (Harris and Knight, 1983a; b). At higher pHs (> 12), for m = 0.5 and 1, the presence of larger, cyclic trimeric species is more pronounced than its linear oligomeric anions. For m > 1, the majority of silicate anions are in Q$^3$ species (the superscript refers to a number of neighbouring Si atoms which are tetrahedrally bonded by bridging oxygen atom). As more silicate is added, at m > 3, all anions are in Q$^4$ structures. Rings and cages are the preferred form of the silicate species, while chains that are larger than trimers are rare at higher m ratios (Dent Glasser, 1984; Dent Glasser and Harvey, 1984). However, these oligomers usually depolymerise quickly at high pH or upon dilution (McCormick and Bell, 1989). In the thesis, the silicate ratios (m) of activating solutions will be varied from 0.0 to 2.0. Therefore, understanding the presence of various anion structures and their chemistry at different silicate concentrations will help to understand the effect of changing silicate concentration on geopolymerisation.

The distribution of silicate anions shifts toward larger species as the cation size increases, as shown in Figure 2.5 (McCormick and Bell, 1989). Wijnen et al. (1990) proposes that the hydration shell of alkali cations becomes the contributing factor to different dynamics of silicate anions. Furthermore, Na$^+$ and Li$^+$ with large hydration shells are known better as water structure formers, while K$^+$, Rb$^+$, and Cs$^+$ are known as
water structure breakers (McCormick and Bell, 1989). The water structure former cations allow the exchange between water and silicate structures to occur, which results in a greater extent of polycondensation.

![Figure 2.5 The distribution of silicate anions with respect to different cation size (McCormick and Bell, 1989). R represents SiO$_2$/M$_2$O ratio, Q$^0$ represents no neighbouring Si atom (a monomer), Q$^1$ represents one neighbouring Si atom (a dimer), Q$^2$ represents a trimer, Q$^3$ represents a cyclic trimer, Q$^4$ represents tetramer, Q$^5$ represents a cyclic tetramer.](image)

The effect of alkali metal cations on the dynamic exchange of silicate anions structure will not be discussed further here, but their effects on the aluminosilicate anions will be, as it is the primary interest of this review to understand the formation of porous solids from aluminosilicate solution.

2.3.4.2 The incorporation of aluminium into silicate anions

In aluminosilicate solution, aluminium ions are in either 4-fold or 6-fold coordination. The type of aluminium anions is relatively simple, i.e. Al(OH)$_4^-$ at high pH, Al(OH)$_4^-$ and Al(H$_2$O)$_6^{3+}$ at low pH condition (Akit et al., 1972). The degree of polymerisation
of aluminosilicate is found to increase with increasing cation radius, silica ratio, and concentration, but decrease with the increase in temperature (McCormick and Bell, 1989; McCormick et al., 1989b; Ray and Plaisted, 1983). Principally, the negative bearing Al(OH)$_4^-$ species is incorporated more easily into silicate species that have less ionic charge. At a low silica concentration, the cyclic trimeric silicate anion, which is the predominant species gives less ionic charge than its linear trimeric silicate (McCormick et al., 1989b). This is because in a cyclic trimetric silicate anion, the charge is distributed in each Si atom, which results in a less repulsive effect toward incoming cations. However, at a higher silicate concentration, larger silicate anions (Q$^3$ and Q$^4$ structures) prevail, with rings and cages being the preferred structures (Dent Glasser, 1984; Dent Glasser and Harvey, 1984). In this condition, the incorporation of aluminium is harder due to the large and stable silicate structure, which can be seen from the longer gelation time at high silicate concentration (Dent Glasser, 1984; Dent Glasser and Harvey, 1984).

It was originally thought that the cage and ring structures in solutions of high silicate concentration controlled the framework of zeolites formed. However, Swaddle (2001) proposed that the kinetics of aluminium and silicate exchange on small, acyclic aluminosilicate species are much faster than either the silicate or cyclic aluminosilicate species. Therefore, contrary to the traditional picture, cyclic and cage-like aluminosilicate species may not be directly involved in the crystallisation but simply serve as reservoirs for small, active, acyclic species responsible for crystal growth. This also means that the silicate or aluminosilicate structures that are dominant among solute species may bear little or no geometric relation to the zeolitic framework.

2.3.4.3 The effect of cations
Dent Glasser and Harvey (1984) observed that increasing the cation size results in the increase in the number of Al-O-Si bonds in aluminosilicate solutions and gels. In addition, larger cations, such as K$^+$ cause a redistribution of Si to larger silicate anions through the cation-anion pairing mechanism. This means K$^+$ prefers to associate with larger silicate anions, which results in a more rapid gelation time at a high silicate concentration (McCormick and Bell, 1989; McCormick et al., 1989a).
Nonetheless, the effects of cations on the aluminosilicate chemistry have been found to be more complicated to explain than a simple cation-anion pairing mechanism because the cations have also been believed to direct the structural formation in zeolites. The following hypotheses are postulated to account for the effect of alkali cations on aluminosilicate gel formation (Kinrade and Pole, 1992):

1. M\(^+\) cations are believed to influence aqueous aluminosilicate to achieve equilibria by stabilising the oligomeric species, so that the formation of crystal structure can be directed appropriately.
2. Hydrated M\(^+\) cations have a templating effect whereby silicate or aluminate species replace the water of hydration sufficiently long that they become bound together within a structural configuration at or near the crystal surface. The intimate association of aluminosilicate and cation species may well be the template for the crystallising zeolite. Therefore, the hydration capacity of different cations can become one of the significant factors that determine the mechanism and kinetics of aluminosilicate gelation. For example, at high Si, and low alkali concentrations, very long gelation time occurs because the species are unable to rearrange to provide the free aluminate essential for the formation of nutrient. In this instance, the gelation process is solely dependent on the hydration capacity of the cation (Wijnen et al., 1990).

Although it is well established that certain cations or other solute species can promote the formation of particular structures, there is often no obvious correlation between the structure and solute speciation in the supernatant liquid. The question of the role of cations and other solutes in the gelation mechanism cannot be simply answered (Swaddle, 2001). The effect of different cation types in geopolymerisation will be discussed in Section 2.4.5.

### 2.4 Geopolymers

The previous sections have established the close relationship between the synthesis, chemistry, and the properties of cement, porous silica (and aluminosilicates), zeolites, and geopolymers. In this section, a review of the history, application, synthesis,
chemistry, and recent development of geopolymers is presented. The aim is to provide background knowledge of geopolymer research in a chronological and systematic fashion.

2.4.1 History and application of geopolymers

The first and foremost drive for the research and commercialisation of geopolymer technology has been the need to find alternative materials to substitute OPC as a construction material. With the need for a greater production for OPC supply, the need to find alternative cleaner materials becomes greater. The calcination of limestone (the main mineral in the cement production) with silico-aluminous minerals at high temperatures (1450-1500 °C) produces green house gas (CO₂) as its by-product (Equation 2.10). Studies have shown that for every tonne cement produced, 0.55 tonnes of chemical CO₂ is generated, which is 8 times higher than emissions resulting from metallurgical activities (Davidovits, 1994).

\[
5\text{CaCO}_3 + 2\text{SiO}_2 \rightarrow (3\text{CaO},\text{SiO}_2) + (2\text{CaO},\text{SiO}_2) + 5\text{CO}_2
\]  (2.10)

From cement manufacturing alone, the forecasted green house gas emission is expected to rise about 6% annually from 1988 to 2015 (Davidovits, 1994). Many programs are aimed at increasing the use of recyclable materials, by blending cements with mineral products in order to reduce the CO₂ emissions. These minerals are of natural origins, like kaolinite or calcined kaolinite (metakaolinite); or industrial by-products, like blast furnace slag, from the iron-steel making industry, and fly ash, from the combustion of coal. These mineral admixtures are at most 30% by weight of OPC mixes. Excess amount of mineral admixtures is likely to be detrimental to the OPC properties (Dhir and Byars, 1993). Apart from replacing cement with mineral admixtures, there is no other known sustainable technology to reduce the use and production of cement any further.

The term ‘geopolymer’ was first coined in the mid 1970's by Davidovits (1991) to describe his findings of a new breed of aluminosilicate binder. Early geopolymers were synthesised by mixing clay derived minerals, i.e. kaolinite with alkali solutions, NaOH
or KOH at temperatures ranging from 25 to 120 °C. In order to achieve a higher reactivity, kaolinite is converted to metakaolinite through calcination at 650 °C for a few hours. The resulting metakaolinite has a high content of amorphous aluminosilicate phases and smaller particle size, which increases the surface area, and results in a higher reactivity upon contact with alkali solution. In this instance, metakaolinite-based geopolymers had been found to exhibit superior mechanical and fire-resistant properties compared to any other organic binders. Early geopolymer materials set rapidly at low temperatures, only a few hours at 30 °C, or a few minutes at 85 °C, or a few seconds in a microwave oven (Davidovits, 1999). They display compressive strength as high as 60 MPa after just one day of curing, and the strength will continue to increase up to 100 MPa. They also exhibit a 4-7 Mohs hardness, and are thermally stable upon subjection to very high temperature (1000-1200 °C), where all organic resins or cement fail to perform (Davidovits and Davidovics, 1998). These findings have made geopolymers potentially useful for ceramic, refractory lining materials, as well as for building materials.

Numerous studies have also used metakaolinite as the base ingredient for the synthesis of geopolymers (Barbosa et al., 2000; Palomo and Glasser, 1992; Rahier et al., 1996a; b; 1997). However, the use of metakaolinite is limited to research purposes because of the low workability and high liquid requirement. Therefore, the choice of raw materials becomes highly dependent on many other factors, e.g. the availability, the cost, the workability and the purpose of application. Theoretically, any aluminosilicate source can be used to make geopolymers, including natural aluminosilicate minerals (Xu and Van Deventer, 2000b; 2002a) and pure aluminosilicate glasses (Hos et al., 2002). A number of authors have utilised waste resources as alternative raw materials, namely fly ashes (Fernandez-Jimenez et al., 2006c; Palomo et al., 1999b; Van Jaarsveld et al., 1997; 1999) and blast furnace slags (Cheng and Chiu, 2003; Krivenko, 2002; Krivenko and Kovalchuk, 2002). The use of waste-based materials has produced cheap, efficient, yet high quality geopolymers. In addition, it has also benefited the environment at least in two aspects: 1) the reduction of cement production, which leads to the reduction of greenhouse gas emission. Geopolymers could utilise 100% fly ashes and/or slags while cement only uses up to 30% of fly ashes and/or slags as admixtures; and 2) it provides
an alternative technology for waste treatment and toxic waste encapsulation (Bankowski et al., 2004; Fernandez-Jimenez et al., 2005b; Khalil and Merz, 1994; Palomo and de la Fuente, 2003; Palomo and Palacios, 2003; Van Jaarsveld et al., 1997; 1999).

In addition, geopolymers have been shown to be a better material than cement and concrete due to the following properties:

1. *The alkali-aggregate reaction (AAR).* AAR is well-known to be a major problem, and usually causes deterioration in the long term strength of concrete (Mindess and Young, 1981). Pozzolanic materials are usually added to the OPC concrete in order to react with alkali solutions or act as fillers to prevent large liquid movement in the pores. However, alkali-activated waste materials concrete, such as slag concrete has less extent of AAR (Davidovits, 1999; Metso, 1982; Talling and Brandstetr, 1989). It is acknowledged that the high alkaline environment causes the carbonation process, although its long term effects are yet to be fully understood.

2. *The fire resistance of geopolymers.* Geopolymers do not reserve water in their structure for further hydration as OPC does. The rigorous movement of water in hardened OPC during drying or high temperature application often causes significant autogenous shrinkage and cracking. It has also been reported that typical OPC fails at 300-400 °C (Neville, 1995), whereas the melting point of geopolymers varies from 650-1200 °C. Recent applications have included organic and inorganic fibres and fillers into making hybrid geopolymer composites that give superior strength and heat properties (Barbosa and Mackenzie, 2003; Cheng and Chiu, 2003; Hussain et al., 2004).

3. *The containment of toxic waste.* The use of porous materials, such as OPC and commercial adsorbents to contain toxic metal waste is common in the mineral and mining industry. Often, the usage is limited by the performance and cost of materials, for example OPC takes a long time to fully harden which makes the containment in a short period difficult. On the other hand, commercial adsorbents, such as zeolites are more expensive than OPC. The use of fly ash- and slag-based geopolymers is shown to be ideal for these types of application (Davidovits, 1996; Phair et al., 2004; Van Jaarsveld et al., 1997; 1999).
2.4.2 The chemical structure and properties of geopolymers

The basic building block of a geopolymer is a tetrahedral silicon and aluminium bonded through sharing of oxygen atoms. Only Al\textsuperscript{IV}, not Al\textsuperscript{V} or Al\textsuperscript{VI} is found to be suitable to replace Si\textsuperscript{IV} in a tetrahedral arrangement. The basic monomer unit is a sialate, with Mn(-(SiO\textsubscript{2})\textsubscript{z}-AlO\textsubscript{2})\textsubscript{n}.wH\textsubscript{2}O to be the empirical formula for polysialates, where z is 1,2,3; M is a monovalent cation, such as potassium or sodium; and n is the degree of polycondensation (Davidovits, 1991).

The sialate structure carries a negative charge due to the substitution of Si\textsuperscript{4+} with Al\textsuperscript{3+}. The excessive charge is balanced by an alkali metal cation (K\textsuperscript{+} or Na\textsuperscript{+}). Based on the number of silicon atoms replaced by aluminium, three different types of monomeric -Si-O-Al- structure are believed to define geopolymers. Davidovits (1999) classified the polymeric forms of -Si-O-Al- into polysialate (PS), polysialate-siloxo (PSS), and polysialate-disiloxo (PSDS). The structures of polysialates and their respective application are listed in Table 2.3. PS and PSS can be easily synthesised using sol-gel chemistry at room temperature, and their ranges of applications extend to the immobilisation of toxic waste and construction products. However, PSDS possesses superior physical and thermal properties compared to the formers, thus it can be used as a refractory lining or tooling composite material (Davidovits, 1991).

Davidovits (1991; 1999) proposed that the macro-molecular structures of PS, PSS resemble those large, cage structures of zeolites based on the similar mechanism and kinetics observed between the hydrothermal synthesis of zeolites and geopolymers from kaolinite. Na-PS (sodium polysialate) resembles the hydroxysodalite framework of Na-phillipsite, K-PS and Ca-PS resemble the frameworks of kalsilite and analcime respectively, while (Na,K)-PSS (sodium, potassium polysialatesiloxo) gives the phillipsite-like framework.

Barbosa and Mackenzie (2003) subjected metakaolinite-based geopolymers (Na- and K-PSS structures) to various thermal analyses and observed that there is an initial water loss at around 200 °C, which is associated with the evaporation of physically-bound water. The water loss at around 200 °C leads to a small degree of shrinkage; however,
the structure of Na-PSS is dimensionally stable at 250-800 °C. Irreversible shrinkage only occurs at 800 °C and higher, i.e. when the gel crystallises. The Na-PSS begins to melt at temperatures ranging from 1200-1300 °C, while the K-PSS shows little sign of melting at 1400 °C. In this instance, it seems that the K-PSS structure has more thermal stability than Na-PSS, and the thermal properties of both geopolymers are affected by the amount of water in the structure as well. At 1000 °C, the amorphous structure of K-PSS is replaced by the crystalline feldspars, leucite, and kalsilite. An NMR study on both systems suggest that charge-balancing alkali cations in the K-PSS and K-PSDS behave similarly to those in Na-PSS and Na-PSDS respectively, i.e. in terms of dehydration and crystalline transformation mechanisms. On the other hand, Rahier et al. (1996b) has found that the glass transition of metakaolinite-based geopolymers occurs at 650 °C, rather than at 800 °C. The difference is mainly caused by the different composition of Si:Al and water content from the geopolymers. In fact, these two factors and also the alkali concentration (Al/M ratio), are parameters that determine the structure and physico-chemical properties of geopolymers.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Monomeric structure</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysialate (PS)</td>
<td>Mn-(Si-O-Al-O-)n</td>
<td>- thermal insulation</td>
</tr>
<tr>
<td>Si:Al = 1:1</td>
<td></td>
<td>- fire-resistant board</td>
</tr>
<tr>
<td>Polysialate siloxo</td>
<td>Mn-(Si-O-Al-O-Si-O-)n</td>
<td>- refractory for aluminium casting</td>
</tr>
<tr>
<td>(PSS) Si:Al = 2:1</td>
<td></td>
<td>- high-performance cements</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- toxic wastes</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- fire resistant composites</td>
</tr>
<tr>
<td>Polysialate disiloxo</td>
<td>Mn-(Si-O-Al-O-Si-O-Si-O)n</td>
<td>- fire resistant composites</td>
</tr>
<tr>
<td>(PSDS) Si:Al = 3:1</td>
<td></td>
<td>- tooling materials for use in the temperature range from 650 - 1000 °C</td>
</tr>
</tbody>
</table>
Barbosa et al. (2000) found that irrespective of composition, curing, and drying method, all types of geopolymers possess a lack of long-range atomic order. This is reflected by the absence of a crystalline XRD pattern and the broad $^{29}$Si NMR resonance. The optimum formation of Na-PSS polymer occurs when the ratio of SiO$_2$/M$_2$O is 4.0 and the ratio of H$_2$O/Na$_2$O is 10. Based on solid-state NMR-MAS study, Barbosa et al. (2000) also proposed a new model for the molecular structure of geopolymer gel, whereby the framework structures are saturated in Al, e.g. SiQ$_4$ (3Al), as shown in Figure 2.6a (SiQ$_4$ (3Al) means there are 3 neighbouring Al atoms for a tetrahedral Si). The new model contains Si and Al tetrahedra which are randomly cross-linked to provide cavities, in order to accommodate the charge-balancing hydrated sodium ions. This arrangement fits with the $^{29}$Si and $^{27}$Al NMR data as the Q$_4$ (2Al) and Q$_4$ (3Al) are believed to be the two predominant species in metakaolinite-based geopolymers. This model is preferred because its structure is in a more disordered state and possesses the ability to accommodate hydrated sodium ions, unlike the previous models suggested by Davidovits (1991), as shown in Figure 2.6b.

2.4.3 The chemistry of geopolymerisation

In terms of synthesis, chemistry, and properties, geopolymers differ slightly from alkali-activated cements (AAC). The synthesis of geopolymers utilises solid sources that are rich in amorphous aluminosilicates and activating solutions, which include both alkali and silicate solutions. However, AAC, as the name suggests, usually blends pozzolans with OPC in order to improve the physical properties by inducing a greater pozzolanic reaction in cement paste. Recent publications (Roy, 1999) have also incorporated 100% waste materials, such as fly ash and slag to synthesise AAC. The activating solutions in AAC include, but not limited to alkali-hydroxide solutions, namely NaOH, KOH, Ca(OH)$_2$, and other alkaline salt solutions (Fernandez-Jimenez and Palomo, 2005). Due to the blending with OPC, the appearance of amorphous aluminosilicate, CSH gel, and other semi-crystalline phases, namely ettringite and monosulphoaluminate is evident in AAC, but rare in geopolymers.
Figure 2.6 (a) A semi-schematic structure for Na-PSS from Barbosa et al. (2000) and (b) A model for Na-PSS from Davidovits (1991). The marked Si atoms indicate the Q4 (2Al) and Q4 (3Al) respectively, where ‘4’ refers to the tetrahedral Si-O structure, and the prefix before Al refers to the numbers of neighbouring Al atoms in tetrahedral Si-O.
Geopolymers are also unique in comparison to any other aluminosilicate materials, (e.g. aluminosilicate gels, glasses, and zeolites). Firstly, the concentration of solid in geopolymerisation is higher than in aluminosilicate gel or zeolite synthesis (see Section 2.2 and 2.3). Geopolymers are believed to be an amorphous metastable phase of zeolites (zeolitic precursors) that can be converted to a more well-defined crystalline phase (zeolites) provided that the right conditions and reactant concentrations are used (Xu and Van Deventer, 2002b). A recent review by Provis et al. (2005c) suggested that that geopolymer is constituted from agglomerates of zeolitic nanocrystals compacted by an amorphous gel phase. The degree of crystallinity is affected by reaction conditions and starting reactant concentration, particularly silicate and alkali concentrations.

Based on an earlier reaction model by Davidovits (1999) and other authors (Xu and Van Deventer, 2000b; 2002a), the reactions in geopolymerisation can be separated into three main mechanistic steps, i.e. dissolution/hydrolysis, restructuring, and polycondensation/gelation. These three mechanisms may occur concomitantly, and are reversible to some extent (Phair and Van Deventer, 2001; Phair et al., 2001). The kinetics of each step vary depending on the type of aluminosilicate solid, the solid to solution ratio, the concentration of silicate, alkali, water content, and the reaction condition. Each step will be discussed in greater detail.

1. The dissolution/hydrolysis step. The geopolymerisation starts with the hydrolysis of H+ with monovalent cations (Na+, K+) from the bulk solution on the aluminosilicate solid surface. This is then followed by continuous dissolution of aluminosilicate precursors. The dissolution proceeds from the breaking of Si-O-Si or Si-O-Al bonds in the aluminosilicate particles (sol) to form reactive precursors Si(OH)4 and Al(OH)4− in the solution. The dissolution step is likely to occur concomitantly with the gelation of aluminosilicate, which occurs usually on the solid surface as the density of gel is higher nearer to the surface (McCormick and Bell, 1989).

2. The restructuring step. In the solution, the aluminosilicate precursors are mobile and are able to partially orientate themselves to obtain a more thermodynamically stable state before they gel through polycondensation mechanism (Lee and Van Deventer, 2002b).
3. The gelation step. The supersaturated condition is reached when the concentrations of dissolved species are higher than the saturated concentrations. At the point of supersaturation, polymerisation of $\text{Al}^{3+}$ and $\text{Si}^{4+}$ occurs immediately. The polymerisation step is also marked by extrusion of molecular water from geopolymer gel, thus shrinkage of material is usually observed as well.

Recently, Provis et al. (2005b) proposed a hypothetical reaction pathway for the synthesis of metakaolinite-based geopolymers, which is illustrated in Figure 2.7 and Table 2.4. The reaction model is based on the weathering of aluminosilicate minerals in alkaline environment (Faimon, 1996). The silicon to aluminium ratio is assumed to remain constant throughout the progress of reaction, i.e. 2:1. The kinetics modelled was compared with the experimental kinetics obtained from activating metakaolinite in Differential Scanning Calorimetry at an isothermal temperature, 35 $^{\circ}$C. So far, this kinetic model has been more fundamental and descriptive than any previous models. However, it still lacks the experimental data to support the validity of each step on different solid-liquid systems, water contents, and reaction temperatures.

![Figure 2.7 The possible reaction pathways in geopolymerisation (Provis et al., 2005b). The description for each symbol is presented in Table 2.4, and the “$k_n$”s represent the kinetic constants for individual reactions.](image)
Table 2.4 The description of symbols in Figure 2.7 (Provis et al., 2005b).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>Metakaolin, $\frac{1}{2}(\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2)$</td>
</tr>
<tr>
<td>S</td>
<td>Silicate monomer, Si(OH)$_4$</td>
</tr>
<tr>
<td>A</td>
<td>Aluminate monomer, Al(OH)$_4$</td>
</tr>
<tr>
<td>O</td>
<td>Aluminosilicate oligomer, AlSi$_2$O$_2$(OH)$_6$ $^-$</td>
</tr>
<tr>
<td>D</td>
<td>Silicate oligomer – unreactive, represented by dimmer, Si$_2$O(OH)$_6$</td>
</tr>
<tr>
<td>P</td>
<td>Amorphous aluminosilicate polymer, formed by combination of two units of species O</td>
</tr>
<tr>
<td>N</td>
<td>Zeolitic nuclei formed from species O</td>
</tr>
<tr>
<td>G</td>
<td>Aluminosilicate (high-silica) gel formed by addition of silicate monomer to species P</td>
</tr>
<tr>
<td>Z</td>
<td>Zeolitic phases (low-silica), formed by addition of A, S, and N</td>
</tr>
</tbody>
</table>

2.4.4 The effect of soluble silicate

The mechanism and kinetics of geopolymerisation are largely affected by at least three factors, namely silicate concentration, type and concentration of alkali metal cations, and curing conditions (e.g. temperature, time, and humidity). The physical properties of metakaolinite-based geopolymer have been found to improve significantly when more silicate is added (Davidovits, 1991; Palomo and Glasser, 1992; Palomo et al., 1999a). The same effect is also seen for fly ash-based geopolymers (Palomo et al., 1999b). Xu and Van Deventer (2002b) observed that optimal geopolymerisation of the stilbite/kaolinite mixture is highly dependent upon the silicate concentration used, and only occurs when silicate solutions are homogeneously dispersed in the presence of alkali (MOH, where M = Na, K) prior to the addition of solid minerals.

The effect of addition of soluble silicate in the synthesis of geopolymer was firstly investigated in a more thorough fashion by Rahier et al. (1996a; b; 1997). Instead of geopolymer, LTIG (Low Temperature Inorganic Gel) is the term used to describe the material, although the synthesis and chemistry bear similar resemblance to those of geopolymer materials. From the study, LTIG is found to have a high yield stress and compressive strength which are comparable to a conventional glass or ceramic material,
but does not require additional drying and sintering during the synthesis. LTIG is synthesised by activating calcined kaolinite (metakaolinite) in Na-silicate solutions with SiO$_2$/Na$_2$O molar ratio of 0.00 - 2.15. Rahier et al. (1996a) proposed that optimum silicate ratio is obtained where Al in metakaolinite is completely consumed in the silicate structure. This means that the optimum Al/Na ratio should be equal to one so that for each Al present in the aluminosilicate structure, one cation is needed to balance the excess charge, as illustrated in Equation (2.11)

\[
(Na_2O)(SiO_2)_{1.4}(H_2O)_x + (Al_2O_3)(SiO_2)_{2}(H_2O)_{0.05} \\
\rightarrow (Na_2O)(Al_2O_3)(SiO_2)_{3.4}(H_2O)_z
\]

(2.11)

where x and z refer to the numbers of water molecules bound in the silicate solution and LTIG respectively. The effect of alkali concentration (H$_2$O/M$_2$O) on the reaction kinetics, heat of reaction, and composition of gel is not as significant as the effect of silicate concentration (SiO$_2$/M$_2$O).

Fernandez-Jimenez and Palomo (2002) used higher silicate concentrations (SiO$_2$/Na$_2$O=1.0 - 6.0) and found an optimum ratio of 1.7 for fly ash-based geopolymers. However, the study does not fundamentally explain the effect of silicate ratio on the chemistry of geopolymerisation. Phair (2001) used non-reactive zirconia particles to investigate the surface chemistry and surface reactions of polysialate species. It is found that the compressive strength of zirconia-incorporated fly ash-based geopolymers is higher than the non-zirconia geopolymers. The basis of this increase in strength has been hypothesised to be due to the formation of specific zirconia associated 3-dimensional polysialate species. It is established that the adsorption of silicate species onto zirconia particles is initially influenced by the concentration of hydrated cation, but the subsequent adsorption is controlled by polycondensation of silicate species. The extent of polycondensation is dependent on the polymerisation of silicate species and amount of co-precipitation of silicate species with sodium, which varies depending on the pH of the solution. As the pH is increased, the concentrations of dissolved silicon and aluminium in the solution are also increased. It is concluded that silicate and
polysialate adsorption onto zirconia are greatest when monomeric silica species is abundantly present in the solution.

Lee and Van Deventer (2002b) investigated the effect of soluble silicate by leaching fly ash in various silicate concentrations at $\text{SiO}_2/\text{M}_2\text{O} = 0.0\text{-}1.0$. The leached fly ash was separated from the supernatant solution, and then subjected to infrared (FTIR) and X-ray diffraction (XRD) analyses, while the solution was subjected to elemental analysis (ICP-OES). There is a threshold of silicate concentration, i.e. at $\text{SiO}_2/\text{M}_2\text{O} \approx 0.2$, whereby further dissolution is inhibited by the formation of secondary polysialate precipitates on the fly ash particles. For fly ash leached in significantly high soluble silicate concentration, the re-structuring of the amorphous aluminosilicates takes place, whereby surface gel with similar morphology and elemental composition is observed. Lee and Van Deventer (2003) also assumed that the extent of dissolution can be used to predict the extent of reaction of fly ash-based geopolymer. By plotting the calibration curve of the peak intensity and the absorption peak of Al-O-Si bonds in the leached fly ash, one can determine the extent of hydrolysis of particle surface, and thus determine the extent of reaction. Although this finding is significant, its reliability and applicability are limited to the dissolution step of geopolymerisation, not the overall process.

Furthermore, Phair and Van Deventer (2002) studied the use of sodium aluminate to synthesise geopolymers. Using $^{27}$Al NMR analysis, they found that the coordination of aluminium reflects the overall mechanism and ion pair formation. Dilution with NaOH solution largely promotes the 6-coordinated Al, while KOH solution largely promotes 4-coordinated Al sites, with both solutions show an increase in the amount of 6-coordinated Al as the concentration of OH$^-$ increases. Whilst it is technically possible to synthesise geopolymer using alkali-aluminate solution, due to cost and other factors, the use of sodium aluminate is not practical.

2.4.5 The effect of cations (Na, K, Ca)
In the chemistry of aluminosilicate solution, Na$^+$ cation is believed to enhance the dissolution of amorphous phase (nucleation) due to its association with monomeric
silicate anion, while K\textsuperscript{+} cation is believed to enhance the growth of gel network due to its association with larger aluminosilicate anions (McCormick and Bell, 1989). The similar behaviour of alkali metal cations is also seen in geopolymerisation. Van Jaarsveld and Van Deventer (1999) showed that the extent of dissolution of aluminium and silicon precursors is larger in Na-, than in K-based geopolymers. However, the degree of gel formation in K-based geopolymers is higher than in Na-based geopolymers.

Xu et al. (2001) studied the geopolymerisation of natural aluminosilicate minerals, mainly stilbite, kaolinite, and feldspars. A model of a five-membered aluminosilicate ring framework using ab-initio Hartree-Fock calculation was established, which is initiated by the high dissolution of stilbite \([\text{NaCa}_4(\text{Si}_{127}\text{Al}_9)\text{O}_{72.3}\text{H}_2\text{O}]\) during leaching with alkali hydroxide solutions (Xu and Van Deventer, 2000a). The dissolution mechanism of stilbite is shown to involve cation-anion pairing mechanism, whereby Na\textsuperscript{+} cation gives a stronger ion-pairing effect, which results in a higher exothermic energy when the five-membered rings structure dissolving in NaOH solution. These findings, however, are limited to a specific mineral dissolution, namely stilbite, and do not represent either the other mineral systems or the complete mechanism in geopolymerisation.

Duxson et al. (2005d) de-convoluted a single broad \(^{29}\text{Si}\) NMR resonance to model the Si/Al distribution in geopolymer gel with respect to the different use of alkali metal cations (Na\textsuperscript{+} and K\textsuperscript{+}). It is found that there is no significant difference in the ordering at Si/Al ratios > 1.65. However, at Si/Al ratio < 1.65, K-based geopolymer appears to exhibit a more random Si/Al distribution and the presence of Al-O-Al linkages. Duxson et al. (2005b) also suggested that alkali metal cations in an aqueous form play a charge balancing role with Al(OH)\textsubscript{4}\textsuperscript{-} in the pore solution, only at low Si/Al ratios (< 1.40). At higher Si/Al ratios, the presence of Al(OH)\textsubscript{4}\textsuperscript{-} and Na\textsuperscript{+}(aq) in the pore solution diminishes.

Through a statistical thermodynamic model for Si/Al ordering in metakaolinite-based geopolymers, Provis et al. (2005a) have shown that Na-geopolymers have higher
dissolution rates, and thus will have more time and freedom to form a highly-ordered crystalline species. However, the K-based geopolymers have higher polycondensation rates, and thus will have less likelihood to form crystalline phases.

Furthermore, it is known that materials with higher calcium contents tend to set quicker because the dissolution rate of Ca\(^{2+}\) is greater than Si\(^{4+}\) or Al\(^{3+}\) (Lee, 2002; Phair, 2001). The content of calcium in metakaolinite is essentially zero, while it is about 5-10 weight % in Class F fly ash, 20 weight % in Class C fly ash, and near 40 weight % in granulated blast furnace slag (GBFS). Therefore, the effect of Ca\(^{2+}\) can be assumed to be significant only in high Ca-loaded sources, such as Class C fly ash and GBFS. Yip (2004) investigated the incorporation of various Ca sources into metakaolinite-based geopolymers. The Ca sources incorporated include CaCO\(_3\), Ca(OH)\(_2\), and GBFS. The coexistence of the amorphous CSH phase with geopolymer gel was identified and characterised using electron microscopy and elemental analysis techniques. The composition of Ca:Si ratio in the CSH derived from GBFS/metakaolinite mix is found to be lower than the CSH obtained from OPC. Yip and Van Deventer (2003) suggested that the formation of CSH phase is dependent on the alkali concentration and the ratio of GBFS to metakaolinite. The higher the alkali concentration, the higher the extent of dissolution of calcium, which is also induced by the presence of soluble silicate in the system. Overall, this results in the precipitation of Ca-phases, such as Ca(OH)\(_2\) and CaCO\(_3\). The CSH phase is, however, more stable at lower alkali and higher soluble silicate concentration. To compensate for the formation of Ca-precipitates, more GBFS should be added (< 60 weight %) in order to obtain phase separation between CSH and geopolymer gel.

2.4.6 The effect of curing temperature and ageing time
Alonso and Palomo (2001a; b) used conduction calorimetry to examine the alkali-activation of metakaolinite with Ca(OH)\(_2\) at 35, 45 and 60 °C. They attributed the calorimetric curves to the dissolution, the precipitation of amorphous aluminosilicate phases, and the formation of zeolitic phases. Alonso and Palomo (2001a; b) also observed that the increase in curing temperature results in the increase of the rate of reaction. The same trend applies to fly ash-based geopolymers, whereby at high
temperature curing, both dissolution and polycondensation are accelerated (Bakharev, 2005; Palomo et al., 1999b). The formation of zeolitic phases, such as hydroxysodalite, chabazite, and Na-P1 is also observed as fly ash is activated with alkali solutions at high temperature (Bakharev, 2005; Katz, 1998). Furthermore, Van Jaarsveld et al. (2002) synthesised and cured geopolymers from kaolinite-fly ash blends, and reported that a prolonged curing at high temperature (70-80 °C) results in the decrease of mechanical strength due to evaporation of pore water and disintegration of geopolymer gel.

The effect of varying curing conditions on slag-based geopolymers is more complicated due to the complex chemistry of GBFS that often results in the formation of various crystalline phases. These crystalline phases are normally observed in OPC, but not in geopolymers (Sioulas and Sanjayan, 2000, 2001). Wang and Scrivener (1995) observed the progressive formation of phases (CSH, Stralingite and Hydrogarnet) at different curing temperature and time. Schneider et al. (2001) activated slag with different alkali sources (e.g. sodium silicate, sodium hydroxide, calcium hydroxide and CaSO₄ or gypsum) under steam, wet, and autoclave curing and found that steam and autoclave curing at high temperature (80 °C) increase the degree of incorporation of Al into CSH. However, steam curing is also found to cause deterioration in the gel structure due to rapid movement of steam during application. The short application of high curing temperature improves early mechanical strength, increases durability, and decreases autogenous shrinkage of slag-based geopolymers (Aldea et al., 2000; Bakharev et al., 1999). Furthermore, Feng et al. (2004) investigated the application of ultrasonic energy in the synthesis of metakaolinite-based geopolymers. Stronger and longer applications of ultrasonic energy result in a stronger chemical bond between solid particles and gel phase due to an enhanced dissolution and polycondensation of geopolymer gel.

Based on the literature presented, it can be seen that few studies has been done on the effect of curing conditions. However, much of the previous work has been directed toward the effect of curing on alkali-activated cements (Katz, 1998), or pozzolanic blended cements (Alonso and Palomo, 2001a; b), rather than geopolymers. In addition, the investigation of the effect of curing conditions is limited to the physical properties of geopolymers, such as strength, durability, and shrinkage of materials (Bakharev, 2005;
Bakharev *et al.*, 1999). This, however, does not provide fundamental and systematic understanding of the effect of curing on mechanism and kinetics of geopolymerisation.

2.5 **Summary and motivations of the thesis**

In summary, geopolymers are essentially a new type of inorganic binder that possesses many superior properties, including high early mechanical strength, hardness, and fire-resistant properties. Geopolymers can be categorised to be an aluminosilicate gel, whereby the chemical structure consists of tetrahedral silicon and aluminium, bonded through sharing of oxygen atoms. The pore structure of geopolymer gel also resembles that of an aluminosilicate gel. The synthesis chemistry of geopolymers is similar to sol-gel methodology that is used to synthesise silica gels and glasses. Recent studies on the reaction mechanism have shown that there are at least 8 reaction steps occurring simultaneously during geopolymerisation, but there are essentially two main reaction steps taking place, i.e. dissolution (hydrolysis) and polycondensation (polymerisation). The progress of each step is dependent on various factors, such as the chemistry of aluminosilicate solid source, alkali and silicate concentration of the activating solution, the type of alkali metal cation, and the reaction condition (e.g. temperature, time, and humidity). Geopolymer gels are also believed to be the amorphous precursors of zeolitic crystals. Although geopolymers are aluminosilicate gels by definition, the macromolecular structure of geopolymers resembles the crystal lattice of zeolites.

The research conducted in the thesis will use fly ash as the main source of aluminosilicate solid. Class F fly ash is chosen as the main raw material because of: 1) its availability as a waste-based material adds value, reduces cost, and enhances the environment, 2) its potential and versatile application in cement and geopolymer technology, 3) its slower kinetics make it suitable to study the mechanism and kinetics in real-time, and 4) its practical workability.

Based on the literature review presented, there are a number of studies that will need to be conducted in order to expand the fundamental understanding of reaction mechanism, kinetics, and physico-chemical properties of geopolymers. The major work presented in the thesis are novel in terms of their approach and methodologies, and have a significant
contribution, filling the current knowledge gap in understanding the chemistry of geopolymerisation, particularly fly ash-based geopolymerisation. The overall research theme is to describe a conceptual model that better explains geopolymerisation based on the key results obtained from the following four mentioned areas.

1. *The effect of curing conditions on the properties of geopolymers.* The current understanding of the effect of curing parameters on the physico-chemical properties of geopolymers is not comprehensive. This is mainly caused by the non-systematic approach, followed in the literature. As a result, there are discrepancies in the reported properties of geopolymer materials. The early chapters of the thesis will attempt to fill this knowledge gap by investigating the effect of curing temperature, time, humidity, and methodology on geopolymerisation in a more thorough and fundamental fashion. It is believed that curing would have a significant effect on the rate and extent of reaction, which in turn affects the strength, porosity, and gel formation.

2. *The development of pore structure of fly ash-based geopolymers.* Despite the similarity drawn between geopolymer gel and that of porous aluminosilicate gel, geopolymers have never been viewed as a porous material due to the lack of investigation on the pore formation in geopolymers. For the first time, the study conducted in the thesis will successfully determine the development of pore structure of fly ash-based geopolymers. The change in the porosity, gel structure, and gel composition will be studied by varying various reaction parameters, namely reaction temperature, reaction time, alkali concentration, and silicate concentration of activating solution. The understanding developed from this work would help to synthesise tailor-made geopolymers with specific physico-chemical properties.

3. *The reaction mechanism of early fly ash-based geopolymerisation.* Previous workers utilised extreme experimental conditions, such as high alkali and high water content in order to study different reaction steps in geopolymerisation. While the results might give insight into understanding the reaction mechanism, the methodologies used are ambiguous because they do not represent actual geopolymerisation.
Therefore, a new approach is needed to study the reaction mechanism and kinetics, closer to actual geopolymerisation conditions. This can be done by measuring the heat of reaction \textit{in-situ}. The behaviour of heat release will be correlated to the dissolution, polymerisation, and crystallisation of aluminosilicate species. The conditions in which polymerisation and/or crystallisation of aluminosilicate species (zeolites) take place, will also be established for the first time.

4. \textit{The reaction mechanism of late fly ash-based geopolymerisation (i.e. after geopolymer materials set).} The effects of reaction parameters (e.g. silicate ratio, alkali concentration, curing temperature and humidity) are minimal after geopolymers set. Instead, a further reaction will be controlled by the rate of diffusion of remaining soluble species in the pore solution onto the fly ash particles or a growing gel network. In order to understand the reaction mechanism and kinetics of the later stages, fly ash-based geopolymers are aged in various alkali and carbonate solutions. By manipulating the concentration of ions in the pore solutions, the equilibrium of ionic precursors can be altered as well, which means that the later reactions might not be \textit{diffusion-limited} anymore.
CHAPTER 3
EXPERIMENTAL AND RESEARCH METHODOLOGIES

Detailed description of experiments is provided in each chapter where appropriate. Provided here is a broad overview of experimental methodologies, synthesis, conditions used, and the theory of instruments. In this study, the experimental methodologies can be divided into two main parts: (1) the synthesis, and (2) the characterisation. Geopolymers will be synthesised by mixing an amorphous aluminosilicate-rich solid, such as fly ash, slag, and metakaolinite, with an activating alkali-silicate solution. The resulting geopolymers and other derived products will be determined by the variations in reactant concentrations and processing conditions (curing conditions). The derived products from geopolymerisation include wet geopolymer gels, dry geopolymer gels, zeolites, and aluminosilicate glasses. A wet geopolymer gel is a non-treated gel, while a dry geopolymer gel is a geopolymer gel, which is dried in a vacuum oven at 105 °C, similar to a xerogel. At higher temperatures and higher alkali to silicate ratios, zeolites are likely to be formed. Aluminosilicate glasses may also be formed at high sintering temperatures (> 300 °C). However, the synthesis of aluminosilicate glasses from gels is beyond the scope of the thesis and will not be discussed further.

Furthermore, the characterisation of geopolymer materials are categorised into two main areas: chemical and physical characterisation. In chemical characterisation, the progress of reaction is monitored from the time of mixing the solid and the activating solution to the time when the material sets. The experiment is usually conducted in-situ, with the aims are to understand the reaction mechanism, kinetics and ion transport mechanism during geopolymerisation. In the thesis, Isothermal Conduction Calorimeter and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) will be the equipment items used for in-situ analyses. In physical characterisation, hardened geopolymers will be subjected to various analyses, which include:
1. *Chemical bonding, crystallinity, and microstructure.* The equipment items used will include: Fourier Transform Infra Red Spectroscopy (FTIR), X-Ray Diffraction (XRD), and Electron Microscopy (EM), coupled with Energy Dispersive Angle X-Ray Spectrometry (EDAX). There are several types of EM used, which include Scanning Electron Microscope (SEM), Environmental Scanning Electron Microscope (ESEM), Field Emission Scanning Electron Microscope (FESEM), and Transmission Electron Microscope (TEM).

2. *Porosity.* The porosity of geopolymers will be characterised using Mercury Intrusion Porosimetry (MIP) and N\textsubscript{2} adsorption. Furthermore, the fractality of geopolymers will be analysed using Small Angle X-Ray Scattering (SAXS).

3. *Physical properties.* This includes the compressive strength testing and permeability measurement.

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### 3.1 Raw materials

In the synthesis of geopolymers, there are essentially two types of raw materials, the aluminosilicate-containing solids and alkali-silicate solutions. The aluminosilicate solids function as sols in the alkali-silicate medium. The sol-liquid will turn into a sol-gel matrix, as is usually done in the sol-gel methodology. The aluminosilicate sources include the commonly used kaolinite and calcined kaolinite, or metakaolinite (Barbosa *et al.*, 2000; Davidovits, 1991; 1999; Davidovits and Davidovics, 1998; Palomo and Glasser, 1992; Rahier *et al.*, 1996a; b; 1997). Others include natural aluminosilicate minerals (Xu and Van Deventer, 2000b; 2002a) and industrial waste-based materials, such as blast furnace slags (Cheng and Chiu, 2003; Yip and Van Deventer, 2003) and fly ashes (Lee and Van Deventer, 2002a; b; Palomo *et al.*, 1999b; Phair and Van Deventer, 2001). In the thesis, three types of raw materials were used, i.e. Class F fly ash (FA), granulated blast furnace slags (GBFS), and metakaolinite (MK), with Class F fly ash being predominantly used as the raw material. The alkali-silicate solutions were made by diluting alkali-hydroxide solids in commercial silicate solutions and water to obtain certain silicate and alkali concentrations, expressed as SiO\textsubscript{2}/M\textsubscript{2}O and H\textsubscript{2}O/M\textsubscript{2}O ratios (where M = Na or K).
3.1.1 Fly ash

Fly ash (FA) is a finely divided residue resulting from the combustion of ground or powdered coal in electricity generating plant. Fly ash consists of earthly minerals, which include silicon, aluminium, iron, calcium, magnesium and traces of titanium and organic matter, such as carbon. The fly ash is solidified while it is being suspended in the exhaust gases, and is collected from the exhaust gases by electrostatic precipitators. Therefore, fly ash particles are generally spherical in shape because the solidification process occurs while the solid is in gas suspension. Furthermore, the collision between particles results in some larger particles or particles made up of several smaller ones bonded together. The particle size of fly ashes ranges from <1 to 200 µm, and the particles are typically spherical in shape (Hemmings and Berry, 1988). Some particles have enclosed pockets of air, or appear to be hollow spheres. It has been found that at least four types of particle morphology are commonly present in fly ash, i.e. solid sphere, plerosphere, clathrosphere, and cenosphere (hollow sphere). The different types of fly ash particles are separated based on their densities, with the density of a solid sphere being the highest (2.4-2.5 g/cm³), and a cenosphere the lowest (≤ 1.4 g/cm³).

FA is complex material with different particle morphologies and chemistry existing in one type of fly ash (Qian et al., 1988). Therefore, similar compositions of two fly ashes that come from different sources may have different physical and chemical characteristics. The types of coal determine the types of fly ash produced. Generally, anthracite and bituminous coals produce fly ashes which are classified as Class F fly ash. In Australia, the majority of ash produced is categorised as Class F – being mainly silica and alumina (80-85 weight %) and < 10 weight % CaO. The fly ash used in the thesis came from Gladstone, Australia (Queensland Cement Limited), which can also be classified as Class F fly ash. Class C fly ash is produced by burning lignite or sub-bituminous coal. Class C fly ash has lower silica and alumina content, but higher CaO content (20-40 weight %). The difference in CaO concentration leads to different chemistries when fly ashes are activated in acidic or basic environment (Hemmings and Berry, 1988). The effect of high calcium concentration typically leads to the acceleration of rate of reaction. In a pozzolanic reaction between fly ash and Ca(OH)$_2$ or calcium silicate phases in cement paste, the early reaction may be so rapid that it will be
unsuited in applications that require longer workability or setting time. Therefore, Class F fly ash is much preferred in cement and geopolymer application due to the high content of amorphous aluminosilicate phases and greater workability.

The oxide compositions of Class F fly ash (FA), granulated blast furnace slag (GBFS), and metakaolinite (MK) used in the thesis are listed in Table 3.1. These were determined using a Siemens SRS3000 X-Ray Fluorescence (XRF) spectrometer. It can be seen from Table 3.1 that the composition of major components in Gladstone FA are 50.0 weight % SiO$_2$, 28.0 weight % Al$_2$O$_3$, and 12.0 weight % Fe$_2$O$_3$. X-Ray Diffraction analysis using the XRD Philips PW 1800 instrument determined that FA was relatively amorphous. The major crystalline phases included α-quartz (SiO$_2$), mullite (3.2 Al$_2$O$_3$ SiO$_2$), hematite (Fe$_2$O$_3$), and magnetite (Fe$_3$O$_4$) (Figure 3.1). It is thought that these crystalline phases are not reactive when fly ash is activated in a basic solution (Hemmings and Berry, 1988) or in geopolymerisation (Fernandez-Jimenez et al., 2006a; b). A quantitative XRD analysis using SiroQuant software showed that GFA contained 17 weight % amorphous Al and 39.1 weight % amorphous Si, which can be fully hydrolysed. Apart from the Si and Al elements, other authors (Hemmings and Berry, 1988; Qian et al., 1988) reported the glassy phases which are associated with calcium, iron and sodium elements in the Class F fly ash. The effect of these glassy phases in the basic reactions is conjectured to be slight, at least when present at low concentrations. Furthermore, using Nitrogen Adsorption on a Tristar instrument, the BET surface area of GFA was determined to be 1.337 m$^2$/g and the mean particle density was 2.34 g/cm$^3$. The particle size distribution of fly ash particles and other solids was determined by Coulter Particle Size Analyser, which is also shown in Table 3.1.

3.1.2 Other aluminosilicate sources
The origins and properties of slag and metakaolinite used in the synthesis of geopolymers are presented in the following section.

3.1.2.1 Granulated blast furnace slag
Blast furnace slag is a non-metallic by-product produced in the manufacturing of iron
Table 3.1 The weight percent compositions and particle size distribution of fly ash (FA), granulated blast furnace slags (GBFS), and metakaolinite (MK) used in the thesis.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>FA</th>
<th>GBFS</th>
<th>MK</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>3.5</td>
<td>43.4</td>
<td>0.10</td>
</tr>
<tr>
<td>SiO₂</td>
<td>50.0</td>
<td>34.4</td>
<td>54.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>28.0</td>
<td>14.1</td>
<td>40.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>12.0</td>
<td>0.11</td>
<td>0.76</td>
</tr>
<tr>
<td>SO₃</td>
<td>-</td>
<td>0.38</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>1.30</td>
<td>6.30</td>
<td>0.41</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.70</td>
<td>0.13</td>
<td>2.52</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.20</td>
<td>0.30</td>
<td>0.07</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>-</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>TiO₂</td>
<td>-</td>
<td>0.56</td>
<td>0.02</td>
</tr>
<tr>
<td>MnO₂</td>
<td>-</td>
<td>0.13</td>
<td>0.01</td>
</tr>
<tr>
<td>LOI</td>
<td>4.30</td>
<td>0.19</td>
<td>0.80</td>
</tr>
<tr>
<td>d₁₀ (µm)</td>
<td>2.1</td>
<td>2.8</td>
<td>1.9</td>
</tr>
<tr>
<td>d₅₀ (µm)</td>
<td>12.4</td>
<td>17.5</td>
<td>5.1</td>
</tr>
<tr>
<td>d₉₀ (µm)</td>
<td>70.0</td>
<td>47.6</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Figure 3.1 The XRD patterns for fly ash, slag, and metakaolinite. Q, M, L represent α-quartz, mullite, and larnite respectively, while Mus, Phil, Mel, and Mag represent muscovite, phillipsite, melilité, and magnetite respectively.
and steel. It consists primarily of silicates, aluminosilicates, and calcium-alumina-silicates. There are different types of slag products depending on the methods used to cool the molten slag, namely air-cooled blast furnace slag (ACBFS), expanded or foamed slag, pelletised slag, and granulated blast furnace slag (GBFS). Only GBFS is used as a replacement material for OPC (Talling and Krivenko, 1997). GBFS has also been used to synthesise alkali-activated cement and geopolymers (Cheng and Chiu, 2003; Fernandez-Jimenez et al., 2003; Yip and Van Deventer, 2003). The process of cooling and solidification of molten slag results in glassy-state materials, which take the form of frit-like fragments. Before being used in cement or geopolymer application, GBFS is usually crushed, and milled to a finer size. The GBFS consists mainly of calcium aluminosilicate glass with crystal inclusions of larnite and melilite (Talling and Krivenko, 1997). Figure 3.1 reveals the presence of these crystalline phases together with K-philipsite. Similarly to fly ash materials, the micro-inhomogeneities and the existence of multiphases within the structure of glassy matters are possible, but not frequent. In this study, GBFS was obtained from Queensland Cement Ltd, Australia. The three main oxide compositions are CaO (43.4 weight %), SiO2 (34.4 weight %), and Al2O3 (14.1 weight %), with the particle size distribution of 2.8 \( \mu \text{m} \) (d10), 17.5 \( \mu \text{m} \) (d50), and 47.5 \( \mu \text{m} \) (d90) (Table 3.1).

3.1.2.2 Metakaolinite

Metakaolinite is obtained from the calcination of kaolinitic clay at temperatures ranging from 500-750 \( ^\circ \text{C} \). The further calcination of kaolinite at higher temperatures leads to the formation of more ordered crystalline phases, such as spinel, mullite and cristobalite (Figure 3.2). It is suggested that firing kaolinite at lower temperatures (< 500 \( ^\circ \text{C} \)) does not give sufficient energy to break the crystalline structure of kaolinite. As a result, amorphous metakaolinite is not formed. However, calcination at higher temperatures, i.e. higher than a threshold temperature turns the metastable phase, metakaolinite, into more ordered crystalline phases, which are non-reactive upon alkali-activation. The high amorphicity of metakaolinite leads to the high reactivity when it is activated in alkali solutions. Figure 3.1 shows that crystalline materials, such as muscovite, quartz, and mullite are also present. The metakaolinite used in the study was obtained from Imerys Ltd in England under the brand name Metastar 501. MK has the smallest particle size in
comparison to FA or GBFS (Table 3.1). The fine and irregular particle shape of MK often mean that MK generally requires more solution for wetting and reaction to take place appropriately. The pozzolanic properties of metakaolinite are also dependent on various factors, such as: 1) the crystallinity of original kaolinite (Kakali et al., 2001; Kaloumenou et al., 1999), where a well-ordered kaolinite gives less pozzolanic active metakaolinite; 2) the calcination temperature (Davidovits, 1999); and 3) the size of metakaolinite particles (Rahier et al., 2003), where smaller particles leads to a larger surface area of contact, which in turn to a higher reactivity.

![Diagram of phase transformation](image)

**Figure 3.2 The schematic diagram of phase transformation from the calcination of kaolinite (Richardson and Ehlers, 1961).**

### 3.1.3 Silicate solutions

Commercial silicate solutions used in the thesis were obtained from *PQ Australia*, while KOH flakes and NaOH pellets were obtained from *Orica Australia*. The composition of solids (Na₂O, K₂O, and SiO₂) in the original silicate solutions is listed in Table 3.2. The compositions of activating solutions were varied according to the purpose of each study, and therefore would be presented separately in the experimental section of each chapter. The wetting requirements were varied depending on the binders (aluminosilicate solids) used. In general, the water required to hydrate the binder increases in this order: FA<GBFS<MK. The different water requirement indicates the different mineralogies, particle sizes and reactivity of different raw materials.

### 3.2 Geopolymer synthesis

Geopolymer materials were made by the mixing of aluminosilicate solid with the activating alkali-silicate solution. The mixture usually forms a slurry paste that will set
in a few hours at ambient temperature. The material as it is setting, is called ‘geopolymer paste’. In various parts of the thesis, silica sand was added to provide additional structural strength and reinforcement. The mixture of geopolymer paste with sand is called ‘geopolymer mortar’. When larger aggregates (> 1mm) are added, the mixture is called ‘geopolymer concrete’. These terms are adopted from cement and concrete applications.

Table 3.2 The product specifications of commercial Na-silicate and K-silicate solutions.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Na-silicate solution (N®)</th>
<th>K-silicate solution (KASIL 2040)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₂O (M = Na or K), weight %</td>
<td>8.9</td>
<td>13.3</td>
</tr>
<tr>
<td>SiO₂, weight %</td>
<td>28.7</td>
<td>26.7</td>
</tr>
<tr>
<td>H₂O, weight %</td>
<td>62.4</td>
<td>60.0</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.38</td>
<td>1.39</td>
</tr>
<tr>
<td>Viscosity (cps)</td>
<td>180</td>
<td>200</td>
</tr>
</tbody>
</table>

The geopolymer binders were synthesised in a plastic container by manually mixing the geopolymer slurry by hand for 5 minutes or longer. An overhead mixer was used when the preparation required larger quantities of samples. The mixing process can be done in ambient temperature or slightly higher (< 50 °C). The resulting consistent slurry was poured into cylindrical plastic moulds, of diameters 2.4, 3, and 5 cm. The aspect ratio between diameter and height varied between 1 to 2. The different mould size was made to fit the specific need for characterisation, for example the compressive strength testing followed the standardised procedure of using cylindrical samples of 5 cm, with the aspect ratio of 2, while the permeability measurement required the aspect ratio of 1. After moulding, samples were sealed, and placed immediately in an air-circulated oven, or a constant temperature water bath to be cured. There were three different curing temperatures used, namely 30, 50, and 75 °C, with the curing time ranged from 4 hours to 7 days.
Figure 3.3 summarises the synthesis methodology implemented in the thesis, starting from the mixing of aluminosilicate solid with activating solution, giving the sol-gel mixture, and through curing getting the geopolymer-derived products. There are five possible outcomes from the procedures implemented in this study, a wet geopolymer gel, a dry geopolymer gel, zeolites, glasses, or a new or extended gel phase formation. The wet geopolymer gel is a reactive gel, whose properties change with time, similar to an aged gel in porous silica synthesis. Although the reaction has largely occurred, further dissolution and precipitation is likely possible due to the presence of solution in the gel pores. The dry geopolymer gel is a geopolymer gel, which is dried in a vacuum oven at 105 °C, similar to a xerogel. It can be assumed that the dry geopolymer gel shrinks slightly from its original wet state, and the reaction ceases almost completely. The drying of specimens was done to prepare specimens for specific tests, such as MIP and gas adsorption. When fly ash-based geopolymer is activated with solutions of high
alkali concentration, at a temperature higher than 50°C, zeolites are likely to form. A further investigation on the formation of zeolites during geopolymerisation will be presented in Chapter 7. In addition, aluminosilicate glasses can also be synthesised sintering aluminosilicate gel at high temperature. However, the synthesis of glasses from gels is beyond the scope of the thesis and will not be discussed further. In Chapter 8, fly ash-based geopolymers will be aged in various alkali and carbonate solutions. As a result of prolonged ageing, new geopolymer gel and zeolitic phases will be formed.

3.3 Characterisation of geopolymers

The primary purpose for characterising geopolymers is: 1) to investigate the physico-chemical properties of various geopolymers, which are synthesised at different conditions; and 2) to understand the underlying mechanism and kinetics that lead to the physico-chemical properties observed. The characterisation and analysis of geopolymers are divided into two main areas, i.e. the chemical and physical, with physical characterisation being divided into microscale and macroscale (Figure 3.4). The aim of chemical characterisation is to understand the reaction mechanism, kinetics and ion transport mechanism during geopolymerisation. To study the progress of reaction during geopolymerisation, the experiment will be conducted in-situ starting from the time when the solids and activating solutions are mixed to the time when the materials completely set. The physical characterisation is conducted after the materials fully set. In the thesis, the physical properties investigated include gel composition, microstructure, porosity, chemical bondings, compressive strength, and permeability of geopolymers (Figure 3.4). The different equipment used in the thesis is described in the following section.

3.3.1 Isothermal Conduction Calorimetry

Previous workers (Lee and Van Deventer, 2003; Phair and Van Deventer, 2001; Van Jaarsveld et al., 1999) attempted to study the reaction steps of fly ash-based geopolymerisation by separating the dissolution and polycondensation steps through various leaching experiments. These two main steps were studied by separately characterising the leached solids and supernatant liquid. The methodology seems to be acceptable because of the ease of experimental procedures. However, it does not take...
into account that more reactions may have taken place, and that they are likely to occur simultaneously, as proposed by Provis et al. (2005b). However, in the thesis, Isothermal Conduction Calorimeter (ICC) was used to monitor the progress of overall reaction steps in-situ. The individual calorimetric curves can be associated with the different reaction steps (dissolution, polymerisation, and crystallisation) in geopolymerisation. In the literature, ICC was used to probe the reaction of metakaolinite with CaOH and alkali solutions (Alonso and Palomo, 2001a; b; Granizo and Blanco, 1998; Granizo et al., 2000). Studies on blast furnace slag (Fernandez-Jimenez et al., 1998) and fly ash (Jalali, 1998; Ma et al., 1994) had also been investigated. However, the work conducted was primarily motivated by the potential use of the waste-based materials for OPC, rather than for geopolymers. In addition, the alkali concentration and water content used in the studies (Alonso and Palomo, 2001b; Granizo and Blanco, 1998) were relatively high, such that they resembled the conditions used in the synthesis of zeolites (Yang and Navrotsky, 2002), and not of geopolymers.

Figure 3.4 Schematic diagram of characterisation techniques for geopolymers.
In ICC, the sample and its holder are in thermal contact, only with a heat-flow sensor, which in turn is mounted on a heat sink. A temperature difference between sample cell and heat sink produces an electric potential, which then is converted into heat output (Wadso et al., 2001). The sample-sensor-heat sink unit is placed in an insulated container, which is then inserted in a constant temperature water bath. In an isothermal calorimeter, the temperature of the cell can be treated as constant.

In the thesis, a *JAF Isothermal Conduction Calorimeter*, manufactured by *Mastrad, England* was used. The older technique of introducing activating solution into solid for reaction (Granizo and Blanco, 1998; Granizo et al., 2000) was improved with a new *direct injection* method. The *direct injection* is a better method because it prevents delay time, caused by the need to stabilise and equalise the calorimeter temperature to the water bath temperature before any measurement can be conducted. The stabilisation temperature can take more than 1 hour, which is disadvantageous because of the rapid early dissolution in geopolymerisation. The solid and activating solution were kept separately at the same temperature and the solution was injected when a stable isothermal temperature was obtained. The heat rate and total heat released were calculated by the JAF Software program, which was based on Tian’s equations (Calvet and Prat, 1963). The plots of heat of reaction against time were smoothed using a three-point analysis.

### 3.3.2 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The use of ICP-OES for studying the reactions in geopolymerisation has been *semi in-situ* (Lee, 2002; Phair, 2001). By *semi-in situ*, it means that incremental time periods are designed to simulate an *in-situ* analysis. In the thesis, the ICP-OES equipment used was a *Perkin Elmer Optima 3000*. The equipment was primarily used to measure the concentration of elements, which were leached from fly ash-based geopolymers as they were immersed in various alkali and carbonate solutions (Chapter 8). In order to obtain feasible results, the aliquout solution should be sufficiently stable, such that no precipitate or colloidal particles exist, as they may prevent complete aerosol formation, which affect the accuracy of measurement (Gustavsson, 1992). The droplet size of
aerosol in the plasma arc should be < 5 μm. To ensure this, the solutions were pre-filtered so that any larger entities could be avoided. Special attention was also placed on the large concentration of elements that might induce formation of oligomeric species or larger, such as alkali cations (Ca⁺, Na⁺, K⁺) and Si⁴⁺. The concentration of Na⁺ and K⁺ (particularly K⁺, which has larger cation radius) should be kept lower than 1000 ppm. In the thesis, all solutions were diluted to 50-100 times the original concentration to ensure the threshold concentration of respective elements was not surpassed. Before analysis the plasma arc was calibrated against a mercury lamp and the intensity of absorption peaks was checked against manganese standard solutions. Triple distilled water was used as a washing solution. A calibration curve was also plotted from standard solutions which were prepared from pre-purchased standard solutions. The concentrations of standard solutions are: 10, 100, and 500 ppm for Al; 10,100, and 1000 ppm for Si; 1, 10, 100 ppm for Ca, Fe, Mg; 10, 100, 1000 ppm for Na and K. The emission wavelengths used were 39.153 nm for Al, 251.611 nm for Si, 280.271 nm for Mg, 238.204 nm for Fe, 317.933 nm for Ca, 766.490 nm for K, 330.237 nm for Na. The Optima 3000 software calculated the concentration of elements by integrating the peak area under the respective emission length.

3.3.3 X-ray Diffraction (XRD) analysis

The XRD data becomes the fingerprint characterisation of crystalline materials and the determination of their structure. The basic underlying principle of XRD uses the characteristic lattice structure of crystalline materials, as illustrated in Figure 3.5.

According to Bragg (Langford and Louer, 1996), when there is a coherent scattering of X-ray from planes of atoms of d in a single crystal, the beams are diffracted in a direction that generate cones with a reflection angle θ.

Therefore, the path difference between 2 waves can be derived as:

\[
2\lambda = 2d \sin(\theta) \tag{3.1}
\]
Figure 3.5 Reflection of x-rays from two planes of atoms in a solid.

For constructive interference between these waves, the path difference must be an integral number of wavelengths, which leads to the Bragg’s equation:

\[ n\lambda = 2d \sin(\theta), \quad (3.2) \]

where \( n \) is an integer of constructive interference, \( \lambda \) is the x-ray wavelength, \( d \) is the characteristic separation between lattice planes and \( \theta \) is the reflection angle. By measuring the reflection, it is possible to determine the d-spacing values for different crystalline phases in the materials.

The X-ray radiation that is most commonly used is that emitted by copper, whose characteristic wavelength for the K radiation is 1.5418\( \text{Å} \). When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 2\( \theta \). The diffracted beam may be detected by using a moveable detector such as a Geiger counter. The counter is set to scan over a range of 2\( \theta \) values at a constant angular velocity. In the thesis, a Philips PW 1800 with CuK\( \alpha \) radiation at 30 mA and 40 kV was used, with the values of 2\( \theta \) ranging from 5\(^{\circ}\) to 70\(^{\circ}\). The scanning step was done at 0.05\(^{\circ}\), and integrated at the rate of 3s per step. Approximately 1-2 g of geopolymers were crushed with agate mortar and pestle, ground to powder form (< 5 microns) and mounted in a sample holder. The crystalline patterns were compared with the standard line patterns from the Powder Diffraction File database supplied by International Centre for Diffraction Data (ICDD). The XRD technique is sensitive to variations in the sample, which include...
particle sizes, the homogeneity of individual particles, the compactness of packing, and the water content in the materials. These factors were taken into consideration during sample preparation.

3.3.4 Fourier Transform Infrared Spectroscopy (FTIR)

Infra-red spectroscopy was used to characterise the chemical functional groups in geopolymers based on the characteristics of vibrational and rotational energies of different molecular bonds in the materials. The use of Fourier Transform Infra Red Spectroscopy (FTIR) to characterise geopolymer materials was studied extensively by Lee (2002) and other authors (Phair, 2001; Van Jaarsveld, 2000). In the thesis, FTIR spectra of geopolymer samples were obtained using a *Bio-Rad FTS 165 FTIR spectrometer* in a transmission mode. Approximately 0.5g of geopolymer powders were pelletised using the *KBr disc* technique. All spectra were taken at 8cm$^{-1}$ resolution and 48 scans per spectrum.

3.3.5 Electron Microscopy (EM) and Energy Dispersive Angle X-ray (EDAX) analysis

In the thesis, the following Electron Microscopes (EM) were used:

1. *High-Vacuum SEM (Phillips XL30 EM)*. With a high vacuum setting ($< 2 \times 10^{-4}$ Torr), less electrons would be scattered, giving a higher image resolution. The highest magnification that can be achieved without reducing resolution is up to 10000 times. In order to achieve high vacuum condition, the sample and the microscope chamber should be free of any moisture. The geopolymer specimen was usually crushed or cut to an approximate size of 200 mm$^3$, then mildly dried (approximately at 60 °C) for 24 hours before being mounted in epoxy resin and polished using graded SiC papers. After polishing, the exposed geopolymer surface was coated with carbon to make the surface conductive for electron transfer. The operating voltage of filament was set at 20 kV.

2. *Environmental SEM (FEI Quanta 200)*. In a typical ESEM equipment, there are three modes of EM that can be used. Every mode was used in the thesis.
   - *High vacuum SEM (HV-SEM)*, as described above.
• *Low vacuum SEM (LV-SEM).* The applied pressure ranged at 0.1-1 Torr. The advantage of the LV technique is the ease of sample preparation. It does not require the sample to be mounted in an epoxy resin, coated with carbon, or dried. The surface, however, should be sufficiently flat to give a good image resolution. The resolution of LV-SEM is expected to be less than HV-SEM for a similar magnification due to the scattering of electrons at low vacuum conditions.

• *Environmental-SEM (ESEM).* In ESEM, the transformation from sol-liquid to gel phase during geopolymerisation was observed in-situ. However, the image resolution might be poor due to the low vacuum environment and non-conductive surface.

3. *Field Emission SEM (Philips XL30 FEG FESEM).* The FESEM has a different type of electron source compared to other electron microscopes. The electron gun is made of a tungsten or platinum wire with a sharpened tip that is mounted in a cathode-ray tube. Electrons are drawn from the tip by a high electrical field and travel toward the screen on which the image is formed. Because of the sharpened tip and large electric field, the operating voltage of filament ranges only from 1-5 kV. The magnification from FESEM can reach up to 25,000 times, 2-3 times higher than HV-SEM.

4. *TEM (Philips CM120 BioTWIN TEM).* In the thesis, selected geopolymer powders were subjected to TEM analysis at 100 kV. The powder technique was preferred to prevent any structural damage caused by rigorous sample preparation. Geopolymers were crushed and ground to a few hundreds microns, and were then suspended in an aluminium TEM grid. In conjunction with TEM, the images of electron diffraction were also taken. Electron diffraction is a technique to identify the crystallinity of phases based on the principle that a particular crystal lattice diffracts electrons in a particular pattern. The diffraction patterns of materials may appear to be continuous, discontinuous, or speckled rings.

Other components that are incorporated into an electron microscope include:

1. *Detectors.* There were two types of detectors used in this study, Secondary Electron (SE) and Back-scattered Electron (BSE) detectors. The SE detector was used to
produce the surface morphology of geopolymer materials. The image contrast is produced by the different topography of phases, rather than the chemical nature of phases. However, the BSE detector was used to distinguish the chemical composition of phases, which is very useful in characterising multi-phase materials, such as fly ash-based geopolymers. The elements with a higher atomic number scatter more electrons thus will appear to be brighter under BSE.

2. Energy Dispersive Angle X-Ray (EDAX) detector. The detectors capture X-ray beams that are reflected from the surface as a result of the bombardment from secondary electrons. The various elemental compositions can be integrated from the area under the peak in which standard characteristic wavelengths are inserted. There are few parameters that should be considered strictly in EDAX analysis:

- The size of interactive volume, which varies depending on the density and composition of phases. In the thesis, twenty measurements were taken across the corresponding gel matrices to obtain a representation of the overall geopolymer gel composition. The spot size for the analyses was normally 2-4 \( \mu \text{m} \), but could be greater than 4 \( \mu \text{m} \), depending on the scale of the microstructure.
- The walking distance (WD) should be at 10 mm, which was approximated to allow most scattered X-Rays to be captured by the detector directly.
- The count rate and dead time. By rule of thumb, the values were set at > 1000 per second and < 30\% respectively. Too low a count rate means there is not enough X-Ray beams detected and too high a dead time means the peaks associated with specific elements are broad, resulting in a poor analysis.

3.3.6 Mercury Intrusion Porosimetry (MIP)

Mercury Intrusion Porosimetry (MIP) was one of the major equipment items used in the thesis. MIP technique provides a wide range of information on the pore properties of geopolymers, such as pore size distribution, the total pore volume or porosity, the skeletal and apparent density, and the specific surface area of a sample (Webb and Orr, 1997). In MIP, the porous sample is located in a glass penetrometer and the measurement is conducted in two steps (Figure 3.6): 1) low pressure step, whereby a vacuum pump is utilised to generate pressure up to 30 psia; and 2) high pressure step,
whereby the porous sample is placed in a pressure chamber, containing hydraulic oil to generate pressure up to 60,000 psia.

Figure 3.6 The apparatus in Mercury Intrusion Porosimetry (Webb and Orr, 1997).

The raw data obtained from MIP is a plot of intruded volume against the applied pressure. The applied pressure is then used to calculate the pore size, which is expressed by the Washburn’s equation (Washburn, 1921):

\[ D = \frac{-4 \gamma \cos \theta}{P} \]  \hspace{1cm} (3.3)

where \( \gamma \) is the interfacial tension, \( \theta \) is the three-phase contact angle, \( P \) is the pressure intruded, and \( D \) is the equivalent pore width.

The pore sizes measured from MIP test range from 3.6 nm to 500 µm. Entry to the pore space is directly correlated with the force applied and is inversely proportional to the opening size of the pore. The above equation holds true if pores are assumed to be one side open and cylindrical. The surface tension force for mercury is usually taken to be 485 dyne/cm at 25 °C and 1 atm. Mercury generally exhibits very high contact angle against most solids. The advancing contact angles between fresh mercury and clean
surfaces range from $112^\circ$ to $142^\circ$ (Leon, 1998). The most accepted value, although not justified for aluminosilicate glasses and cementitious products is $130^\circ$. This contact angle was used in the thesis. The receding angles are typically about $30^\circ$ less than the advancing ones (Leon, 1998). The different contact angles between intrusion and extrusion can be attributed to the hysteresis phenomenon (Kloubek, 1981), whose mechanism is illustrated in Figure 3.7 (Giesche, 2002). During intrusion, mercury enters and fills pores, however most of the pore opening forms an ink-bottle structure that hinders the total removal of mercury during extrusion. This causes some mercury to remain in the pores thus produces a different pressure-volume relation from the intrusion process.

![Figure 3.7 The hysteresis phenomenon associated with intrusion-extrusion mechanism (Giesche, 2002).](image)

In the thesis, MIP was used to measure the dry geopolymer gel. The wet geopolymer gel was cut, dried in a vacuum oven at $105^\circ$C for 24 hours or until a constant sample weight was obtained. The dried geopolymer was then subjected to MIP test (Autopore II 9220). The pressure applied was from 0.5 psia to 60,000 psia at 15 seconds equilibration time, based on the standard practice used for any aluminosilicate material (Webb and Orr, 1997). The pore size distribution was derived based on the interconnected tubular pore network model developed from Washburn’s equation (Washburn, 1921). The pore distribution however is more meaningful if the smoothing
of the volume-pore size curve is carried out, which results in the plot of log differential intrusion against diameter, \((\text{d}V/\text{d}\log D)\) vs \(D\). The latter plot is particularly enlightening because the peaks will plot with equal areas on the logarithmic diameter axis when a sample has pores concentrated in distinct size ranges containing the same total volume (Giesche, 2002). Furthermore, external surface area can be related to pore volume using \(A = 4 \ V/D\) expression, where \(V\) is the volume and \(D\) is the equivalent pore diameter.

The interpretation of intrusion and extrusion data is usually complicated by the complex and irregular pore geometry. This has been thoroughly investigated by Diamond (2000) on cementitious materials. In OPC, the intrusion of larger pores in porosimetry may be avoided if there are long percolative chains of intermediate pores with varying sizes and shapes, which leads to a greater volume and area measured than are actually present. This phenomenon may apply to any porous aluminosilicate materials, including geopolymers. However, geopolymers have a more regular pore network, originating from the stacking of aluminosilicate particles. Therefore, the problems associated with irregular pore geometry may be avoided (Diamond, 2004).

In the thesis, the porosimetry data were also used to characterise the fractality of geopolymers. The common methodologies used to determine surface fractal dimension (\(D_s\)) from MIP data include:

1. *Friesen’s method* (Friesen and Laidlaw, 1993; Friesen and Mikula, 1987; Mahamud *et al.*, 2003), which is expressed in Equation (3.4).

\[
\log \frac{dV_m(P)}{dP} \propto (D_s - 4) \log (P)
\]  

(3.4)

The \(D_s\) can be obtained from the gradient of the logarithmic plot between the differential volume-pressure against the intruded pressure.

2. *Thermodynamic method* (Mahamud *et al.*, 2003; Sahouli *et al.*, 1999b). This method is based on the same assumption used in the first formula. However, it appears more
straightforward because the actual surfaces \((W_v)\) are considered. The surface area can be calculated from Equation (3.5).

\[
W_v = \frac{-1}{\gamma \cos \theta} \int_0^\gamma P \, dV
\]  

(3.5)

which leads to the following correlation:

\[
\log W_v \propto (D_s - 2) \log P
\]

(3.6)

Similarly, the \(D_s\) can be calculated from the gradient of the logarithmic plot between surface area and the intruded pressure.

### 3.3.7 \(\text{N}_2\) adsorption

Similar to MIP, \(\text{N}_2\) adsorption is widely used to characterise the pore structure of ceramics, adsorbents, cement and concrete, silica gels and glasses and other porous materials (Garci Juenger and Jennings, 2001; Gille et al., 2003; Ravikovitch and Neimark, 2000; Ravikovitch et al., 1997). Tristar equipment from Micromeritics Inc was used in the thesis to characterise the porosity of geopolymers. The principle of the gas adsorption technique is based on the complex phenomenon of gas adsorption on solid surface, where mass and energy interacts, causes the transformation of phases to take place simultaneously (Webb and Orr, 1997). The adsorption data constitute two isotherms, adsorption and desorption. The original data are the plot of adsorbed volume against the relative pressure \((P/P_0)\), where \(P\) is the actual gas pressure and \(P_0\) is the vapour pressure. The test was conducted at a cryogenic temperature, i.e. at the boiling point of liquid \(\text{N}_2\) \((77.35 \text{ K at 1 atm})\), and the equilibration time was set at 15 seconds.

In the context of physisorption (adsorption-desorption by physical means), the pore sizes can be classified into three classes (Sing et al., 1985):

1. Macropores, pores that exceed 50 nm.
2. Mesopores, pores that falls within the range of 2-50 nm.
3. Micropores, pores that are smaller than 2 nm.
In the current work, only the BJH model (Barret et al., 1951) was used to calculate pore parameters from the gas adsorption data because the method is simple and comprehensive for geopolymer materials. The relationship between relative gas pressure, volume and radius of liquid menisci during gas adsorption and condensation can be expressed by the classical Kelvin’s equation (Gregg and Sing, 1982):

\[
\ln \frac{P^*}{P_0} = -\left(\frac{2\gamma \nu \cos \theta}{RTm}\right)
\]  \hspace{1cm} (3.7)

where \(P^*\) is the critical condensation pressure, \(P_0\) is the saturation pressure of adsorptive gas (N\(_2\)), \(\gamma\) the liquid surface tension, \(\nu\) the molar volume of the condensed adsorptive, \(\theta\) the contact angle between the solid and condensed phase, and \(m\) is the mean radius of curvature of the liquid meniscus. If it is assumed that all pores are open-ended, cylindrical and connected, Equation (3.7) can be re-written as Equation (3.8) for adsorption, and Equation (3.9) for desorption, where \(t\) is equal to the thickness of N\(_2\) condensate on solid surface.

\[
\ln \frac{P^*}{P_0} = -\left(\frac{\gamma \nu \cos \theta}{RT}\right) \quad \text{for adsorption} \hspace{1cm} (3.8)
\]

\[
\ln \frac{P^*}{P_0} = -\left(\frac{2\gamma \nu \cos \theta}{RT(r-t)}\right) \quad \text{for desorption} \hspace{1cm} (3.9)
\]

Based on Equations (3.8) and (3.9), Barret, Joyner, and Halenda (BJH) (1951) developed an adsorption model by considering an imaginary emptying of condensed adsorptive in the pores in a stepwise manner, as the pressure decreases. The adsorptive lost in each step represents the core volumes of pores emptied in that step. The thickness of adsorptive layer is obtained from Equation (3.10) (Webb and Orr, 1997).
In order to obtain pore volume and area, a right circular cylinder model is assumed (Volume = \( \pi r^2L \), and Area=2\( \pi rL \)). The pore volume and surface area were calculated using \textit{Win 3000} Software. It should be noted that the measured pore volume and area from MIP and BJH are external pore parameters. Pores that have small openings or exhibit the \textit{ink-bottle} effect prohibit full intrusion and/or adsorption in the overall pore space. This may mean that the results do not represent the ‘real’ pore volume and area. Furthermore, only the N\(_2\) desorption branch was compared with MIP intrusion. The evaporation volume of adsorbed gas decreases step-wise as the pore size decreases, a similar process to the MIP, where Hg intrudes from larger to smaller pores sequentially.

Similar to MIP, the gas adsorption isotherms can be used to determine fractal dimensions of porous materials. The two methodologies developed to determine surface fractal dimension (\( D_s \)) from the adsorption data include:

1. \textit{Frenkel-Halsey-Hill (FHH) Theory} (Sahouli \textit{et al.}, 1996; 1999a). This method assumes a multilayer adsorption to the fractal surfaces. The following equation is commonly used:

\[
\ln \left( \frac{V}{V_m} \right) \propto (D_s - 4) \ln(\frac{P_0}{P})
\]  

(3.11)

2. \textit{Thermodynamic method} (Sahouli \textit{et al.}, 1996; 1999a). Thermodynamic method for N\(_2\) adsorption was firstly described by Neimark and Unger (1993), i.e. using the real surface area to derive the surface fractal. Based on the Kiselev’s equation (Gregg and Sing, 1982), the surface area at each pressure increment can be expressed as:

\[
S = \frac{RT}{\sigma} \int_{N}^{N_{max}} \ln(\frac{P_0}{P}) \, dN
\]  

(3.12)
The surface fractal is incorporated in the logarithmic plot of surface area and inverse relative pressure by the following equation:

\[
\ln S \propto (D_s - 2) \ln(\frac{P_0}{P})
\]  

(3.13)

### 3.3.8 Small Angle X-ray Scattering (SAXS)

The application of Small Angle Scattering using X-Rays or Neutrons for analysing the fractality of porous silica and aluminosilicate solids has been widely investigated (Brenner et al., 1995; Brinker, 1988; Brinker et al., 1984; Pernyeszi and Dekany, 2003; Pouxviel et al., 1988; Vollet et al., 2004). The small-angle scattering measurements of both X-rays and neutrons can provide structural details on a length scale from 1 nm to >100 nm (Schmidt, 1988). The scattering of X-ray radiation in porous materials can arise from (Ramsay, 2002): (1) the assemblage of small particles in air or vacuum, comprising a porous material; (2) solid materials containing voids or pores; (3) solid solutions, such as alloys; and (4) colloidal dispersions of particles and polymers in liquids. In most porous silica solids, including geopolymers, the scattering pattern originates from the density difference between gel mass and void pores. The distinct structure of solids causes the fluctuations in the electron intensity, \( I(q) \), and scattering length, \( qd \). The \( q \) value is the momentum transfer, as expressed in Equation (3.14).

\[
q = 4\pi\lambda^{-1}\sin(\theta/2)
\]  

(3.14)

where \( \lambda \) is the wavelength of x-rays or neutrons and \( \theta \) is the reflective angle (only a few degrees) (Schmidt, 1988).

The data obtained from SAXS can be plotted as a logarithmic plot of the Intensity, \( I(q) \) against \( qd \), as shown in Figure 3.8. In the plot of \( I(q) \) vs \( qd \), there is a power law region, i.e. Porod region, whereby fractal dimensions are usually derived. This region is only applied to a small \( q \) range (qd>>1). The gradient of this plot is correlated to fractal surface dimension, as shown in Equation (3.15). Equation (3.15) assumes the “two phase approximation” (Schmidt, 1988), which can be used as long as the scattering at
small angle is not affected by the atomic scale structure. The “two phases approximation” assumes one phase is the solid, and the other is the empty pores. The SAXS equipment used in the thesis was a Bruker Nanostar in the long configuration (106 cm).

![Graph: Logarithmic plot of scattering intensity, I(Q) against the scattering length, Qd (Ramsay, 2002).]

\[ \ln I \propto (D_v - 6) \ln q \]  

(3.15)

### 3.3.9 Compressive strength and permeability testing

Geopolymers were subjected to compression tests using an ELE International Auto Test Compression Machine in accordance with the procedures described in AS 1012.9-1999. It is realised that inhomogeneities in geopolymers were prevalent, even if the materials were synthesised from the same batch. The variations in microstructure and physicochemical properties from one sample to the other may also cause significant variations in compressive strength testing. Therefore, the average strength of at least 3 specimens
were presented in the thesis. Prior to strength testing, both ends of cylindrical samples were capped with dental plaster (gypsum) in order to have flat surfaces.

Geopolymers were subjected to permeability measurement using Leeds permeability equipment, as shown in Figure 3.9 (Bamforth, 1987; Cabrera and Lysndale, 1988; Cabrera et al., 1989). The reproducibility of the permeability cells to measure the permeability of cement mortar and concrete was reported to be consistent (Cabrera et al., 1989). It will be shown in Chapter 5 that the reproducibility of the technique for geopolymers is also satisfactory.

![Figure 3.9 The Leeds Permeability Cells (Cabrera et al., 1989).](image)

The cell consists of a hollow stainless steel cylinder with a cap, whereby a percolating fluid, usually $N_2$ flows in from the top and come out at the bottom after passing through pores and channels in the porous materials. Inside the cell, there is a hollow, truncated rubber cone, which is fitted into the cell wall perfectly. The rubber cone holds the porous cylindrical sample inside its hole. The cone is custom made from Silastic 9161 RTV silicon rubber to withstand the pressure and leakage associated with nitrogen flow.
Nitrogen gas (N\textsubscript{2}) was used for the test because it was considered to be inert and non-adsorptive to geopolymer surface at ambient condition. Prior to each permeability test, geopolymer samples were weighed and dried at 105 °C for 24 h according to the procedures described in AS 1012.21-1999. After drying, the geopolymer mortars, which are cylindrical with 5 cm diameter x 10 cm height dimension, were cut into two pieces from the centre length followed by another 1 cm cut from the end. The two 4 cm length samples were tested consecutively, and the results of the two were averaged. To ensure a unidirectional flow through the sample, and to prevent leakage, the surface of geopolymer mortar was coated with epoxy at approximately 0.5 mm thickness.

The intrinsic permeability coefficient, \( k_g \) was derived using the expression proposed by Grube and Lawrence (Cabrera and Lynsdale, 1988):

\[
\frac{2\mu P_A vl}{A(P_1^2 - P_2^2)}
\]  

(3.16)

where \( k_g \) is an intrinsic gas permeability coefficient (m\textsuperscript{2}), \( v \) is the flow rate (cm\textsuperscript{3}/s), \( A \) is the cross-sectional area of specimen (m\textsuperscript{2}), \( l \) is the length of specimen (m), \( \mu \) is the viscosity of the fluid at ambient temperature (Ns/m\textsuperscript{2}), \( P_1 \) is absolute applied pressure at the entrance, and \( P_2 \) is the pressure at which the flow rate is measured (usually 1 bar). Equation (3.16) assumes a steady state gas flow. In practice, it took some time before a steady state condition was achieved. Therefore, the measurement of flow rate was taken only after the steady state flowrate was obtained, i.e. when the flow rate was constant.

3.4 Summary

In this chapter, the research methodologies, experimental procedures, and theory of equipment used have been described. The methodologies used can be divided into two main parts: the synthesis and characterisation of geopolymers. The resulting geopolymers and the derived products are determined by the variations in reactant concentrations and processing conditions (curing conditions). The derived products include wet geopolymer gels, dry geopolymer gels, zeolites, and aluminosilicate glasses.
The characterisation of geopolymer materials is further categorised into two main areas: chemical and physical characterisation. In the chemical characterisation, the analysis is conducted \textit{in-situ}, with the aims to understand the reaction mechanism, kinetics and ion transport mechanism during geopolymerisation. In the physical characterisation, the analysis is undertaken after geopolymers are fully hardened. The aims are to investigate the physico-chemical properties of geopolymer materials, and to understand the reaction mechanisms that lead to the observed properties. Using the various experimental methodologies presented in this chapter, the mechanism, kinetics, and properties of geopolymers, particularly fly ash-based geopolymers will be investigated in the following chapters.
CHAPTER 4
AN OVERVIEW OF THE PROPERTIES OF GEOPOLYMERS

In this chapter, the physico-chemical properties of geopolymers derived from metakaolinite (MK), granulated blast furnace slag (GBFS), and fly ash (FA) are investigated. The purpose of this study is to describe the complexities involved in studying geopolymers prepared from different raw materials due to the differences in chemical composition, mineralogies, and particle size distribution.

In all geopolymers, the de-polymerisation (or dissolution) of aluminosilicate phases is seen in the XRD patterns, by the shift of amorphous shoulder from the 2θ values of 20-30° to 25-35°. FTIR spectra also show a shift of the Si-O asymmetric stretching band peaks to lower wavenumbers, ~1021-1031 cm⁻¹, depending on the raw materials used. The peak shift suggests a higher content of non-bridging oxygen present due to the hydrolysis of aluminosilicate surface, i.e. more Si atoms in Si-O-Si (or Si-O-Al) structure are replaced by M atoms (M = Na or K). In addition, MK-based geopolymers display a fine porous and homogeneous gel structure, but GBFS- and FA-based geopolymers are characterised by non-reacted grains and porous gel structure. The results suggest the close connection between chemical reaction and the development of gel structure of geopolymers. From the amount of heat released, XRD, FTIR spectroscopy, SEM analyses, and compressive strength testing, the early reactivity of different geopolymers is seen to decrease in the following order: MK > GBFS > FA. It is likely that the higher composition of amorphous aluminosilicate and the larger surface area of metakaolinite particles lead to a higher reactivity.

4.1 Introduction

The physico-chemical properties of MK-based geopolymers had been extensively investigated by a number of workers (Barbosa et al., 2000; Davidovits, 1999; Duxson et
al., 2005a; c; Palomo and Glasser, 1992). In general, MK-based geopolymers possess superior early strength than other geopolymers due to high early reactivity. The early reactivity is caused by the amorphicity and large surface area of metakaolinite particles. However, the properties of GBFS-based geopolymers is found to be complicated by the inclusion of calcium and other impurities (Richardson and Cabrera, 2000; Richardson and Groves, 1992; 1997). Calcium is believed to control the rate and extent of reaction (Yip, 2004), and also induces the formation of CSH phases in a predominantly geopolymer gel matrix (Richardson and Groves, 1992; Yip, 2004). The properties of FA-based geopolymers are complicated by the inclusion of non-reactive aluminosilicate crystalline phases, e.g. mullite, quartz. The non-reactivity of these phases leads to the lack of reactivity in FA-based geopolymers. Nonetheless, the concentration of calcium in class F fly ash is less significant, thus its reactivity during geopolymerisation can be neglected.

The reactivity of MK-, GBFS-, and FA-based geopolymers will be compared by measuring the heat released during the activation of each raw material with 5M KOH solution. The physicochemical properties of these geopolymers (e.g. crystallinity, chemical bondings, microstructure, and compressive strength) will be investigated accordingly. The purpose of the study is to provide a preliminary understanding of the reactions and physico-chemical properties of geopolymers, and to highlight the complexities of studying geopolymers prepared from different raw materials. A detailed study on the mechanism, kinetics, and properties of geopolymers, particularly on FA-based geopolymers will be conducted in the following chapters.

### 4.2 Experimental methods

The rate of heat and total heat released during the alkali-activation of MK, GBFS, and FA was measured using JAF Isothermal Conduction Calorimeter. All raw materials were activated using 5M KOH solution at 30 °C. For comparison, the heat of hydration of Ordinary Portland Cement (OPC) with water was also measured.

Table 4.1 shows the oxide compositions of FA, GBFS, and MK, and the molar ratios of Si/Al, M/Al (where M = Na or K), and Ca/Al of each raw material. Hardened
geopolymers were subjected to powder XRD analysis (Philips PW 1800), and the FTIR spectra of geopolymers were obtained using a Bio-Rad FTS 165 FTIR spectrometer. Microstructures of geopolymers were studied using PHILLIPS XL30 SEM, operated at 20 keV. The elemental composition of gel structure was determined using a coupled EDAX instrument. The procedures and instrumentation for XRD, FTIR, and SEM-EDAX were detailed in Chapter 3.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>FA (weight %)</th>
<th>GBFS (weight %)</th>
<th>MK (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>3.5</td>
<td>43.4</td>
<td>0.10</td>
</tr>
<tr>
<td>SiO₂</td>
<td>50.0</td>
<td>34.4</td>
<td>54.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>28.0</td>
<td>14.1</td>
<td>40.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>12.0</td>
<td>0.11</td>
<td>0.76</td>
</tr>
<tr>
<td>SO₃</td>
<td>-</td>
<td>0.58</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>1.30</td>
<td>6.30</td>
<td>0.41</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.70</td>
<td>0.13</td>
<td>2.52</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.20</td>
<td>0.30</td>
<td>0.07</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>-</td>
<td>-</td>
<td>0.11</td>
</tr>
<tr>
<td>TiO₂</td>
<td>-</td>
<td>0.56</td>
<td>0.02</td>
</tr>
<tr>
<td>Mn₂O₃</td>
<td>-</td>
<td>0.13</td>
<td>0.01</td>
</tr>
<tr>
<td>LOI</td>
<td>4.30</td>
<td>0.19</td>
<td>0.80</td>
</tr>
<tr>
<td>Si/Al (molar ratio)</td>
<td>6.06</td>
<td>8.28</td>
<td>4.60</td>
</tr>
<tr>
<td>M/Al (molar ratio)</td>
<td>0.04</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>Ca/Al (molar ratio)</td>
<td>0.46</td>
<td>11.21</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.1 The composition of raw materials, based on XRF analysis in Table 3.1 (in weight %).

For compressive strength testing each raw material was reacted at different water to binder ratios because of the different water requirement, originating from the different mineralogy and physical properties. The composition of geopolymers and their activating solutions are shown in Table 4.2. The theoretical M/Al ratio is calculated based on the assumption that all amorphous aluminium (as determined by quantitative XRD analysis) will dissolve and participate in geopolymerisation. This assumption is
not totally correct, as some glassy phases are more reactive than the others, but is sufficiently accurate for the purpose of the analysis in the study. Moreover, uniform-sized river sand (180µm) was added to fresh geopolymer mix at a constant weight ratio of 2:1 (sand:binder).

Table 4.2 MK-, GBFS-, and FA-based geopolymers synthesised with alkali-silicate solutions ([SiO₂] = 2.5M) at ambient condition (25 ± 2 °C, 50 ± 5 % RH, with RH = Relative Humidity). The theoretical M/Al ratios are calculated based on the assumption that all amorphous aluminium are fully reacted.

<table>
<thead>
<tr>
<th>System</th>
<th>[KOH], M</th>
<th>H₂O/M₂O</th>
<th>Density (g/L)</th>
<th>SiO₂/M₂O (M = Na or K)</th>
<th>M/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK1</td>
<td>10</td>
<td>7.26</td>
<td>1515</td>
<td>0.44</td>
<td>2.04</td>
</tr>
<tr>
<td>MK2</td>
<td>5</td>
<td>14.85</td>
<td>1355</td>
<td>0.78</td>
<td>1.58</td>
</tr>
<tr>
<td>MK3</td>
<td>2.5</td>
<td>26.00</td>
<td>1287</td>
<td>1.27</td>
<td>1.20</td>
</tr>
<tr>
<td>GBFS1</td>
<td>10</td>
<td>7.26</td>
<td>1515</td>
<td>0.44</td>
<td>4.55</td>
</tr>
<tr>
<td>GBFS2</td>
<td>5</td>
<td>14.85</td>
<td>1355</td>
<td>0.78</td>
<td>2.33</td>
</tr>
<tr>
<td>GBFS3</td>
<td>2.5</td>
<td>26.00</td>
<td>1287</td>
<td>1.27</td>
<td>1.72</td>
</tr>
<tr>
<td>FA1</td>
<td>10</td>
<td>7.26</td>
<td>1515</td>
<td>0.44</td>
<td>0.95</td>
</tr>
<tr>
<td>FA2</td>
<td>5</td>
<td>14.85</td>
<td>1355</td>
<td>0.78</td>
<td>0.74</td>
</tr>
<tr>
<td>FA3</td>
<td>2.5</td>
<td>26.00</td>
<td>1287</td>
<td>1.27</td>
<td>0.54</td>
</tr>
</tbody>
</table>

4.3 The heat of reaction of geopolymers

In this chapter, the analyses and discussions on the heat of reaction are intended to be preliminary. The purpose is to correlate the evolution of heat with various possible reaction steps that occur during the activation of MK, GBFS, and FA. A more detailed investigation of heat of reaction, particularly of FA-based geopolymerisation will be presented in Chapter 7.

Figures 4.1a and 4.1b show the rate of heat and total heat released during the activation of OPC, MK, GBFS, and FA at 30 °C respectively. For alkali-activated MK, there is a narrow heat curve for the first hour (inset in Figure 4.1a). The subsequent heat curve is rather long, lasting 14 hours (Figure 4.1a). Granizo and co-workers (1998; 2000)
reported that the initial heat release was associated with the heat of dissolution of $\text{Si}^{4+}$.

Figure 4.1 (a) The rate of heat and (b) the total heat of reaction of hydrated OPC, alkali-activated MK, GBFS, and FA for 24 hours. The inset in Figure 4.1a shows the rate of heat released in the first 1.6 hours. The dotted circle in Figure 4.1b indicates the possible formation of zeolites.
and Al\(^{3+}\) precursors. The subsequent heat release is likely to be caused by the coprecipitation of these precursors to form aluminosilicate gel (Krivenko, 1994). Following these reactions, further dissolution and precipitation still take place, but to a lesser extent. This can be seen from the continuing heat dissipation, even after 14 hours of reaction (Figure 4.1b).

The initial heat release from the activation of GBFS is characterised by a single heat curve, lasts approximately 4 hours (Figure 4.1a). It is believed that this heat release is associated with the dissolution of aluminosilicate precursors and precipitation of aluminosilicate gel, which is induced by a high alkali concentration in the activating solution. Nonetheless, it seems that the dissolution and precipitation might not be the only reactions contributing to the observed heat trend. From the kinetics study of alkali-activated GBFS, Fernandez-Jimenez et al. (1998) proposed that CSH is formed along with the polymerisation of aluminosilicate gel. The content of calcium in GBFS is known to be significantly high, such that it affects the incorporation of aluminium into silicate structure, i.e. calcium accelerates the gelation of aluminosilicate gel and induces the formation of CSH phases (Fernandez-Jimenez et al., 1998; Wang and Scrivener, 1995). So even though a distinct heat of CSH formation is not clearly seen, it is possible that the observed heat of reaction also incorporates the heat of CSH formation. The formation of CSH in GBFS-based geopolymers will be evident from the XRD and FTIR analyses, presented later in the next section.

For comparison, the heat of hydration of OPC was also measured (Figure 4.1). Firstly, the initial heat curve from OPC hydration is associated with the wetting of lime (CH). This is followed by a fast hydration of Tricalcium aluminate (C\(_3\)A) and gypsum (CaSO\(_4\)) to form ettringite (Bezjak, 1980). It can be seen that the time for initial heat release is very short, lasting ~0.3 h (inset in Figure 4.1a). This heat curve is also observed in activated GBFS because of the presence of C\(_3\)A and gypsum in GBFS (Talling and Krivenko, 1997). However, the amount of heat released in GBFS is small, and the heat curve is likely to be overlapped by the larger subsequent heat curve (inset in Figure 4.1a).
The subsequent heat curve (starting from the 2nd hour in Figure 4.1a) from the hydration of OPC is believed to be attributed to the heat of hydration of calcium silicate phases, C$_3$S and C$_2$S (Barker, 1990; Bezjak, 1980). In contrast to alkali-activated GBFS, the formation of CSH in OPC can be clearly seen from the heat released. In addition, the total heat released in OPC is also greater than in alkali-activated GBFS, which is likely to indicate a greater extent of CSH being formed (Figure 4.1b).

The amount of heat released from the alkali-activated FA is smaller than from alkali-activated MK or GBFS (Figure 4.1b). This is caused by a smaller content of reactive aluminosilicate phases (amorphous), smaller surface area, and the contribution of reactivity and kinetics of particle size and Si:Al ratio (Fernandez-Jimenez et al., 2006d). However, there is also a second heat release, observed approximately after 18-20 hours of reaction (highlighted in Figure 4.1b). It is hypothesised that this heat release is associated with the formation of zeolitic phases. During the formation of zeolites, there is usually an induction period after the dissolution of precursors, whereby aluminosilicate precursors partially orientate to nucleate, gel, and finally grow into crystals (Barrer, 1989). This induction period is shown by the delayed heat release, i.e. up to 18 hours of reaction time (Figure 4.1b).

The formation of zeolites during geopolymerisation has been widely documented, namely in MK- (Palomo and Glasser, 1992), GBFS- (Krivenko, 1994), and FA-based geopolymerisation (Bakharev, 2005). Nonetheless, most zeolites are more successfully synthesised from alkali-activated FA (Murayama et al., 2002; Querol et al., 1995; 1997a; b). In Chapter 7, the polymerisation and crystallisation of aluminosilicate species during fly ash-based geopolymerisation will be further investigated. The conditions in which zeolites are formed will be determined.

### 4.4 The chemical structure of geopolymers

In the following section, the crystallinity and aluminosilicate structure (chemical bonding) in geopolymers synthesised from MK, GBFS, and FA are characterised using XRD and FTIR.
4.4.1 The crystallinity of geopolymers

The XRD patterns of raw materials and their-derived geopolymers are shown in Figure 4.2. MK shows a strong shoulder at 20 ranging from 20 to 30°, indicating the presence of amorphous aluminosilicate phases (Barbosa et al., 2000; Palomo and Glasser, 1992; Puertas et al., 2000). In GBFS and FA, the intensities of these shoulders are weak, indicating smaller amount of amorphous phases present. Other crystalline peaks are observed in XRD patterns of the raw materials (Figure 4.2). MK contains muscovite, quartz, and mullite, which are formed due to calcination of kaolinite at high temperatures (Holm, 2001). GBFS contains calcium aluminosilicate glass with its crystal inclusions of larnite, melilite, and phillipsite (Talling and Krivenko, 1997). FA contains α-quartz, mullite, calcite, and magnetite (Qian et al., 1988).

Figure 4.2 The XRD patterns of MK, GBFS, FA, and their derived geopolymers (refer Table 4.2 for the compositions of geopolymers). Q, M, L, Mus, Phil, Mel, Cal, and Mag represent α-quartz, mullite, larnite, muscovite, phillipsite, melilite, calcite, and magnetite respectively. The dotted line highlights the characteristic diffraction angle of the amorphous aluminosilicate phases in raw materials (20° < 20 < 30°), while the dotted circle highlights the amorphous aluminosilicate phases in geopolymers (25° < 20 < 35°).
Upon activation, some crystalline components in MK and GBFS disappear from the diffractograms (Figure 4.2). In addition, there is a shift of aluminosilicate shoulder to greater values of 20 after activation, i.e. to 25-35°. The shift of amorphous shoulder peaks from their original position is induced by the hydrolytic attack of alkali metal cations, which results in de-polymerisation of the aluminosilicate structure on solid surface (Palomo and Glasser, 1992; Palomo et al., 1999b). In GBFS-based geopolymers (GBFS2), CSH is also formed (Figure 4.2). The identified CSH phases have the diffraction patterns that resemble tobermorite and heulandite minerals, which possess Al in their hydrated structures, as reported by Fernandez-Jimenez et al. (2003).

### 4.4.2 The aluminosilicate structure of geopolymers

Figure 4.3 shows the absorption spectra (in transmission mode) of raw materials and geopolymers. Table 4.3 lists the assignment of wavenumbers (or frequencies) for molecular vibrations that are apparent in the absorption spectra of geopolymers. In general, geopolymers consist of a short-range network of tetrahedrally-bonded Si-O-Si or/and Si-O-Al, loaded with water and carbonate species (Figure 4.3). The structure of molecular water in geopolymer gel is characterised by the O-H stretching band, with its broad absorption shoulders ranging from 3200 cm⁻¹ to 3700 cm⁻¹ (Figure 4.3). The peaks of these absorption shoulders range from 3440 cm⁻¹ to 3480 cm⁻¹. Weak absorption peaks at 2928 cm⁻¹ and 2855 cm⁻¹ correspond to O-H vibrational frequencies, while 1650 cm⁻¹ corresponds to H-O-H bending frequency. A sharp peak at 1450 cm⁻¹ is assigned to the vibrational stretching frequency of C-O in carbonates. In the synthesis of geopolymers, unreacted alkali cations react with dissolved CO₂ to form carbonate in the gel matrix (Barbosa et al., 2000). After the materials set, alkali-containing pore solution is likely to diffuse to the surface through ‘capillary pores’ due to a developing concentration gradient between the core and surface of specimen. The transport of alkali metal cations leads to the precipitation of carbonates on the surface, known as efflorescence (Neville, 1995). Therefore, from the peak intensities observed in the FTIR spectra, the amounts of molecular water and carbonate are greater in geopolymers than in raw materials.
Figure 4.3 The FTIR spectra (in a transmission mode) of: (a) MK and MK2; (b) GBFS and GBFS2; and (c) FA and FA2 (refer Table 4.2 for the compositions of geopolymers).
Table 4.3 Vibrational frequency assignments for geopolymers (Efimov et al., 2003; Farmer, 1988; Lee and Van Deventer, 2003; Onorato et al., 1985; Takei et al., 1999).

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Vibrational assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3440-3480</td>
<td>Adsorbed O-H stretching</td>
</tr>
<tr>
<td>2855, 2930</td>
<td>Adsorbed O-H stretching</td>
</tr>
<tr>
<td>1650-1655</td>
<td>Adsorbed H-O-H bending</td>
</tr>
<tr>
<td>1420-1480</td>
<td>C-O stretching (carbonates)</td>
</tr>
<tr>
<td>865-875</td>
<td>O-C-O bending (carbonates)</td>
</tr>
<tr>
<td>950-1250</td>
<td>Asymmetric Si-O-Si and/or Al-O-Si stretching</td>
</tr>
<tr>
<td>950-980</td>
<td>Si-O stretching (Si-O-M), M = Na or K</td>
</tr>
<tr>
<td>870</td>
<td>Si-OH stretching</td>
</tr>
<tr>
<td>600-800</td>
<td>Al-O bands</td>
</tr>
<tr>
<td>797</td>
<td>Network Si-O-Si (or Si-O-Al) stretching</td>
</tr>
<tr>
<td>558</td>
<td>Network Si-O-Si (or Si-O-Al) symmetric</td>
</tr>
<tr>
<td>461</td>
<td>Network Al-O-Si bending</td>
</tr>
</tbody>
</table>

In MK, network Si-O-Si (or Si-O-Al) bending band is observed at 440-482 cm⁻¹ in Figure 4.3a (Farmer, 1988). Network aluminosilicates are essentially tetrahedral silicon and aluminium, which are arranged in long-ordering structures, such as in the cage or ring structures. However, MK contains a significant amount of amorphous aluminosilicate, thus the network absorption bands are reasonably weak. Upon activation, there appears to be a slight change of peak position of network Si-O-Al, i.e. there is a shift to a lower wavenumber (447-478 cm⁻¹), with a stronger absorption intensity (Figure 4.3a). There is also a perturbation of a small shoulder peak, located at 822 cm⁻¹, which shifts to a higher wavenumber at 837 cm⁻¹ after geopolymerisation. This indicates the dissolution of tetrahedral Al-O from Al₂O₃ in MK (Alkan et al., 2005; Tarte, 1967). In addition, the disruption in Al-O environment at 600-800 cm⁻¹ is observed (Alkan et al., 2005; Barbosa et al., 2000).

The spectra of asymmetric Si-O stretching bands (950-1250 cm⁻¹) in MK and MK-based geopolymers are broad because of the overlapping of various types of Si-O- bonds.
These bonds include Si-O-Si, Si-O-Al, and Si-O-M (where M = Na or K), resulting from the presence of various phases surrounding the silica structure. Therefore, only those vibrations that are unique and do not interfere with other silicate minerals are observed distinctly in the IR spectrum (Farmer, 1988). The Si-O- peak in MK is seen to be at 1085 cm$^{-1}$ (Figure 4.3a). Upon activation, there is a shift of this peak to a lower wavenumber, 1021 cm$^{-1}$, suggesting a higher content of non-bridging oxygen due to hydrolysis, i.e. more Si atoms in Si-O-Si (or Si-O-Al) are replaced by M atoms (Clark et al., 1976).

In GBFS, the network Si-O-Si (or Si-O-Al) band is also observed at 440-478 cm$^{-1}$ (Figure 4.3b). Upon activation, the absorption is stronger with a significant alteration in the spectra of Al-O structure (600-800 cm$^{-1}$). In contrast to MK, there is no tetrahedral Al-O stretching band from Al$_2$O$_3$ phase. This is attributed to the lack of ‘pure’ Al$_2$O$_3$ in GBFS because aluminium is incorporated in other mineral phases (Talling and Krivenko, 1997). The silica spectra at 985 and 1123 cm$^{-1}$ appear as one broad shoulder peak. Again, the absorption in this region tends to be broad due to the overlapping of various aluminosilicate bands. It is believed the calcium-silicate phases in GBFS contribute to the lower stretching frequency at 985 cm$^{-1}$, while the aluminosilicate phases contribute to a higher frequency at 1123 cm$^{-1}$ (Fernandez-Jimenez et al., 2003; Puertas et al., 2000; Yu et al., 1999). Upon activation, there is a shift to lower wavenumbers at 957 and 1030 cm$^{-1}$ respectively.

In FA, the absorption bands at 467, 575, 733 cm$^{-1}$ are clear indication of network tetrahedral aluminosilicates from mullite (Figure 4.3c) (Vempati, 1994). Upon activation, there is no perturbation of these network bands because of the non-reactivity of mullite and other crystalline minerals from FA (Pietersen et al., 1988). Calcite peak is also observed at 876 cm$^{-1}$, both in original FA and FA-based geopolymers (FA2). Similar to MK, there is a small shoulder, centred at 802 cm$^{-1}$ indicating Al-O vibrational frequency in Al$_2$O$_3$. However, upon activation, this peak totally disappears, but stronger network tetrahedral aluminosilicates are observed (575 and 733 cm$^{-1}$). The strongest absorption peak of Si-O band is centred at 1098 cm$^{-1}$ (Iyer, 2002; Vempati, 1994). Upon activation, this peak shifts to a lower wavenumber at 1021 cm$^{-1}$, as shown in MK- and
4.5 Microstructure of geopolymers

Figure 4.4 shows the BSE (backscattered electron) images of MK2, GBFS2, and FA2 respectively. Figure 4.4a shows the microstructure of MK-based geopolymers, which is characterised by a reasonably homogeneous gel structure. The homogeneous gel structure is attributed to the high reactivity, resulting from the high content of amorphous aluminosilicate phases and large surface area of metakaolinite particles. The macro-crack shown in Figure 4.4a is caused by the drying shrinkage, a physical property, inherent of the gel. The gel shrinkage occurs because the removal of water during polycondensation creates capillary tension within the gel matrices (Brinker and Scherer, 1990).

The average gel composition in MK2 is $M_{1.4}AlSi_{1.8}$ (where M=Na or K). The Si:Al ratio in the gel is close 2.0, which is the Si/Al ratio in the poly-sialatesiloxo structure (Davidovits, 1999). In addition, the M/Al ratio is 1.4, which is greater than 1. In an ‘ideal’, i.e. a completely reacted system, the ratio of M/Al should be equal to 1 because every Si-O’-Al structure requires only one alkali cation to balance its excess negative charge. The high alkali concentration in the gel, however, is likely to be caused by the high liquid to solid ratio used in the synthesis, as more water is required to coat the surface of fine MK particles to initiate early reaction (Table 4.2). The measured high alkali concentration is also caused by limited dissolution of aluminium from MK due to restricted reaction conditions, such as low temperature and high concentration of soluble silicate in the activating solution. In following chapters, the effect of alkali-silicate concentration, water content, reaction temperature, and time on the mechanism and kinetics of geopolymerisation will be investigated thoroughly. It will be found that the properties and composition of gel structure vary depending on those parameters.

In contrast to MK, the microstructure of GBFS-based geopolymers is heterogeneous, and is characterised by the presence of slag grain residues and geopolymer gel (Figure 4.4b). The slag grains show a high concentration of calcium, but a low concentration of alkali ($Ca_{2.9}M_{0.1}AlSi_{2.8}$). The slag grains possess irregular cubic shape, and appear to be
in brighter contrast under SEM. The geopolymer gel has a high concentration of calcium and alkali cations (Ca$_{2.2}$M$_{1.5}$AlSi$_{2.2}$). A high concentration of calcium in the gel mainly results from the dissolution and precipitation of amorphous Ca-based minerals in GBFS. The geopolymer gel is also more continuous and in darker contrast under SEM. Similar to MK-based geopolymers, the concentration of alkali in the gel is rather high (M/Al = 1.5), which is caused by a high water to solid ratio initially used in the synthesis.

Figure 4.4 (a) The microstructure of MK-based geopolymers (MK2), (b) GBFS-based geopolymers (GBFS2), and (c) FA- based geopolymers (FA2) at 28 days. “x“ indicates an unreacted slag grain, “y“ indicates unreacted fly ash particles, and “z“ indicates iron and/or calcium-based phases.
In this study, the CSH phases have been partly identified from XRD and FTIR spectra, but are not seen under SEM. It is likely that CSH phases do not form readily under the conditions investigated in this study. Even if they are formed, it will be a ‘localised’ reaction, i.e. in a region of low alkali and silicate concentration (Richardson and Groves, 1992; Yip, 2004).

The microstructure of FA-based geopolymers is a mixture of non- or partly-reacted fly ash grains, residual alkaline precipitates, and geopolymer gel (Figure 4.4c). In contrast to MK and GBFS, the chemistry and composition of FA are more complex, whereby the variations from one particle to another are commonly observed (Hemmings and Berry, 1988; Qian et al., 1988). From Figure 4.4c, the iron and calcium-containing particles, namely magnetite and calcite appear to be ‘brighter’ under SEM. The other ‘darker’ structures are amorphous and/or crystalline aluminosilicates. Upon activation, only amorphous aluminosilicate phases dissolve to a large extent. The iron and calcium phases also dissolve (Pietersen et al., 1988), but to smaller extents, and are not incorporated into the aluminosilicate gel structure. This can be seen from the XRD results, whereby the crystalline structures of calcium and iron phases remain to be non-reactive (Figure 4.2). The gel structure of FA-based geopolymers is more porous and heterogeneous than MK- or GBFS-based geopolymers. The average composition of the gel is MAiSi_{1.6}O_{5.5}. Unlike in MK and GBFS, less water is required to wet the larger and spherical FA particles. As a result, there is also less alkali used in FA-based geopolymerisation, as shown by the theoretical M/Al ratio = 1. The lower reactivity of fly ash particles and the lower alkali concentration lead to the lower reactivity of FA-based geopolymers.

4.6 The compressive strength of geopolymers

The strength of geopolymers is believed to originate from the strong chemical bondings in the aluminosilicate gel formed, as well as the physical and chemical reactions occurring between the geopolymer gel, non- or partly-reacted phases, and particulate aggregates. From earlier results and discussions, a preliminary understanding on early reactions and structures of MK-, GBFS-, and FA-based geopolymers has been established. In this section, the compressive strength of these geopolymers is
determined in order to correlate the chemical to the physical properties of geopolymers.

The compressive strength of various geopolymers at 7, 28, and 90 days is shown in Figure 4.5. The strength of MK-based geopolymers originates from the fine and homogeneous gel structure and the effects of unreacted particles and impurities are minimal (Figure 4.4a). Overall, MK-based geopolymers display a high early strength (7 days), but only a slight increase of strength after 7 days. Again, this is attributed to a higher content of amorphous aluminosilicate phases, finer particle size, and the ability of MK to release Si and Al for reaction immediately, which altogether results in a higher early reactivity. The rapid increase in strength may also be attributed to the higher alkali concentration used to activate metakaolinite, as shown by a dramatic decrease in strength as the alkali concentration decreases (Figure 4.5). The low alkalinity in the activating solutions causes less hydrolytic attack on the raw materials, thus inhibits the dissolution of aluminosilicate precursors. As a result, there is a lack of viable silicate and aluminate species to polymerise into aluminosilicate gel.

![Figure 4.5 The compressive strength of MK-, GBFS-, and FA-based geopolymers synthesised with various alkali-silicate solutions at 30 °C (refer to Table 4.2 for the composition of studied geopolymers).](image)
In contrast to MK-based geopolymers, the structural strength of GBFS- and FA-based geopolymers comes from the intimate bonding between partly reacted phases and geopolymer gel (Figures 4.4b and 4.4c). Besides aluminosilicates, GBFS-based geopolymers might contain CSH, CaOH, and other Ca-residues (Krivenko, 1994; Richardson and Groves, 1997; Yip, 2004). The interaction between slag grains, CSH, Ca-residues, and geopolymer gel is believed to contribute to the observed physical strength (Richardson and Groves, 1997). Similar to MK, GBFS-based geopolymers also have a high early reactivity, particularly those synthesised with solutions of high alkali concentration.

From Figure 4.5, it appears that the early strength of FA-based geopolymers is always lower than MK- or GBFS-based geopolymers (7 days). This may be attributed to: (1) lower alkali concentration in the activating solutions (compare the different Al/M ratios for the same activating solution used in Table 4.2), and/or (2) the rate of reaction of fly ash-based geopolymers is inherently slower. In contrast to MK, FA has a lower content of reactive aluminosilicate phase (with amorphous Si:Al ratio close to 2) and smaller surface area. Most of the crystalline phases existing in fly ash, such as quartz, mullite, haematite, and calcite are relatively inert upon contact with alkaline solution at room temperature (Hemmings and Berry, 1988). In addition, the calcium content in Class F fly ash is too low to cause any significant effect in geopolymerisation. These factors have accounted for the slower reaction observed in FA-based geopolymerisation.

4.7 Conclusions

Based on the measurement of the heat of reaction, XRD, FTIR, and SEM analyses, it can be concluded that the reactivity of MK is greater than for GBFS and FA. The extent of reaction in MK is higher due to a greater amount of amorphous aluminosilicate and a larger surface area of MK particles. The microstructure of MK-based geopolymers reveals a fine porous and homogeneous gel structure, which is reflected in a high early compressive strength as well. The microstructures of GBFS- and FA-based geopolymers show more heterogeneous gel structures, characterised by non-reacted particle grains and geopolymer gel.
The dissolution of amorphous aluminosilicate in raw materials can be seen from the changes in the XRD patterns and FTIR spectra. Upon activation, there is a shift of the shoulder from the 2θ values of 20° - 30° to 25° - 35°, which is the characteristic diffraction of amorphous aluminosilicate gel in geopolymers. In addition, the absorption peaks of surface silica band are shifted to lower wavenumbers (approximately 1021-1030 cm⁻¹), depending on the type of raw materials used. The shift of peaks signifies the presence of non-bridging oxygen due to hydrolysis, i.e. more Si atoms in Si-O-Si (or Si-O-Al) are replaced by M atoms (M = Na and/or K).

In conclusion, each geopolymer possesses different reactivity, chemical structure, and physical properties due to the variation in composition of raw materials, particle size, and mineralogies. It is therefore impossible to compare the geopolymerisation of MK, GBFS, and FA due to the different mechanism and kinetics of individual reaction steps from each material. Therefore, in the following chapters, a large volume of work will be devoted to understanding the chemistry of fly ash-based geopolymerisation further.
CHAPTER 5
THE EFFECT OF CURING CONDITIONS ON
THE PROPERTIES OF FLY ASH BASED-
GEOPOLYMERS

In this chapter, the effect of curing temperature, relative humidity, and curing time on the physico-chemical properties of fly ash-based geopolymers is investigated systematically. The geopolymers that are cured at a high temperature (75 °C) possess high compressive strength and low permeability due to a greater rate and extent of reaction. It is believed that higher temperatures activate aluminosilicate phases in fly ash that are otherwise not reactive at lower temperatures. While elevated temperature is required to achieve a higher degree of activation, the rate of reaction is also accelerated at high temperatures, resulting in the geopolymers setting rapidly. Therefore, the choice of optimal curing temperatures should be a balance between enhancing dissolution of aluminosilicate precursors and preventing rapid setting of the materials.

At high curing temperatures (e.g. 50 and 75 °C), the peaks corresponding to the asymmetric stretching of Si-O in the FTIR spectra shift gradually to lower wavenumbers, indicating a greater extent of de-polymerisation of aluminosilicate on the fly ash surface. The carbonation process is also less likely to occur in geopolymers cured at high temperature and RH. From EDAX analysis, the composition of geopolymers that are cured at 30 °C has a high M/Al ratio (M/Al > 1, where M = Na or K). This indicates low reactivity, i.e. a low aluminium content in the gel. In contrast, geopolymers that are cured at 75 °C show two regions of gel phase. Firstly, the geopolymer gel, which is characterised by a low M/Al ratio (M/Al < 1) and a denser gel structure, indicating a gel of higher reactivity. Secondly, the ‘islands’ of alkaline precipitates, which are characterised by a high M/Al ratio (M/Al > 1) and a coarser pore structure. Such phase separation occurs because the rate of reaction is accelerated at high temperatures, which results in a quick ‘entrainment’ of pore solution that contains...
residual alkali.


5.1 Introduction

In the literature, the effect of curing conditions on pozzolanic-blended cements, such as MK- (Bai et al., 2002; Curcio et al., 1998; Dunster et al., 1993; Poon et al., 2001; Rojas and Cabrera, 2002; Rojas and Sanchez de Rojas, 2003; Wild et al., 1996); GBFS- (Aldea et al., 2000; Bakharev et al., 1999; Ma et al., 1994; Shi, 1996); and FA-blended cements (Bleszynski and Thomas, 1998; Brough et al., 2001; Lee et al., 1997; Li et al., 2000; Pietersen and Bijen, 1994) has been widely investigated. However, few (Bakharev, 2005; Barbosa et al., 2000; Van Jaarsveld et al., 2002) have actually investigated the effect of curing conditions on the properties of ‘geopolymers’. As a result, the effect of curing on the reaction mechanism and kinetics of geopolymerisation has never been thoroughly investigated nor has it been fully elucidated. The lack of systematic studies on curing conditions also leads to differences in the physical and chemical properties reported. The aim of the current study is to understand the effect of changing curing parameters (eg. temperature, humidity, and time) on the physico-chemical properties of geopolymers (eg. strength, permeability, and gel structure).

The rate and extent of reaction from activating fly ash with alkali-silicate solutions at different temperatures will be determined by measuring the heat of reaction. The compressive strength of geopolymers, which are cured at different temperature and humidity will be tested and correlated with the permeability values. It is believed that temperature accelerates the rate of activation of fly ash, thus increasing early reactivity and strength of geopolymers, while the effect of humidity is rather unclear (Bakharev, 2005; Van Jaarsveld et al., 2002). The strength of binders usually correlates with the porosity and permeability (Davis and Sing, 2002). The porosity is used to define the volume unoccupied by solid in the porous materials. The permeability is used to define
the open and inter-connected pores. The pore connectivity is more significant than individual (or discrete) pores because it determines the resistance to chemical attack, the resistance to freeze-thawing cycle, and weathering conditions (Neville, 1995). The permeability in fly ash-based geopolymers is likely to originate from: (1) the porous gaps between the geopolymer gel and sand aggregates and partially reacted fly ash particles, (2) the channels and pores created in the material by water movement during curing, (3) the inherent porous nature of the geopolymer gel, and (4) the partially reacted fly ash particles themselves.

5.2 Experimental methods

1g of fly ash was activated with alkali-silicate solution in JAF conduction calorimeter at 30, 40, and 50 °C for 48 hours. In a separate set of experiment, geopolymers were synthesised according to the procedures described in Chapter 3. The composition of the activating solution was fixed at SiO$_2$/M$_2$O = 0.79 and H$_2$O/M$_2$O = 14.85 (where M = Na or K, same as FA2 in Table 4.2). For compressive strength and permeability measurements, uni-sized river sand (180µm) was added to fresh geopolymer pastes at the sand to binder ratio of 2 to 1. Then, freshly mixed geopolymers were subjected to various curing regimes, as listed in Table 5.1.

Table 5.1 Various curing regimes applied on fly ash-based geopolymers. RH refers to relative humidity.

<table>
<thead>
<tr>
<th>Geopolymers</th>
<th>Curing method</th>
<th>Curing time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30°C – 30% RH</td>
<td>4, 24, 48</td>
</tr>
<tr>
<td>B</td>
<td>50°C – 30% RH</td>
<td>4, 24, 48</td>
</tr>
<tr>
<td>C</td>
<td>75°C – 30% RH</td>
<td>4, 24, 48</td>
</tr>
<tr>
<td>D</td>
<td>30°C – 75% RH</td>
<td>4, 24, 48</td>
</tr>
<tr>
<td>E</td>
<td>50°C – 75% RH</td>
<td>4, 24, 48</td>
</tr>
<tr>
<td>F</td>
<td>75°C – 75% RH</td>
<td>4, 24, 48</td>
</tr>
</tbody>
</table>

The compressive strength of Geopolymers A to F was tested at 7, 28, and 90 days, while the permeability was measured at 90 days. The strength result was the average of 3 consecutive tests, while the permeability coefficient was the average of 6 measurements.
In the study, the intrinsic permeability of fly ash-based geopolymers was measured using Leeds permeability cells that were commonly used to measure the intrinsic permeability in cement and concrete. The experiment was conducted according to the procedures described in Section 3.3.9, and the equations used to calculate intrinsic permeability coefficient was expressed in Equation 3.16 (in Chapter 3).

Furthermore, fly ash-based geopolymers were crushed, and subjected to powder XRD (Philips PW 1800) and FTIR analyses (Bio-Rad FTS 165 FTIR spectrometer). To simulate an in-situ hardening process of geopolymer gel, fly ash was reacted in Environmental SEM (FEI Quanta 200) at 30 °C, 30% RH, and micrographs were taken at 0, 70, and 100 minutes reaction time. The micrographs of hardened geopolymers were produced using a PHILLIPS XL30 SEM, operated at 20 keV. The elemental composition of geopolymers was also obtained using a coupled EDAX instrument.

5.3 The effect of temperature on heat of reaction of fly ash-based geopolymers

Figure 5.1 shows the rate and total heat of reaction from activating fly ash at 30, 40, and 50 °C. In Chapter 4, it was mentioned that the initial heat release was associated with the dissolution of Si\(^{4+}\) and Al\(^{3+}\) precursors from amorphous aluminosilicate (Alonso and Palomo, 2001a; b). After initial heat release, further dissolution and polycondensation of aluminosilicate still take place, which can be seen from the continuing heat dissipated (Figures 5.1a and 5.1b). As the temperature of reaction is increased, there is an increase in the amount of heat released, which indicates a greater extent of reaction has taken place. It has been known that fly ash particles possess a variation in composition and structure and therefore a different reactivity when it is reacted at different temperatures (Hemmings and Berry, 1988; Pietersen et al., 1988). It is thought that an increase in the reaction temperature results in a higher degree of activation of those phases that are otherwise not reactive at lower temperatures. Apart from the extent of reaction, elevated temperatures also increase the rate of reaction. For example, at 50 °C, the rate of heat increases significantly, but reduces at a higher rate than at lower temperatures (Figure 5.1a). Figure 5.1b also shows the total heat released at 50 °C increases for ~ 36 hours, at which point the total heat released gradually reduces. This behaviour, however, is not
Figure 5.1 (a) The rate of heat and (b) total heat released in fly ash-based geopolymerisation at 30, 40, and 50 °C. The inset in Figure 5.1a plots the rate of heat released in the first 2 hours.
observed at lower temperatures (Figure 5.1b). The reduction of heat at 50 °C is attributed to the endothermic heating of hardened geopolymers. Geopolymers absorb heat, which is supplied by the calorimeter to maintain an isothermal condition (50 °C). A late reduction of heat only appears in geopolymers, which are reacted at higher temperatures because the reaction rate has been accelerated, thus geopolymers set early.

A high reaction temperature (50 °C) may not be required to activate most reactive phases in fly ash. Instead, provided that a sufficient amount of reaction time is given, the reactivity at lower temperatures can be higher than the reactivity at higher temperatures because the reactive phases will finally dissolve and polymerise to gel (compare the heat of reaction at 40 °C with 50 °C in Figure 5.1b). This occurs because low-temperature curing ‘delays’ reactivity by preventing the rapid setting of geopolymer materials. Nonetheless, curing at elevated temperatures is still required to achieve a high degree of fly ash activation. Therefore, the choice of optimal curing temperatures should be a balance between enhancing dissolution of precursors and preventing the rapid setting of materials. The beneficial effect of ‘delayed’ reactivity is reflected in the physical properties of geopolymers as well, which will be shown in Section 5.4.

5.4 The effect of curing conditions on the physico-chemical properties of fly ash-based geopolymers

The effect of curing conditions (e.g. curing temperature, humidity, and time) on the physico-chemical properties (e.g. compressive strength, permeability, aluminosilicate structure, and microstructure) is presented in the following section.

5.4.1 Compressive strength

The compressive strength of fly ash-based geopolymers at the age of 7, 28, and 90 days is shown in Figure 5.2. Elevating curing temperatures from 30 to 75 °C increases the early strength of geopolymers immediately due to an increase in the rate and extent of reaction. In general, there is an increase of strength from 7 to 28, and 90 days, showing that continuous dissolution and polycondensation still take place, even when the curing application has ceased. The effect of temperature in controlling the rate of reaction can
be seen from the different rate of strength increase with increasing temperature. At 30 °C, there is essentially no increase regardless of the length of curing time. However, at higher temperatures 50 and 75°C, there is a continual increase of strength at longer curing time. While there is a significant increase of strength at 50 °C, there is only a slight increase at 75 °C from 24 to 48 hours. This confirms the beneficial effect of a ‘delayed’ reactivity at an intermediate temperature (50 °C) over a higher temperature (75 °C).

Figure 5.2 The compressive strength of fly ash-based geopolymers subjected to the various curing regimes in Table 5.1 at the age of (a) 7 days, (b) 28 days, and (c) 90 days.
From Figure 5.2, it also appears that temperature has a more significant effect on compressive strength than relative humidity. Regardless of temperature and time, the compressive strength of geopolymers at 30% RH is slightly higher than at 75% RH. It is reasonable to assume that a low humidity environment would accelerate reaction by removing water earlier. This can be seen from a marginally higher loss of water from drying in Geopolymer A and C than in Geopolymer D and F (Table 5.2). As a result of water removal, smaller pores usually collapse, leading to the shrinkage of gel structure (Brinker and Scherer, 1990).

Table 5.2 The water loss during drying at 105 °C. RH refers to relative humidity.

<table>
<thead>
<tr>
<th>Curing conditions (Time: 48 hours)</th>
<th>Water loss (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: 30°C – 30%RH</td>
<td>1.98</td>
</tr>
<tr>
<td>B: 50°C – 30%RH</td>
<td>1.77</td>
</tr>
<tr>
<td>C: 75°C – 30%RH</td>
<td>1.64</td>
</tr>
<tr>
<td>D: 30°C – 75%RH</td>
<td>1.96</td>
</tr>
<tr>
<td>E: 50°C – 75%RH</td>
<td>1.80</td>
</tr>
<tr>
<td>F: 75°C – 75%RH</td>
<td>1.50</td>
</tr>
</tbody>
</table>

The gel shrinkage at low humidity (30% RH) is illustrated by observing fly ash-based geopolymerisation in-situ under an Environmental SEM (Figure 5.3). Figure 5.3a shows the microstructure of non-reacted fly ash, while Figures 5.3b and 5.3c show the microstructures of activated fly ash after 70 and 100 minutes, respectively. During dissolution, a large proportion of gel volume is occupied by the activating solution. However, when gelation takes place, aqueous solution is expelled from the aluminosilicate gel matrices, which results in the gel shrinkage observed. In this particular instance, the rate of reaction is accelerated by exposing the specimen to a vacuum (< 0.1 Torr) and a low humidity environment. At a higher humidity, the gel shrinkage is likely to be less and slower.
Figure 5.3 (a) The spherical structure of fly ash particles, (b) the fly ash particles in alkali-silicate solution after 70 minutes, and (c) the transformation of sol-liquid into gel after 100 minutes. The micrographs were taken using ESEM at 30 °C, 30% RH (RH = Relative Humidity). Regions labelled ‘x’ indicate dissolving fly ash particles.

In addition, prolonged curing at high temperature and low humidity (for 48 hours) is detrimental to the long-term strength of geopolymers. After 90 days, the strength of Geopolymer C (75 °C and 30% RH) is weaker than Geopolymer F (75 °C and 75% RH) because of the early removal of activating solutions (or water). For these reasons, it seems that increasing initial curing temperatures is beneficial to increase the rate at which Al and Si precursors are dissociated and polymerised into aluminosilicate gel. In contrast, the humidity may not be significant because the aqueous solution in the gel is...
an appropriate medium to facilitate the reaction to take place. However, when the geopolymer sets, followed by the expulsion of water, the temperature would have a less significant role. Instead, the reaction would be driven by the need for the gel to become more highly hydrated. As a result, maintaining a high curing temperature for a longer curing time may not be as effective as applying high temperature for a short curing time, then followed by high humidity.

5.4.2 Permeability

For the measurement of permeability, an inert gas, N₂ should be passed through the geopolymer specimens at a steady state condition to comply with Darcy’s Law of gas flow (Bamforth, 1987; Cabrera and Lynsdale, 1988). The consistency of this technique was pre-tested on a weaker geopolymer, namely Geopolymer A (30°C and 75% RH for 4 hours). It is reasonable to assume that weaker geopolymer reflects a lower reactivity. Thus, the porosity is also large and susceptible to a permeable fluid. Geopolymer A was subjected to five pressure flow rates, which were increased from 60 to 150 kPa consecutively. The steady state flow rates were measured, and the values of \( \frac{v}{(P_1^2 - P_2^2)} \) were tabulated against the applied pressures (Table 5.3). The relationship between flow rate and \((P_1^2 - P_2^2)\) is not a perfect linear relationship due to the Klinkenberg effect (Bamforth, 1987; Cabrera and Lynsdale, 1988), which is caused by the effect of slip in gas flow. Nonetheless, this deviation is expected and the reproducibility of the test is considered to be consistent and satisfactory. In addition, 100 kPa was taken as the operating pressure for other geopolymers as well.

The calculated intrinsic permeability \((k_g)\) of geopolymers is shown in Figure 5.4. It can be seen that \(k_g\) decreases by two orders of magnitude as temperature is increased from 30°C to 75°C. A decrease in permeability indicates that a higher degree of gel polymerisation has taken place, thus there are less gaps between the existing grains (sand aggregate, partly-reacted, and/or non-reacted fly ash particles). In general, less permeable geopolymers lead to stronger geopolymers and vice versa. However, there seems to be an exception, whereby the permeability values are not in agreement with the observed strength. For example, after 48 hours of curing, Geopolymer B and E (50°C) have greater values of \(k_g\) (more permeable) than Geopolymer C and F, (75°C). Yet, the
strengths are slightly higher (Figures 5.2 and 5.4). The observed discrepancies are likely to be caused by the effect of pore solutions (aqueous) in both tests. It should be noted that permeability testing was done on ‘dry geopolymers’, while compressive strength was on ‘wet geopolymers’. When pores are filled with solution, the compressive strength of materials tends to be higher than when pores are empty (Trithart and Haussler, 2003). The rate of crack propagation from one discrete pore to the next will be decelerated if pores are filled with water. In a more porous gel (50°C), there are considerably more water-filled pores than a less porous gel (75°C). A greater amount of water content at 50°C is evident from Table 5.2. As a result, the compressive strength is also higher because pore solution reduces rate of crack propagation during strength testing.

Table 5.3 Statistical analysis of reproducibility of the measurement of nitrogen flow at different pressures through a geopolymer sample (Age: 90 days). The ratio of \( \frac{\nu}{(P_1^2 - 1)} \) is not constant, but continuously decreases when pressure deviates from 100 kPa.

<table>
<thead>
<tr>
<th>Measurement number</th>
<th>Flow rate (ml/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 kPa</td>
</tr>
<tr>
<td>1</td>
<td>2.01</td>
</tr>
<tr>
<td>2</td>
<td>2.00</td>
</tr>
<tr>
<td>3</td>
<td>1.98</td>
</tr>
<tr>
<td>4</td>
<td>1.98</td>
</tr>
<tr>
<td>5</td>
<td>1.98</td>
</tr>
<tr>
<td>6</td>
<td>1.97</td>
</tr>
<tr>
<td>Mean</td>
<td>1.98</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.01</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>0.72</td>
</tr>
<tr>
<td>Ratio of ( \frac{\nu}{(P_1^2 - 1)} )</td>
<td>1.27</td>
</tr>
</tbody>
</table>
5.4.3 Aluminosilicate structure

In Chapter 4, the absorption spectra reveal that geopolymers are essentially an aluminosilicate structure with large amounts of molecular water and carbonates. The water and carbonates are usually associated with residual cations, namely Na\(^+\), K\(^+\), and Ca\(^{2+}\). The frequency assignments for water and carbonate molecular vibrations are listed in Table 4.3. In this chapter, geopolymers that are cured at lower temperatures also display high intensity of carbonate absorption peaks (≈ 879 cm\(^{-1}\) in Figure 5.5). At lower temperatures, the rates of reaction are low, which means the rate and extent of hydrolysis are low. As a result, more ‘free and available’ alkali cations react with CO\(_2\) to form carbonate phases. In contrast, when the reaction occurs rapidly (i.e. due to the activation at high temperature), the material becomes compact thus becoming more
difficult for CO₂ to penetrate the matrix (Criado et al., 2005). The intensity of carbonate peaks appears to be less dominant at higher relative humidity (75%), which is likely caused by the forming pores being water-logged preventing the rapid spread of gas (Criado et al., 2005). From this study, there seems to be no direct correlation between the increase in the rate of strength increase and high RH, although high RH is believed to prevent the carbonation process. Criado et al. (2005) suggested that the carbonation process is likely to slow down the progress of reaction due to the acidification of the overall system. This has an impact in the progress of later reaction, which in turn affects the strength development of materials.

![Figure 5.5](image)

*Figure 5.5 The FTIR spectra of fly ash (FA) and its derived geopolymers, as listed in Table 5.1. The dotted line indicates the shift of asymmetric Si-O stretching band in fly ash-based geopolymers.*
Figure 5.5 shows the absorption spectra of various molecular structures in fused silica (amorphous silica), quartz (crystalline silica), fly ash (FA) and fly ash-based geopolymers, cured at various curing regimes (Table 5.1). The fused silica and quartz are used as reference materials to analyse the FTIR spectra from FA and its derived geopolymers. For fused silica, the main absorption peaks are observed at 1119, 818, and 474 cm\(^{-1}\), while quartz display absorption peaks at 1088, 791, 694, 513, and 463 cm\(^{-1}\) (Figure 5.5). However, there are only Si and O present in fused silica and quartz (assume the impurities are insignificant), thus all identified absorption peaks can be assumed to associate with Si-O molecular vibrations. The shoulder band at 1250-1000 cm\(^{-1}\) corresponds to the overlapping asymmetric stretching frequencies of Si-O molecular vibrations, while 400-800 cm\(^{-1}\) corresponds to the network Si-O bands (Farmer, 1988). Due to the amorphicity of fused silica, the Si-O stretching band displays a dominant peak at 1119 cm\(^{-1}\). In contrast, quartz displays strong network Si-O-Si bands, but weak Si-O stretching bands (Figure 5.5).

FA spectra shows characteristic absorption peaks at 1089, 797, 575, and 467 cm\(^{-1}\) (Figure 5.5), indicating a mixture of crystalline and amorphous silica and/or aluminosilicate in the gel structure. The shift of peak of Si-O band in original FA from 1089 cm\(^{-1}\) to lower wavenumbers in alkali-activated FA is associated with the de-polymerisation of Si-O-Al from fly ash, i.e. the dissolution of Al and Si precursors (Palomo et al., 1999b; Yousuf A Mollah et al., 1994). The shift of peak positions is associated with the replacement of Si in glassy Si-O-Si (or Al) with other cations, such as Al, Na, K, Ca, which means more non-bridging oxygens (Si-O-Na and/or Si-O-K) are likely to be present (Clark et al., 1976). By de-convoluting the overlapping spectra in the Si-O band, Lee and Van Deventer (2003) proposed that the extent of peak shift from the Si-O band in fly ash-based geopolymers can be used to measure the degree of activation/reactivity.

Figure 5.6 shows the peak positions of the Si-O band (1000-1250 cm\(^{-1}\)) in fly ash-based geopolymers, which are cured at various curing conditions. In general, increasing curing temperature and time results in a gradual shift of Si-O peak positions to lower wavenumbers (1003-1020 cm\(^{-1}\)). This concurs with earlier observations that increasing
temperature and time results in the increase of reactivity. It is interesting to note that the largest shift from 4 to 48 hour is observed at 50 °C, and not at 30 or 75 °C, which is in agreement with the earlier hypothesis, i.e. a ‘delayed’ reactivity at an intermediate temperature (50 °C) results in a higher degree of activation. As expected, changing humidity has less significant effect on the aluminosilicate structure of geopolymers, as shown in the FTIR spectra.

![FTIR spectra graph](image)

**Figure 5.6** The peak positions of Si-O band (1000-1250 cm⁻¹) in fly ash-based geopolymers cured at various temperatures and relative humidities.

The X-ray diffractograms of fly ash-based geopolymers are shown Figure 5.7. In FA, there is a shoulder at the diffraction angles (2θ) ranging from 20 to 30°. This shoulder is associated with the amorphous aluminosilicate phases in fly ash (Palomo et al., 1999b). Activation of fly ash with alkali-silicate solution results in the shift of amorphous shoulder to 25 to 35°, which has been identified as the characteristic diffraction patterns of geopolymers (Palomo and Glasser, 1992; Palomo et al., 1999b). High reaction temperature is also believed to induce the formation of crystalline phases in alkali-activated fly ash and/or fly ash-based geopolymers (Bakharev, 2005; Katz, 1998).
Nonetheless, the formation of crystalline phases at varying reaction temperatures and humidity has not been supported by the observations from this study. The observations made apply strictly to a specific concentration of activating solution (SiO₂/M₂O = 0.79 and H₂O/M₂O=14.9), water content, and particular type of fly ash. In Chapter 7, the formation of zeolites and other crystalline phases is observed during the synthesis of fly ash-based geopolymers, which is favourable at low silicate concentration and elevated reaction temperature.

![X-ray diffractograms](image)

Figure 5.7 X-ray diffractograms of unreacted fly ash and fly ash-based geopolymers (as listed in Table 5.1) at various curing conditions for 48 hours. M, Q, and H refer to mullite, quartz, and hematite respectively. The dotted circle highlights the characteristic diffraction angle of the amorphous aluminosilicate phases in geopolymers.
5.4.4 Microstructure

The BSE images of fly ash-based geopolymers that are cured at 30 °C and 75 °C (30% RH), are shown in Figures 5.8a and 5.8b respectively. The geopolymers that are cured at 75% RH are shown in Figures 5.8c and 5.8d. Elevating reaction temperatures from 30 to 75 °C results in the formation of a denser gel, indicating a higher rate and extent of reaction. Nonetheless, the non- and partly-reacted fly ash particles still exist, even at a higher temperature, 75 °C, whereby a greater degree of reaction is expected.

From EDAX analysis, the composition of the gel in fly ash-based geopolymers that are cured at 30 °C shows a high M/Al ratio (M/Al > 1, where M = Na or K in Table 5.4). This indicates a low reactivity because of the low aluminium concentration in the gel. Geopolymers that are cured at 75 °C show two regions of gel phase. Firstly, the geopolymer gel (indicated as Geopolymer Gel II in Table 5.4), which is characterised by a low M/Al ratio (M/Al < 1) and a denser gel structure, indicating a gel of high reactivity. Secondly, the ‘islands’ of alkaline precipitates (indicated as Geopolymer Gel I in Table 5.4), which are characterised by a high M/Al ratio (M/Al > 1) and a coarser pore structure. Such phase separation occurs because the rate of reaction is accelerated at high temperatures. As a result, there is an ‘entrapment’ of pore solution (the pore solution contains residual alkali), which creates ‘islands’ of alkaline precipitates when the geopolymer rapidly sets. A heterogeneous microstructure may also occur due to a number of other reasons, namely uneven mixing, low reactivity, or a heterogeneous solid. However, the first mechanism is believed to be the predominant factor in the formation of such a microstructure.
Figure 5.8 SEM micrographs of (a) 30°C – 30%, (b) 75°C – 30%, (c) 30°C – 75%, and (d) 75°C – 75%. A-the un-reacted fly ash particles, B – Geopolymer Gel, C-Geopolymer Gel I – alkaline precipitates, D – Geopolymer Gel II – geopolymer gel, E – Geopolymer Gel, F- Geopolymer Gel I – alkaline precipitates, and G–Geopolymer Gel II – geopolymer gel.
Table 5.4 The experimental K/Al and Na/Al ratios of various gel regions in fly ash-based geopolymers (see Figure 5.8).

<table>
<thead>
<tr>
<th>System Region</th>
<th>K/Al</th>
<th>Na/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>30°C – 30%RH Geopolymer Gel (B)</td>
<td>1.23 ± 0.27</td>
<td>0.17 ± 0.02</td>
</tr>
<tr>
<td>75°C – 30%RH Geopolymer Gel I (C – K precipitates)</td>
<td>0.88 ± 0.25</td>
<td>0.23 ± 0.02</td>
</tr>
<tr>
<td>Geopolymer Gel II (D)</td>
<td>0.60 ± 0.08</td>
<td>0.20 ± 0.10</td>
</tr>
<tr>
<td>30°C – 75%RH Geopolymer Gel (E)</td>
<td>1.39 ± 0.39</td>
<td>0.23 ± 0.09</td>
</tr>
<tr>
<td>75°C – 75%RH Geopolymer Gel I (F – K precipitates)</td>
<td>0.95 ± 0.90</td>
<td>0.16 ± 0.03</td>
</tr>
<tr>
<td>Geopolymer Gel II (G)</td>
<td>0.52 ± 0.33</td>
<td>0.13 ± 0.09</td>
</tr>
</tbody>
</table>

5.5 Conclusions

Higher temperatures activate more aluminosilicate phases in fly ash that are otherwise not reactive at low temperatures. Elevated temperatures are required to achieve a higher degree of activation, but the rate of reaction is also accelerated at high temperatures. As a result, the material sets rapidly, and prevents further reaction from occurring. Therefore, the choice of optimal curing temperatures should be a balance between enhancing dissolution of precursors and preventing rapid setting of geopolymers. Nonetheless, varying relative humidity from 30 to 75 %RH has less pronounced effect on the physical strength and permeability observed.

The stronger and less permeable geopolymer has a denser and finer pore in the gel structure, and vice versa. Furthermore, geopolymers that are cured at 30 °C have high M/Al ratios (M/Al > 1, where M = Na or K), indicating low aluminium content, attributed to the low reactivity of these geopolymers. In contrast, geopolymers that are cured at 75 °C show two regions of gel phase: (a) Firstly, the geopolymer gel, which is characterised by a lower M/Al ratio (M/Al < 1) and a denser gel structure; (b) Secondly, the ‘islands’ of alkaline precipitates, which are characterised by a higher M/Al ratio (M/Al > 1) and a coarser pore structure. Such phase distinction occurs because the rate of reaction is accelerated at high temperature. As a result, there is an ‘entrapment’ of pore solution (contains residual alkali) that creates ‘islands’ of alkaline precipitates when the geopolymer rapidly sets. In Chapter 6, a thorough investigation on the development of pore structure in fly ash-based geopolymers will be conducted.
A novel study on the development of pore structure and gel composition of fly ash-based geopolymers has been undertaken. The pore structure of fly ash-based geopolymers was analysed using Mercury Intrusion Porosimetry (MIP), Nitrogen Adsorption, and Electron Microscopy. Based on the elemental analysis performed by SEM-EDAX, fly ash-based geopolymer can be classified as mesoporous aluminosilicate gel, with the Si/Al composition varying from 1.51 to 2.24. The gel composition (expressed as the Si/Al ratio) and pore structure of fly ash-based geopolymers have been found to vary depending upon the reaction temperature, time, silicate concentration (SiO$_2$/M$_2$O, M = Na or K), and alkali concentration (H$_2$O/M$_2$O, M = Na or K) of the activating solutions.

Elevating reaction temperature from 30 $^\circ$C to 75 $^\circ$C increases the extent and rate of reaction as shown by an increase in mesopore volume, surface area, and an accelerated setting time. The effect of temperature on the rate of reaction, however, becomes less significant once the material sets. Increasing the soluble silicate concentration also enhances geopolymerisation, as shown by an increase in mesopore volume and area of fly ash-based geopolymers. However, a high silicate ratio (SiO$_2$/M$_2$O $\geq$ 2.0) is believed to reduce reactivity. Furthermore, the pore structure of K-based geopolymer is found to be more susceptible to a change in temperature than for Na-based geopolymer. The increase in alkali concentration usually results in a higher reactivity due to a higher extent of dissolution that provides more nuclei for further reaction to take place. Nonetheless, in this study, high alkalinity is found to slow down the polymerisation step due to the availability of more alkali metal cations that prolong the dissolution process. Therefore, a moderate alkali concentration (e.g. at H$_2$O/M$_2$O ratio = 12.5) may balance the rates of dissolution and polymerisation; although the dissolution is extended, it is not
at the expense of polymerisation thus giving an optimum rate and extent of reaction throughout.

A prolonged reaction time (from 24 hours to 48, 96, and 168 hours) at a constant temperature of 50 °C leads to higher reactivity. This can be seen from a shift in pore volume distribution from mesopore (3.6 – 50 nm) to ‘sub-mesopore’ region (2-3.6 nm), which occurs because larger pores are filled with the newly formed gel. Continuous curing at higher temperatures (e.g. at 75 °C for 24 or 48 hours) accelerates both the rate of nucleation and gelation to an extent that the gel structure disintegrates. An optimum curing scheme is found when geopolymers are cured initially at a lower temperature (30 or 50 °C), followed by a higher temperature (75 °C). This allows for more nutrients to be available initially without causing the overall sol-gel system to gel rapidly.

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Parts of the work presented in this chapter are based on the manuscript: Sindhunata, Van Deventer, J. S. J., Lukey, G. C., and Xu, H., Effect of curing temperature and silicate concentration on fly ash-based geopolymerisation, Industrial and Engineering Chemistry Research, 45, 10, 3559-3568, 2006.

### 6.1 Introduction

A number of authors (Querol et al., 1997a; b; Zhao et al., 1997) have successfully synthesised zeolite-like materials from fly ashes. Others (Chang et al., 1999; Kumar et al., 2001) have shown that fly ash can be converted to mesoporous aluminosilicate materials through the fusion process of NaOH and fly ash at elevated temperatures. The Si:Al composition of this fly ash-derived material is 13.4, and its pore structure resembles that of MCM-41, a mesoporous material with higher Si:Al composition, which is commonly used as molecular sieves.

The porosity of fly ash-based geopolymers results predominantly from the inherent porous nature of geopolymer gel. The pore structure in the gel is formed during the drying process, when the aqueous pore solution evaporates, leaving empty voids within the gel matrices (Hench and West, 1990). In the synthesis of porous silica gel, this type
of gel is known as dried gel or xerogel (Iler, 1979). Secondly, in a non-reacted or less reactive system, the geopolymer gel is rarely formed. Instead, the dissolved ionic species, such as Si, Al, Ca, Fe, which are leached from various glassy phases in the fly ash, precipitate on the surface of fly ash particles. Therefore, there is insufficient geopolymer gel to fill the gaps between two or more partially reacted fly ash particles. These voids are generally large (micron scale) and can be distinguished easily from the typical porous gel structure. Finally, the porosity could originate from within the partially reacted fly ash particles. As mentioned in Chapter 3 that there are at least four types of particle morphology commonly present in fly ash, i.e. solid sphere, plerosphere, clathrosphere, and cenosphere (hollow sphere) (Hemmings and Berry, 1988; Pietersen et al., 1988). Upon reaction, only a partially reacted cenosphere is likely to leave a significant hollow space, which could be accessible to fluid penetration (an open pore) and affect the pore structure analysis. The density of Gladstone Fly Ash (GFA), the Class F fly ash used in this study, is 2.34 g/cm³. Based on the measured density, the amount of cenosphere is believed to be minimal. Furthermore, in a well-reacted geopolymer, it is likely that the hollow spaces originating from partly reacted cenosphere are filled with forming geopolymer gel.

Understanding the development of pore structure of fly ash-based geopolymers is essential for explaining the observed physico-chemical properties of geopolymers. The development of pore structure of fly ash-based geopolymers will be determined using MIP (Mercury Intrusion Porosimetry), N₂ adsorption and high resolution electron microscopy (FESEM and TEM). The effect of different temperature, alkali concentration, silicate concentration (SiO₂/M₂O, where M = Na or K), and alkali metal cation type on fly ash-based geopolymerisation is discussed from the perspectives of pore volume, pore surface area, and setting time. The findings will have significant practical applications as it is believed that porous geopolymers can also be tailored to produce specific material properties, such as mechanical strength, flexibility, durability and fluid permeability.
6.2 Experimental methods

The chemical composition and mineralogy of Gladstone Fly Ash (GFA) were detailed in Chapter 3. The activating solutions were prepared by diluting NaOH solids in sodium silicate and water and KOH solids in potassium silicate and water. The composition of activating solutions used is listed in Table 6.1.

Table 6.1 The composition of fly ash based geopolymers synthesised with a constant \( \frac{H_2O}{M_2O} = 14.85 \), where \( M = K \) or \( Na \). *The Si/Al ratio is calculated based on the assumption that all amorphous silicon and aluminium in the fly ash are fully reacted \( \frac{Al}{M} = 1.5 \).

<table>
<thead>
<tr>
<th>Geopolymer</th>
<th>( \frac{SiO_2}{M_2O} ) ratio in the solution</th>
<th>Theoretical Si/Al*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0K</td>
<td>0</td>
<td>1.95</td>
</tr>
<tr>
<td>0.79K</td>
<td>0.79</td>
<td>2.21</td>
</tr>
<tr>
<td>1.40K</td>
<td>1.40</td>
<td>2.42</td>
</tr>
<tr>
<td>2.0K</td>
<td>2.0</td>
<td>2.62</td>
</tr>
<tr>
<td>0.0Na</td>
<td>0</td>
<td>1.95</td>
</tr>
<tr>
<td>0.79Na</td>
<td>0.79</td>
<td>2.21</td>
</tr>
<tr>
<td>1.40Na</td>
<td>1.40</td>
<td>2.42</td>
</tr>
<tr>
<td>2.0Na</td>
<td>2.0</td>
<td>2.62</td>
</tr>
</tbody>
</table>

In this study, the weight ratio of water to fly ash was kept constant at 0.3. This would give a constant solid:solution ratio for each mix. If the amorphous content of Si- and Al-associated phases is assumed to be fully reacted, while the crystalline phases are assumed not to be reactive, the theoretical gel composition can be calculated. Clearly, this is an approximation, as some glassy phases are known to be more reactive than others. Also, any secondary reaction products such as zeolites or silica gel that might form, even in minute quantities, are not considered here. The theoretical Si/Al ratio for every geopolymer studied is shown in Table 6.1.

The resulting slurry was cast in 35 x 75 mm cylindrical vials, sealed and vibrated for 2 minutes in order to eliminate the air entrapped during mixing, which would affect the
pore structure analysis. Three different curing temperatures were used (30 °C, 50 °C, and 75 °C), and the curing period varied from 24 to 168 hours. The approximate setting time was determined by tilting the clear plastic vials containing geopolymers (Nishino et al., 2004). The setting time is defined as the time when geopolymer paste stops flowing. The setting time is a more appropriate terminology than gelation time or precipitation time because the dissolution and polycondensation are believed to take place simultaneously in the course of geopolymerisation, thus there is no clear time distinction between the two processes.

To investigate the effect of changing alkali concentration, three different activating solutions were prepared by varying the H2O/K2O ratios at 14.85, 12.5, and 10.0 (SiO2/K2O = 0.79). By keeping the water to binder ratio constant at 0.3, and assuming that reactive aluminium in fly ash is fully reacted, the theoretical Al/M ratios of the formed gel will be 1.0, 1.25, and 1.5 respectively. These geopolymers were also reacted at three different curing temperatures, 30, 50 and 75 °C for 24 hours.

After the designated curing times, hardened geopolymers were de-moulded and cut in cross section to four pieces. The two middle pieces were dried in a vacuum oven at 105 °C for 24 hours or until there was no reduction in the sample weight. Although this drying step changed the pore structure, it was essential to obtain consistent results. These dried geopolymers were subjected to MIP (Autopore II 9220) and N2 adsorption tests (Tristar equipment). The applied pressure was used to calculate the pore size, which was calculated using the Washburn’s equation and assuming an interconnected tubular pore network model (Webb and Orr, 1997). In addition, the pore size distribution from desorption isotherm was calculated using the BJH method (Barret et al., 1951). The mesopore volume (Vp) and surface area (Sp) obtained from BJH method were calculated using Win 3000 Software. Further experimental details relating to porosimetry and adsorption techniques used to study the pore structure of geopolymers were described in Chapter 3.

A Philips XL30 FEG Field Emission Scanning Electron Microscope (FESEM) was used to obtain the micrographs of fly ash-based geopolymers. At a voltage of 2kV, the
particles of geopolymer gel can be clearly observed. The sample preparation for FESEM started with the crushing of geopolymers into pieces of approximately 0.1 cm$^3$ in volume. The crushed geopolymers were mounted in an epoxy resin, and polished with graded SiC papers. Using EDAX, the composition of Al, Si, K, Na, Ca, and Fe in the gel was routinely determined, but only the Si/Al ratio is presented. Twenty measurements were taken across the corresponding gel matrices to obtain a representative geopolymer gel composition. The powder samples were also subjected to Transmission Electron Microscopy (TEM) using a Philips CM120 BioTWIN TEM at 100 kV.

6.3 The development of gel structure of fly ash-based geopolymers

In this section, the mechanism of gel formation in fly ash-based geopolymers is investigated by analysing changes in the microstructure and gel composition as geopolymers are activated at various curing conditions and silicate concentrations.

6.3.1 The development of microstructure

The microstructure of fly ash-based geopolymers is presented as a series of electron micrographs in Figure 6.1. Figure 6.1a shows the spherical morphologies of original fly ash particles, which vary in chemical composition and size. Figure 6.1b depicts the microstructure of Geopolymer 0.0K, which is synthesised with a KOH solution (H$_2$O/K$_2$O=14.85) at 75 °C. The Geopolymer 0.0K shows typical microstructure of a non-reactive system, whereby geopolymer gel is formed only to a very limited extent. Instead, the dissolved ion precursors, such as silicon, aluminium, and trace of calcium and iron, precipitate on the surface of spherical fly ash particles. In addition, all unreacted fly ash particles are loosely connected by ‘necks’, which are believed to be precipitates of dissolved species. If any geopolymer gel is formed, the gel growth would concentrate on the surface of the particles, which functions as the initial points of nucleation (McCormick and Bell, 1989). Figures 6.1c and 6.1d are the micrographs of Geopolymer 0.79K, which is cured at 30 °C and 75 °C respectively. They reveal different gel morphologies to Geopolymer 0.0K, whereby a greater degree of reaction has taken place, and the gaps between fly ash particles have been filled with the formed
geopolymer gel. At 30 °C, the microstructure of fly ash-based geopolymers shows larger pores at the interfacial region between fly ash particles and geopolymer gel (Figure 6.1c), indicating a low degree of gel formation. However, this is not observed at a higher curing temperature, 75 °C (Figure 6.1d). Figure 6.1e is the microstructure of Geopolymer 2.0K, which is synthesised at 75 °C, while Figure 6.1f is the same geopolymer at a higher magnification. At a higher magnification, the fly ash-based geopolymer gel is comprised of aluminosilicate particulates, which are connected and forming nano-channels and pores, as has been reported elsewhere (Kriven et al., 2003).

It is thought that the colloidal sizes of these aluminosilicate particulates determine the pore parameters observed, e.g. a network of larger particles results in a larger pore volume and mean pore width, but a lower surface area. The opposite is true for a gel network consisting of smaller particles. TEM results show a dense gel (darker, at the top) and another porous gel (lighter, at the bottom) of Geopolymer 2.0K, which is cured at 75 °C (Figure 6.2a). Figures 6.2b and 6.2c are taken at a higher resolution for Geopolymer 0.79K and 2.0K respectively. The porous gel clearly depicts the typical pore structure of geopolymer gel. The microstructure consists of aluminosilicate particles that are not exactly spherical, but they are homogeneous in size, with a nano-scale dimension. Electron diffraction from both geopolymers shows patterns of broad circular rings without traces of bright speckles around the rings. This indicates a short-range ordering between neighboring atoms, which is the characteristic of an amorphous-like material. The distinct pore structures of the two geopolymers can be clearly seen; Geopolymer 0.79K, which is synthesised at a lower silicate ratio, comprises of larger particles than Geopolymer 2.0K, which is synthesised at a higher silicate ratio. The growth of controlled mono-disperse silica particles was observed initially by Stober and co-workers (1968). Presumably, the silica particles stop growing after reaching a critical size because they are electrostatically stabilised (mutually repulsive) (Brinker, 1988). Stabilisation prevents particles from condensing with other particles, but it does not preclude continued condensation between particles and monomeric silicate species. Similarly, the formation of uniform pore structure in aluminosilicate particles through a sol-gel chemistry is also commonly observed (Setzer et al., 2002). The particle size can
be easily modified by changing the reaction temperature, curing time, and silicate ratio, as has also been observed in this study.

Figure 6.1 The electron micrographs of: (a) Fly ash, (b) Geopolymer 0.0K, cured at 75 °C, (c) Geopolymer 0.79K, cured at 30 °C, (d) Geopolymer 0.79K, cured at 75 °C, (e) Geopolymer 2.0K, cured at 75 °C, and (f) Same as (e), but at a higher magnification. Phases marked with ‘x’ are non- or partly-reacted fly ash particle, ‘y’ is geopolymer gel, and ‘z’ are phases with high silicon concentration.
From the microstructural observation, there are phase inhomogeneities showing regions of high silicon concentration, indicated as ‘z’ in Figures 6.1d and 6.1e. Based on the elemental analysis, the average Si/Al ratio of geopolymer gel is ≈ 2 (Figure 6.1e), while the ‘z’ region is found to have a significantly high silica content (Si/Al ≈ 4-5). The region of high silica content is frequently found in fly ash-based geopolymers that are synthesised at higher silicate concentration. It is easily spotted because of its distinctive
less porous microstructure than a typical geopolymer gel. It is important to note that while the finding applies to fly ash-based geopolymers, more reactive geopolymers, such as those of metakaolin-based geopolymers, do not show much variation in the gel composition (Rahier et al., 1997). Therefore, a more accurate and advanced technique, such as the MAS-NMR, which uses a smaller sampling volume may not be suitable for the characterisation of fly ash-based geopolymers if phase separation is a problem. The phase inhomogeneities in the gel are likely caused by the different release rates of silicon and aluminum from fly ash particles. The rates are affected by the reaction temperature, silicate concentration, and local variations in fly ash composition, as is shown in Table 6.2. It is likely that homogenisation cannot be achieved before complete dissolution takes place. At the onset of gelation (polycondensation), the viscosity increases rapidly, hence, the formed gel will further hinder homogenisation. Thus species coming into solution after gelation will react locally, without many possibilities of homogenisation.

6.3.2 The gel composition
The Si/Al ratios of synthesised geopolymers are presented in Table 6.2. The elemental analysis has taken into consideration the variations in composition due to the regions of high silica concentration by taking average readings at various spots in the microstructure. Overall, the geopolymer gel gives a Si/Al molar ratio ranging from 1.51-2.24. Davidovits (1999) classified this Si-O-Al structure as a polysialate with Si/Al composition of 1.0-2.0. Although not shown, the composition of trace elements, such as calcium (Ca) and iron (Fe) from each geopolymer varies from 2-4 molar % of the total composition, and is found to be homogeneously distributed across the gel matrix. Calcium and iron-associated glassy phases in fly ash dissolve at high pHs (Pietersen et al., 1988), which means that these phases are likely to participate in geopolymerisation. However, the effect of these cations on geopolymerisation has not been fully elucidated yet, and is beyond the scope of the thesis. In this instance, the effect of these cations on geopolymerisation will be assumed to be minimal (Pietersen et al., 1988; Qian et al., 1988).
Table 6.2 The Si/Al ratios of fly ash-based geopolymers as determined by EDAX analysis. Twenty measurements were taken across each gel matrix. All geopolymers were cured for 24 hours.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (°C)</th>
<th>Si/Al molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0K</td>
<td>75</td>
<td>1.51 ± 0.34</td>
</tr>
<tr>
<td>0.79K</td>
<td>30</td>
<td>1.62 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.66 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1.75 ± 0.15</td>
</tr>
<tr>
<td>1.4K</td>
<td>30</td>
<td>1.59 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.63 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1.97 ± 0.25</td>
</tr>
<tr>
<td>2.0K</td>
<td>30</td>
<td>2.01 ± 0.18</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.14 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>2.06 ± 0.14</td>
</tr>
<tr>
<td>0.0Na</td>
<td>75</td>
<td>1.53 ± 0.07</td>
</tr>
<tr>
<td>0.79Na</td>
<td>30</td>
<td>1.61 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.78 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1.60 ± 0.12</td>
</tr>
<tr>
<td>1.4Na</td>
<td>30</td>
<td>1.98 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2.24 ± 0.32</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>1.79 ± 0.30</td>
</tr>
<tr>
<td>2.0Na</td>
<td>30</td>
<td>1.97 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>1.90 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>2.03 ± 0.21</td>
</tr>
</tbody>
</table>

The Si/Al ratio varies depending on the curing temperature and silicate solution (Table 6.2). As the curing temperature is increased, the Si/Al ratio in the geopolymer gel generally increases. It is proposed that the difference in Si/Al ratios is caused by the different rates of release of Si\(^{4+}\) and Al\(^{3+}\) precursors. Pietersen et al. (1988) found that fly ash dissolved Al\(^{3+}\) faster than Si\(^{4+}\) when it was activated with alkali solution. The dissolution of Al\(^{3+}\) is constrained by a limited amorphous content because a large fraction of aluminium composition in fly ash is included in mullite, which is non-
reactive in alkali solution (Catalfamo et al., 1993). Hence, as the reaction progresses, the rate and extent of Si\(^{4+}\) dissolution will be greater than Al\(^{3+}\) dissolution. Therefore, at lower temperatures, the Si/Al ratio in the gel is low because the gel is formed when the rate of Al dissolution is high. However, high temperatures accelerate the rate of reaction. As a result, the gel is formed when Al source is exhausted, while Si dissolution is high, which leads to a higher Si/Al ratio in the gel.

Furthermore, Rahier et al. (1997) found that increasing the silicate concentration in the activating solution (SiO\(_2\)/M\(_2\)O = 0.0 - 1.9) leads to a decrease in the average Al substitution around Si in a geopolymer gel. This finding is in accordance with the EDAX results presented in Table 6.2, whereby at higher silicate concentration, the ratio of Si/Al is higher. There are some exceptions, however, especially at higher silicate concentrations, where the increasing Si/Al ratio trend is not fully followed.

The correlation between experimental and theoretical Si/Al ratio for geopolymers cured at 75 \(^{0}\)C is shown in Figure 6.3. The experimental Si/Al ratios are consistently lower than the theoretical ratios at any silicate concentration. There are two explanations for the lower Si/Al ratio observed: 1) the actual reactive amorphous phase is less than estimated, and 2) the glassy silica and alumina phases from fly ash are not fully dissolved. This is highly possible considering that the theoretical Al/M ratio used in this study is 1.5, thus there is insufficient alkali available for dissolving all amorphous Al. This means there is a direct correlation between the extent of dissolution and the observed Si/Al ratio. The deviation of the experimental Si/Al ratio from its theoretical value is calculated using Equation (6.3), and is presented in Table 6.3. The average deviation of K- and Na-based geopolymers is 21 % and 25 % respectively. Although, it is not feasible to assume that all dissolved precursors will polymerise to form aluminosilicate gel, the deviation still partly reflects the reactivity of geopolymers of different alkali metal cations. It is speculated that solutions containing K\(^+\) are more efficient either in the dissolution and/or polycondensation than solutions containing Na\(^+\), based on the observation that the Si/Al ratios of K-based geopolymer are closer to the theoretical ratios.
Figure 6.3 Experimental and theoretical Si/Al ratios from K- and Na-based geopolymers, cured at 75 °C.

\[
\text{Deviation} = \frac{(Si/Al)_{\text{theoretical}} - (Si/Al)_{\text{experimental}}}{(Si/Al)_{\text{theoretical}}} \times 100\% \quad (6.3)
\]

Table 6.3 The deviation of the experimental Si/Al ratios from their theoretical values.

<table>
<thead>
<tr>
<th>Theoretical Si/Al</th>
<th>The deviation of the experimental Si/Al ratio</th>
<th>K-geopolymer</th>
<th>Na-geopolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.95</td>
<td>22 %</td>
<td>22 %</td>
<td>22 %</td>
</tr>
<tr>
<td>2.21</td>
<td>21 %</td>
<td>28 %</td>
<td>28 %</td>
</tr>
<tr>
<td>2.42</td>
<td>19 %</td>
<td>26 %</td>
<td>26 %</td>
</tr>
<tr>
<td>2.62</td>
<td>21 %</td>
<td>23 %</td>
<td>23 %</td>
</tr>
<tr>
<td>Average</td>
<td>21 %</td>
<td>25 %</td>
<td>25 %</td>
</tr>
</tbody>
</table>
6.4 Pore structure of fly ash-based geopolymers

In the previous section, it is seen that curing temperature and silicate concentration affect the formation of aluminosilicate particles and chemical composition in geopolymer gels. It is believed, therefore, the pore structure of geopolymers can be altered easily upon activation at different curing temperature and silicate concentration.

6.4.1 The effect of drying method on pore structure characterisation

Prior being subjected to MIP and gas adsorption, geopolymer specimens were pre-dried to remove molecular water in the pores. Drying is believed to alter the pore structure of geopolymers, as it has been found to alter the pore structure of porous silica gels (De Witte and Uytterhoeven, 1996; Dieudonne et al., 2000; Gevelyuk and Doycho, 2000; Titulaer et al., 1994a; Vendange et al., 1996). Rigorous drying at high rates and temperatures usually leads to the collapse of smaller pores and creates more capillary pores. The collapse of pores during drying is induced by the stress exerted on the pore surface as water leaves the pores, known as drying shrinkage (Scherer, 1999). Therefore, the effect of different drying methods on the pore structure of geopolymers will be investigated.

Geopolymer 0.79K, cured at 30 °C was subjected to different drying methods, i.e. drying in an air-circulated oven at 60 °C and 105 °C, in a vacuum at 105 °C, and freeze drying for 24 hours. Due to low reactivity, Geopolymer 0.79K (30 °C) will be more susceptible to any changes in drying temperature immediately, thus it is the ideal specimen to be tested. Figure 6.4 shows that the pore volume of Geopolymer 0.79K (30 °C) dried at 60 °C for 24 hours is lower than the pore volume of geopolymers that are either dried at 105 °C, or subjected to the freeze-drying method. This suggests that drying at 60 °C results in less water evaporated, and therefore more water remaining in the pores. However, the intruded pressure region at 60 °C does not deviate significantly from the other drying conditions, i.e. remains at approximately 100 psia. Hence, the pore structure (size) of geopolymers can be assumed not to be affected significantly by the different drying temperatures. Out of the four drying methods, freeze-drying is found to be the most optimum method because it removes water as effectively as in vacuum drying (a similar pore volume). At the same time, the intruded pressure region
is on a higher pressure side, which correlates to a smaller pore size region. This shows that the collapse of smaller pores, which is induced by the stress exerted on the pore surface has been prevented.

Figure 6.4 The comparison between four different drying methods and their effects on the pore structure of Geopolymer 0.79K cured at 30 °C.

6.4.2 The development of pore structure of fly ash-based geopolymers

The volume of Hg intruded into fly ash particles and fly ash-based geopolymers is presented in Figure 6.5a. The intrusion loop of fly ash reveals a ‘breakthrough pressure’ starting from 80 psia. This indicates the pressure when liquid Hg starts filling up the interstitial spaces of fly ash particles (inter-particle pores). After the gaps are fully filled, the intruded volume ceases to increase, which shows that within the fly ash particles, there are no accessible pores. For Geopolymer 0.0K cured at 75 °C and Geopolymer 0.79K cured at 30 °C, a similar breakthrough pressure is observed, but the intrusion curve is shifted slightly to a higher pressure region for Geopolymer 0.0K. Moreover,

![Figure 6.4](image-url)
Figure 6.5 (a) Cumulative intruded volume vs pressure and (b) Pore size distribution of fly ash and fly ash-based geopolymers. 0K-75 means Geopolymer 0.0K, cured at 75 °C; while 0.79K-30, 0.79K-50, and 0.79-75 refer to Geopolymer 0.79K, cured at 30 °C, 50 °C, and 75 °C respectively.
geopolymers that are cured at higher temperatures 50 °C and 75 °C, give an intrusion at higher pressure regions and greater cumulative pore volume.

The intruded pressure can be correlated to the equivalent pore size by the Washburn’s equation (Washburn, 1921). As a result, the pore volume distribution of geopolymers can be plotted (Figure 6.5b). Fly ash particles reveal a narrow pore size distribution, i.e. only within 2-4 microns. Geopolymer 0.0K displays a wider pore size distribution with a greater total pore volume than the fly ash particles. Adding soluble silicate into the activating solution results in a smaller pore size (Geopolymer 0.79K). Increasing temperature also results in a smaller pore size, with bimodal and wide pore size distributions shown at 50 °C and 75 °C.

Based on the pore size distribution, it is possible to designate three distinct regions of porosity in geopolymer materials derived from fly ash. The following hierarchical pore structure can be used, i.e. mesopores (3.6-50 nm), macropores (50-200 nm), and pores larger than 200 nm. The demarcation between meso- and macropores (50 and 200 nm) is based on the results shown in Figure 6.5b, even though this classification deviates slightly from the IUPAC definition (Giesche, 2002). Each designated pore size range is believed to originate from different pore formation mechanisms. The mesopores are the main porous structure, which is the cluster(s) of aluminosilicate particles that constitute the Si-O-Al’ network (polysialate) (Davidovits, 1999). The macropores as defined (50-200 nm) are the larger pores that are formed during the early stage of reaction. As gel continues to form, larger macro pores are being filled, and longer chains and branches are being formed, thus transforming macropores into mesopores. Macropores are apparent in fly ash-based geopolymers that are cured at medium temperature (50 °C). The presence of pore sizes larger than 200 nm is characteristic of less reacted geopolymers. There are two systems which show pores larger than 200 nm: (i) Geopolymers that are synthesised with alkali hydroxide solutions (Geopolymers 0.0K and 0.0 Na), and (ii) Geopolymers that are synthesised at low temperature (30 °C).

6.4.3 MIP versus N₂ desorption (BJH method)

In this section, a quantitative comparison between two techniques, MIP and N₂ adsorption in measuring pore volume of geopolymers is shown. Figures 6.6 and 6.7
show the pore volume distribution and surface area respectively (determined by MIP), for fly ash-based geopolymers cured at different curing temperature and time.

Based on MIP, a large proportion of pores in geopolymers lies within the mesoporous region, i.e. within 3.6-50 nm (Figures 6.6 and 6.7). N₂ adsorption is capable of measuring pores smaller than 3.6 nm, which are commonly referred to as micropores. However, it is found that the volume and area of micropores in fly ash based geopolymers at any reaction conditions are relatively low. In order to get a fair comparison between the MIP and BJH methods, only the mesopore parameters are presented, i.e. mesopore volume (Vₚ) in Figure 6.8 and mesopore area (Sₚ) in Figure 6.9. Furthermore, geopolymers which are cured at 30 °C and/or with alkali hydroxide solutions (0.0K and 0.0 Na) have low reactivity, thus the mesopore volume of these geopolymers is negligible. These geopolymers were not subjected to gas adsorption.

![Figure 6.6](image.png)

**Figure 6.6** The cumulative pore volume distribution of various fly ash-based geopolymers, as determined by MIP. Vp, referred to later is the mesopore volume and shown as the striped segments in the graph.
Figure 6.7 The pore surface area distribution of various fly ash-based geopolymers, as determined by MIP. Sp, referred to later is the mesopore surface area and shown as the striped segments in the graph.

Figures 6.8 and 6.9 show that $V_p$ and $S_p$ values from the MIP method are consistently greater than the $V_p$ and $S_p$ values obtained from the BJH method. For example, the $V_p$ and $S_p$ of Geopolymer 0.79K, which is cured at 75 °C, are 0.212 cm$^3$/g and 60.9 m$^2$/g respectively from the MIP measurement, but are only 0.131 cm$^3$/g and 55.1 m$^2$/g from the BJH method. These quantitative discrepancies are also apparent in Na-based geopolymers, but vary depending on the silicate ratio. There are a number of reasons to explain the differences in pore parameters obtained from the two techniques. Firstly, the physical adsorption of non-wetting liquid (Hg) is very different from N$_2$ adsorption, which involves a complex mechanism between gas and liquid condensation on the solid surface. Secondly, it is likely that the ‘true’ pore structure of geopolymers affects the quantitative measurement. In both MIP and BJH methods, an interconnected tubular pore model must be assumed in order to derive the predicted volume and area of the pores, which means that the ‘real’ pore network and shape cannot be determined from
Figure 6.8 Effect of elevated curing temperature (50 °C and 75 °C) on the mesopore volume ($V_p$) of fly ash-based geopolymers. Due to low reactivity, geopolymers that were cured at 30 °C, were not subjected to N$_2$ adsorption.

Figure 6.9 Effect of elevated curing temperature (50 °C and 75 °C) on the mesopore surface area ($S_p$) of fly ash-based geopolymers. Due to low reactivity, geopolymers that were cured at 30 °C, were not subjected to N$_2$ adsorption.
these two methods alone. Diamond (2000) reported that long percolative chains of intermediate pores with varying sizes and shapes, leading to larger pores in concrete will give false volumes and areas in mercury porosimetry. This phenomenon may apply to any porous aluminosilicate materials, including geopolymers. The more porous the geopolymer gel is, the more complex the pore structure is likely to be.

There are a number of other techniques that can be used to complement the study of pore structure of geopolymers, which include quantitative analysis from Transmission Electron Microscopy (TEM) and Small Angle Neutron/X-Ray Scattering (SANS and SAXS). These techniques have been successfully implemented to analyse pore structures in aluminosilicate gels (Kerch et al., 1990; Lin et al., 2004; Lindsay et al., 1999; Ramsay, 2002; Sinko and Mezei, 2001; Tao et al., 2004). Despite the apparent differences in $V_p$ and $S_p$ values, the trends in pore structure evolution with respect to the variations in curing temperature and $SiO_2/M_2O$ ratio agree with each other quite well. The MIP and BJH methods may not give a quantitative determination of the pore parameters, unless an accurate pore network model is applied. Yet, the effect of various reaction conditions on the pore structure of geopolymers can still be studied using these two techniques.

6.5 The effect of temperature on fly ash-based geopolymerisation

In Chapter 5, elevating curing temperature was found to increase the rate and extent of reaction through an increase in the heat of reaction, increase of compressive strength, and a finer gel structure. In this chapter, the effect of temperature on fly ash-based geopolymerisation is discussed from the perspectives of pore volume, area, and setting time. Generally, there is an increase in total pore volume ($V$) and surface area ($S$) as the curing temperature is elevated. Also, a greater degree of reaction is indicated particularly by the increase in mesopore volume and area as the curing temperature is raised (Figures 6.6 and 6.7). The geopolymers that are cured at 30 °C and those synthesised with alkali solution only (Geopolymers 0.0K and 0.0Na) are very porous. Yet, there is a low level of mesopores observed. As the reaction temperature is raised from 30 °C to 50 °C and 75 °C, the $V_p$ and $S_p$ of fly ash based geopolymers increase.
significantly (Figures 6.6 and 6.7). This trend applies to both K and Na-based geopolymers at any SiO₂/M₂O ratios. The extent of increase in Vₚ and Sₚ, however, varies depending on the silicate ratios used. Elevating the reaction temperature is known to increase the extent of dissolution of precursors (primarily Al and Si) from the glassy phases in fly ash (Pietersen et al., 1988). Increasing the amount of precursors leads to an increase in nucleation rates, and thus polycondensation, as it can be seen that the apparent setting times (tₛ) of geopolymers reacted at higher temperatures (50 °C and 75 °C) are generally shorter than for those geopolymers reacted at a lower temperature (30 °C, Table 6.4), except for Geopolymer 0.0K, which shows an unexpected gelation behavior. The tₛ of Geopolymer 0.0K increases when the temperature is raised from 30 °C to 50 °C, and decreases again when the temperature is increased to 75 °C (Table 6.4).

It is proposed that the anomalous gelation behaviour of K-based geopolymer at high alkalinity results from a reduction in the number of nuclei at 50 °C because of increased solubility, causing the reaction to proceed longer (North et al., 2001). At 30 °C, the solubility is low, so that setting is faster due to the precipitation of dissolved species, rather than polycondensation of monomeric silicate with aluminate. So, even though the samples appear to have set, they are also weak because of insufficient gel that functions as binder to existing fly ash particles. At 75 °C, the increased rate of gel growth may compensate for the reduction in the numbers of nuclei and thus, gelation times begin to decrease again. The ‘unexpected’ gelation behaviour of particular K⁺ solutions was also noted by Dent Glasser and Harvey (1984).

It also appears that the pore structure of K-based geopolymers is more susceptible to variations in temperature than Na-based geopolymers. The Vₚ and Sₚ of K-based geopolymers increase systematically as curing temperature is raised from 30 °C to 75 °C (see the values for mesopores in Figures 6.6 and 6.7). On the other hand, for Na-based geopolymers, there is a significant increase in both Vₚ and Sₚ from 30°C to 50°C, but a plateau from 50 °C to 75 °C. The trends apply to K- and Na-based geopolymers irrespective of the SiO₂/M₂O ratios. It has been shown that the effect of temperature on the kinetics of different geopolymers can be elucidated from their setting behaviour (Table 6.4). However, in this particular case, the tₛ of both K- and Na-based geopolymers decrease slightly as the temperature is raised from 50 °C to 75 °C (except
in Geopolymer 0.0K and 0.0Na), despite the significant difference observed in the pore structure of both geopolymers. It is believed that a large decrease in $t_s$ is not observed because of the highly concentrated sol-gel system.

Table 6.4 The apparent setting time, $t_s$ of various fly ash-based geopolymers, cured at 30 °C, 50 °C, and 75 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>30 °C</th>
<th>50 °C</th>
<th>75 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0K*</td>
<td>240 min &lt; $t_s$ &lt; 250 min</td>
<td>12 h &lt; $t_s$ &lt; 13 h</td>
<td>125 min &lt; $t_s$ &lt; 130 min</td>
</tr>
<tr>
<td>0.79K</td>
<td>≈ 40 min</td>
<td>≈ 18 min</td>
<td>≈ 17 min</td>
</tr>
<tr>
<td>1.4K</td>
<td>≈ 44 min</td>
<td>≈ 18 min</td>
<td>≈ 18 min</td>
</tr>
<tr>
<td>2.0K</td>
<td>≈ 40 min</td>
<td>≈ 21 min</td>
<td>≈ 20 min</td>
</tr>
<tr>
<td>0.0Na</td>
<td>&gt; 24 h</td>
<td>180 min &lt; $t_s$ &lt; 192 min</td>
<td>67 min &lt; $t_s$ &lt; 71 min</td>
</tr>
<tr>
<td>0.79Na</td>
<td>≈ 45 min</td>
<td>≈ 16 min</td>
<td>≈ 14 min</td>
</tr>
<tr>
<td>1.4Na</td>
<td>≈ 72 min</td>
<td>≈ 24 min</td>
<td>≈ 22 min</td>
</tr>
<tr>
<td>2.0Na</td>
<td>≈ 68 min</td>
<td>≈ 25 min</td>
<td>≈ 24 min</td>
</tr>
</tbody>
</table>

* Geopolymers are weak due to the lack of gel content.

The effect of elevated temperature on the compressive strength of fly ash-based geopolymers is presented in Figure 6.10. The increase in compressive strength at higher curing temperature concurs with the increase in mesopore volume and area observed in Figures 6.6 and 6.7. The results confirm that high temperature increases the early rate and extent of reaction, shown by a significantly higher strength from geopolymers that are cured at 75 °C after 7 days, while the rate of strength increase decreases after 28 days. There is a complex correlation between the compressive strength and the pore structure of fly ash-based geopolymers synthesised at different silicate ratios (Figures 6.6 and 6.10). The short-term strength (7 days) decreases for K-based geopolymers synthesised at SiO$_2$/K$_2$O = 2.0, while the long-term strength (28 days) is similar at any silicate ratios. In contrast, the short- and long-term strengths increase for Na-based geopolymers synthesised at increasing silicate ratios. In general, however, the short-term compressive strength of both geopolymers concur with the change in the mesopore...
volume, whereby a greater pore volume correspond to a greater degree of gel formation, thus a higher compressive strength.

Figure 6.10 The compressive strength of geopolymers at various curing temperatures (30, 50, and 75 °C) and silicate concentrations (SiO\textsubscript{2}/M\textsubscript{2}O = 0.0, 0.79, 1.4, and 2.0). The reactivity of Geopolymer 0.0K at 75 °C was too low, thus the strength of the binder was insignificant.

6.6 The effect of silicate concentration (SiO\textsubscript{2}/M\textsubscript{2}O ratio) and alkali metal cation type on fly ash-based geopolymerisation

The effect of silicate concentration on fly ash-based geopolymerisation can be understood by considering two aspects: 1) the interaction between alkali metal cations (K\textsuperscript{+} or Na\textsuperscript{+}) and silicate (and aluminate) anions in the solution, and 2) the distribution of various aluminosilicate anions at different SiO\textsubscript{2}/M\textsubscript{2}O ratios.
Firstly, the $V_p$ and $S_p$ of geopolymers synthesised at SiO$_2$/M$_2$O ratio = 0.0 are significantly lower than the $V_p$ and $S_p$ of geopolymers synthesised at higher SiO$_2$/M$_2$O ratios (Figures 6.8 and 6.9). The extent of dissolution of aluminium and silica in the alkali-containing solution is known to be less than if soluble silicate is present in the solution (Iler, 1979), because de-polymerisation of Si-O-Al and Si-O-Si bonds is enhanced with the presence of more soluble silicate species. A lower extent of dissolution decreases the rate of nucleation. As a result, Geopolymers 0.0K and 0.0Na, which are cured at lower temperatures (30 °C and 50 °C) hardly set (even after 24 hours), while at 75 °C, these geopolymers take longer time to set than other geopolymers prepared at higher silicate ratios (Table 6.4).

At SiO$_2$/M$_2$O = 0.0, the $V_p$ and $S_p$ of Na-based geopolymer are significantly greater than for K-based geopolymers (Figures 6.8 and 6.9). It is likely that the large porosity in Geopolymer 0.0Na is attributed to the formation of zeolites (the characterisation of zeolites is not presented in this study). A number of authors (Inada et al., 2005; Murayama et al., 2002; Querol et al., 1995; 1997a) reported the formation of zeolitic phases namely faujasite, hydroxysodalite, and Na-A when Class F fly ash was activated with NaOH or KOH solutions. In order to form zeolitic crystals from fly ash, a significant hydrolysis of glassy phases needs to be achieved, which usually involves reactions at high solution to solid ratio and elevated temperatures, at least above 50 °C, preferably in NaOH solutions. Further investigations on the formation of zeolites and their reaction conditions during geopolymerisation will be presented in Chapter 7.

A slight addition of soluble silicate (from SiO$_2$/M$_2$O = 0.0 to 0.79) results in a more mesoporous structure (Figures 6.8 and 6.9), which means that more geopolymer gel is likely being formed. For example, the $V_p$ and $S_p$ of Geopolymer 0.79K are larger than those of Geopolymer 0.0K. This is also the case for its Na-counterpart, although the difference is not as significantly large as for K-based geopolymer. A slightly higher soluble silicate concentration in the solution accelerates the reaction rate of K-based geopolymerisation significantly, as can be seen from the reduction of $t_s$ to $\approx$ 17 minutes. For Na-based geopolymers, the rate of reaction is accelerated slightly more, with the $t_s$ being shortened to $\approx$ 14 minutes at 75 °C. Although the curing at higher temperature
increases the rate of dissolution, the faster gel growth resulting from the coagulating ability of Na$^+$ with monomeric silicate (Dent Glasser, 1984; Wijnen et al., 1990) will cause faster setting. This is not the case for K-based geopolymers that will not induce the gelation step to proceed, unless there is sufficient supply of nutrients (larger aluminosilicate anions) for gel growth (Dent Glasser and Harvey, 1984).

As the silicate ratio is increased from 0.79 to 2.0 at 75 °C, there is a general increase in $V_p$, $S_p$, and $t_s$. This means that addition of soluble silicate generally enhances geopolymerisation, but too high silicate concentration ($\text{SiO}_2/\text{M}_2\text{O} \geq 2$) is likely to reduce reactivity. Speculatively, it is proposed that in a very high silicate solution, the high concentration of cyclic silicate species inhibits further condensation. This can be seen from the delayed setting time as the silicate ratio is increased from 0.79 to 2. In condensation, only the un-complexed tetrahedral aluminate $\text{Al(OH)}_4^-$ reacts with monomeric $\text{Si(OH)}_4$ or larger linear silicate anions (Harris et al., 1997). Linear silicate species can be easily de-polymerised as the bulk conditions are changed, allowing polymerisation to take place easily through the polycondensation of silicate and aluminate monomers. On the other hand, the large cyclic structures, such as cage or ring silicate species slow down the kinetics, and only serve as reservoirs for small, acyclic species that are more responsible for gel growth (Swaddle, 2001).

There is an anomaly observed in the pore structure of K-based geopolymers as the silicate ratio in the solution changes from 0.79 to 1.4 and 2. Geopolymer 0.79K shows a larger $V_p$, but a smaller $S_p$ than Geopolymers 1.4K and 2.0K. This is not observed in Na-based geopolymers (Figures 6.8 and 6.9). From TEM and MIP results, it can be established that Geopolymer 0.79K comprises of aluminosilicate particles that are larger than for Geopolymer 2.0K. The former may have a larger porosity (greater pore volume), but the gel network consisting of larger particles leading to a significant decrease in the pore surface area. Furthermore, the $V_p$ of K-based geopolymers at $\text{SiO}_2/\text{M}_2\text{O} = 1.4$ and 2.0 are only slightly larger than their Na-counterparts when both samples are cured at 75 °C (Figure 6.8). Yet, the $S_p$ values of K-based geopolymers are significantly larger (Figure 6.9). A larger $V_p$ and $S_p$ can be associated with a greater extent of reaction because of the increasing amount of porous gel in the matrix. A larger
Sp can also be attributed to a more uniform, smaller particle array that constitutes an extended pore network. Based on the available results, it is not yet feasible to establish that K-based geopolymer is more reactive than Na-based geopolymer. It has been speculated earlier that K-based geopolymer is more efficient in the dissolution step because the observed Si/Al ratios of K-based geopolymers are closer to the theoretical values. Wijnen et al. (1990) suggested that the larger hydration shell of K⁺ results in a weaker interaction between K⁺ and water molecules thus resulting in a better dissolution, which is essential for nucleation to proceed. Numerous authors (Dent Glasser, 1984; McCormick et al., 1989b) have suggested that the larger K⁺ cation size contributes to the increase in the number of Al-O-Si bonds due to its association with larger aluminosilicate anions, which results in an extended gel growth. These two factors seem to explain the differences in pore structure between Na and K geopolymers. Nonetheless, the effect of cation size on the mechanism of aluminosilicate gel formation, such as geopolymer gel is still ambiguous (Azizi et al., 2002; Swaddle, 2001). The increase of soluble cations is known to affect the distribution of anionic species and the structure of porous aluminosilicate by increasing the de-polymerisation of larger silicate anions thus enhancing nucleation and gel growth. Yet, the effects of cation size are complex and do not correspond to simple extensions of the reasoning for alkali metal cations, but are interrelated with various variables, such as silicate and alkali concentrations. Therefore, a definitive assessment of the distinct pore structure characteristics of K-based and Na-based geopolymers is not yet feasible.

6.7 The effect of alkali concentration (H₂O/M₂O ratio) on fly ash-based geopolymerisation

In this study, the concentration of alkali in the activating solutions is expressed as the H₂O/M₂O ratio (R), e.g. R = 10.0, 12.5, and 14.85. This means that R is small when the alkali concentration is high. The pore volume and surface area distribution of fly ash-based geopolymers at R = 10.0, 12.5, and 14.85 are presented in Figures 6.11 and 6.12 respectively.
Figure 6.11 The pore volume distribution of fly ash-based geopolymers at R = 10.0, 12.5, and 14.85 (R = H₂O/M₂O). The SiO₂/K₂O and water/binder ratios were kept constant at 0.79 and 0.3 respectively.

Figure 6.12 The pore surface area distribution of fly ash-based geopolymers at R = 10.0, 12.5, and 14.85 (R = H₂O/M₂O). The SiO₂/K₂O and water/binder ratios were kept constant at 0.79, and 0.3 respectively.
At 50\(^{\circ}\)C, the largest pore volume is shown by geopolymers that are activated at R=12.5 (Figure 6.11), while the pore surface area is similar at any R ratios (Figure 6.12). At 75\(^{\circ}\)C, the largest pore volume and area are also for geopolymers activated at R=12.5, but with a significant increase in the pore surface area at R=10.0 because of the increase in the amount of pores in the 2-3.6 nm region, classified as the ‘sub-mesopore’ region here. It is interesting that the highest pore volume and area are not observed in the geopolymers that are reacted at high alkali concentration (R = 10.0). It is believed that high alkali concentration increases the extent of dissolution (hydrolysis), but often at the expense of prolonging reaction time. Granizo and Blanco (1998) observed the delay in reaction completion in geopolymers that were activated at increasing alkali concentration. It is likely that higher alkali concentration, despite providing more nuclei (by hydrolysis) for further reaction to take place, also slows down the polymerisation step due to the availability of more alkali metal cations in the solution. However, large volume and area, particularly of that ‘sub-mesopores’ are obtained when geopolymers are reacted at R = 10.0 (at 75\(^{\circ}\)C) because even though there is an increase in the extent of hydrolysis, the rate of reaction (dissolution and polymerisation) is likely to be accelerated with the increase in curing temperature, resulting in a greater extent of the overall reaction. On the other hand, a moderate alkali concentration (R=12.5), may balance the competing rates of dissolution and polymerisation; although the dissolution is extended, it is not at the expense of polymerisation thus giving an optimum rate and extent of reaction throughout.

Figure 6.13 shows that the increase in the curing temperature and alkali concentration (smaller R) results in the increase of Si/Al ratio of the gel, indicating a higher degree of Si and Al incorporation in the gel. Although there is a significant increase in the measured Si/Al ratio in R = 10.0 with an increase in the temperature, the error bars are so significant that the Si/Al ratios could, in fact, be similar when curing takes place under different alkali concentrations, but at the same temperature.

Nonetheless, the effect of alkali concentration on geopolymerisation has not been thoroughly investigated during this study. The hypotheses made are simply based on the changes observed in the pore volume and gel composition (Si/Al ratio), and applies only
to the condition specified ($\text{SiO}_2/\text{K}_2\text{O} = 0.79$). It is expected that varying the silicate concentration or changing the type of alkali cations may cause the effect of high alkalinity to become more or less dominant.

![Graph showing the experimental Si/Al ratios of fly ash-based geopolymers at different alkali concentrations.](image)

**Figure 6.13** The experimental Si/Al ratios of fly ash-based geopolymers at $R = 10.0$, $12.5$, and $14.85$ ($R = \text{H}_2\text{O}/\text{M}_2\text{O}$). The $\text{SiO}_2/\text{K}_2\text{O}$ and water/binder ratios were kept constant at 0.79, and 0.3 respectively.

### 6.8 The effect of prolonged curing time on fly ash-based geopolymerisation

The increase in reaction temperature, silicate concentration, and alkali concentration has been shown to have a substantial effect on fly ash-based geopolymerisation, i.e. changing the rate and extent of geopolymerisation. In this section, the effect of prolonged curing on the pore structure and gel composition of K-based geopolymer is presented. Figures 6.14a and 6.14b show the experimental Si/Al ratio and the pore volume distribution of Geopolymer 0.79K, cured using various curing temperature schemes.
Figure 6.14 (a) The experimental Si/Al ratios and (b) The pore volume distribution of Geopolymer 0.79K, which were cured using various temperature schemes. N$_2$ adsorption was used to determine the porosity of geopolymers. Note: 50-24 h represents curing at 50 °C for 24h, while 30 and 75 means curing at 30 °C for 24 hours, followed by 75 °C for 24 hours.
For Geopolymer 0.79K, there is almost no increase in the experimental Si/Al ratio as the curing time at 50 °C is increased from 24 to 168 hours (Figure 6.14a). However, given the statistical errors, the differences become insignificant. The minor change in Si/Al ratio of the gel in Figure 6.14a suggests that there is a point in the course of geopolymerisation when the effect of temperature at a longer curing time becomes insignificant. Prior to this, significant dissolution usually occurs because of the alkali and silicate species existing in the solution, which are needed for nucleation and gel growth to proceed (Hench and West, 1990). Near supersaturation, however, dissolution is replaced predominantly by the polycondensation process, resulting in water being expelled from the solidified gel matrices (although it is believed that both dissolution and polycondensation processes occur simultaneously, they are separated conceptually here). In this instance, some of the alkali cations are bonded into the aluminosilicate gel network, which leads to a decrease of alkali concentration in the pore solution. The reaction kinetics are thus slowed down. Further reactions beyond this are likely to be controlled by the diffusion of remaining ion precursors to reach equilibrium with partly reacted fly ash, whereby dissolution and condensation may still take place, but at a lower extent and rate.

While a prolonged curing time does not change the Si/Al ratio of the gel, a higher reactivity might have been obtained. The evidence for higher reactivity can be seen from an increase in the volume of ‘sub-mesopores’ (2-3.6nm) when the curing time is prolonged (Figure 6.14b). This occurs because a greater degree of reaction results in more gel being formed. Consequently, larger pores are being filled with the forming gel. The total pore volume, however, seems to decrease, which is likely to be caused by the syneresis process (Scherer, 1999). The syneresis of drying gel is a physical, rather than a chemical reaction, which means that despite the total pore volume decreasing due to shrinkage, the gel composition (chemistry) remains the same. It can be concluded that while it is good to prolong curing time in order to obtain a finer pore structure, the syneresis process should not be neglected because it leads to the collapse of pores, which may potentially bring damage to the gel structure due to shrinkage of the materials.
In contrast to prolonged curing at 50 °C, there is a general increase in the Si/Al ratio and ‘sub-mesopore’ volume whenever the reaction temperature is raised to 75 °C or whenever successive low-high temperatures are applied, e.g. for geopolymers that are reacted at 30 °C or 50 °C for 24 hours, followed by 75 °C afterwards (Figure 6.14a). In this instance, it is thought that the rate and extent of gel formation is controlled by the rate of nucleation (dissolution) and gelation (polycondensation). These two reactions occur simultaneously and competitively depending on the applied reaction time and temperature. Continuous curing at a high temperature (75-24h and 75-48h) accelerates both the rate of nucleation and gelation to an extent that the integrity of gel structure deteriorates (75-48 h). However, a step-wise curing (30 and 75 or 50 and 75) provides longer time for dissolution to occur. As a result, more nutrients are available for gel growth without causing the sol-gel system to gel rapidly. This means that the available nutrients are in a ‘dormant’ state until further reactions occur, which can be induced by an external condition, such as applying heat. The results also suggest that the step-wise curing of 50 and 75 appears to be more optimal than 30 and 75. This has shown that even at an initial temperature of 50 °C, the extent of dissolution can be enhanced without resulting in a significant increase of the rate of gelation. Once again, as has been shown in Chapter 5, an optimum reaction temperature and time can be obtained by balancing the rates of nucleation (dissolution) and gelation (polycondensation).

Figures 6.15a and 6.15b show the experimental Si/Al ratio and pore volume distribution of Geopolymer 2.0K, cured using the same curing schemes. In Geopolymer 2.0 K, there is no alteration observed in the Si/Al ratio, which is the same behaviour observed in Geopolymer 0.79K (compare Figure 6.14a with 6.15a). Although there is a fluctuation in the Si/Al ratio from one curing scheme to another, the calculated standard deviation nullifies any differences. The pore structure, however, seems to suggest otherwise, and provides a better understanding of the effect of prolonged curing (Figure 6.15b). Similar to Geopolymer 0.79K, prolonged curing leads to a higher reactivity, shown by a large shift of volume to the ‘sub-mesopore’ region (2-3.6 nm in Figure 6.15b). Once again, it appears that reacting geopolymers at a higher and/or successive temperatures is more beneficial than if only a low temperature is applied, even for a longer period of time.
Figure 6.15 (a) The experimental Si/Al ratios and (b) The pore volume distribution of Geopolymer 2.0K, which were cured using various temperature schemes. N$_2$ adsorption was used to characterise the porosity of geopolymers. Note: 50-24 h represents curing at 50 $^\circ$C for 24h, while 30 and 75 means curing at 30 $^\circ$C for 24 hours, followed by 75 $^\circ$C for 24 hours.
Furthermore, the pore structure of Geopolymer 2.0K seems to be resilient to shrinkage (syneresis), i.e. when different curing schemes are applied. Speculatively, geopolymers synthesised at a higher silicate concentration may give a more stable polysialate structure (Si/Al ≈ 2).

6.9 The fractal characterisation of fly ash-based geopolymers

The surface fractality is purely a mathematical definition often used for describing the inherent disorder on the solid surface. In a simpler term, a surface geometry is defined as fractal if it can be divided into repeating N numbers of length unit, or yardstick size (Avnir, 1989). To some extent, the surface fractal geometries can be correlated to the surface roughness of porous solids. In this work, the surface fractal dimensions of different geopolymers were calculated based on the experimental data obtained from porosimetry (MIP), adsorption isotherm (N₂ adsorption) and small angle x-ray scattering (SAXS). The aim of the analysis is to provide preliminary information on the fractality of geopolymers, which is essential for the practical applications of geopolymer materials. In addition, fractal studies may provide new insight into understanding the mechanism and kinetics of geopolymerisation. A brief interpretation of the calculated fractal dimensions will be presented.

Figures 6.16 and 6.17 show the surface fractal dimensions (Dₛ) derived from applying Friesen’s and the Thermodynamic methods on the porosimetry data. Figure 6.18 shows the Dₛ values derived from applying the FHH’s and the Thermodynamic methods on the gas adsorption data, and Figures 6.19 and 6.20 show the Dₛ values obtained from SAXS data. The derivations of equations for different methods were described in Chapter 3. A summary of Dₛ obtained from different methods is shown in Table 6.5.

It can be seen that the calculated fractal dimensions vary depending on the measurement techniques (Table 6.5). This is likely to be caused by the different physico-chemical interactions between adsorbents and solid surface (i.e. for MIP and N₂ adsorption). In general, the surface fractal dimensions (Dₛ), which are obtained from MIP data are larger than 3.0 (Dₛ ≥ 3). This applies particularly to well-cured geopolymers, i.e. geopolymers that are cured at high temperatures. Nonetheless, a surface geometry can
be considered fractal only if the rule of $2 < D_s < 3$ is followed, whereby 2 refers to the concept of smooth flat area and 3 refers to the totally rough surface (Avnir, 1989). The values of $D_s > 3$ indicate a *fuzzy* interface (Neimark, 2002), which means that the surface of geopolymers is non-fractal. The application of *FHH Theory* on N$_2$ adsorption data shows that geopolymer surfaces can be considered to be fractal, i.e. $2 < D_s < 3$ (Table 6.5). However, the application of the *Thermodynamic method* reveals non-fractal properties, i.e. the $D_s > 3$. The discrepancies of values between the two methods were reported earlier for porous carbon (Sahouli *et al.*, 1996). It was suggested that the different relative pressure regions used to derive the fractal dimensions causes the observed discrepancies.

Similar to N$_2$ adsorption, the SAXS data seem to show that geopolymers possess fractal dimensions, i.e. $2 < D_s < 3$ (Table 6.5). However, the different values of $D_s$ are obtained for dried and wet geopolymers. For wet geopolymers, the presence of pore fluid seems to disturb the X-ray scattering, thus resulting in a higher $D_s$. This is also observed in time-resolved analysis of wet geopolymers. Of the three measurement techniques, SAXS is believed to be the most optimal method for fractal characterisation of geopolymers because it is not ‘destructive’ to the specimen, and has a better resolution. Based on the results shown, a comprehensive fractal characterisation of fly ash-based geopolymers is not possible. Further experimental data and analysis of measurements using SAXS and/or SANS are required.
Figure 6.16 The fractal dimensions ($D_s$) of Geopolymers 0.79K (a-c) and 2.0K (d-f) as determined by Friesen’s method using porosimetry data.
Figure 6.17 The fractal dimensions (D_s) of Geopolymers 0.79K (a-c) and 2.0K (d-f) as determined by Thermodynamic method using porosimetry data.
Figure 6.18 The fractal dimensions ($D_s$) as determined by FHH method (a-d) and Thermodynamic method (e-h) using gas adsorption data.
Figure 6.19 The fractal dimensions (D_s) of wet and dried geopolymers as determined using SAXS data. The intensity (I) scales of different geopolymers are adjusted for clarity (the real intensities for different geopolymers are similar).

Figure 6.20 Time-resolved SAXS for Geopolymer 0.79K.
Table 6.5 Summary of fractal dimensions calculated from MIP, N\textsubscript{2} adsorption, and SAXS.

<table>
<thead>
<tr>
<th>Geopolymer Temperature ((^\circ)C)</th>
<th>Fractal dimensions, D*&lt;sub&gt;s&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MIP</td>
</tr>
<tr>
<td></td>
<td>Friesen</td>
</tr>
<tr>
<td>0.79K</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>75</td>
</tr>
<tr>
<td>2.0K</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>75</td>
</tr>
</tbody>
</table>

* The values are obtained with a correlation coefficient (R²) at 0.910 < R² < 0.970.

6.10 Conclusions

The work in this chapter shows a direct correlation between the degree of reaction and the development of pore structure of fly ash-based geopolymers. The curing temperature, silicate concentration, alkali concentration, and prolonged curing time determine the rate and extent to which aluminosilicate precursors dissolve, nucleate, and grow into porous gel network. Fly ash-based geopolymers can be classified as a mesoporous (3.6-50 nm) aluminosilicate gel, with the Si/Al composition varying from 1.51 to 2.24. Three regions of porosity exist in fly ash-based geopolymers, i.e. mesopores (3.6-50 nm), macropores (50-200 nm), and pores larger than 200 nm. Each designated pore size originates from a different mechanism. The mesopores are the main porous structure, which is essentially the cluster(s) of aluminosilicate particles that constitute the Si-O-Al network (polysialate). The macropores are formed in earlier stages of reaction, i.e. when reactivity is low. As gel continues to form, these macropores are being filled, and longer chains and branches are being formed, thus transforming these macropores into mesopores. Pores larger than 200 nm exist in less reacted geopolymers, i.e. when lower silicate, alkalinity, and temperature are used.
Increasing temperature leads to an increase in the extent and rate of reaction, as shown by an increase in the mesopore volume, the Si/Al ratio, and an accelerated setting time. The effect of temperature on the rate of reaction, however, becomes less significant once the geopolymer materials set. Increasing soluble silicate concentration in the activating solutions also enhances geopolymerisation, as shown by an increase in mesopore volume and the Si/Al ratio in the gel. At SiO$_2$/M$_2$O $\geq$ 2.0 (where M = Na or K), the reactivity is reduced. The pore structure of K-based geopolymers appears to be more susceptible to variations in temperature than for Na-based geopolymers. Nonetheless, in this study, it is found that the effect of alkali metal cations on geopolymerisation is complex and subtle, thus requiring further investigation. The increase in alkali concentration often leads to prolonging dissolution, at the expense of delaying polymerisation of aluminosilicate gel. The application of a moderate alkali concentration (e.g. H$_2$O/M$_2$O = 12.5) is able to balance the competing rates of dissolution and polymerisation; although the dissolution is extended, it is not at the expense of polymerisation thus giving an optimum rate and extent of reaction throughout. A prolonged curing time at a constant temperature of 50 °C leads to a higher reactivity, shown by an increase in the mesopore volume. An optimum curing scheme is found when geopolymers are cured step-wise, i.e. starts at a lower temperature (e.g. 30 °C or 50 °C) for 24 hours, followed by a higher temperature (e.g. 75 °C) for 24 hours. This allows for more nutrients to be available initially without causing the sol-gel system to gel rapidly.

A comprehensive fractal analysis of geopolymers derived from MIP, N$_2$ adsorption, and SAXS measurement is not feasible due to the lack of experimental data. It is suggested that SAXS and/or SANS are more suitable techniques to characterise fractality of geopolymers due to the better resolution, and are non-destructive to the specimens. In Chapter 7, the formation of zeolites during geopolymerisation will be studied. The results will further support the results and discussions presented in this chapter.
CHAPTER 7
THE MECHANISM OF EARLY FLY ASH-BASED GEOPOLYMERISATION

In this chapter, the mechanism of early fly ash-based geopolymerisation is studied based on the heat of reaction, which was measured by Isothermal Conduction Calorimeter. The work is novel, as there has not been any study conducted which investigates the correlation between the heat of reaction and reactivity of fly ash-based geopolymers. The study involves varying only the silicate concentration (SiO₂/M₂O ratio, where M = Na or K) of the activating solutions while the alkali concentration (H₂O/M₂O ratio) and temperature of reaction will be kept constant at 1.0 and 50 °C respectively.

Essentially, there are two calorimetric curves observed as fly ash is activated with alkali-silicate solutions. The first heat curve lasts for approximately the first 1-2 hours and is attributed to the wetting of fly ash particles, the dissolution of aluminosilicate precursors, and polycondensation of aluminosilicate gel. Increasing the silicate concentration results in an increase in the total heat released, indicating a greater extent of reaction. The second heat curve lasts longer (more than 16 hours) and is associated with the crystallisation of zeolites. The formation of zeolites is only observed at low silicate concentrations (SiO₂/M₂O = 0.0 and 0.2), and mainly when Na-silicate is used as an activating solution. Na-silicate solution tends to enhance nucleation, which leads to a greater extent of crystal growth. K-silicate solution tends to enhance polycondensation, which results in a greater extent of geopolymer gel to be formed. The types of zeolites formed include hydroxysodalite, analcime-o, faujasite, and cancrinite when Na-silicate solution is used; and kalsilite, K-philipsite, and F-linde zeolite when K-silicate solution is used.

Large quantity of zeolites formed are localised on the fly ash particle surface. The progressive formation of zeolites during geopolymerisation is monitored by simulating a time-resolved XRD analysis. It is hypothesised that the competition between
crystallisation and polymerisation of aluminosilicate during fly ash-based geopolymerisation is dependent on the rates of dissolution of Al$^{3+}$ and Si$^{4+}$ precursors. The early dissolution of aluminium results in the formation of zeolites with high aluminium compositions. This is shown by the low Si/Al ratios of the zeolites formed initially, e.g. hydroxysodalite and cancrinite. The Al$^{3+}$ cation is believed to be the limiting nutrient because of the limited amount of reactive aluminium (amorphous) in fly ash. Therefore, the growth of zeolites is inhibited when the availability of Al-nutrient is exhausted. These findings show new insight into understanding the role of aluminium dissolution in fly ash-based geopolymerisation.

The work presented in this chapter is based on the manuscript: Sindhunata, Van Deventer, J. S. J., Lukey, G. C., and Xu, H., The mechanism of early fly ash-based geopolymerisation: polymerisation and crystallisation of aluminosilicate, Colloids and Surfaces A, submitted 2006.

7.1 Introduction

The difficulties in studying geopolymerisation arise from the various complex reaction steps, which occur simultaneously and competitively during the course of reaction. Provis et al. (2005b) suggested that there are at least 8 reaction steps, but only two are predominant, i.e. dissolution and polycondensation. Earlier workers (Lee, 2002; Van Jaarsveld et al., 1997; 1999; Xu and Van Deventer, 2002a; Yip, 2004) attempted to separate the dissolution and polycondensation steps experimentally. The results from their investigations provided valuable insight into understanding the role of individual reaction step, but they did not reflect actual geopolymerisation because of the constrained experimental conditions and methodologies.

The aim of this chapter is to address the mechanism of early fly ash-based geopolymerisation from the perspectives of three reaction steps, i.e. dissolution, polycondensation, and crystallisation of aluminosilicate. These reaction steps occur simultaneously in geopolymerisation, however they will be conceptually separated in this study. Furthermore, the individual step considered is an exothermic reaction
(Davidovits, 1999; Rahier et al., 1996b), thus the progression of each step can be studied by observing the characteristics of the rate and amount of heat released during geopolymerisation. Similar to Chapters 4 and 5, the release of heat was measured in-situ using a JAF Isothermal Conduction Calorimeter, which has commonly been used to study the hydration chemistry of cement-based materials (Barker, 1990; Kaminski and Zielenkiewicz, 1982; Mostafa and Brown, 2005; Winslow et al., 1994).

To the author’s knowledge, there has not been any published literature for the heat of reaction of alkali-activated fly ash, although there have been studies conducted for alkali-activated metakaolinite (Alonso and Palomo, 2001a; b) and slag (Fernandez-Jimenez et al., 1998; Shi and Day, 1995). Alonso and Palomo (2001a; b) reported that there were two calorimetric curves as metakaolinite was activated with alkali solution. The first heat curve is attributed to the surface wetting of solid and the dissolution of precursors. The second heat curve is associated with the precipitation of aluminosilicate phases. Occasionally, there is additional heat released, which is believed to be due to the formation of zeolites. Nonetheless, these early studies (Alonso and Palomo, 2001a; b; Granizo and Blanco, 1998) used high alkali concentration and water content. As a result, a prolonged dissolution and delayed precipitation were often observed. It will be shown that delayed precipitation will not occur in fly ash-based geopolymerisation that utilises low alkali concentration and water to solid ratio.

It has always been believed that the process of geopolymerisation is analogous to the synthesis of zeolites (Davidovits, 1991; Provis et al., 2005b), and that geopolymers are the amorphous precursors of zeolitic crystals (Van Jaarsveld et al., 1997; Xu and Van Deventer, 2002a). The synthesis of zeolites from alkali-activated fly ash has been investigated to some extent (Larosa et al., 1992; Lin and Hsi, 1995; Murayama et al., 2002; Querol et al., 1995; 1997a; b; Shigemoto and Hayashi, 1993). However, the formation of zeolitic components from fly ash has not been observed previously under the synthesis conditions for geopolymer materials, e.g. low alkalinity, low water to solid ratio, and high soluble silicate concentration. From this study, zeolites are found to form during the early fly ash-based geopolymerisation. The relationship between the mechanism of early geopolymerisation and the formation of zeolites is established.
Furthermore, the preference for crystallisation in either Na- or K-based geopolymerisation will be discussed.

7.2 Experimental methods

1 g of fly ash was mixed with various alkali-silicate solutions (Table 7.1). The heat of reaction was measured using JAF Isothermal Conduction Calorimeter by applying the direct injection method, which is preferred to the conventional methods (Alonso and Palomo, 2001a; b; Granizo and Blanco, 1998), because it eliminates the delay time caused by a stabilisation of temperature in the conduction calorimeter. The delay may take more than an hour during which all information on the early reaction might be neglected. Both fly ash and activating solutions were at the same temperature when they were mixed, i.e. at 50 °C. This eliminated the effect of initial heat transfer (from solid to liquid or vice versa). The sampling rate in the data acquisition was once every 30 seconds. Due to the absence of preliminary mixing, the mixture is expected to be inhomogeneous, but its effect has been reduced by using a higher liquid to binder (fly ash) ratio, i.e. the weight ratio of water to fly ash was kept constant at 0.4. If the amorphous content of Si- and Al-associated phases is assumed to be fully reacted, while the crystalline phases are assumed to be not reactive, the elemental composition of geopolymer gel can be calculated. Once again, this assumption is not entirely correct because of different reactivities of amorphous phases in fly ash, but is sufficient for the purpose of analysis. The theoretical Al/M ratio is kept constant at 1.0, while the theoretical Si/Al ratios of geopolymers are tabulated in Table 7.1.

The rate of heat and the total heat released were calculated by JAF Calorimeter Software using Tian’s equations (Calvet and Prat, 1963). Based on the heat release, the time at which reaction completes can be estimated. However, the time when the sample sets is unknown. Some geopolymer specimens might never have set, particularly geopolymers synthesised at low silicate concentrations (Table 6.4 in Chapter 6). At 48 hours, geopolymers were taken out from the calorimeter, washed, dried and characterised using powder XRD analysis. Micrographs of selected specimens were also obtained using an ESEM FEI XL30, which was operated at 20keV. The elemental analysis was conducted using a coupled Oxford EDAX instrument.
Table 7.1 The composition of synthesised geopolymers (constant $H_2O/M_2O$ ratio = 14.85, which leads to the theoretical $Al/M$ ratio = 1.0, $M = Na$ or $K$). The $Al/M$ and $Si/Al$ ratios are calculated-based on the assumption that all amorphous silicon and aluminium in the fly ash are fully reacted.

<table>
<thead>
<tr>
<th>Geopolymer</th>
<th>$SiO_2/M_2O$ ratio in the solution</th>
<th>$Si/Al^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0Na</td>
<td>0.0</td>
<td>1.95</td>
</tr>
<tr>
<td>0.2Na</td>
<td>0.2</td>
<td>2.04</td>
</tr>
<tr>
<td>0.5Na</td>
<td>0.5</td>
<td>2.17</td>
</tr>
<tr>
<td>0.79Na</td>
<td>0.79</td>
<td>2.30</td>
</tr>
<tr>
<td>2.0Na</td>
<td>2.0</td>
<td>2.85</td>
</tr>
<tr>
<td>0.0K</td>
<td>0.0</td>
<td>1.95</td>
</tr>
<tr>
<td>0.2K</td>
<td>0.2</td>
<td>2.04</td>
</tr>
<tr>
<td>0.5K</td>
<td>0.5</td>
<td>2.17</td>
</tr>
<tr>
<td>0.79K</td>
<td>0.79</td>
<td>2.30</td>
</tr>
<tr>
<td>2.0K</td>
<td>2.0</td>
<td>2.85</td>
</tr>
</tbody>
</table>

A separate set of experiments was also conducted to characterise zeolites formed during fly ash-based geopolymerisation. Fly ash was mixed with alkali-silicate solution, and then immediately placed in sealed plastic bags to be cured in water bath at 50°C. At designated periods, the reacted solid was separated from the solution, washed, and subjected to XRD analysis, thus the progressive formation of zeolites at different reaction times can be investigated. The intensities of the three strongest peaks from zeolites formed were normalised against the peaks from reference zeolites to calculate the relative degree of crystal formation in geopolymers (Equation 7.1),

$$\text{Relative crystallinity} = \frac{(I)_t - (I)_0}{(I)_{ref} - (I)_0} \times 100\% \quad (7.1)$$

whereby $(I)_t$ refers to peak intensity of the zeolites in geopolymers at time $t$; $(I)_0$ refers to initial peak intensity (prior to reaction); and $(I)_{ref}$ refers to peak intensity of the reference zeolite. The results presented are the average calculations from three strongest
peaks of respective zeolites.

The reference zeolites were directly synthesised from fly ash (Querol et al., 1997b; Shigemoto and Hayashi, 1993). Initially, fly ash was fused with NaOH/KOH solids at 650 °C. After 4 hours, the fused solid was taken out from the furnace, left to cool down to ambient temperature. The solid was then mixed with water at a water/solid ratio of 2.0, and stirred at ambient temperature for 24 hours. Before being subjected to a hydrothermal reaction at 90 °C, approximately 10 ml of the mixture slurry was taken. The solid was separated from the supernatant liquid, washed, filtered, and subjected to XRD analysis. The solid here is expressed as ‘S’, which essentially is the residue of fly ash particles that has not dissolved. ‘S’ was characterised in order to estimate the extent of dissolution of the crystalline phases from fly ash. ‘S’ may also contain zeolites that are formed during dissolution. The remaining slurry was heated up to 90 °C and maintained at that temperature for 24 hours in a sealed tube, thus the generated pressure was an autogenous pressure (water vapour). After 24 hours of reaction, the solid (containing zeolites) was separated from the supernatant liquid, washed, filtered, and dried for 24 hours before being subjected to XRD analysis. In order to obtain accuracy and reproducibility of the quantitative technique, the experiments were repeated three times, and the plotted results were the average of the three. The crystalline phases in fly ash become more reactive due to the fusion with hydroxide solids at 650 °C, and the use of very high alkali concentration in the synthesis. Table 7.2 lists the theoretical Al/M ratios for different mixtures of fly ash and alkali hydroxide. The theoretical Al/M ratios are calculated assuming that both amorphous and crystalline phases in fly ash are fully reacted.

### 7.3 Mechanism of fly ash-based geopolymerisation

Based on the heat released during geopolymerisation, there are at least two reaction steps observed: (1) dissolution and polycondensation, which occur simultaneously, and lead to the formation of aluminosilicate gel; and (2) crystallisation of zeolites. The occurrences of these reaction steps will be discussed in the following section.
Table 7.2 The composition of solid residue (S) and synthesised zeolites (Z). S refers to the residue of fly ash particles after dissolution. Z refers to zeolites formed after hydrothermal reaction. The water/fly ash ratio used was 2.0. The Al/M ratios are calculated assuming that both crystalline and amorphous Al are fully reacted.

<table>
<thead>
<tr>
<th>Solid (S)</th>
<th>Zeolite (Z)</th>
<th>Al/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1 (M=Na)</td>
<td>Z1</td>
<td>0.62</td>
</tr>
<tr>
<td>S2 (M=Na)</td>
<td>Z2</td>
<td>0.31</td>
</tr>
<tr>
<td>S3 (M=Na)</td>
<td>Z3</td>
<td>0.90</td>
</tr>
<tr>
<td>S4 (M=K)</td>
<td>Z4</td>
<td>0.62</td>
</tr>
<tr>
<td>S5 (M=K)</td>
<td>Z5</td>
<td>0.31</td>
</tr>
</tbody>
</table>

7.3.1 Simultaneous dissolution and polycondensation

Figures 7.1 and 7.2 show the rate of heat and total heat released as fly ash is reacted with Na-silicate and K-silicate solutions respectively at a constant temperature (50 °C) for 48 hours. For clarity, the rates of heat in Figures 7.1a and 7.2a are shown for the first 20 hours only, even though the experiment was conducted for 48 hours. The apparently high background noise from the calorimetric curves is attributed to the small amount of sample used (1 g of fly ash). The mixing of fly ash and solutions was initiated after the first 0.1 hour (insets in Figures 7.1a and 7.2a). Generally, there are two heat curves of interest. For all silicate concentrations studied, the first heat curve generally occurs between 0-2 hour, with a maximum in the rate of heat observed approximately at 10 minutes (0.15 h) depending on the silicate concentration used (inset in Figure 7.1a). The first heat curve is associated with the wetting of solid and continuous dissolution of Si\(^{4+}\) and Al\(^{3+}\) species into the solution (Alonso and Palomo, 2001a; b). The rate of heat released increases rapidly to a maximum rate, but decreases comparatively gradually thereafter (inset in Figure 7.1a). This seems to suggest that the extent of dissolution might have been reduced as the reaction progresses. Alonso and Palomo (2001b) reported an incomplete first curve from alkali-activated metakaolinite because of the time required for temperature stabilisation. From their study, the heat released due to the polycondensation (or gelation) of aluminosilicate was also observed at a significantly later time, due to the high water to solid ratios and alkali concentrations used to activate metakaolinite. In contrast, a distinct heat released from polycondensation is not
Figure 7.1 (a) The rate of heat and (b) The total heat released from activating fly ash at various Na-silicate concentrations. The inset in Figure 7.1a shows the rate of heat released for the first 0.5 hour. For clarity, the rate of heat in Figure 7.1a is shown for the duration of 20 hours only.
Figure 7.2 (a) The rate of heat and (b) The total heat released from activating fly ash at various K-silicate concentrations. The inset in Figure 7.2a shows the rate of heat for the first 0.5 hour. The dotted circle highlights the appearance of second heat curve in Geopolymer 0.0K. For clarity, the rate of heat in Figure 7.2a is shown for the duration of 20 hours only.
observed in this study. It is believed that simultaneous dissolution and polycondensation occur when water and alkali concentrations are lower, as are the conditions used in this study. The occurrence of the second heat curve is seen to be dependent on the silicate concentration (i.e. is only seen at \( \text{SiO}_2/\text{Na}_2\text{O} = 0.0 \) and 0.2 in Figure 7.1a) and the duration of reaction (i.e. at least 4 hours to observe the curve in 0.0Na, and 9 hours in 0.2Na). These heat curves are believed to be attributed to the heat released due to formation of zeolitic phases, which will be discussed later.

The quantities of heat released in the first 4 hours at different silicate concentrations are presented in Table 7.3. The 4 hours duration accounts for the completion of the first heat curves for all silicate concentrations, and excludes the contribution of second curves from Geopolymers 0.0Na and 0.2Na. It is seen that with increasing silicate ratio from 0.0 to 0.79, there is an increase in total heat released for the first 4 hours, i.e. from 15.6 J (0.0Na) to 37.9 J (0.79Na), as shown in Table 7.3. An exception is observed at \( \text{SiO}_2/\text{Na}_2\text{O} = 0.5 \) (26.4 J), whereby a slightly smaller quantity of heat released is observed than at 0.2 (27.9 J). This is believed to be due to the rise of second heat curve at \( \text{SiO}_2/\text{Na}_2\text{O} = 0.2 \), which partly contributes to the higher quantity of heat measured in the first 4 hours. The increase in total heat of reaction suggests that increasing silicate ratio from 0.0 to 0.79 has increased the extent of reaction, as also observed in Chapter 6. It is believed that at higher silicate ratios, the concentration of larger silicate oligomers is higher, thus favouring the polycondensation of aluminosilicate gel (Roozeboom et al., 1983). Lee and Van Deventer (2002b) have proposed that the re-organisation of silicate structure on fly ash particle surface probably increases the extent of dissolution and polymerisation of aluminosilicate as the silicate concentration is increased. However, as the silicate concentration becomes very high (e.g. \( \text{SiO}_2/\text{Na}_2\text{O} = 2.0 \)), the total heat released decreases (26.5 J), suggesting a less reactivity. Once again, it is speculated that larger silicate species, e.g. cage and ring structures, which are present in solutions of high silicate concentration slow down the kinetics of reaction, thus are unable to promote condensation of aluminosilicate gel (Swaddle, 2001).

The quantity of heat released differs significantly between Na- and K-based geopolymerisation. After 48 hours of reaction, the Na-based geopolymerisation liberates
a total heat ranging from 38.6 to 161.3 J (Table 7.3). The greatest amount of heat
liberated originates from the geopolymerisation at lower silicate concentrations, i.e. at
SiO$_2$/Na$_2$O = 0.0 and 0.2. At these concentrations, a greater fraction of the heat released
can be ascribed to the appearance of the second, rather than the first heat curve (Figure
7.1a). However, the K-based geopolymerisation only liberates a total heat ranging from
29.1 to 108.5 J. Furthermore, in contrast to Na-based geopolymerisation, K-based
gopolymerisation releases the greatest amount of heat at higher silicate concentrations,
i.e. at SiO$_2$/K$_2$O = 0.5, 0.79, and 2.0. A larger fraction of heat released originates from
the contribution of the first, and not the second heat curve. The second heat curve,
which is associated with the formation of zeolites, is insignificant in K-based
gopolymerisation (Figure 7.2).

Table 7.3 The maximum rate of heat, heat of first curve (from 0-4h), and total heat
of reaction after 48 hours.

<table>
<thead>
<tr>
<th>Geopolymer</th>
<th>Max Rate of heat, mW (Time, h)</th>
<th>Total heat from the first curve, J (0-4h)</th>
<th>Total heat, J</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0Na</td>
<td>18.59 (0.12)</td>
<td>15.6</td>
<td>104.3</td>
</tr>
<tr>
<td>0.2Na</td>
<td>7.71 (0.14)</td>
<td>27.9</td>
<td>161.3</td>
</tr>
<tr>
<td>0.5Na</td>
<td>9.35 (0.14)</td>
<td>26.4</td>
<td>38.6</td>
</tr>
<tr>
<td>0.79Na</td>
<td>15.33 (0.14)</td>
<td>37.9</td>
<td>63.9</td>
</tr>
<tr>
<td>2.0Na</td>
<td>7.87 (0.19)</td>
<td>26.5</td>
<td>59.6</td>
</tr>
<tr>
<td>0.0K</td>
<td>20.79 (0.12)</td>
<td>10.7</td>
<td>44.6</td>
</tr>
<tr>
<td>0.2K</td>
<td>7.17 (0.13)</td>
<td>15.8</td>
<td>29.1</td>
</tr>
<tr>
<td>0.5K</td>
<td>10.28 (0.12)</td>
<td>30.9</td>
<td>88.6</td>
</tr>
<tr>
<td>0.79K</td>
<td>23.28 (0.11)</td>
<td>43.7</td>
<td>108.5</td>
</tr>
<tr>
<td>2.0K</td>
<td>22.93 (0.14)</td>
<td>29.2</td>
<td>74.8</td>
</tr>
</tbody>
</table>

7.3.2 The formation of zeolites
Na-silicate solutions appear to be more effective at lower silicate ratios, probably
because Na$^+$ induces a greater extent of dissolution, but a lower extent of
dissolution (Provis et al., 2005a; Xu et al., 2001). A higher extent of dissolution
leads to nucleation, which in turn to formation of zeolites favourably. In contrast, K-
silicate solutions appear to be more effective at higher silicate concentrations because \( K^+ \) induces a greater extent of polycondensation, but a lower extent of dissolution. A greater extent of polycondensation means that a geopolymer gel is more likely than zeolites to be formed. In Chapter 6, it is observed that the experimental Si/Al ratios of K-based geopolymers are consistently closer to the theoretical Si/Al ratios than the Na-based geopolymers, and K-based geopolymers possess a more uniform and refined pore structure. These observations confirm that a greater extent of gel being formed.

It is suggested that the rise of the second heat curve indicates the formation of zeolites, rather than that of a delayed gelation. There are two fundamental reasons why these curves are attributed to the formation of zeolites. Firstly, there is a delay between the disappearance of the first and the rise of the second curve, the length of which is approximately 4 hours for Geopolymer 0.0Na, 9 hours for Geopolymer 0.2Na (Figure 7.1a), and 5 hours for Geopolymer 0.0K (Figure 7.2a), but the second heat curve is not very pronounced for Geopolymer 0.2K. In the synthesis of zeolites, this is commonly referred to as an *induction* period. The *induction* period is the time, whereby the aluminosilicate precursors dissolve and rearrange themselves in order to find the most thermodynamically-stable state for nucleation, re-dissolution, and crystal growth (Nishi and Thompson, 2002). On the other hand, the aluminosilicate species do not require a long time to polymerise, particularly under the conditions used in this study (low water content and alkali concentration). Secondly, the second heat curve represents a significantly greater amount of heat, which is characteristic of crystal formation. A significantly high heat of reaction contributes to the highly-ordered, crystalline structure of zeolites (Nishi and Thompson, 2002). Finally, the formation of crystals at low silicate concentrations is also confirmed from the XRD analyses (Figure 7.3) and ESEM micrographs (Figure 7.4).
Figure 7.3 The XRD patterns of (a) Na-based geopolymers and (b) K-based geopolymers, cured at 50°C for 48 hours. The following abbreviations are used: H-hydroxysodalite, A-analcime-o, F-faujasite, C-cancrinite, K-kalsilite, P-K-philipsite, and L-F-linde zeolite.
Figure 7.4 The crystal-like phases under ESEM. The composition of phases marked ‘X’ are as follows: (a) $\text{Na}_{0.4}\text{AlSi}_{0.9}\text{O}_{4}$ in 0.0Na, the chemical composition is similar to hydroxysodalite; (b) $\text{NaAlSi}_{1.9}\text{O}_{7.9}$ in 0.0Na, similar to analcime-o; (c) $\text{Na}_{0.6}\text{AlSi}_{1.1}\text{O}_{4.2}$ in 0.2Na, similar to faujasite. The phases marked “Y” have similar crystal morphologies and compositions with the phases marked “X” in Figure 7.4a; and (d) $\text{K}_{0.7}\text{AlSi}_{1.1}\text{O}_{5}$ in 0.0K, similar to kalsilite. Refer to Table 7.4 for the estimated compositions of respective zeolites.

It is seen that the extent of zeolite formation is greater for Na- than K-based geopolymerization (Figure 7.3). Previous workers (Barrer, 1982; Larosa et al., 1992; Provis et al., 2005a; Querol et al., 1995; 1997a; b; Shigemoto and Hayashi, 1993;
Vucinic et al., 2003) also reported the preferential formation of zeolites in Na-based solutions. It is believed that the smaller cation radius of Na\(^+\) enables the formation of smaller network of aluminosilicate species that grow into nuclei and crystals more rapidly. In contrast, K\(^+\) facilitates reactions that lead to the formation of larger nuclei, which usually result in less crystallinity, but more aluminosilicate polycondensation. The different behaviour of alkali metal cations is believed to be due to the ability of each cation to order water molecules to provide a template for incorporation of aluminate into the silicate structure (Wijnen et al., 1990). Provis et al. (2005a) went further to explain the tendency of Na\(^+\) cation to crystallise based on the calculated minimum energy penalty for the Si/Al ordering in geopolymer materials. They suggested that Na-based geopolymers will have more time and freedom to find a minimum-energy state, and so will be more highly ordered and more crystalline. In contrast, K-based geopolymers will not have the same freedom to rearrange into lower energy states, thus polycondensation is preferred over crystallisation. The formation of K-based zeolites is still highly possible during fly ash-based geopolymerisation, provided that the right conditions are applied. These reaction conditions include high alkali concentration, high temperature, and longer reaction time. The formation mechanisms of zeolites in early geopolymerisation are not so much limited by the thermodynamic properties of zeolites formed, but rather in finding the kinetic pathway that leads to formation of the respective zeolites.

7.4 The mechanism of zeolite formation during early geopolymerisation

In this section, the mechanism of zeolite formation at low silicate concentrations (SiO\(_2\)/M\(_2\)O = 0.0 and 0.2, where M = Na or K) is proposed by analysing the formation of various zeolites at different reaction times. There are various factors that determine the type and extent of zeolites formed. These factors include temperature, ageing method and time, reactant type and concentration, and the presence of seeds. In this study, the effect of temperature can be omitted because every reaction was carried out isothermally at 50 \(^\circ\)C. Similar to temperature, ageing method and time can also be omitted because all experiments were conducted in the same controlled environment, i.e. in an isothermal calorimeter with identical reaction times and methodologies.
Therefore, the only variables are the composition of reactants (e.g. fly ash and silicate concentration in the activating solutions) and the presence of seeds, i.e. non- or partly-reacted fly ash particles.

### 7.4.1 The formation of zeolites at low silicate ratios (SiO$_2$/M$_2$O = 0.0 and 0.2, where M = Na or K)

There are four types of zeolites formed from the activation of fly ash with Na-silicate solutions, which include hydroxysodalite (H), analcime-o (A), faujasite (F), and cancrinite (C) (Figure 7.3a). H and A are formed at SiO$_2$/Na$_2$O = 0.0, while F is predominantly formed at SiO$_2$/Na$_2$O = 0.2, with trace amounts of H and C also being present (Figure 7.3a). There are three types of crystalline phases, which are formed from the activation of fly ash with K-silicate solutions, which include kalsilite (K), K-phillipsite (P), and F-linde zeolite (L), as shown in Figure 7.3b. Here, K is a framework aluminosilicate, while P and L are zeolites. At SiO$_2$/K$_2$O = 0.0, K and L are formed, with K being formed predominantly. At SiO$_2$/K$_2$O = 0.2, P and L are formed, with L being formed predominantly. The simultaneous formation of different phases is common in the process of zeolite synthesis. These zeolitic phases are considered to be in metastable states, which means that they are likely to change to a more thermodynamically-stable phase by re-dissolution into the solution phase or solid state reaction, depending on reactant concentrations and reaction conditions (Serrano and Van Grieken, 2001). Table 7.4 lists the types of zeolites that could be formed from the activation of fly ash with alkali solutions, including their respective chemical formulae, Si:Al ratios, and JCPDS database numbers, supplied by International Centre for Diffraction Data (ICDD).

Characteristically, the formation of zeolites during geopolymerisation occurs only when low silicate concentrations are used (SiO$_2$/M$_2$O = 0.0 and 0.2, M = Na or K), and mainly in Na-silicate solutions (Figure 7.3). In a rich Al-nutrient environment, zeolites are formed favourably because a higher aluminium content leads to a greater chance for aluminium to be incorporated into silicate structures (De Witte and Uytterhoeven, 1996). A lack of silicate species is significant in keeping the concentration of dissolved Al$^{3+}$ high in the solution because the supply of Al-nutrient is limited to the extent of
amorphous Al phases dissolving from fly ash particles (Catalfamo et al., 1993). With a higher probability of Al incorporation, the number of nuclei being formed is greater, which leads to an expansive growth of the crystals. As the reaction progresses, however, there will be a high supply of Al- and Si-nutrients, which would cause the overall sol-gel phase to set rapidly. This condition has a counter-effect on the crystal growth. The favourable reaction would be the gelation of aluminosilicate species, which is also enhanced at a higher silicate concentration (Harvey and Dent Glasser, 1989).

Table 7.4 The list of zeolitic phases that could be formed from the activation of fly ash with alkali-containing solutions.

<table>
<thead>
<tr>
<th>Zeolites</th>
<th>Chemical formula</th>
<th>Si:Al ratio</th>
<th>JCPDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxysodalite (H)</td>
<td>1.08Na2OAl2O3.1.68SiO2</td>
<td>0.84:1</td>
<td>31-1271</td>
</tr>
<tr>
<td>Faujasite (F)</td>
<td>Na2Al2Si2.4O8.8.6.7H2O</td>
<td>1.2:1</td>
<td>12-0246</td>
</tr>
<tr>
<td>Cancrinite (C)</td>
<td>Na6Ca1.5Al6Si6O24(CO3)1.6</td>
<td>1:1</td>
<td>34-0176</td>
</tr>
<tr>
<td>Anacime-O (A)</td>
<td>Na(Si2Al)O6.H2O</td>
<td>2:1</td>
<td>19-1180</td>
</tr>
<tr>
<td>Kalsilite (K)</td>
<td>KAlSiO4</td>
<td>1:1</td>
<td>11-0579</td>
</tr>
<tr>
<td>F-linde zeolite (L)</td>
<td>K2Al2Si2.08O8.16.3H2O</td>
<td>1.04:1</td>
<td>25-0619</td>
</tr>
<tr>
<td>K-Phillipsite (P)</td>
<td>K2Al2Si3O10.3H2O</td>
<td>1.5:1</td>
<td>30-0902</td>
</tr>
</tbody>
</table>

Figure 7.4 depicts the morphologies of crystal-like phases (marked as ‘X’ and ‘Y’ phases) that are formed during the synthesis of geopolymers. The elemental composition of these phases was analysed using EDAX, and found to be similar to the theoretical composition (i.e. the Si/Al ratio) of known zeolites (Table 7.4). It is observed that the growth of crystals mainly occurs on the surface of fly ash particles. This suggests that the main nucleation is likely to occur on the surface, rather than in the gel matrix. The un-reacted and/or partly reacted fly ash particles might function as seeds to induce a heterogeneous nucleation to take place. Even when nucleation takes place in the gel, the density of forming gel is relatively lower than forming crystal. As a result, the remaining gel would need to dissolve to reach the crystal surfaces (McCormick and Bell, 1989). However, previous workers (Katz, 1998; Larosa et al., 1992; Querol et al., 1997a) had synthesised zeolites from fly ash exclusively and observed their formation in
gel phase of the activated fly ash-based materials. It is believed that for nucleation in the gel to occur, the nucleation mechanism should be slow and homogeneous, which normally occurs in the synthesis of zeolites from a clear, homogeneous, and seed-less solution (Schoeman et al., 1994; Zhang et al., 2003). This will result in the formation of smaller and uniform nuclei. This mechanistic pathway can be obtained by increasing the alkali concentration and water content, which are opposite to the conditions used in this study.

7.4.2 The mechanism of zeolite formation during fly ash-based geopolymerisation

In order to formulate a hypothesis for the formation mechanism of various zeolites during early geopolymerisation, a further quantitative analysis is required. Therefore, it is important to obtain pure zeolites as reference materials. However, the compositions, origins, and physico-chemical properties of pure zeolites may differ from the zeolites synthesised from activated fly ash. In this study, the reference zeolites were synthesised directly by activating fly ash with alkali-hydroxide. In order to obtain a high reactivity, fly ash was pre-fused with NaOH/KOH solids before being subjected to a hydrothermal reaction (Shigemoto and Hayashi, 1993). The fusion process breaks down the crystalline structures in fly ash particles, so that a higher dissolution of aluminosilicate phases (i.e. crystalline and amorphous phases) can be obtained. Figure 7.5a shows the XRD patterns of S, which essentially is the residue of fly ash particles after dissolving fused fly ash in water, i.e. before being subjected to hydrothermal reaction. The theoretical Al/M ratios for different fly ash-hydroxide mixtures are also shown in Figure 7.5. Figure 7.5b shows the XRD patterns of zeolites (Z) formed after the hydrothermal reaction at 90 °C. It appears the crystallisation of zeolites and their degree of crystallisation are optimum at high alkali concentration, i.e. at Al/M = 0.31 (Figures 7.5a and 7.5b). This is shown by a large proportion of crystalline aluminosilicates (e.g. quartz and mullite) that dissolve at Al/M = 0.31, in both NaOH and KOH activation (as highlighted in S2 and S5 in Figure 7.5a). Zeolites are also formed favourably at this concentration, e.g. C and H (Z2 in Figure 7.5b), and L (Z5 in Figure 7.5b). In the activation with KOH, new crystalline phases, like kalsilite (K) and F-linde zeolite (L) have already been formed, even before being subjected to hydrothermal reaction (see S4
and S5 in Figure 7.5a). When the alkali concentration is reduced to \( \text{Al/M} = 0.62 \) (S1 and S4 in Figure 7.5a), the extent of dissolution of mullite and \( \alpha \)-quartz is less. However, zeolites are also formed at this concentration, e.g. H and F (in Z1) and K (in Z4). At \( \text{Al/M} = 0.9 \) (S3 in Figure 7.5a), there is little dissolution of either mullite or quartz, and the formation zeolite is not observed clearly at this concentration (Z3 in Figure 7.5b).

From Figure 7.5, it is seen that H, C, and F can be used as the reference materials to determine the amount of zeolites, which are progressively formed during Na-based geopolymerisation (Figures 7.6a and 7.6b). Table 7.5 lists H, C, and F as reference zeolites. However, the degree of crystallinity in K-based geopolymerisation was not determined because the amount of zeolites formed was too small for a substantial quantitative analysis without significant statistical error and ambiguous interpretation (Figure 7.6c). Furthermore, despite analcime-o (A) was formed in Geopolymer 0.0Na (Figure 7.6a), it was not obtained as one of the final zeolitic products in the fusion of fly ash with NaOH (Figure 7.5b). This is probably due to the fact that A forms in its metastable phase, and changes into a more stable zeolitic phase. The instability in the amount of A formed means it would be inappropriate to use A as a reference zeolite. Therefore, the degree of A formed in Geopolymer 0.0Na will not be quantitatively determined here, but the formation of A will still be discussed qualitatively. Finally, the peak intensities of H, C, and F from Geopolymers 0.0Na and 0.2Na were normalised against the peak intensities from the reference zeolites to obtain the relative degree of crystallinity (Figure 7.7, to be presented later).

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Source</th>
<th>Al/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxysodalite (H)</td>
<td>Z2</td>
<td>0.31</td>
</tr>
<tr>
<td>Cancrinite (C)</td>
<td>Z2</td>
<td>0.31</td>
</tr>
<tr>
<td>Faujasite (F)</td>
<td>Z1</td>
<td>0.62</td>
</tr>
</tbody>
</table>
Figure 7.5 The XRD patterns of (a) solid residues (S) and (b) synthesised zeolites (Z). S refers to Solid residue after the dissolution of fused fly ash. Z refers to Zeolites formed after hydrothermal reaction. The numbering system from 1 to 5 was introduced in Table 7.2, and refers to the theoretical Al/M ratios, which are calculated assuming that both crystalline and amorphous Al are fully reacted. The dotted circles highlight the dissolution of mullite (M) and α-quartz (Q). The following abbreviations are used for zeolites: H-hydroxysodalite, A-analcime-o, F-faujasite, C-cancrinite, K-kalsilite, P-K-phillipsite, and L-F-linde zeolite.
(a) The intensity of H increases.

(b) F starts forming.
C and H start forming.
Figure 7.6 The formation of: (a) H and A in 0.0Na, (b) H, F, and C in 0.2Na, and (c) K in 0.0K. The dotted circles highlight the amorphous aluminosilicate in geopolymers, while the dotted lines highlight various peaks of the dominant zeolites. The ? indicates an un-identified metastable phase in 0.0K, which is formed at 6 hours, but disappears quickly in later stages.

It can be seen that apart from the growth of various zeolites, the XRD analyses also show the diffraction patterns, which are characteristic of amorphous aluminosilicate in geopolymers (highlighted in Figures 7.6a to 7.6c). The amorphous aluminosilicate phase(s) is indicated by a broad shoulder peak at diffraction angles (2θ) ranging from 25-35° (Davidovits, 1999). At the initial stages of reaction (≈ 8-10h), i.e. when zeolites are seen to form, the appearance of these shoulder peaks is not obvious. However, it becomes more apparent as the reaction progresses to 48 hours, indicating a greater amount of geopolymer gel being formed. This seems to suggest that the formation of zeolites is initiated early, obtaining nutrients directly from the dissolution of aluminosilicate in fly ash. In the later stages of reaction, however, the polymerisation of aluminosilicate gel is the more dominant reaction.
It is known that hydroxysodalite (H) and analcime-o (A) are formed when fly ash is activated at SiO$_2$/Na$_2$O = 0.0 (Figure 7.3a). From the heat of reaction data (Figure 7.1a), the broad secondary heat curve does not show a distinction in the time of formation of H and A; neither does it show the extent of zeolites formed. However, XRD analysis shows that H is likely to start growing between 4-6 hours of reaction, and will continue growing until the reaction ceases at 48 hours (Figure 7.6a). In contrast, A is seen to start growing between 8-10 hours of reaction. Figure 7.6a also shows that H is formed to a greater extent and over a longer period of time than A. Therefore, it is hypothesised that the formation of the later phase, A, is likely not to be caused by the transformation of the earlier phase, H (i.e. neither through a re-dissolution nor through a solid-state transformation of H), but rather, controlled by the dissolution behaviour of Al$^{3+}$ and Si$^{4+}$ from fly ash. This can be explained by comparing the Si:Al ratios of the two zeolites (Table 7.4). H possesses a lower Si:Al ratio of 0.84:1, which originates from the early dissolution of Al$^{3+}$ cation. Solutions containing Al-rich nutrients tend to crystallise easier than solutions containing Si-rich nutrients (McCormick and Bell, 1989). Catalfamo et al. (1993) suggested that in the initial leaching of fly ash, the rate of dissolution of Al$^{3+}$ is higher than Si$^{4+}$. The higher dissolution of Al$^{3+}$ induces the formation of amorphous precursors that grow into nuclei immediately. This means that the early Al-rich phase formed is located nearer to the surface of fly ash particles (Fernandez-Jimenez et al., 2005a; 2006d), thus the growth of H is also localised on the surface of fly ash particles, and not in gel matrices (the crystalline phases shown in Figure 7.4a possess similar composition to H). However, as reaction progresses, the dissolution of Al$^{3+}$ is inhibited by the depletion of available amorphous Al. The extent and rate of dissolution of Si$^{4+}$ continue to increase due to a greater composition of amorphous silica in fly ash. As a result, the growth of zeolites is mostly affected by the dissolution of Si$^{4+}$. At this stage of reaction, A is likely to be formed, as shown by its higher Si:Al ratio (2:1). In a system, whereby the extent of Al$^{3+}$ dissolution is not limited, the formation of H will be uninhibited. This can be seen in the synthesis of zeolites from the fusion of fly ash and NaOH, whereby a high yield of H is obtained due to the availability of Al from both crystalline and amorphous phases (see Z2 in Figure 7.5b). In contrast, the crystallisation of A is not observed.
At $\text{SiO}_2/\text{Na}_2\text{O} = 0.2$, there are three types of zeolites forming, namely C, H, and F. From Figure 7.6b, C and H are seen to start appearing predominantly after 10 hours, while F starts appearing after approximately 10-12 hours of reaction. However, similar to 0.0Na, the broad second heat curve at 0.2 Na (i.e. indicating the formation of zeolites) does not distinctively separate the crystallisation of one zeolite from the others (Figure 7.1a). It is hypothesised that the crystallisation of cancrinite (C) occurs earlier than F (Figure 7.6b) due to the early dissolution of Al and Ca, as shown by the low Si/Al ratio (1:1) and the incorporation of calcium into its crystal structure (Table 7.4). The quick dissolution of calcium from fly ash (Pietersen et al., 1988) enhances the crystallisation of C because calcium is able to stabilise the structure of zeolites better than other alkali cations, such as sodium or potassium (Singh and Dutta, 1998). However, the composition of calcium in fly ash used is relatively low (< 4 weight %). As a result, the extent of growth of C is limited, compared to other zeolites, namely H and F. In a similar mechanism to C, the crystallisation of H occurs earlier than F because of the early dissolution of aluminium, as shown by its low Si:Al ratio (0.84:1). The degree of crystallisation of H at $\text{SiO}_2/\text{Na}_2\text{O} = 0.2$ is lower than at 0.0 (Figure 7.7). It has been mentioned earlier that adding soluble silicate reduces the extent of formation of Al-rich phases, which in turn reduces the crystallisation of zeolites which have high aluminium contents. Therefore, at $\text{SiO}_2/\text{Na}_2\text{O} = 0.2$, the amount of H formed is less than that of F (Figure 7.7). Furthermore, F is formed at a later time because of the incorporation of more Si and less Al into the solution, evident from its higher Si:Al ratio (1.2:1), as shown in Figure 7.6b.

It also appears that the amount of H and C formed fluctuate during the course of reaction (Figure 7.7). This seems to suggest that these zeolites (H and C) probably re-dissolve to feed the crystallisation of a more stable zeolite, e.g. F in the solution phase. The increase of the amount of C and H afterwards is, however, induced by the continuous dissolution of aluminosilicate precursors from fly ash. It is acknowledged that the obtained results are currently insufficient to prove the dominance of one mechanism over the other, and therefore, will be considered to be a subject of further investigation.
Figure 7.7 The degree of crystallinity of H in 0.0Na, and C, F, and H in 0.2Na. The relative crystallinity was calculated using Equation 7.1, starting from the time of formation as shown in Figures 7.6a and 7.6b.

The early dissolution of aluminium also controls the formation of crystalline phases during K-based geopolymerisation. At SiO$_2$/K$_2$O = 0.0, the predominant phase formed is kalsilite (K), which possesses a Si:Al ratio close to 1 (Table 7.4). At SiO$_2$/K$_2$O = 0.2, two types of zeolites are formed, namely K-philipsite (the Si:Al ratio of 1.5:1) and F-linde zeolite (the Si:Al ratio of 1.04:1), in which F-linde zeolite is a more predominant zeolite (Figure 7.3b). Both conditions show that the predominant phases and crystals have lower Si:Al ratios.

### 7.5 Conclusions

The mechanism of early fly ash-based geopolymerisation activated by alkali-silicate solutions of different silicate concentrations (SiO$_2$/M$_2$O, where M = Na or K) has been elucidated. The work is novel, as there has not been any study conducted that investigates the correlation between heat of reaction, time-resolved XRD, and reactivity of fly ash-based geopolymers. The heat of reaction data suggests that the alterations in
silicate concentration and alkali metal cation types control the rate and extent of dissolution, polymerisation, and crystallisation of aluminosilicate species in geopolymerisation.

The formation of zeolites in a predominantly aluminosilicate gel is only observed in Na-silicate solutions with low silicate concentrations (SiO$_2$/Na$_2$O = 0.0 and 0.2). The lack of soluble silicate enhances the early dissolution of Al from fly ash and leads to a higher extent of nucleation and crystallisation of zeolites with high aluminium content. It is proposed that the competition for nutrients between polymerisation of aluminosilicate gel and crystallisation of zeolites during early geopolymerisation is controlled by the dissolution rates of Si$^{4+}$ and Al$^{3+}$ precursors. The dissolution of Al$^{3+}$ is, however, limited by the content of amorphous aluminium in fly ash. Once the source of Al is exhausted, it is thought that the formation of zeolites will cease. The findings show new insight into understanding the role of aluminium dissolution in fly ash-based geopolymerisation. In Chapter 8, the later reaction stages in geopolymerisation (i.e. after geopolymers set) will be investigated by ageing geopolymers in various alkali and carbonate solutions.
In the previous chapters, the reaction mechanisms of early fly ash-based geopolymerisation were studied by correlating the development of pore structure and heat of reaction with the formation of geopolymer gel and zeolites in geopolymerisation. The competition between crystallisation of zeolites and polycondensation of aluminosilicate gel (or geopolymer gel) is found to be controlled by the rate of releasing Si$^{4+}$ and Al$^{3+}$ precursors from fly ash particles. However, it is known that once geopolymers set, the reactivity of the geopolymers is reduced because the reaction becomes diffusion-limited. As a result, further reaction steps become dependent on the concentration of dissolved species in the pore solution. In this chapter, the later reaction stages of geopolymerisation (i.e. after geopolymers set) have been studied by ageing (immersing) geopolymers in various alkali and carbonate solutions. The transport of precursors (Si$^{4+}$ and Al$^{3+}$) between pore and ageing solutions has been indirectly investigated by measuring the concentration of the dissolved Si$^{4+}$ and Al$^{3+}$ in the ageing solutions. As a result of immersion, the concentration of precursors in the pore solution of geopolymers is altered, which in turn affects the reactivity of later reaction.

The transport of ions, the alterations in the porosity, and microstructure are evidence, which indicate that reaction is enhanced when geopolymers are immersed in alkali solution. Nonetheless, a high alkali concentration (5M MOH, where M = Na or K) is found to be detrimental to the structure of geopolymers because of prolonged dissolution. There are two conditions which favour higher reactivity: 1) a moderate alkali concentration (e.g. 1 M MOH) to promote dissolution, but without delaying precipitation; and 2) the availability of aqueous solutions to facilitate the transport of precursors, so that dissolution and precipitation can occur continuously. As a result of ageing, new crystalline phases (zeolites) are also formed. However, ageing in solutions of neutral pH, such as water and carbonates is found to give a ‘buffering effect’, which
inhibits transport of alkali cations into and out of pore solution, such that the rate and extent of dissolution are greatly reduced. Hence, there is essentially no change in the pore structure as geopolymers are aged under these solutions. These findings have significant practical application because of the age-dependent properties of geopolymers. It is known that the properties of geopolymers change with time. Therefore, by ageing geopolymers in solutions, which provide a ‘buffering effect’, the properties of geopolymers can be preserved.

The results and discussions presented in this chapter are empirical. It is acknowledged that a full fundamental understanding which explains the change in physico-chemical properties observed as a result of ageing cannot be provided based on the current results alone. Therefore, further investigations are recommended, though this work falls outside the scope of the thesis.


8.1 Introduction

The practice of ageing cementitious materials in water or alkali-containing solutions, such as Ca(OH)$_2$ and CaCO$_3$ has been done to prolong the hydration of calcium silicate hydrates (Bleszynski and Thomas, 1998; Neville, 1995). Apart from the prolonged hydration, curing cement paste or concrete in Ca-containing solutions also increases durability of materials by preventing alkali-silica reactions, ASR (Kurtis and Monteiro, 2003; Prezzi et al., 1997; 1998; Rodrigues et al., 1999) and efflorescence (Neville and Brooks, 1990).

In the synthesis of aluminosilicate gels and glasses, the porosity and other physico-chemical properties can be tailored by ageing wet gel in various alkali solutions (Goworek et al., 1999; Venezia et al., 2001; Willey, 1980), salt solutions (Setzer et al., 2002; Willey, 1980), and organic solvents (De Witte et al., 1996; Nakanishi et al.,
Regarding the use of alkali solutions, it is found that the alteration of pore structure in wet and dry silica gel (xerogel) is largely dependent on the ageing time, concentration, and pH of solutions (Davis et al., 1992; 1994; Setzer et al., 2002; Titulaer et al., 1994a; b). A longer ageing time results in an increase in pore size and decrease in specific surface area by eliminating narrower pores (Goworek et al., 1999; Willey, 1980). Ageing in high pH solutions leads to the formation of mesoporosity, while low pH leads to the formation of microporosity because of the incorporation of Al$^{3+}$, which gives rise to a stronger network condensation (Davis et al., 1994; De Witte et al., 1996). Furthermore, ageing or washing in a neutral pH (near to 7) results in a porous gel with a higher pore volume and lower surface area than ageing or washing at lower pHs. The alteration of pore structure in porous silica gels follows the Ostwald's ripening mechanism (Iler, 1979). Along with a higher extent of aluminosilicate condensation, the growth of neck occurs between larger particles at the expense of dissolution of smaller particles. As a result, the pore volume and mean pore size increase, but the specific surface area decreases.

The effect of ageing in alkali and carbonate solutions on the physico-chemical properties of fly ash-based geopolymers has never been investigated before. In this study, fly ash-based geopolymers will be immersed in various alkali and carbonate solutions. The transport behaviour of ionic precursors, porosity, crystallinity, and morphologies of aged gels will be investigated. It is known that once geopolymers set, the effects of various reaction parameters, such as silicate ratio, alkali concentration, curing temperature and humidity are found to be minimal because the reactions are diffusion-limited (Provis et al., 2005b), i.e. controlled by the diffusion of remaining soluble species in the pore solution onto the fly ash particles or growing gel network. However, it is expected that by ageing geopolymers in alkali and carbonate solutions, the equilibrium of ionic precursors will be affected such that further reaction steps will not be diffusion-limited.

In this chapter, the following questions will be addressed:

1. Is ageing of geopolymers in alkali or carbonate solutions beneficial for practical applications?
2. What are the factors contributing to the alterations in the physico-chemical properties observed in non-aged and aged geopolymers?

3. How does ageing affect the porosity and crystallinity of geopolymers?

### 8.2 Experimental methods

Table 8.1 lists the composition of synthesised geopolymers with their theoretical Si/Al ratios, which are calculated assuming all amorphous Si and Al in fly ash are fully reacted. The water to binder ratio was kept constant at 0.3, which results in a constant Al/M ratio of 1.5. Geopolymers were synthesised by mixing fly ash and alkali-silicate solutions according to the procedures described in Chapter 3. The consistent geopolymer slurry was cast in 70 cm³ cylindrical moulds, cured at 50 and 75 °C for 24 hours. A longer curing time of 48 hours was applied to Geopolymers 0.0K and 0.2K in order to achieve a higher reactivity (or until the samples were sufficiently hard to be de-moulded). Geopolymers were de-moulded, and left to cool to room temperature, which then aged (immersed) in various alkali and carbonate solutions (100 ml), namely NaOH, KOH, Na₂CO₃, K₂CO₃, and distilled water (Table 8.2). A 3 ml aliquot was taken every 2h, 4h, 8h, 24h, 48h, 168h (7 days), 336h (14 days), 672h (28 days), and 2160h (90 days). The aliquot solution was diluted (a ratio of 1:100 for every solution) before being subjected to elemental analysis (Al³⁺, Si⁴⁺) using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Then, the relative concentrations of Si⁴⁺ and Al³⁺ were plotted against the duration of immersion. The relative concentration refers to the difference between the concentration of cations in the ageing solution prior to immersion and the concentration at the time of measurement. The direct extraction of pore solution from hardened geopolymers for analysing the Si⁴⁺ and Al³⁺ concentrations was deemed inappropriate for geopolymer gel due to the very high pressures which would need to be applied. High pressure causes the fusion of gel and solution, which will lead to measurement errors (Barneyback Jr and Diamond, 1981).

At 14, 28, and 90 days, geopolymers were cut into two cylindrical pieces of approximately 5 cm³ each using a diamond saw (Leco VC-50). One was crushed, dried at 105 °C for 24 hours, and subjected to N₂ adsorption (Tristar) and XRD (Philips PW 1800 XRD) analyses; while the other was dried at 60 °C, and then subjected to ESEM-
EDAX analysis (PHILLIPS XL30 Environmental Electron Microscope).

Table 8.1 The theoretical Si/Al ratios of geopolymers synthesised in this study.

<table>
<thead>
<tr>
<th>Geopolymer</th>
<th>SiO₂/M₂O ratio in the solution (m)</th>
<th>Si/Al*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0Na</td>
<td>0.0</td>
<td>1.95</td>
</tr>
<tr>
<td>0.2Na</td>
<td>0.2</td>
<td>2.02</td>
</tr>
<tr>
<td>0.79Na</td>
<td>0.79</td>
<td>2.21</td>
</tr>
<tr>
<td>2.0Na*</td>
<td>2.0</td>
<td>2.62</td>
</tr>
<tr>
<td>0.0K</td>
<td>0.0</td>
<td>1.95</td>
</tr>
<tr>
<td>0.2K</td>
<td>0.2</td>
<td>2.02</td>
</tr>
<tr>
<td>0.79K</td>
<td>0.79</td>
<td>2.21</td>
</tr>
<tr>
<td>2.0K*</td>
<td>2.0</td>
<td>2.62</td>
</tr>
</tbody>
</table>

*The Si/Al ratios are calculated based on the assumption that all amorphous aluminosilicate phases are fully reacted. Geopolymers 2.0Na and 2.0K were damaged during immersion in alkali solutions after 48 hours. Therefore, the experiment was discontinued for these geopolymers.

Table 8.2 The concentration of various ageing solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH / KOH</td>
<td>1</td>
</tr>
<tr>
<td>NaOH / KOH</td>
<td>5*</td>
</tr>
<tr>
<td>NaOH / KOH</td>
<td>8</td>
</tr>
<tr>
<td>Na₂CO₃ (saturated) / K₂CO₃</td>
<td>2.5*</td>
</tr>
<tr>
<td>Distilled water</td>
<td>-</td>
</tr>
</tbody>
</table>

*Note that the concentration of alkali metal cations, [Na⁺] or [K⁺], was kept constant at 5M for hydroxide and carbonate solutions. The concentration of 5M KOH/NaOH is equal to the initial alkali concentration used in the synthesis of geopolymers.
8.3 The transport behaviour of Si\(^4+\) and Al\(^3+\) cations

The dissolution of Si\(^4+\) and Al\(^3+\) from geopolymers into ageing solutions may initiate from the various existing phases, namely: 1) non- or partly-reacted fly ash particles, 2) silicate residues, and 3) early geopolymer gel (or precursors). Firstly, the greater proportion of dissolved ions should originate from residual fly ash particles. Secondly, the residual silicates dissolve because of colloidal silicas present in the activating solutions with high silicate concentration. Colloidal silicas are usually unstable at high pHs, and thus readily dissolve into their monomeric species, Si(OH)\(_4\) (Iler, 1979). However, is the dissolution of early geopolymer gel possible? Similar to zeolites, the early geopolymer gel (or aluminosilicate gel) is likely to be in a metastable phase, which is formed by kinetics-, rather than thermodynamic-driven mechanism (Navrotsky et al., 1995), and thus is easily transformed at changing reaction conditions. In the results presented later, the re-structuring of gel network is observed when geopolymers are aged in various alkali solutions, shown by the changes in gel porosity, microstructure, and gel composition.

The amounts of Si\(^4+\) and Al\(^3+\) cations dissolved from Na-based geopolymers that are immersed in water, alkali, and carbonate solutions are presented in Figure 8.1. It is seen that the relative concentrations of dissolved Si\(^4+\) and Al\(^3+\) increase as the ageing time increases. However, the discerning reader will be aware of the extremely low/zero concentrations of Si\(^4+\) and Al\(^3+\) to be expected initially in water or carbonate solutions, and note the unusual, negative relative concentrations reported for some of their measurements in Figure 8.1. Since the solutions began without Si\(^4+\) and Al\(^3+\) cations, it is physically impossible for the concentration of these precursors to fall below zero. The negative readings are suspected of being artefacts generated as a result of the ICP-OES equipment’s inability to measure accurately at the very low concentrations near zero, thus giving false values. Hence, it is most sensible to interpret these negative values to indicate zero concentration.

In 1M, 5M, and 8M NaOH solutions, the rates of release of Si\(^4+\) generally increase significantly in the first 48 hours, then decline slightly afterwards. However, the dissolution of Si\(^4+\) continues after 28 days (after 672 hours in Figures 8.1a, 8.1c, and
In these solutions, the rates of release of Al\(^{3+}\) also generally increase in the first 48 hours, decline slightly afterwards, then finally result in reduced concentrations after 28 days (after 672 hours in Figures 8.1b, 8.1d, and 8.1f). The concentration of Al\(^{3+}\) decreases after a prolonged ageing period (28 days) because the supply of Al\(^{3+}\) is probably limited, as most Al is contained in the crystalline structure of mullite (Catalfamo et al., 1993). The initial increase in the concentration of dissolved Si\(^{4+}\) and Al\(^{3+}\) is likely caused by the hydrolysis of Na\(^+\), which leads to the dissolution of Si\(^{4+}\) and Al\(^{3+}\). When the concentration of OH\(^-\) is increased, the initial rate and extent of dissolution also increase. The extent of dissolution is reduced only when aluminosilicate species re-precipitates. As the ageing time is prolonged, the precipitation of aluminosilicate eventually dominates. The dissolution and re-precipitation result in a more condensed gel structure at 90 days (Figure 8.12d, to be discussed later). The physical evidence for aluminosilicate precipitation is seen from the change of an initially clear to become a cloudy ageing solution, which is filled with opaque flakes, indicative of aluminosilicate gel (Nishino et al., 2004). Apart from the Si\(^{4+}\) and Al\(^{3+}\), the Fe\(^{3+}\) and Ca\(^{2+}\) cations also dissolve, which are evident from the formation of brownish precipitates (possibly Fe(OH)\(_3\)) after longer ageing periods (at least 28 days). The precipitates exist only in solutions of high alkali concentrations (5M and 8M NaOH).
Figure 8.1 The relative concentrations of Si$^{4+}$ and Al$^{3+}$ cations for: (a) and (b) Geopolymer 0.0Na; (c) and (d) Geopolymer 0.2Na; and (e) and (f) Geopolymer 0.79Na. All geopolymers were pre-cured at 50°C for 24 hours, unless otherwise indicated. The prefix 75°C-NaOH and 75°C-Na$_2$CO$_3$ refer to geopolymers, pre-cured at 75°C and aged in 5M NaOH and 2.5M Na$_2$CO$_3$ respectively. Lines are drawn to highlight 48 and 672 hours ageing time.
It is also seen that the concentrations of dissolved ionic precursors are dependent on the silicate ratios of original geopolymers. For Na-based geopolymers, the concentrations of dissolved Si$^{4+}$ and Al$^{3+}$ cations increase in the following order: 0.0Na < 0.2Na < 0.79Na (Figure 8.1). The concentrations of Si$^{4+}$ and Al$^{3+}$ precursors are higher in geopolymers synthesised at higher silicate concentrations because there are more readily available precursors to dissolve once geopolymers are ‘activated’ (i.e. by immersing in alkali-containing solutions). The increase of available precursors can be directly correlated to a higher rate and extent of polymerisation in high-silicate geopolymers (Chapter 6).

The concentrations of dissolved Si$^{4+}$ and Al$^{3+}$ from K-based geopolymers increase in the following order: 0.79K < 0.2K < 0.0K (Figure 8.2). Geopolymers 0.0K and 0.2 K are known to be less reactive than Geopolymer 0.79K, hence there is a larger porosity due to a lack of gel formation, as shown in Figure 8.6 (to be discussed later). Upon ageing in alkali solutions, a larger porosity allows the transport of K$^+$ to become easier, which leads to an increase in the extent of aluminosilicate dissolution from fly ash. In addition, the amounts of dissolved Si$^{4+}$ and Al$^{3+}$ from K-based geopolymers are consistently greater than for Na-based geopolymers at any silicate ratio. For low-silicate ratios (SiO$_2$/M$_2$O = 0.0 and 0.2), because of low reactivity, many partly-reacted fly ash particles possibly dissolve more Si$^{4+}$ and Al$^{3+}$ into the alkali solutions. For higher silicate ratios (SiO$_2$/M$_2$O = 0.79), Geopolymer 0.79K is likely to be more reactive than Geopolymer 0.79Na (Chapter 6). As a result, there are more readily available precursors in Geopolymer 0.79K to support dissolution.

An interesting trend is observed as Na-based geopolymers are aged in KOH solution. Firstly, after a prolonged ageing time (more than 48 hours), the concentrations of dissolved Si$^{4+}$ and Al$^{3+}$ in 5M NaOH are generally higher than in 5M KOH solution for all Na-based geopolymers (Figure 8.1). Similarly, the concentrations of Si$^{4+}$ and Al$^{3+}$ in K-based geopolymers dissolved in 5M NaOH are consistently higher than in 5M KOH solution (Figure 8.2). Speculatively, the different degrees of dissolution of geopolymers in NaOH and KOH solutions are caused by the different chemistry of alkali metal cations. It has been shown that while Na$^+$ tends to dissolve continuously, K$^+$ tends to polycondensate quickly. This is due to the preferential association of Na$^+$ with
monomeric aluminosilicate, while K⁺ with oligomeric aluminosilicate species (Dent Glasser, 1984; Dent Glasser and Harvey, 1984; McCormick and Bell, 1989; Provis et al., 2005a). As a result, it is thought that ageing geopolymers in NaOH solution will cause a greater rate and extent of dissolution, whereas ageing in KOH solution will cause a greater rate and extent of polycondensation.
Figure 8.2 The relative concentrations of Si$^{4+}$ and Al$^{3+}$ cations for: (a) and (b) Geopolymer 0.0K; (c) and (d) Geopolymer 0.2K; and (e) and (f) Geopolymer 0.79K. All geopolymers were pre-cured at 50 °C for 24 hours, unless otherwise indicated. The prefix 75 °C-KOH and 75 °C-K$_2$CO$_3$ refer to geopolymers, pre-cured at 75 °C and were aged in 5M KOH and 2.5M K$_2$CO$_3$ respectively. Lines are drawn to highlight 48 and 672 hours ageing time.

The transport of precursors in H$_2$O and Na$_2$CO$_3$ solutions is different from the transport behaviour observed in the OH⁻ solutions. In H$_2$O and Na$_2$CO$_3$ solutions, the slopes of the curves of Si$^{4+}$ and Al$^{3+}$ dissolution are seen to increase slightly for an initial 48 hours, but decrease afterwards (all Na-based geopolymers in Figure 8.1). In water, initial dissolution (for 48 hours) is likely to be ‘initiated’ by the residual alkali cations in the pore solution, which are able to ‘move’ freely upon contact with aqueous solutions. The decrease in the concentrations of dissolved Si$^{4+}$ and Al$^{3+}$ after 48 hours is probably caused by the decrease in the extent of hydrolysis due to the lack of alkali supply in the solution (the pH of water is neutral). However, the saturated Na$_2$CO$_3$ solution probably prevents any ionic transport from pores into ageing solutions, and vice versa to occur. As a result, the dissolution of Si$^{4+}$ and Al$^{3+}$ ceases early. Similar to Na-based
Geopolymers, the concentrations of dissolved Si$^{4+}$ and Al$^{3+}$ from K-based geopolymers are relatively low in H$_2$O and K$_2$CO$_3$ solutions (Figure 8.2). Nonetheless, K-based geopolymers that are immersed in 2.5M K$_2$CO$_3$ solution show a higher extent of dissolution of Si$^{4+}$ and Al$^{3+}$ than in water, probably because 2.5 M K$_2$CO$_3$ is not a saturated solution, thus facilitating the transport of precursors easily.

Geopolymers pre-cured at 75 °C (Geo-75 °C) were also aged in alkali and carbonate solutions along with those pre-cured at 50 °C (Geo-50 °C) (Figures 8.1 and 8.2). For Na- and K-based geopolymers, the amount of dissolved Si$^{4+}$ from Geo-75 °C is higher than for Geo-50 °C. In contrast, the amount of dissolved Al$^{3+}$ from Geo-75 °C is generally lower than for Geo-50 °C. There are two cumulative factors, which can explain the observed behaviour. Firstly, it has been known that higher curing temperatures lead to the formation of geopolymer gels with higher Si:Al ratios (Chapter 6). Consequently, there are more Si$^{4+}$ than Al$^{3+}$ cations available, and readily dissolve upon contact with alkali solutions. Secondly, the content of amorphous Al in fly ash is limited (Catalfamo et al., 1993). Therefore, if the dissolution of fly ash is prolonged, more Si$^{4+}$, and less Al$^{3+}$ will dissolve.

In summary, the alterations of the concentration of Si$^{4+}$ and Al$^{3+}$ precursors in the ageing solutions are found to be related to the extent of dissolution and precipitation of these precursors in aged fly ash-based geopolymers. Increasing OH$^{-}$ concentration of the ageing solutions leads to a higher rate and extent of dissolution, thus ageing (immersing) in OH$^{-}$ solutions for a prolonged period results in a higher extent of reaction. Nonetheless, solutions of neutral pH, such as water and saturated carbonate solutions give a ‘buffering effect’, which inhibits the transport of alkali cations into and out of the pore solution. As a result, the rate and extent of dissolution and precipitation are also reduced.

### 8.4 The alteration of pore structure

In the following section, effects of ageing on the pore structure of geopolymers will be investigated. The extent of reactivity (dissolution and precipitation) can be seen from the changes in the porosity of geopolymers.
8.4.1  The pore structure of Na-based geopolymers

The effect of ageing in various alkali and carbonate solutions on the pore structure of Na-based geopolymers is presented in this section.

8.4.1.1  Non-immersed geopolymers

The porosity of fly ash-based geopolymers that are aged for 1, 14, and 28 days are presented in Figure 8.3. From Chapter 7, it is known that zeolites are formed in Na-based geopolymers that are activated at low silicate concentrations (SiO$_2$/Na$_2$O = 0.0 and 0.2). In Figure 8.3, the porosity of zeolites in Na-based geopolymers can be seen from the significant pore volume in the ‘sub-mesopore’ region (2-3.6 nm in Figures 8.3a and 8.3b). In addition, there is also significant volume in the mesopore region, i.e. at 3.6-50 nm. The pore volume distribution at SiO$_2$/Na$_2$O = 0.0 and 0.2 encompasses the porosity of both zeolites and geopolymer gel. As the ageing time is prolonged to 28 days, there is a shift of pore size distribution to be predominantly in the ‘sub-mesopore’ region (2-3.6 nm in Figures 8.3a and 8.3b), which probably suggests that more zeolites are being formed. At SiO$_2$/M$_2$O = 0.79 (M = Na or K), the pore structure of Na- and K-based geopolymers is classified mainly in the mesopore region, 3.6 – 50 nm (Figures 8.3c and 8.3d). As the ageing time is prolonged to 28 days, there is a shift of pore size distribution to smaller pore region, e.g. < 10 nm. This shows that a higher extent of aluminosilicate condensation results in more formation of aluminosilicate gel, leading to large pre-existing pores being filled.

8.4.1.2  Ageing by immersion in various alkali and carbonate solutions

The effect of ageing by immersion in various alkali and carbonate solutions on the pore structure of Geopolymers 0.0Na, 0.2Na, and 0.79Na for 14 days is shown in Figure 8.4. At low Na-silicate concentrations (SiO$_2$/Na$_2$O = 0.0 and 0.2), ageing in 1M NaOH solution results in a shift of pore distribution towards the ‘sub-mesopore’ region (Figures 8.4a and 8.4b). Table 8.3 also shows an increase in the pore volume when Geopolymers 0.0Na and 0.2Na are immersed in 1M NaOH solution. For Geopolymer 0.79Na, there is a significant shift in the pore volume towards smaller pores, e.g. < 10 nm (Figure 8.4c). It is believed that the external supply of alkali cations (Na$^+$) from 1M NaOH enhances hydrolytic attack on fly ash and geopolymer gel, which results in a
higher extent of dissolution and re-precipitation of new gel.

Figure 8.3 The pore volume distribution of non-immersed geopolymers: (a) 0.0Na, (b) 0.2Na, (c) 0.79Na, and (d) 0.79K at 1, 14, and 28 days. The dotted circles indicate the increase of volume in ‘sub-mesopore’ region, 2-3.6 nm, while the dotted lines separate pore volume with mean pore widths above and below 10 nm.
Figure 8.4 The pore volume distribution of: (a) 0.0Na, (b) 0.2Na, and (c) 0.79Na after 14 days of immersion. All geopolymers were pre-cured at 50 °C for 24 hours, except 75 °C-NaOH, which was pre-cured at 75 °C, and immersed in 5M NaOH solution. The dotted lines separate pore volume with mean pore widths above and below 10 nm.
It was seen earlier that as the alkali concentration of ageing solution increased (5M and 8M NaOH), the extent of dissolution of Si$^{4+}$ and Al$^{3+}$ precursors from all Na-based geopolymers also increased (Figure 8.1). The transport of precursors from Na-based geopolymers thus results in a significant decrease in the total pore volume (Table 8.3). The decrease in the total pore volume is attributed to the shift of pore volume distribution from the mesopore, 3.6 – 50 nm to a larger pore size region (Figure 8.4). In addition, when aged in a 5M NaOH solution for 14 days, Geo-75 $^0$C appears to have a similar pore volume distribution with Geo-50 $^0$C (Figure 8.4). However, the total pore volume of Geo-75 $^0$C is slightly smaller than Geo-50 $^0$C (Table 8.3). This shows that Geo-75 $^0$C, which is originally a more-reacted geopolymer, is susceptible to further dissolution upon contact with alkali solutions. This is speculated as being due to the abundance of ‘mobile’ and ‘active’ precursors contained in geopolymers pre-cured at 75 $^0$C, and these precursors are readily dissolved upon contact with ageing solutions.

Ageing in saturated Na$_2$CO$_3$ solution and water slightly changes the pore volume distribution of Geopolymers 0.0Na and 0.2Na at 14 days (Figures 8.4a and 8.4b). The slight increase in total pore volume is also observed at 14 days (Table 8.3). However, for Geopolymer 0.79Na, there is essentially no change in the pore volume distribution (Figure 8.4c). Firstly, it is believed that Na$_2$CO$_3$ (sat) solution provides a ‘buffering effect’ that inhibits the transport of ions between pore and ageing solution, which leads to low reactivity. Hence, the porosity of geopolymers aged in Na$_2$CO$_3$ (sat) solution only changes slightly from the original non-immersed geopolymers. Secondly, while water also gives further dissolution and re-precipitation, the extent of reaction is less because of the lack of alkali metal cation for hydrolysis to occur continuously. These findings have a practical significance because it is known that the properties of geopolymers change with time (or age-dependent). Therefore, by ageing geopolymers in solutions that provide a ‘buffering effect’, the initial properties of geopolymers can be preserved.
Table 8.3 The cumulative pore volume (cm$^3$/g) of Na- and K-based geopolymers under different ageing conditions. *Data from Geopolymer 0.0K and 0.2K are not available due to the low reactivity of the geopolymers. #Only Geo-75 °C in 5M NaOH was subjected to N$_2$ adsorption.

<table>
<thead>
<tr>
<th>Time (d)</th>
<th>0.0Na</th>
<th>0.2Na</th>
<th>0.79Na</th>
<th>Time (d)</th>
<th>0.0K</th>
<th>0.2K</th>
<th>0.79K</th>
</tr>
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<tr>
<td>Na-based geopolymers (non-immersed)</td>
<td></td>
<td></td>
<td></td>
<td>K- based geopolymers (non-immersed)</td>
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<tr>
<td>1d</td>
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<td>0.067</td>
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<td>0.005</td>
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<td>0.053</td>
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<tr>
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<td>0.028</td>
<td>0.014</td>
<td>14d</td>
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<td>0.005</td>
<td>0.038</td>
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<td>28d</td>
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<td></td>
<td></td>
<td>Geo – 75 °C in 5M KOH*</td>
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<tr>
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<td>2.5M K$_2$CO$_3$</td>
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<td>0.011</td>
<td>0.008</td>
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</tr>
<tr>
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<td>0.076</td>
<td>0.093</td>
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<td>-</td>
<td>-</td>
<td>0.130</td>
</tr>
<tr>
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<td>0.072</td>
<td>0.079</td>
<td>90d</td>
<td>-</td>
<td>-</td>
<td>0.110</td>
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<td></td>
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<tr>
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<td>0.053</td>
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<td>0.167</td>
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<td>0.077</td>
<td>0.100</td>
<td>90d</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>
The effect of ageing in 1M NaOH, Na₂CO₃ (sat), and H₂O on the pore structure of Geopolymers 0.0Na, 0.2Na, and 0.79Na over longer ageing periods (14, 28, and 90 days) is further investigated, and the pore volume distributions are presented in Figure 8.5. The change in the pore structure of Na-based geopolymers is dependent on the silicate concentration and type of ageing solution. Firstly, for low-silicate geopolymers (Geopolymers 0.0Na and 0.2Na), ageing in solutions of 1M NaOH, Na₂CO₃ (sat), and H₂O leads to an increase in the total pore volume at 14 and 28 days, but a slight decrease in the pore volume at 90 days (Table 8.3). The increase in total pore volume is attributed to the increase in the pore volume at the sub-mesopore region, 2-3.6nm at 14 and 28 days, but not at 90 days (Figures 8.5a to 8.5f). It appears that the reaction is enhanced at 14 and 28 days, but is reduced afterwards. Secondly, Geopolymer 0.79Na that is aged in H₂O and Na₂CO₃ (sat) does not show any significant change in the pore structure at 14, 28, and 90 days (Figures 8.5h and 8.5i). However, Geopolymer 0.79Na that is aged in 1M NaOH shows an increase in the total pore volume at 90 days (Table 8.3), predominantly at the pore sizes smaller than 10 nm (Figure 8.5g). The significant increase in the total pore volume after a prolonged ageing period is caused by two reasons: (1) the formation of zeolites, and (2) the formation of condensed geopolymer gel. The XRD analyses show the formation of new zeolites, hydroxysodalite and faujasite, which are not present initially in Geopolymer 0.79Na (Table 8.5, to be discussed later). The micrograph from ESEM also depicts the transformation from a porous to a more condensed gel structure at 90 days (Figure 8.12d, to be discussed later). This shows that high reactivity (indicated by formation of zeolites and condensed gel) is possible even after geopolymers set. This can occur because the concentration of precursors in pore solution has been modified significantly, e.g. by ageing geopolymers in alkali solution. There are two ageing conditions that favour high reactivity: (1) a not too high, but moderate alkali concentration (e.g. 1M MOH, M = Na or K) to promote dissolution, but without delaying polymerisation (or precipitation); and (2) aqueous solutions to facilitate the transport of precursors, so that dissolution and precipitation may occur continuously.
Figure 8.5 The pore volume distribution of Geopolymers 0.0Na (a-c), 0.2Na (d-f), 0.79Na (g-i), immersed in 1M NaOH, 2.5M Na$_2$CO$_3$, and H$_2$O for 14, 28, and 90 days. The dotted circle highlights a significant increase in the pore volume at pore widths < 10 nm.
8.4.2 The pore structure of K-based geopolymers

The pore structure of K-based geopolymers is slightly different from Na-based geopolymers. At low silicate ratios (SiO\textsubscript{2}/K\textsubscript{2}O = 0.0 and 0.2), there is essentially no mesoporous structure, shown by the low pore volume in the mesopore region (Figures 8.6a and 8.6b). This can be attributed to the low reactivity of K-based geopolymers. The absence of ‘sub-mesopores’ (2-3.6 nm) is also mainly due to the tendency of K\textsuperscript{+} not to direct crystallisation. It was observed in Chapter 6 and 7 that the formation of geopolymer gel, particularly in K-based geopolymerization is favourable when there is a high concentration of soluble silicate present. This can be seen from a significant increase in pore volume of K-based geopolymers as the silicate ratio is increased to 0.79 (Table 8.3). For a similar silicate ratio (SiO\textsubscript{2}/M\textsubscript{2}O = 0.79, where M = Na or K), K-based geopolymers also have a greater pore volume, with a narrower range of pore sizes than Na-based geopolymers.

Ageing Geopolymers 0.0K and 0.2K in 1 M KOH generally results in a slight increase of pore volume in the mesopore region, 3.6 – 50 nm (Figures 8.6a and 8.6b), indicating the formation of more geopolymer gel. However, ageing in solutions of high alkali concentration, e.g. 8M KOH leads to a significant reduction of pore volume in the mesopore region. Ageing in water for 14 days also results in the increase of pore volume of these geopolymers (Figures 8.6a, 8.6b, and Table 8.3). It is likely the aqueous pore solution containing high concentration of residual alkali (i.e. result from the lack of reactivity of the original geopolymers) facilitates in prolonging reaction.

The alterations in the pore structure of Geopolymer 0.79K (Figure 8.6c) due to ageing in alkali and carbonate solutions, are slightly different from the alterations observed in Geopolymer 0.79Na (Figure 8.4c). For example, ageing Geopolymer 0.79K in water and carbonate solution results in the shift of pore volume distribution to smaller and larger pore size respectively, but ageing in either solutions result in the increase of total pore volume at 14 days (Table 8.3). In 1M KOH solution, the pore volume distribution does not change significantly. Nonetheless, ageing Geopolymer 0.79K in 5M KOH results in the decrease of total pore volume (Figure 8.6c and Table 8.3).
Figure 8.6 The pore volume distribution of: (a) 0.0K, (b) 0.2K, and (c) 0.79K after 14 days of immersion. All geopolymers were pre-cured at 50 °C for 24 hours, except 75°C-KOH, which was pre-cured at 75 °C, and immersed in a 5M KOH solution. The dotted lines separate pore volume with mean pore widths above and below 10 nm.
The effect of ageing in 1M KOH, 2.5M K$_2$CO$_3$, and H$_2$O on the pore structure of Geopolymer 0.79K is further investigated and the pore volume distributions of aged geopolymers at 14, 28, and 90 days are shown in Figure 8.7. For all ageing solutions, there is an increase in the total pore volume, and a shift of pore volume distribution to a smaller pore size region (< 10 nm), which is observed at 14 and 28 days (Figure 8.7). However at 90 days, there is a decrease in the total pore volume as compared to the value observed at 28 days, but the shift of pore distribution to smaller pore size region remains to be observed. Firstly, in 1M KOH, the increase in volume of smaller pores (e.g. < 10 nm) indicates the possible growth of zeolites and a greater extent of gel being formed. Secondly, in contrast to Na$_2$CO$_3$ (sat) solution, there is a significant change of pore structure as Geopolymer 0.79K is aged in K$_2$CO$_3$ solution (Figure 8.7b), showing that the ‘buffering effect’ is not applicable because K$_2$CO$_3$ solution at 2.5M is not a saturated solution. Instead, there will be significant transport of K$^+$ into and out of pore solution, which can be seen from a higher concentration of Si$^{4+}$ and Al$^{3+}$ dissolving in K$_2$CO$_3$ than in saturated Na$_2$CO$_3$ solutions (Figures 8.1 and 8.2).

8.5 The growth of crystalline phases

It is seen that the pore structure of geopolymers is generally altered to a greater extent when geopolymers are aged (immersed) in alkali-containing solutions. For example, ageing in a moderate alkali concentration (e.g. 1M MOH, where M = Na or K) allows the increase of hydrolytic attack due to the supply of external alkali from ageing solutions. The dissolution of Si and Al is enhanced, but without inhibiting the precipitation of gel from occurring, thus resulting in a refined gel structure. It is believed that the increase in pore volume at pore sizes < 10 nm (Figures 8.4 and 8.6) is primarily due to an extended formation of product phases, i.e. zeolites and geopolymer gel. XRD will be used to prove the formation of new phases after prolonged ageing time.
Figure 8.7 The pore volume distribution of Geopolymer 0.79K, immersed in (a) 1M NaOH, (b) 2.5M Na$_2$CO$_3$, and (c) H$_2$O for 14, 28, 90 days. The dotted lines separate pore volume with mean pore widths above and below 10 nm.

Figures 8.8 to 8.11 show the XRD patterns of Geopolymers 0.0Na, 0.2Na, 0.79Na, and 0.79K before and after being aged in water, 1M MOH, 5M MOH, and 2.5M M$_2$CO$_3$ (where M = Na or K) for 14, 28, and 90 days. The different types of zeolites, crystalline phases, and their chemical formulae are summarised in Table 8.4. The extent of zeolites and other crystalline phases formed in different geopolymers are shown in Table 8.5.

H is originally formed in non-immersed Geopolymer 0.0Na (Figure 8.8). Upon ageing this geopolymer in alkali solutions (1M and 5M NaOH) after 28-90 days, other zeolites are also formed, namely F, and a sodium aluminosilicate phase, which gives crystalline patterns similar to a synthetic zeolite, ZK-5 (Kerr, 1963, 1966a). The formation of phases F and ZK-5, which possess high Si:Al ratios, 1.2:1 and 3:1 respectively (Table 8.4) suggest that the reactivity of geopolymers has been enhanced by including more Si into the new phases formed, as observed in Chapter 7. Upon ageing Geopolymer 0.0Na in either water or carbonate solution, no zeolite is formed (Figure 8.8). Again, this
confirms the ‘buffering effect’ of water and carbonate solutions, which essentially terminates further reaction from occurring. However, calcite (CaCO₃) and natrite (Na₂CO₃) form easily, particularly in carbonate solutions. It should be noted that the Calcite (Cal) detected at a prolonged ageing time (90 days) is the re-growth of dissolved calcium, which is originated from fly ash. It is possible that the precipitation of both Cal and Nat is induced by the high concentration of dissolved carbonates from the carbonate solution.

In Geopolymer 0.2Na, H and F are formed initially (Figure 8.9 and Table 8.5). Upon ageing in alkali solutions (1M and 5M NaOH), F remains, H dissolves slightly. This shows the stability of F as a latter product (i.e. with a higher Si:Al ratio). Essentially, no new aluminosilicate phase formed as the ageing period is prolonged to 90 days. The re-growth of Cal and Nat is, however, observed. Similar to ageing in alkali solutions, ageing in water and carbonate also shows little reactivity, but with a significant amount of Cal and Nat precipitated.

In Geopolymer 0.79Na, the formation of H is observed after ageing in 1M and 5M NaOH solutions, while F is only observed in 1M NaOH after 90 days (Figure 8.10 and Table 8.5). In water or carbonate solutions, H and F are not formed, but the re-growth of Cal and Nat occurs (Table 8.5). Furthermore, there is an increase in the intensity of amorphous aluminosilicate shoulders (at 2θ = 25-35°) as Geopolymer 0.79Na is immersed in 1M and 5M NaOH solutions (highlighted in Figure 8.10), and a slight increase in the intensity if this geopolymer is immersed in water or carbonate solutions. The amorphous shoulders are also becoming ‘sharper’ at 90 days. Currently, there is no definitive explanation of such observed behaviour. It is speculated that the cycle of dissolution and re-precipitation of geopolymer gel has resulted in a condensed gel that is structurally close to aluminosilicate crystals. Provis et al. (2005c) proposed that geopolymer materials are actually collective zeolitic crystals that appear to be amorphous under conventional XRD measurement. Therefore, prolonged ageing, higher alkali solution, and higher water content from ageing solutions may have induced the formation of larger crystals that can be clearly observed in this study.
The growth of zeolites in aged K-based geopolymers is not as extensive as in Na-based geopolymers (Figure 8.11 and Table 8.5). Ageing K-based geopolymers in alkali solutions results in the dissolution of metastable K (only listed in Table 8.5, not shown in Figure 8.11 because the peak intensities are too weak), which has a low Si:Al ratio (1:1). The other zeolites, such as F-linde (L) and K-phillipsite (P) are also formed. The latter products, F-linde (L) possess a higher Si:Al ratio, 1.04:1, while K-phillipsite (P) possess a ratio of 1.5:1. Their stable structures are evident at high alkali concentration (5M KOH) and over longer ageing periods (90 days, Figure 8.11). A new crystalline phase, with crystalline patterns that resembles latiumite (Lat) is also formed at high alkali concentrations (5M KOH and 2.5M K₂CO₃). Lat contains Ca, K, SO₄, and CO₃ in its crystalline structure (Table 8.4). Based on the current results, there is no definitive explanation for the formation of Lat. It is speculated that the combination of various factors, namely the absence of Na⁺, the tendency of K⁺ not to direct crystallisation, the availability of dissolved carbonate species, and the high concentration of dissolved Ca²⁺ have probably induced the crystallisation of Lat in K-based geopolymers. Nonetheless, there is essentially no new crystalline phase formed as K-based geopolymer is aged in water (Table 8.5). In contrast to Na-based geopolymer, the re-growth of Cal from dissolved calcium is not apparent at high alkali concentration, but the formation of K₂CO₃ precipitate is observed (Table 8.5). Ageing in 2.5M K₂CO₃ solution results in the formation of L and Lat because the carbonate solution is not saturated at 2.5M, thus the ‘buffering effect’ is not observed, but results in the same effect as immersing geopolymers in solutions of high alkali concentration, i.e. enhances reaction in the gel.
Figure 8.8 The XRD patterns of Geopolymer 0.0Na, aged in H₂O, 1M NaOH, 2.5M Na₂CO₃, and 5M NaOH solutions for 14, 28, and 90 days. The following abbreviations are used: F-faujasite, Cal-calcite, Nat-natrite, H-hydroxysodalite, ZK-5 – a synthetic zeolite. Crystalline phases which are obvious in the XRD are marked, for other phases formed refer to Table 8.5.
Figure 8.9 The XRD patterns of Geopolymer 0.2Na, aged in H₂O, 1M NaOH, 2.5M Na₂CO₃, and 5M NaOH solutions for 14, 28, and 90 days. The following abbreviations are used: F-faujasite, Cal-calcite, Nat-natrite, H-hydroxysodalite. Crystalline phases which are obvious in the XRD are marked, for other phases formed refer to Table 8.5.
Figure 8.10 The XRD patterns of Geopolymer 0.79Na, aged in H₂O, 1M NaOH, 2.5M Na₂CO₃, and 5M NaOH solutions for 14, 28, and 90 days. The following abbreviations are used: F-faujasite, Cal-calcite, Nat-natrite, H-hydroxysodalite. Crystalline phases which are obvious in the XRD are marked, for other phases formed refer to Table 8.5. The dotted circle highlights the increase in peak intensity of amorphous aluminosilicate in geopolymers.
Figure 8.11 The XRD patterns of Geopolymer 0.79K, aged in H$_2$O, 1M NaOH, 2.5M Na$_2$CO$_3$, and 5M NaOH solutions for 14, 28, and 90 days. The following abbreviations are used: Cal-calcite, L–F-linde zeolite, P-K-phillipsite, Lat-latiumite. Crystalline phases which are obvious in the XRD are marked, for other phases formed refer to Table 8.5. The dotted circle highlights the increase in peak intensity of amorphous aluminosilicate in geopolymers.
Table 8.4 The types of crystalline phases formed in both non-immersed and immersed geopolymers.

<table>
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<th>Crystalline phases (some are zeolites)</th>
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<th>JCPDS</th>
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<td>Cancrinite (C)</td>
<td>Na6Ca1.5Al6Si6O24(CO3)1.6</td>
<td>1:1</td>
<td>34-0176</td>
</tr>
<tr>
<td>Analcime-O (A)</td>
<td>Na(Si2Al)O6.H2O</td>
<td>2:1</td>
<td>19-1180</td>
</tr>
<tr>
<td>Kalsilite (K)</td>
<td>KAlSiO4</td>
<td>1:1</td>
<td>11-0579</td>
</tr>
<tr>
<td>F-linde zeolite (L)</td>
<td>K2Al2Si2.08O8.16.3H2O</td>
<td>1.04:1</td>
<td>25-0619</td>
</tr>
<tr>
<td>K-phillipsite (P)</td>
<td>K2Al2Si3O10.3H2O</td>
<td>1.5:1</td>
<td>30-0902</td>
</tr>
<tr>
<td>Synthetic aluminosilicate zeolite (ZK-5)</td>
<td>NaAlSi3O8.xH2O</td>
<td>3:1</td>
<td>18-1198</td>
</tr>
<tr>
<td>Latiumite (Lat)</td>
<td>(Ca,K)4(Al,Si)5O11(SO4CO3)</td>
<td>1:1</td>
<td>25-1202</td>
</tr>
<tr>
<td>Natrite (Nat)</td>
<td>Na2CO3</td>
<td>-</td>
<td>37-0451</td>
</tr>
<tr>
<td>Calcite (Cal)</td>
<td>CaCO3</td>
<td>-</td>
<td>47-1743</td>
</tr>
<tr>
<td>Potassium carbonate</td>
<td>K2CO3</td>
<td>-</td>
<td>27-1348</td>
</tr>
</tbody>
</table>
Table 8.5 The crystalline phases formed in Na- and K-based geopolymers after being aged in alkali and carbonate solutions. Refer to Table 8.4 for the abbreviations used for various crystalline phases. * (s) and (w) refer to strong and weak peak intensities respectively; if not indicated, it refers to medium peak intensity.

<table>
<thead>
<tr>
<th>Geopolymer</th>
<th>Non-immersed</th>
<th>1M MOH (M=Na or K)</th>
<th>H₂O</th>
<th>5M MOH (M=Na or K)</th>
<th>2.5M M₂CO₃ (M=Na or K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0Na H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>A (w) F (w)</td>
<td>A (w) F (s)</td>
<td>A (w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZK-5 Cal (s)</td>
<td>ZK-5 Cal (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cal (w) Nat (w)</td>
<td>Cal (w) Nat (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nat (w) Nat (s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2Na H</td>
<td>H</td>
<td>H (w) F</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>F (s) Cal</td>
<td>F</td>
<td>F</td>
<td>Cal (s) Nat (s)</td>
</tr>
<tr>
<td></td>
<td>C (w) Cal (s)</td>
<td></td>
<td>Nat (s) Cal (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.79Na No</td>
<td>H (w) F (s)</td>
<td>No crystal Nat (s)</td>
<td>H</td>
<td>Cal (s) Nat (s)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cal (s) Nat (s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0K* K</td>
<td>K (w) No crystal</td>
<td>No crystal</td>
<td>L (w)</td>
<td>No crystal Lat</td>
<td>K₂CO₃ (s) K₂CO₃ (s)</td>
</tr>
<tr>
<td>0.2K* L</td>
<td>K₂CO₃ (s) No crystal</td>
<td>L</td>
<td>P(w) P (s) Lat</td>
<td>K₂CO₃ (s) K₂CO₃ (s)</td>
<td></td>
</tr>
<tr>
<td>P (w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.79K No</td>
<td>P (w) No crystal</td>
<td>No crystal</td>
<td>L (w)</td>
<td>L (w) Lat</td>
<td>K₂CO₃ (s) K₂CO₃ (s)</td>
</tr>
<tr>
<td>crystal</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
8.6 The microstructure of aged geopolymers

Figure 8.12 shows a series of micrographs depicting the microstructures of Na-based geopolymers, which are aged in 1M NaOH solution. Figure 8.12a is the microstructure of Geopolymer 0.0Na at 14 days. The inset in Figure 8.12a shows Geopolymer 0.0Na at a higher magnification. It can be seen that the aluminosilicate gel network in fly ash-based geopolymers is composed of non-spherical aluminosilicate particles, as observed in Chapter 6. Despite significant nucleation takes place due to ageing, the extent of gel growth is minimal in Geopolymer 0.0Na. Thus, the gel matrix is porous, and not as condensed as in high-silicate geopolymers, i.e. Geopolymer 0.2Na and 0.79Na (Figures 8.12b and 8.12c). Figure 8.12d shows the microstructure of Geopolymer 0.79Na, which is immersed in 1M NaOH for 90 days. The prolonged ageing time has changed the microstructure of gel significantly, such that the overall gel matrix becomes more homogeneous and condensed (region ‘y’ in Figure 8.12d). This is in accordance with the results obtained from the N$_2$ adsorption, whereby there is a significant increase in the pore volume of smaller pore size region (e.g. < 10 nm) at 90 days (Figure 8.5g). The continuous cycle of dissolution and re-precipitation is believed to fill the original larger pores, and leads to the formation of gel with finer pores. The residual Na$_2$CO$_3$ precipitates are also present (region ‘x’ in Figure 8.12d), but are formed outside the geopolymer gel matrix.

Figure 8.13 shows the microstructure of Geopolymer 0.79Na and the crystal-like phases formed after ageing in 5M NaOH for 28 days. The crystal-like phases are distributed un-evenly, and are seen to be localised on the surface of fly ash particles. Figure 8.13a shows an aged (immersed) gel microstructure, with its Si/Al ratio is determined to be 1.9. This ratio is slightly higher than the composition of a non-immersed geopolymer gel, i.e. ≈ 1.8 (Chapter 6), indicating that reaction has been enhanced during immersion. Figure 8.13b depicts cube-like crystalline phases on the surface of partly-reacted fly ash particles. These phases have average Si/Al ratio < 1, low Na, Fe and Ca contents, which seem to indicate the composition of a zeolitic phase. Other crystal-like phases include iron and calcium precipitates, which are shown in Figures 8.13c and 8.13d respectively.
Figure 8.12 (a) Geopolymer 0.0Na (the inset shows a magnified region in the gel), (b) Geopolymer 0.2Na, (c) Geopolymer 0.79Na immersed in 1M NaOH for 14 days, while (d) Geopolymer 0.79Na immersed in 1M NaOH for 90 days. The region marked “x” are sodium-based precipitates, and “y” indicates highly condensed geopolymer gel.
Figure 8.13 The morphologies of crystalline structures in Geopolymer 0.79Na, immersed in 5M NaOH for 28 days. The composition of “x” in different figures are as follows: (a) Na$_{0.6}$Si$_{1.9}$AlO$_{5.6}$, (b) Na$_{0.2}$Si$_{0.8}$AlO$_{2.7}$, (c) Fe$_{5.6}$ Na$_{0.6}$Si$_{1.9}$AlO$_{4.7}$, and (d) Ca$_{6.4}$K$_{1.3}$Si$_{1.76}$AlO$_{12}$. 
8.7 Conclusions

It is known that the reactivity of geopolymer gel is greatly reduced when the reaction has become diffusion-limited, i.e. when the material sets. Any further reactions are dependent on the concentration of dissolved species in the pore solution. From the study conducted in this chapter, it has been shown that ageing in water, alkali and carbonate solutions alter the concentration of dissolved precursors, the porosity, and the gel structure of geopolymers. The formation of new product phases, including crystalline phases (zeolites) and geopolymer gel are observed during ageing in alkali-containing solutions. This shows that reaction (e.g. crystallisation and polymerisation) can be enhanced, even in the later stages (i.e. after geopolymers set).

The rate and extent of reactivity of geopolymers during ageing vary depending on the silicate concentration, the concentration and type of ageing solutions, and the ageing time. The amounts of dissolved Si$^{4+}$ and Al$^{3+}$ precursors during ageing are generally greater in high-silicate geopolymers (SiO$_2$/M$_2$O = 0.79, where M = Na or K) than in low-silicate geopolymers (SiO$_2$/M$_2$O = 0.0 and 0.2) because there are more readily available precursors (Si$^{4+}$ and Al$^{3+}$) in the pore solution for dissolution to proceed. In general, the extent of dissolution of Si$^{4+}$ and Al$^{3+}$ precursors increases as the OH$^-$ concentration of ageing solutions is increased. The increase in dissolution at high alkali concentrations (e.g. 5M and 8M NaOH/KOH) results in the formation porous gel structure, which is detrimental to geopolymers. However, at a lower alkali concentration (1M NaOH/KOH), the balance between dissolution and re-precipitation is obtained. Thus, there is a significant increase in gel growth, shown by the formation of a less porous and more condensed gel structure. Two conditions are believed to favour higher reactivity: (1) a moderate alkali concentration to promote dissolution, without delaying precipitation; and (2) aqueous solutions to facilitate the transport of precursors, so that dissolution and precipitation can be enhanced. In contrast, ageing geopolymers in water and carbonate solutions results in little reactivity. This is caused by a ‘buffering effect’, which leads to a limited transport of alkali cations into and out of pore solutions. As a result, there is less dissolution (hydrolysis). This means that the availability of alkali cations and aqueous solutions is not significant. This finding is very important for curing applications because the properties of geopolymers are known
to be age-dependent. By ageing geopolymers in solutions, which provide a ‘buffering effect’, the long-term properties of geopolymers may be preserved.
CHAPTER 9
CONCEPTUAL MODEL OF GEOPOLYMERISATION

The work undertaken in the thesis has provided an improved understanding of the physico-chemical properties of geopolymers, and also the mechanism and kinetics of geopolymerisation. In essence, there are at least three novel areas covered during this investigation. Firstly, the development of pore structure in geopolymers has been thoroughly investigated and understood. Secondly, the effects of altering silicate concentration and the type of alkali metal cations on the competition between dissolution, polymerisation, and crystallisation of aluminosilicate gels during geopolymerisation are established. Finally, the systematic and novel investigations on the ageing of geopolymers in alkali and carbonate solutions have been conducted, which provide insight into the reaction mechanisms of late geopolymerisation.

In this chapter, a conceptual model of geopolymerisation is described to consolidate the novel results and key learnings presented in the previous chapters. The effect of various parameters (e.g. aluminosilicate solids, activating solutions, curing conditions, and ageing conditions) on the reaction steps in geopolymerisation (dissolution, polymerisation, and crystallisation) is presented. Firstly, it is found that using different aluminosilicate solids primarily affects the dissolution of Si and Al, and probably other impurities (e.g. Ca, Fe) into solution. Secondly, the concentration of silicate in solution and the types of alkali metal cation affect the competitive rates and extent of reaction in each reaction step (dissolution, polymerisation, and crystallisation). In general, increasing silicate concentration results in an increase in the extent of reaction (both dissolution and polymerisation). The optimum silicate concentration is found to be 0.79 < SiO₂/M₂O < 2.0, where M = Na or K. At low Na-silicate concentrations (SiO₂/Na₂O = 0.0 - 0.2), the polymerisation of aluminosilicate gel is not preferred. Instead, the dissolved precursors tend to form zeolites or framework aluminosilicates. The preferential crystallisation over polymerisation of aluminosilicates is believed to be
influenced by early dissolution of Al and the preference for Na\(^+\) to crystallise. Thirdly, the effect of curing parameters (e.g. temperature, time, and humidity) is primarily kinetic. It is found that while elevated temperature (75 °C) is required to achieve a higher degree of activation, the rate of reaction is also accelerated at higher temperatures. As a result, the geopolymer materials set rapidly, preventing further reaction from occurring. Therefore, the choice of optimal curing temperatures and curing time should be a balance between enhancing dissolution and preventing rapid setting of the materials. Finally, ageing geopolymers by immersing in a solution of moderate alkali concentration (1M MOH, M = Na or K) enhances reaction further, better than if they are not aged by immersion. The findings from the thesis will be used as a basis for further research of geopolymer materials, particularly of fly ash-based geopolymers.

9.1 Introduction

The effect of reactant parameters (aluminosilicate solids and activating solutions) and reaction conditions (curing and ageing) on the properties, reaction mechanisms, and kinetics of geopolymerisation are illustrated in a conceptual model of geopolymerisation in Figure 9.1. The reaction steps in geopolymerisation are complex, because they usually occur simultaneously. However, for the purpose of discussion, the reaction steps will be conceptually simplified and separated into three main steps: dissolution, polymerisation, and crystallisation of aluminosilicate. Dissolution is initiated by the hydrolytic attack of alkali metal cations on the aluminosilicate structure of the solids. The hydrolysis is then followed by the dissolution of Al and Si precursors into solution, in which the Al and Si precursors reorganise to form chains, which finally grow to become nuclei (Iler, 1979). Immediately after the initiation of the dissolution process, polycondensation (polymerisation) occurs simultaneously with dissolution, leading to the formation of geopolymer gel. Under special conditions, which will be discussed later, crystallisation probably occurs at the same time as gel formation. In this conceptual model, the kinetics of reaction are important because they control the reaction pathway.
Figure 9.1 Conceptual model of geopolymerisation. The bold arrow lines indicate the cause and effect relationship of various components in geopolymerisation. The dotted arrow lines highlight the significant effect of major reaction parameters to the respective reaction steps.
Depending on the values of influencing parameters, the sequence and extent of reaction steps are also altered. Consequently, the product phases formed are also controlled by the values of influencing parameters. The products of geopolymerisation can be divided into three types: precipitates, geopolymer gels (aluminosilicate gels), and zeolites (or crystalline aluminosilicates). The precipitates are alkali-based phases, or other ionic impurities originating from raw materials, e.g. iron, calcium, etc. These precipitates are formed mainly in less-reacted geopolymers due to the lack of dissolved silicon and aluminium available in the solution for nucleation and gel growth. Sometimes, localised alkali regions are observed in a predominantly geopolymer gel matrix (Figure 5.8 in Chapter 5) due to the heterogeneous reaction or instantaneous entrapment of residual alkali in the pore solution. The other two product phases, geopolymer gels and zeolites, are formed in more reacted geopolymers because of the abundance of Si and Al nutrients in the solution for nucleation, thus favouring polymerisation and crystallisation processes.

The formation of product phases alters the physico-chemical properties of geopolymers, e.g. porosity or permeability, strength, microstructure and gel composition. In the thesis, the development of the pore structure of geopolymers, particularly in fly ash-based geopolymers has been thoroughly investigated for the first time. It is found that well-reacted fly ash-based geopolymers can be classified as mesoporous aluminosilicate gels (2-50 nm). The geopolymer gel is constituted from an array of non-spherical aluminosilicate particles. An increase in the formation of these aluminosilicate particles leads to an increase in mesopore volume and area. The formation of these particles also increases the mechanical strength of geopolymers. Furthermore, greater gel formation results in a higher Si/Al ratio and a condensed gel structure. In the next section, the effect of each influencing parameter on the reaction steps in geopolymerisation is discussed in detail.

9.2 Aluminosilicate composition and mineralogy
The use of different raw materials in the synthesis of geopolymers provides a glimpse of the difficulties in understanding the complex chemistry of geopolymerisation. In the conceptual model illustrated in Figure 9.1, different aluminosilicate solids primarily
affect the dissolution step; which in turn affect the other reaction steps in geopolymerisation.

9.2.1 Aluminosilicate composition and mineralogy

Geopolymerisation is initiated with the dissolution of Si and Al into solution phase. Therefore, the rate and extent of Si and Al dissolution determine the mechanism and kinetics of geopolymer gel formation. It is known that the composition of SiO₂ and Al₂O₃ in the raw materials can be ranked in increasing order as follows: GBFS<FA<MK (Table 3.1 in Chapter 3). MK is shown to give the highest reactivity due the greater amount of amorphous Si and Al available in the material and the ability to release Si and Al for reaction immediately. Given the right concentration of reactants (e.g. high alkalinity, M/Al = 1), amorphous Si and Al can theoretically be fully dissolved into alkali-silicate solution. However, some Si and Al are not readily dissolved, particularly those contained in crystalline structures. For example, a high concentration of Al in fly ash is contained in mullite, which does not dissolve readily upon alkali activation. This contributes to the lower reactivity of fly ash-based geopolymers. The reactivity of crystalline and amorphous structure in raw materials, although significant, is beyond the scope of the thesis, and should be considered as a subject for further investigation.

9.2.2 The rate of dissolution of Si and Al

The rate of dissolution of aluminosilicate precursors correlates strongly with the mineralogy of the raw material. From the work conducted in the thesis (Chapter 6 and 7), it is hypothesised that Al can dissolve earlier than Si during fly ash-based geopolymerisation. This can be seen from: (a) less reactive geopolymers typically have low measured Si/Al ratios, while highly reactive geopolymers have higher Si/Al ratios (close to 2.0), which indicate the progressive inclusion of Si into the formation of the gel; (b) the progressive formation of zeolites starting from hydroxysodalite, with a low Si:Al ratio (0.84:1), to faujasite (1.2:1) or analcime-o (2:1).
9.2.3  **The physical properties of raw materials**

The particle shape and size of raw materials also have an impact on the requirements for activation and the alteration in the reaction steps of geopolymerisation. For example, MK requires a higher water to binder ratio (>1 by weight) for activation because of its higher surface area. FA is usually activated at lower water to binder ratio (> 0.3 by weight) because of a ‘lubricating effect’, attributed to the spherical particle shape of fly ash. Although not investigated, the various shapes of spherical fly ash particles (e.g. solid sphere, plerosphere, clathrosphere, and cenosphere) may also affect the geopolymerisation to a certain extent (Hemmings and Berry, 1988).

9.2.4  **Impurities**

The effect of impurities (e.g. calcium, iron, and magnesium) in raw materials was not investigated in the thesis. The effect of these impurities is almost negligible in MK. However, the concentration of Ca and Mg is high in GBFS. It is seen that the activation of GBFS can give a high early rate of heat release (Figure 4.1a in Chapter 4). This is believed to be due to the high Ca content, which accelerates the polymerisation step in geopolymerisation (Yip, 2004). The incorporation of Ca into the gel seems to suggest that CSH is probably formed in GBFS-based geopolymers. In FA, the dissolution of Ca and Fe also occurs, but their effects on geopolymerisation are rather unknown, and therefore, it should be subjected to further investigation.

9.3  **Activating solutions**

The experiments reported in the thesis suggest that alterations in mechanism, kinetics, and properties of geopolymers are mainly caused by the variations in activating solution composition. The factors considered in Figure 9.1 are discussed in the following sections.

9.3.1  **Silicate concentration**

The silicate concentration in the activating solution is expressed as the SiO$_2$/M$_2$O ratio (M= Na and K). In the thesis, the SiO$_2$/M$_2$O ratio was set at 0.0, 0.2, 0.5, 0.79, 1.4, and 2.0. By keeping a constant alkali concentration (constant H$_2$O/M$_2$O ratio = 14.85), the effect of changing soluble silicate concentration on geopolymerisation was investigated.
Firstly, the silicate concentration controls the dissolution and polymerisation of Si and Al nutrients in the solution. It is found that the increase of silicate concentration (SiO$_2$/M$_2$O) from 0.0 to 0.79 leads to an increase in the mesopore volume, area, and measured Si/Al ratio in the gel, which together suggest a higher degree of reaction has taken place. It is believed that at higher silicate concentration, the concentration of larger silicate oligomers is higher, thus favouring the condensation of aluminosilicate precursors (Roozeboom et al., 1983). The crystallisation of zeolites is favourable, particularly at very low silicate concentrations (SiO$_2$/M$_2$O = 0.0 and 0.2), which will be discussed later.

It is also found that increasing silicate concentration to a SiO$_2$/M$_2$O ratio of 2.0 leads to a reduction in reactivity, shown by the decrease in the amount of heat released, mesopore volume, and area of geopolymer gels. The setting time of geopolymers is also longer than at lower silicate concentration (SiO$_2$/M$_2$O = 0.79), suggesting an inhibition in the reaction. It has been speculated that solutions of high silicate concentration contain larger silicate species (e.g., ring or cage structures), which do not participate directly in the polymerisation of aluminosilicate, rather serve as a reservoir for monomeric silicates to grow (Swaddle, 2001). Therefore, an optimum silicate concentration for geopolymerisation is found in the range of 0.79 < SiO$_2$/M$_2$O < 2.0. The optimum silicate concentration range will vary, nonetheless, depending on the alkali concentration and the type of alkali metal cation used.

Secondly, the silicate concentration controls the competition between polymerisation and crystallisation of aluminosilicate. It is found that at low silicate ratios (SiO$_2$/M$_2$O = 0.0 and 0.2), the polymerisation of aluminosilicate gel is not favoured. Instead, the dissolved precursors tend to form zeolites or framework aluminosilicates. In contrast, at higher silicate concentrations (SiO$_2$/M$_2$O = 0.5, 0.79, and 2.0), the formation of zeolites is not observed, as the conditions will favour the polymerisation of aluminosilicate. The crystallisation of aluminosilicate at low silicate concentrations (SiO$_2$/M$_2$O = 0.0-0.2) is shown by the appearance of a secondary heat curve, which is identified as the heat associated with the formation of zeolites. In the absence of silicate, nucleation is favoured due to the incorporation of Al into monomeric silica, which grow easily into
crystals (McCormick and Bell, 1989). At higher silicate concentrations, the larger silica species present are likely to hinder crystallisation. The preferential crystallisation over polymerisation of aluminosilicate at low silicate concentration is seen to be influenced by the available Si and Al precursors in the solution during the dissolution step. The early dissolution of aluminium results in the formation of zeolites with high aluminium composition, such as hydroxysodalite (Si:Al = 0.84:1), while faujasite (Si:Al = 1.2:1) and analcime-o (Si:Al = 2:1) are formed in the later stages. Nonetheless, the extent of Al dissolution is limited because a large proportion of aluminium is included in mullite, which is essentially non-reactive toward alkali activation. It is hypothesised that the growth of zeolites during fly ash-based geopolymerisation is therefore inhibited when the availability of Al-nutrient is exhausted. The findings provide insight into the role of aluminium dissolution in fly ash-based geopolymerisation.

9.3.2 The types of alkali metal cations
In the thesis, there were only two types of alkali metal cations investigated, i.e. Na\textsuperscript{+} and K\textsuperscript{+}. The effects of using different types of cations in the solution are complex and are interrelated with various variables, such as silicate and alkali concentrations. Nonetheless, their effects are evident in the dissolution, polymerisation, and crystallisation steps. Firstly, it is observed that Na-solution appears to be more ‘reactive’ at low silicate concentrations (SiO\textsubscript{2}/M\textsubscript{2}O = 0.0 and 0.2). The ‘reactivity’ is closely related to the dissolution of aluminosilicate, which leads to crystallisation rather than polymerisation. This is believed to be due to the preference of Na\textsuperscript{+} to associate with monomeric silicate species, which presumably exists in a greater amount in solutions with low silica content (Harris and Knight, 1983a; b). The preference for Na\textsuperscript{+} to direct the crystallisation of aluminosilicate during geopolymerisation was also suggested by Provis et al. (2005a). In contrast, K\textsuperscript{+} is observed to be more reactive at high silicate concentrations (SiO\textsubscript{2}/M\textsubscript{2}O = 0.0, 0.79, and 2.0), which is evident from the high heat of reaction released. Again, this is believed to be due to the preference of K\textsuperscript{+} to associate with available oligomeric or larger silicate species, thus extending the polymerisation of aluminosilicate gel. Nonetheless, even at low silicate concentrations (SiO\textsubscript{2}/M\textsubscript{2}O = 0.0, 0.79 and 2.0), the formation of crystalline phases, such as zeolites is not favoured.
9.3.3 The concentration of alkali solution (H₂O/M₂O ratio)

In the thesis, the concentration of alkali is expressed as H₂O/M₂O ratio, or R (e.g. R = 10, 12.5, 14.85). This means solutions with higher alkali concentration have lower H₂O/M₂O ratios. The effect of alkalinity is investigated by varying R, while keeping the SiO₂/M₂O ratio constant at 0.79, and water to binder ratio constant at 0.3 (w/w). This results in theoretical Al/M ratios equal to 1.0, 1.25, and 1.5 respectively. It is seen that there is an optimum alkali concentration, where a balance exists between increasing the extent of dissolution (hydrolysis) without significantly altering the rate of reaction. The optimum alkali concentration from this study is shown to be at R = 1.25, indicated by the large pore volume, area, and Si/Al ratio in the gel. Interestingly, increasing alkali concentration to R = 10.0 (R = H₂O/M₂O) does not seem to show high reactivity (or formation of more geopolymer gel) in the beginning, but once the rate of reaction is abruptly accelerated, e.g. by increasing temperature, the dramatic increase in the extent of reaction can be observed, evident from the formation of small nuclei (i.e. a significant increase of pore volume in the ‘sub-mesopore’ region, 2-3.6nm). It is believed that high alkali concentration increases the extent of dissolution (hydrolysis), but often at the expense of prolonging reaction time. This can be seen from the delay of reaction observed in geopolymers synthesised at higher alkali concentrations (Granizo and Blanco, 1998). Therefore, activation at moderate alkali concentration (e.g. R = 12.5) may balance the competing rates between dissolution and polymerisation of aluminosilicate.

9.3.4 Water content (water to binder ratio)

Water is believed to be the medium for dissolution and polymerisation of Al and Si precursors to take place appropriately. In the thesis, the effect of water to binder ratio was not thoroughly investigated. It is reasonable to suggest that increasing water content during geopolymerisation will prevent the system from reaching supersaturation, thus the dissolution of precursors is likely to be prolonged, resulting in slow gel formation. Nonetheless, the silicate concentration, alkali concentration, and the type of alkali cation used are other, more dominant factors in altering the rate and extent of reactivity, not the water content.
9.4 Curing conditions

Curing conditions are defined as the external environmental conditions applied to enhance geopolymerisation. The factors in curing are explored in the following sections.

9.4.1 Temperature

The effect of curing temperature on the kinetics of geopolymerisation was thoroughly investigated in the thesis. It is found that an increase in temperature (30 to 75 ⁰C) leads to an increase in the rate and extent of reaction (dissolution and polymerisation). The increase in the reactivity is shown by an increase in the amount of heat released during reaction, an increase in the mesopore volume and area, an increase in the compressive strength, and a decrease in the permeability of geopolymers. From the FTIR spectra, there is also a consistent shift of peak positions of the Si-O absorption band (at 1000-1250 cm⁻¹) to lower wavenumbers (1005-1025 cm⁻¹) as the curing temperature is increased. The shift of peaks indicates a greater amount of non-bridging oxygen due to the hydrolysis of aluminosilicate surface, i.e. the Si atoms in the glassy Si-O-Si (or Al-O-Si) structure are replaced by M atoms (M = Na or K). It is also found that while elevated temperatures are required to achieve a higher degree of activation, the rate of reaction is also accelerated at higher temperatures. As a result, the geopolymer materials set rapidly, preventing further reaction from occurring. Therefore, the choice of optimal curing temperature should be a balance between enhancing dissolution of precursors and preventing rapid setting of the materials.

9.4.2 The curing time and temperature scheme

In the thesis, two types of experiments were conducted: (1) prolonged curing at a medium temperature (50 ⁰C) for 24h to 168 h; and (2) step-wise curing temperature from low to high temperatures (30 ⁰C to 75 ⁰C and 50 ⁰C to 75 ⁰C) and continuous curing at a high temperature (75 ⁰C for 48 h).

It is found that prolonged curing time (24h – 168h) at a medium temperature (50 ⁰C ) increases the extent of reaction, indicated by an increase in the pore volume of ‘sub-mesopores’ (2-3.6nm). Although there is a significant increase in the pore volume, the measured Si/Al ratio is essentially the same at 50 ⁰C. It is suggested that there is a point
in the course of geopolymerisation when the effect of temperature over a prolonged curing time becomes insignificant. Prior to setting, significant dissolution usually occurs because the rate and extent of reaction have been increased by the application of high temperature. Near supersaturation, however, dissolution is replaced predominantly by the polymerisation step (or gel growth). In this instance, the concentration of alkali cations in the pore solution is also reduced. The reaction kinetics are therefore decreased. Further reactions are likely to be controlled by the diffusion of remaining ion precursors to reach equilibrium with partly-reacted fly ash, whereby dissolution and condensation may still take place, but at a lower extent and rate.

Continuous curing at a high temperature (75 °C for 48h) accelerates both the rate of nucleation and gelation to the extent that the integrity of gel structure is deteriorated. However, step-wise curing (30 °C and 75 °C or 50 °C and 75°C) enhances the reaction by allowing more nutrients to be available for gel growth without causing the overall sol-gel system to gel rapidly at 30 °C or 50 °C. The available nutrients are likely to be in a ‘dormant’ state until further reactions occur, which can be induced by external conditions, such as the application of high temperature. It also appears that the curing at 50 °C and 75°C is more optimal than at 30 °C and 75 °C. Even at an initial temperature of 50 °C, the extent of dissolution can be enhanced without resulting in a significant increase in the rate of gelation. Once again, it is shown that an optimum reaction temperature and time can be obtained by balancing the competing rates of dissolution and polymerisation (or gelation).

9.4.3 Humidity
In the thesis, the effect of humidity (RH = 30 to 75%) was investigated along with the effect of curing temperature. In contrast to increasing curing temperature, there is essentially little change in the physical properties of geopolymers with the change in relative humidity. It is found that curing at high RH seems to prevent the carbonation process, although there is no direct effect on the strength of the materials. The high RH keeps the pores being water-logged preventing the rapid spread of gas. The role of humidity can also be correlated to the function of water in geopolymerisation. It is known that water functions as a medium to initiate and facilitate reactions to take place
appropriately in geopolymerisation, during which external humid environment may not be significant. However, when the materials set, and water is expelled as a direct result of polycondensation step, the effect of humidity would be more significant because the reaction would be driven by the need for the gel to become more highly hydrated. Thus, maintaining a high curing temperature over a longer curing time may not be as effective as applying high temperature for a short curing time, and then followed by high humidity.

9.5 Ageing
The ageing of geopolymers is defined as the application of external conditions to enhance geopolymerisation after the synthesis of geopolymers is completed. It has been shown that curing conditions affect the reaction mechanism and kinetics of early geopolymerisation by controlling the competing rates and extents of dissolution and polymerisation. On the other hand, the late geopolymerisation (ageing) is likely to be controlled by the diffusion of residual precursors in the pore solution. The extent and rate of further reactions are less and slow because there is a lack of viable nutrients to enhance the geopolymerisation of aluminosilicate species. In the thesis, two ageing conditions were applied: ageing geopolymers at ambient condition (sealed, 25 ± 2 °C, 55% RH), and immersing geopolymers in alkali and carbonate solutions.

9.5.1 Non-immersed
Ageing geopolymers under ambient conditions for extended periods (up to 28 days) leads to reaction being enhanced. This can be seen from the shift of pore volume distribution to the smaller pore size region (e.g. < 10 nm). This shows that a higher extent of aluminosilicate condensation results in the formation of more aluminosilicate gels and in the filling of pre-existing large pores. In addition, as polycondensation of aluminosilicates expels water from the gel matrix, the transport of water often carries residual alkali to the the surface of specimen, which leads to the formation alkali-based precipitates. This is caused by the reaction of alkali metal cations with CO₂ in the atmospheric air.
9.5.2 Immersed in alkali and carbonate solutions

It is found that geopolymerisation is also enhanced when geopolymers are aged in alkali solution of moderate concentration (e.g. 1M MOH, M = Na or K), shown by an increase in the pore volume and a shift of pore distribution to smaller pore size region (< 10 nm). The extent of pore volume increase is significantly higher than if geopolymers are not immersed. However, prolonged ageing at high alkali concentrations (5M and 8M MOH) leads to a large extent of dissolution of Al and Si, which is detrimental to the original gel structure. The formation of more product phases, including new geopolymer gel and zeolites is also observed during ageing in alkali-containing solutions. This shows that extended polymerisation and crystallisation of geopolymer gel in the later stages of reaction (after geopolymers set) are highly probable, especially when the precursors in pore solution are disrupted.

Fly ash-based geopolymers that are aged in saturated carbonate solution and water have little reactivity, shown by the consistent pore structure throughout the ageing period. This is mainly caused by the lack of available alkali to facilitate hydrolysis, which in turn results in a lower extent of dissolution (hydrolysis). This finding is very important for practical curing applications because the properties of geopolymers are known to be age-dependent. By ageing geopolymers in these solutions, the structure of geopolymer gels can thus be preserved.

9.6 Conclusions

A conceptual model of geopolymerisation describing the effect of various reaction parameters (aluminosilicate solids, activating solutions, curing conditions, and ageing conditions) on the mechanism and kinetics of geopolymerisation has been presented. The influencing parameters of aluminosilicate solids include the composition and mineralogy of amorphous aluminium and silicon, the rate of dissolution of aluminium and silicon, impurities and particle properties. These parameters primarily affect the early dissolution of aluminosilicate precursors. In the work conducted, it is found that at low silicate concentrations (SiO₂/ M₂O = 0.0 and 0.2, M = Na or K), the crystallisation of zeolites is favourable due to the availability of Al nutrients. At higher silicate concentrations (SiO₂/M₂O = 0.5, 1.79, and 2.0, M = Na or K), the polymerisation of
geopolymer gel is favoured. The crystallisation of zeolites is also more favourable in Na-silicate than in K-silicate solutions. The effect of curing parameters is primarily kinetic. The optimum curing conditions can be achieved by balancing the competing rates of dissolution and polymerisation, so that a higher extent of reaction can be obtained throughout. Finally, ageing in the solutions of moderate alkali concentration (e.g. 1M MOH, M = Na or K) increases the extent of reaction, shown by the formation of more condensed gel and zeolitic phases.

9.7 Recommendations

Future investigations will be required to explain some aspects of geopolymerisation that were not addressed in the current work. These aspects include:

1. The fundamental understanding of the roles of Na\(^+\) and K\(^+\) cations in the mechanism and kinetics of geopolymerisation.

2. A quantitative description between the rate (and extent) of reaction and reaction parameters, namely temperature, time, water content, alkali concentration, and silicate concentration.

3. A mathematical model should be developed in order to provide a quantitative understanding. The model should provide a correlation between heat of reaction and the dissolution, polymerisation, and crystallisation of aluminosilicate. The modelling will need to consider various factors, such as the particle size of fly ash, particle morphology of fly ash, the individual crystalline and amorphous composition in fly ash, alkalinity, temperature fluctuation, and the diffusion of precursors. A numerical model of the mechanism of zeolite formation during fly ash-based geopolymerisation is also essential, and should be considered as extended work.

4. So far, it has been suggested that re-activation of fly ash particles causes the re-dissolution of aluminosilicate precursors, which enhances later reactions, as observed from the work conducted in Chapter 8. Further investigations are required to understand whether the crystals formed are also caused by the re-dissolution of geopolymer gel, which forms a metastable intermediate phase in the solution before crystallising in the gel matrix (homogeneous), or simply by a solid-state transformation (heterogeneous).


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