GEOPOLYMERISATION OF
ALUMINOSILICATE MINERALS

by

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Dedicated to Steve, Lily and Lucy
ABSTRACT

Geopolymerisation can transfer Al and Si containing wastes into geopolymers with a high mechanical strength and high fire, acid and bacteria resistances. This thesis investigates the geopolymerisation of natural aluminosilicate minerals which cover a wide range of structures, minerals groups, hardness, densities and Al₂O₃ and SiO₂ contents. The study of fifteen selected Al-Si minerals shows that the framework structured Al-Si minerals with a high CaO content and a lower K₂O content, have a higher potential to undergo geopolymerisation in KOH solution with resulting geopolymers possessing a higher compressive strength. The NaOH solution is observed to leach more Al and Si complexes from the solid reactants than KOH solution, while KOH solution produces geopolymers with a higher mechanical strength than NaOH solution does.

The addition of silicate solution during geopolymerisation is one of the essential conditions. However, it is found in this thesis that the added silicate solution actually catalyses the geopolymerisation and initiates the polymerisation between the large silicate oligomers and the aluminate monomers. The alkalinity M₅O/H₂O, the ratio of added silicate, the SiO₂/M₅O ratio, the alkali metal cation K⁺ and the setting pressure positively affect the geopolymerisation of the stilbite/kaolinite matrix. The procedure that mixes alkaline solution with silicate solution prior to the addition of solid reactants is proven to be the best due to the best homogeneity obtained.

A method of combining XRD, MAS NMR, SEM/EDX, TEM/EDX and HREM techniques has been established to characterise the structural composition of geopolymers. The results on the geopolymers synthesised from stilbite/kaolinite matrices reveal that the mechanical strength of geopolymers is determined by the gel phase as the binder, the undissolved solid reactants as the filler and the ratio of average surface area and undissolved particles.
The mechanisms involved in leaching and geopolymerisation can be explained by the cation anion ion pair theory. The Na\(^+\) cation, with a smaller size, better stabilises the smaller silicate oligomers, such as monomer and dimer. K\(^+\), possessing a larger size, preferentially coordinates with the larger silicate oligomers. During the dissolution of Al-Si minerals, only silicate monomer and dimer exist, which are better stabilised by NaOH so as to result in a higher extent of dissolution. Along with the addition of silicate solution, the amount of larger silicate oligomers increases greatly. These larger silicate oligomers are stabilised by the K\(^+\) cation, which eventually leads to a higher extent of geopolymerisation.

The cation anion ion pair theory is theoretically verified in the steps of dissolution, the formation of silicate oligomers and the formation of geopolymer precursors by using ab initio calculations. The calculated reaction energies for the dissolution and the energies for the formation of the silicate oligomers and geopolymer precursors indicate that the mechanisms involved in leaching and geopolymerisation can be explained by the ion pair theory.

Finally, a study is conducted on the interaction between the alkali metals structured in the Al-Si minerals and the alkali metal cations in the alkaline solutions. Both Na-feldspar (albite) and K-feldspar (microcline) are selected to embody this research, and the results show that a certain ratio of Na/K in the gel phase significantly affects the geopolymerisation and the compressive strength of the geopolymers formed. When the molar ratio of Na/K in the gel phase ranges from 1.5 to 77.9, the geopolymers synthesised can reach a high compressive strength. If the molar ratio of Na/K drops to < 0.1, the formed geopolymers crack after 28 days setting and hardening at 45 °C. The Na-feldspar and K-feldspar, when respectively geopolymerised in KOH and NaOH solution, reach 24.4 MPa. and 25MPa. after 28 days setting and hardening at 45 °C.

The work done in this thesis indicates that a large variety of natural aluminosilicate minerals have the potential to be used in geopolymerisation to form strong monolithic materials that could be applied in the construction industry in the near future.
DECLARATION

This is to certify that

(i) the thesis comprises only my original work except where indicated in the preface,

(ii) due acknowledgement has been made in the text to all other material used,

(iii) the thesis is less than 100,000 words in length, exclusive of tables, maps, bibliographies and appendices.

Hua Xu
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CHAPTER ONE

INTRODUCTION

Geopolymers, invented in 1978 (Davidovits, 1989), are a kind of inorganic polymer with AIO$_4$ and SiO$_4$ tetrahedra being the structural units. Possessing excellent mechanical strength and fire, acid and bacteria resistance, geopolymers show a high potential to replace traditional cement in the near future (Davidovits, 1991; 1994). Moreover, geopolymers are produced by making use of wastes as reactants, for instance, fly ash, furnace slag, construction wastes and mining tails so that they are environmentally friendly materials from the point of view of reducing green house effects caused by CO$_2$ emission from the manufacturing of Portland cement. Due to these advantages, geopolymers and geopolymerisation have been studied for the last two and a half decades. Before 1995, the study of this technique was focussed on the manufacturing of geopolymeric products and their industrial applications by using either kaolinite or metakaolinite as the sole reactant. Since 1995, more waste materials have been used in the geopolymerisation process. Theoretically, any aluminium and silicon containing materials can undergo geopolymerisation and form geopolymers under certain conditions. Naturally occurring aluminosilicate minerals are the most abundant Al and Si sources existing in the world. It is important to know whether these minerals can be geopolymerised if geopolymers are to be commercialised extensively.

Geopolymerisation occurs in alkaline solution with silicate solution or solids added as catalyst. The reaction environment and the reactants in geopolymerisation are analogous to those in silicate polymerisation and the synthesis of zeolite. Chapter 2 lists the structural and physical properties of the natural Al-Si minerals and discusses the basic dissolution behaviours for aluminates, silicates and aluminosilicates, respectively. The differences between the polymerisation of silicates and the synthesis of zeolite as well as geopolymerisation have been discussed in order to aid readers to understand the results presented in the following chapters. A detailed review of the research into
geopolymerisation conducted from the 1970's to 2001 is presented in chapter 2 to show readers where this thesis starts and why it is necessary to carry out the study on geopolymerisation of natural aluminosilicate minerals.

Chapter 3 illustrates the methodology applied throughout the thesis. These methods or a combination of these methods are effective in characterisation of both reactants and geopolymers. Despite the fact that these analytical methods are not applied here for the first time in the characterisation of geopolymers, a combination of them is found to be effective in the characterisation of geopolymeric reactants and geopolymers.

Fifteen natural aluminosilicate minerals, kaolinite, Na-feldspar and K-feldspar have been investigated in this thesis. Chapter 4 studies the leaching and geopolymerisation of the fifteen Al-Si minerals. These minerals possess Al₂O₃ and SiO₂ contents varying from 1.59% to 57.78% and 27.57% to 64.38%, respectively. Four crystal structure groups and six minerals groups are included in these fifteen minerals, which cover a wide range of Al-Si minerals. The results obtained from chapter 4 show that natural aluminosilicate minerals can be applied in geopolymerisation. Chapter 4 also reveals a series of problems centred on how to better understand the geopolymerisation and how to improve the geopolymers formed.

The effect of alkali metal cations (Na⁺ and/or K⁺) on the geopolymerisation of fly ash has been investigated previously by Van Jaarsveld and Van Deventer (1999a). Chapter 5 discusses the factors that affect the geopolymerisation of natural Al-Si minerals in detail by using mixtures of stilbite/kaolinite as a case study. Alkali metal cations and concentration of alkaline solutions as well as the added silicate solution, sample setting pressure and sample preparing procedures are investigated in Chapter 5. The study discovers that the alkalinity, the added silicate solution and the setting pressure show positive effects on the geopolymerisation. The investigation on sample preparing procedures indicates that the procedure of mixing alkaline solution with silicate solution prior to addition of solid reactants can generate the best homogeneous paste and result in geopolymers with high compressive strength.
Geopolymers synthesised nowadays are the mixtures of amorphous gel phase and undissolved crystalline source particles. The mechanical strength of geopolymers is, therefore, contributed by the gel phase as binder, the undissolved particles as filler and the ratio of gel phase/undissolved particles. The characterisation of the geopolymers in terms of both structure and composition is essential to the understanding of geopolymerisation and the improvement of the geopolymers. A few characterisation studies on geopolymers have been carried out previously in the literature, but they are all at a qualitative level. Chapter 6, for the first time, establishes a method of combining XRD, MAS-NMR, SEM/EDX, TEM/EDX and HREM techniques to characterise the geopolymers and reactants at a semi-quantitative level. The method proposed in Chapter 6 can also be applied to related materials such as cement and concrete.

The study of geopolymerisation and geopolymer has been conducted for more than two decades. However, little, if any work has been done on the mechanisms involved in geopolymerisation. Chapter 4 indicates that the cation-anion ion pair theory can satisfactorily explain the experimental observations obtained from the study of the fifteen aluminosilicate minerals. The ion pair theory has been established by researches in the field of zeolite synthesis. Considering that geopolymerisation is an analogue of zeolite synthesis, this theory is borrowed to explain the mechanisms involved in leaching as well as in geopolymerisation. In order to verify this theory, a series of theoretical calculations by using ab initio simulation have been conducted in Chapter 4 and Chapter 7. Chapter 4 simulates the silicate monomer and dimer forming energies and the geopolymer precursors forming energies. The calculation results match well with the experimental observations as well as the ion pair theory. Chapter 7 models the dissolution of stilbite in water, and NaOH and KOH solutions, with the calculated dissolution energies in good agreement with both experimental results and ion pair theory. The verification of ion pair theory done by ab initio calculations in Chapters 4 and 7 indicates that the mechanisms involved in both leaching and geopolymerisation can be explained by the ion pair theory.
Chapter 8 further verifies the model of stilbite at a higher theoretical level by calculating the vibrational frequencies of stilbite and comparing these frequencies with the experimental IR and Raman spectra, respectively.

Alkaline solution (NaOH or KOH) is one of the essential reactants in geopolymerisation. The alkali metals (Na and/or K) are the most common metals structured in the natural aluminosilicate minerals, so that the interaction between the alkaline solution and the alkali metals structured in Al-Si minerals is an interesting and important aspect for the study of geopolymerisation of natural Al-Si minerals. Chapter 9 investigates the geopolymerisation of the alkali-feldspars (Na-feldspar and K-feldspar) in both NaOH and KOH solutions with the purpose to reveal how the alkali metals structured in Al-Si minerals affect the geopolymerisation and how alkali metals structured in Al-Si minerals interact with the alkaline solutions applied.

The work conducted in this thesis starts from the study of geopolymerisation of natural Al-Si minerals. The characterisation of geopolymers formed, the investigation of mechanisms involved in leaching and geopolymerisation, and the interaction between alkali metals structured in Al-Si minerals and the alkali metal cations contained in alkaline solutions, are discussed in subsequent individual chapters. All the chapters contained in this thesis are written in a stand-alone fashion and address an individual topic. The integration of these topics to form a coherent model of geopolymerisation is summarised at the end of the thesis in Chapter 10. Each of chapters 4 to 9 is based on a published or submitted manuscript.
CHAPTER TWO

THE CHEMISTRY OF ALUMINOSILICATES AND GEOPOLYMERS

The geopolymerisation of aluminosilicate minerals is a new topic, despite the fact that geopolymerisation has been studied for more than two decades. Before presenting the research results found in this thesis, an introduction to aluminosilicate minerals as well as the similarities and differences between aluminosilicate minerals and geopolymers will aid the understanding of the work described in the following chapters. In this thesis, a wide range of natural Al-Si minerals have been investigated, in particular, kaolinite, zeolites and alkali-feldspars have been intensively studied. Moreover, geopolymers are believed to be the synthetic analogues of zeolites (Davidovits, 1991; 1994). Thus, a basic understanding of aluminosilicates, kaolinite, alkali-feldspars, zeolites and the chemistries of synthesis of zeolites and geopolymerisation will be essential in understanding of the whole thesis. The objective of this chapter is, therefore, to serve as a literature review for the thesis and some of the contents presented in this chapter will be discussed in more detail later in the following chapters.

2.1 ALUMINOSILICATES

2.1.1 General

Both silicon and aluminium are the commonest elements existing on earth. More than 75% of the earth's continental crust consists of silicates and aluminosilicates (Dietrich and Skinner, 1979). Silicon has the oxidation state +4 in the environment. Under normal conditions of temperature and pressure each silicon atom is nearly always found bonded to four oxygen atoms. Thus, the basic unit of Si found in silicates and aluminosilicates can be written simply as \( \text{SiO}_4^{4-} \). The tetrahedral units of Si have a strong tendency to polymerise each other by eliminating one oxide ion and sharing another one to form silicate minerals. The ratio of Si to O, along with an increase in
the extent of polymerisation, decreases from 1:4 for ortho-silicates containing single SiO₄⁴⁻ units, to 1:2 for the fully polymerised 3D-framework structure. Every oxygen atom contained in the framework structure is shared between two silicon atoms.

Aluminium is a highly electropositive element and is observed exclusively as Al³⁺ in combination with oxygen atoms (Cox, 1995). As the covalent radii for silicon and aluminium are 1.17 and 1.26 Å respectively (Shriver et al., 1990), during polymerisation of SiO₄⁴⁻, a replacement of Si atoms by Al atoms is possible from the viewpoint of the atomic size. However, the negative charge will increase; for example the layer [Si₂O₅]²⁻ becomes [Si₂AlO₁₀]³⁻ when one in four silicon atoms is substituted by aluminium. Metal cations are, therefore, needed to compensate this charge, which eventually gives an enormous variety of formulae and structures for aluminosilicate minerals.

Loewenstein indicated in 1954 (Loewenstein, 1954) that the maximum substitution of silicon in three-dimensional frameworks and plane networks of tetrahedral aluminosilicate oxide by aluminium is 50%. Therefore, tetrahedrally framework and plane network structured aluminosilicate minerals are always silicon rich minerals. Silicon is always tetrahedrally structured as SiO₄⁴⁻, while aluminium can be tetrahedrally or octahedrally structured. For most of octahedrally structured aluminosilicate minerals, for instance, andalusite (Al₂SiO₅), kyanite (Al₂SiO₃), sillimanite (Al₂SiO₅) and mullite (Al₆Si₂O₁₃) (Deer et al., 1992), more Al than Si atoms could be contained in their formulae. When aluminium atoms are in octahedral structure (ortho-, ring and chain structures), the aluminosilicate minerals are often aluminium rich minerals. The distances of Al-O bond in tetrahedral and octahedral structures are 1.77Å and 1.91 Å (Deer et al., 1992) respectively. Also the bond energies recorded for Al₂O₃ at four and six coordination number are 1.3 and 0.9 eV (Van der Put, 1998) respectively. Despite the Al-O bond being subjected to the environmental SiO₄⁴⁻ tetrahedral unit, the four fold structured Al-O bond is observed to be more stable than the six fold structured Al-O in aluminosilicate minerals.

Aluminosilicate minerals are a large group of minerals that comprise Al and Si oxides, but possess differences in chemical composition, crystal structure, density, hardness and paragenesis. Basically, aluminosilicate minerals can be classified on the
basis of their structural groups as ortho- and ring, chain, sheet and framework groups (Deer et al., 1992). Table 2.1 lists the 20 selected common aluminosilicate minerals and their physical and structural properties.

2.1.2 Ortho- and ring structured aluminosilicates

Ortho- and ring structured aluminosilicate minerals are very stable in terms of temperature and pressure. The melting temperature for these minerals is roughly between 1100 to 1890 °C (Deer et al., 1992) at atmospheric pressure. Ortho- and ring structured aluminosilicate minerals also have the highest average hardness and density (Table 2.1). The chemistry of aluminosilicate minerals in this group is significantly different, however, aluminium atoms structured in aluminosilicate minerals are mostly in six fold and the structural unit of Al-O is octahedral (AlO₆). The paragenesis of metal cations in ortho- and ring structured aluminosilicate minerals is mainly Ca, Fe, Mg, Ti, Mn and Zr despite Cr, Zn, Li, Be, Ce, La, Y, Th, Na and K being observed as minor elements. The common anions in ortho- and ring structured aluminosilicate minerals are F, Cl and (OH).

2.1.3 Chain structured aluminosilicates

Chain structured aluminosilicates occur as a wide variety of igneous rocks, and are particularly characteristic constituents of gabbros, dolerites and basalts. They occur also, but less frequently, in ultrabasic and intermediate rocks. The average hardness and density for chain structured aluminosilicates are higher than for sheet and framework structured aluminosilicates and slightly lower than for ortho- and ring structured aluminosilicates (Table 2.1). The structure unit of Al-O in chain structured aluminosilicates is more four fold tetrahedral AlO₄ than six fold octahedral AlO₆. Chain structured aluminosilicates are normally rich in Fe, Ca, Mg, Na, Li, Cr and Ti cations. The anions often revealing paragenesis in chain structured aluminosilicates are F and (OH). The melting temperature for chain structured aluminosilicates is about 1000 °C at atmospheric pressure, thus an extremely wide range of chemical substitutions leads to their existence in a variety of igneous and metamorphic petrogenetic conditions.
2.1.4 Sheet aluminosilicates

Mica and clay are the two largest groups in sheet aluminosilicates. The basic structure of mica is a composite sheet in which a layer of octahedrally coordinated metal cations is sandwiched between two identical layers of linked (Si, Al)O₄ tetrahedrons. The principal metal cation replacements which occur in mica aluminosilicates are Na, K, Ca, Mg, Mn and Ti. When heated to a temperature between 500 to 1000°C, most mica aluminosilicates are not stable and will decompose.

The structures of clay aluminosilicates are composite layers built from components with tetrahedrally and octahedrally coordinated cations. Most clay aluminosilicates occur as platy particles in fine-grained aggregates which, when mixed with water, yield materials showing varying degrees of plasticity. The commonest metal cation paragenesis in clay minerals is Na, K, Ca, Mg and Fe. Sheet structured clay aluminosilicates possess a lower hardness and density compared with ortho-, ring and chain structured aluminosilicates.

The most important mineral in the clay group is kaolinite. The fundamental structural unit of kaolinite is an extended sheet which can be regarded as having two constituents. One is the layer of (Si₄O₁₀)⁺⁺ formed by the linkage of SiO₄ tetrahedra in a hexagonal array with the bases of SiO₄ tetrahedra being approximately coplanar and their vertices all pointing in one direction. Another is the layer of (OH)₆-Al₄-(OH)₂O₄ formed over the centres of (Si₄O₁₀)⁺⁺ hexagons by the linkage of AlO₆ octahedra. Plane and elevation views of this composite Al₄Si₄O₁₀(OH)₈ layer are shown in Figures 2.1 and 2.2. Only two out of each set of three available sites are occupied by Al ions. When treated by heating at 750°C, kaolinite will be deformed and transferred to metakaolinite; the structure unit of Al-O, therefore, will be changed from octahedral (AlO₆) to tetrahedral (AlO₄).
2.1.5 Framework structured aluminosilicates

Feldspar, sodalite and zeolite are the three largest and commonest groups in framework structured aluminosilicates. As the structural unit of Al-O in framework structured aluminosilicates is mostly tetrahedra (AlO₄), the majority of framework structured aluminosilicates are silicon rich minerals because of the Loewenstein’s rule (Loewenstein, 1954). The average lower density possessed by most framework structured aluminosilicates is attributed to their cage-like or tunnel-like inner structures, however, the average hardness of them is higher than for sheet structured aluminosilicates.

The feldspar group is the most abundant constituent of igneous rocks. The majority of feldspars may be classified chemically as members of the ternary system NaAlSi₃O₈ (albite), KAlSi₃O₈ (K-feldspar) and CaAl₂Si₂O₈ (anorthite). Feldspars NaAlSi₃O₈ and KAlSi₃O₈ are referred to as alkali feldspars and those between NaAlSi₃O₈ and CaAl₂Si₂O₈ as plagioclase feldspars. The alkali feldspars generally contain less than 5 to 10 per cent of the calcium feldspar in solid solution. The structure of alkali feldspars is typical framework aluminosilicates in which tetrahedra of (Si, Al)O₄ are linked to one another (by shared oxygen) in all directions rather than in chains or in sheets. Although discrete chains of tetrahedra do not exist in the structure, its nature may be more easily understood by considering the atomic arrangement as the linking of chains in two directions perpendicular to their length. The chains themselves are formed by the linking of horizontal rings of four tetrahedrons as shown in Figure 2.3a. The repeat distance in the chain direction is approximately four times the height of a tetrahedron. When viewed in the direction of the chain axis a horizontal ring appears approximately as in Figure 2.3b and this can be further simplified in its representation as in Figure 2.3c. The configuration shown in Figure 2.3(a to c) is often described as a “double crankshaft” and the upward and downward pointing tetrahedra in a horizontal ring are labelled as U and D respectively.

The sodalite group is formed by the linkage of SiO₄ and AlO₄ tetrahedra in approximately equal numbers, each corner oxygen being shared by two tetrahedra and Al and Si are completely ordered. In sodalite, cage-like cubo-octahedral units are formed (Figure 2.4) by binding six rings of four tetrahedra parallel to \{100\} and eight
rings of six tetrahedra parallel to \{111\}. The six-membered rings define a set of channels which intersets to form large cavities. The cavities are occupied by chlorine ions and these are tetrahedrally coordinated by sodium ions as well. Sodalite is the sodium-rich mineral of the sodalite group and differs from the other minerals of the group in containing chlorine as an essential constituent. There is variation in the Na content beyond a slight substitution of Na by both K and Ca in sodalite.

The zeolite group is best defined as aluminosilicates with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement permitting ion exchange and reversible dehydration. Chemically, they are related to feldspars when subjected to thermal metamorphism. The basic structure of the zeolite group is composed of \((\text{Si,Al})_4\) tetrahedra, each oxygen of which is shared between two tetrahedra. The net negative charge on the framework is balanced by the presence of cations, in most cases Ca, Na, or K. The feature of zeolite is also embodied in the structures of the feldspar minerals. However, feldspars have compact structures in which Na, K and Ca ions are in relatively small cavities and are completely surrounded by oxygens of the framework. The cations and frameworks are strongly interdependent in feldspars so unless framework bonds are broken, the replacement of Na, K by Ca necessarily involves a change in the structure and the Si/Al ratio. The chemistry of zeolites is rather variable and sometimes deviates considerably. Generally, zeolites form a well-defined group of hydrated aluminosilicates with the alkalis or alkaline earths and with the ratio of \(\text{SiO}_2/\text{Al}_2\text{O}_3\) always \(\geq 2:1\).

2.2 DISSOLUTION OF ALUMINOSILICATES

2.2.1 Dissolution of silicates

As in most silicates, the silicon atom is surrounded by four oxygen atoms in a tetrahedral arrangement. A study of dissolution of silicates is actually a study of silicate species (\(\text{H}_4\text{SiO}_4\)) in solution. The simplest silicate mineral is quartz which is generally recognised as the most stable silica mineral at normal temperatures and
pressures. The solubilities of the different forms of silica and silicate species are listed in Table 2.2 (Lindsay, 1979). The solubility for silica minerals and silicate species in terms of $H_2SiO_4^-$ (chemicals represented with "\(=\)" are their aqueous species with no charge) is expected to range from $10^{-2.71}$ M (where M represents Molar concentration) to $10^{-4.95}$ M respectively. An obvious lower solubility for silicate species than silica minerals as showed in Table 2.2 indicates that the solubility is studied under the condition of lower pH values (lower than 8.5). Iler (1979) pointed out that along with the increase in pH from 9 to 10.7, an apparent increase occurs in the solubility of amorphous silica, owing to the formation of silicate species in addition to the monomer [\(\cdot\)OSi(OH)$_3$] which is in equilibrium with the solid phase. Moreover, above pH 10.7 and to pH 14, all the solid phase of amorphous silica dissolves to form soluble silicate. This trend is caused by the fact that at high pH (pH = 14) the concentration of Si(OH)$_4^-$ is greatly lowered by conversion to ionic species \(\cdot\)OSi(OH)$_3$ and \(\cdot\)OSi(OH)$_2$O$^-$ (Babushkin et al., 1985) through cation-anion pairing.

2.2.2 Dissolution of aluminates and aluminosilicates

Aluminates are known to have a higher solubility in acid solution. Table 2.3 lists the equilibrium reactions of aluminium minerals and complexes at 25°C (Lindsay, 1979). In strong acid solutions, dissolved aluminium species are found to dominantly form the octahedral cation Al(H$_2$O)$_6^{3+}$ (Barrer, 1982). From pH 6 upwards Al(OH)$_4^-$ or very simple dehydration products such as AlO$_2^-$ is dominant (Barrer, 1982). The Al(OH)$_4^-$ is tetrahedral in configuration and so should favour the formation of tectoaluminosilicate with silicates and further to polymerise into 3-dimensional crystalline networks.

The dissolution of aluminosilicate minerals in acidic solutions is reasonably well known. Table 2.4 lists the solubility of several aluminosilicate minerals in terms of the activities of Al$^{3+}$, H$^+$ and $H_2SiO_4^-$. For example, the dissolution of kaolinite can be described as

$$\text{Al}_2\text{Si}_2\text{O}_5 (\text{OH})_4 + 6\text{H}^+ \rightleftharpoons 2\text{Al}^{3+} + 2\text{H}_2\text{SiO}_4^- + \text{H}_2\text{O} \quad (2.1)$$

Since
\[
\log K^\circ = 5.45 \quad \text{(} K^\circ \text{ represents the equilibrium constant in terms of activity)}
\]

\[
\frac{[Al^{3+}]^2[H_4SiO_4^\circ]^2}{[H^+]^6} = 10^{5.45}
\]

\[
\log [Al^{3+}] + 3\text{pH} = 2.73 - \log [H_4SiO_4^\circ]
\]  
(2.2)

By selecting different values for \(\log [H_4SiO_4^\circ]\), Eq. 2.2 can be solved for \(\log [Al^{3+}] + 3\text{pH}\) to give a series of values. Figure 2.5 plots the relationship of \([Al^{3+}], \text{pH and } [H_4SiO_4^\circ]\) for some selected common aluminosilicate minerals.

However, the solubility of aluminosilicate minerals in alkaline solutions is much lower than in acidic environment. Due to the higher ability of gelling between \(Al(OH)_4^-\) and \(OSi(OH)_4\) species, the information about the solubility of aluminosilicate minerals in alkaline solution is not easy to obtain, but is related and limited to the bauxite processing industry (Breuer et al., 1963) and zeolite synthesis (McCormick and Bell, 1989). Gasteiger et al. (1992) studied the solubility of aluminosilicates in alkaline solutions by establishing a thermodynamic equilibrium model. They found that the solubility of aluminosilicates in alkaline solutions depended on the charges of aluminium and silicon as well as on the hydroxide ion concentration, ionic strength and temperature. At the concentrations of 1M and 3M for NaOH solution, the observed concentrations were 4.14±0.04 and 4.31±0.03 for \(10^3 [Al]\) (Molar concentration) and 1.38±0.04 and 1.36±0.05 for \(10^3 [Si]\) (Molar concentration) respectively. They also noticed that the ratio of apparent aluminium and silicon species ([Al]/[Si]) in alkaline solutions ranged from 0.076 to 50 at the specific hydroxide ion concentration, ionic strength and temperature. It is worth noting that there is no general common rule for dissolution of aluminosilicate minerals found in the literature. Moreover, there is little research conducted on individual aluminosilicate minerals to understand their dissolution behaviour (Chou and Wollast, 1985; Hellmann, 1994; Gérard et al., 1998; Blum and Stillings, 1995). For aluminosilicate minerals investigated in this thesis, their dissolution behaviour in alkaline solutions has been studied individually by the author.
2.3 POLYMERISATION OF SILICATES AND ALUMINOSILICATES

2.3.1 Polymerisation of silicates

2.3.1.1 General

Monosilicic acid Si(OH)$_4$ is known to have a high tendency to polymerise with itself in solution, although generally, Si(OH)$_4$ is stable in water at 25°C for long periods of time if its concentration is less than about 100 ppm as SiO$_2$ (Iler, 1979). When a solution of monomer, Si(OH)$_4$, is formed at a concentration greater than about 200 ppm as SiO$_2$, the monomer starts to polymerise by condensation and forms dimer, trimer and higher oligomers. It is found (Iler, 1979) that silicic acid polymerises in such a way that there is a maximum of siloxane (Si-O-Si) bonds and a minimum of uncondensed SiOH groups in the polymer. Thus at the earliest stage of polymerisation, condensation quickly leads to ring structures, for example, the cyclic tetramer, followed by addition of monomers to these and linking together the cyclic polymers to larger three-dimensional molecules. The resulting three-dimensional molecules are, in effect, the nuclei for the further polymerisation, which eventually develops to the larger particles. Since small particles are more soluble than larger ones, the polymeric particles grow in average size and diminish in numbers along with the dissolution of the smaller ones and the depositing upon the larger ones. Basically there are two processes in polymerisation of silicic acid solution, formation of nuclei at the expense of silicic monomers in the solution, and growth of larger particles by the deposition of silicic acid species. It is found that the latter step is the slower process and consequently is the speed-controlling step (Lindsay, 1979).

2.3.1.2 Effect of pH

The overall effect of pH on both nuclei formation and particles growth is depicted in Figure 2.6 (Iler, 1979). Curve ABC represents the behaviour of silica in the absence of salts. Curve DEF demonstrates the general trend when an electrolyte such as NaCl
or Na$_2$SO$_4$ is present at a concentration about 0.2-0.3 N. It is noted from Figure 2.6 that sodium salts lower the gelling time significantly.

It is believed that the nuclei formation involved an ionic mechanism (Iler, 1979). At pH above 2, the rate of nuclear formation is proportional to the concentration of OH\(^-\) ion and below 2, it is proportional to the H\(^+\) ion. At low pH the silica particles bear very little ionic charge and thus can collide and aggregate each other into chains and then gel networks. If the concentration of SiO$_2$ is more than 1% such aggregation may begin as soon as the first small particles are formed. However, at lower concentrations and at pH around 2, the monomer is converted largely to discrete particles before they begin to aggregate. On the other hand, at pH 5-6, monomer is converted rapidly to particles which simultaneously aggregate and gel so that it is not possible to separate the two processes. The rate of aggregation increases rapidly with concentration so that in any case with more than 1% silica present, aggregation probably involves not only particles but also oligomers. At the pH above 6 or 7, and up to 10.5, the silica particles are negatively charged and repel each other. Therefore they do not collide, so that particle growth continues without aggregation. However, if salt (for instance, NaCl and Na$_2$SO$_4$) is present at a concentration greater than 0.2-0.3 N, as when sodium silicate is neutralised with acid, the charge repulsion is reduced and aggregation and gelling occur.

It is observed from Figure 2.6 that sols have a minimum temporary stability around pH 5-6. Above about pH 7, no gel is formed since the particles are charged and only particle growth occurs. However, for curve DEF, since salts lower the ionic charge on particles, the gelling time is reduced greatly. Also in the neutral region, the pH of minimum stability is higher (E higher than B) when salt is present.

2.3.1.3 Polymerisation above pH 7

The polymerisation of silica in solution below pH 7 differs from that above pH 7 for the following reasons:
1) It is only at low pH that the polymerisation is sufficiently slow to allow the early stages to be followed. Changes that occur in hours at pH 2 are completed in minutes or seconds at pH 8 – 9.

2) The polymer units or particles formed at low pH bear no charges and unless the silica concentration is very low, aggregation begins to occur soon after polymeric particles are formed. This happens not only because of the lack of charge on the particles, but also because the particles are extremely small and cease to grow after they reach a diameter of 2-3 nm. Since the rate of aggregation depends mainly on the number of particles per unit volume and less on their size, aggregation occurs even at very low silica concentrations.

3) At pH above 7, particle growth continues up to a larger diameter, depending mainly on the temperature, unless aggregation or gelling takes place when an electrolyte is present in an amount approaching the critical coagulation concentration at the pH of the sol.

At pH above 7, the ionisation of silicate polymer species is much higher so that the monomer polymerises and decreases in concentration very rapidly. At the same time, the particles grow rapidly with the rate of growth depending on the distribution of particle sizes. This is because the growth of the particles occurs as a result of more smaller particles being dissolved and the silica being deposited upon the larger ones. Generally, the distribution of particle sizes is not known, but with the assumption of a Gaussian distribution, the increase in average size continues at a given temperature until the size is so large that the difference in solubility of smaller versus larger particles becomes negligible. Therefore the final size of polymeric silicate particles depends on the temperature. Table 2.5 and Figure 2.7 show the rate of growth of silica particles at 50 °C and 90 °C and different pH values respectively (Iler, 1979). It is observed from Table 2.5 and Figure 2.7 that the particle sizes aged at 90 °C (A, B and C) are significantly larger than that aged at 50 °C (D, E and F). It is also noted that the initial distribution of particle sizes in the sol will have a marked effect on the final size reached.

The mechanisms involved in polymerisation of silica sols above pH 7 are particle-to-particle attraction by van der Waals forces and particle-to-particle bridging by the
flocculating or coagulating agent (Iler, 1979). In the first case, the attraction leads to coagulation when repulsion force between particles is reduced by addition of a critical concentration of salt coagulant. On the other hand, flocculation is caused by inter-particle bonding through the cations contained in salt coagulant above pH 11. Figure 2.8 shows the bonding mechanism between Na⁺ and silica particles. The sodium cation in solution is surrounded by the oxygen atoms of six water molecules or hydroxyl anions. When a sodium cation is adsorbed on the surface of a silica particle, one or more of the oxygen atoms can be displaced by the oxygens of the surface silanol groups (SiOH), which thus become linked directly to sodium. The positive charge of sodium cation thus neutralises the negative charge of the adjacent adsorbed hydroxyl anion and a neutral adsorption complex is formed. At high sodium cation concentrations above the “critical coagulation concentration”, more water or hydroxyl surrounded Na⁺ link outwardly with other silanol groups on the surface of a second colliding particle. Then sodium cation bridges two silica particles.

2.3.2 Polymerisation of aluminosilicates

It has been stated previously in section 2.1 that the SiO₄ tetrahedra in tectosilicates can be replaced by tetrahedral AlO₄ to form tectoaluminosilicates, which, like the crystalline silicates, have three-dimensional framework structures. The most discussed polymerisation of aluminosilicates in the literature so far is the synthesis of zeolite. The chemical precursors to zeolite formation are more complex and varied than are those involved in polymerisation of silicates. Nevertheless the stages of zeolite formation and synthesis of silicates are very similar: small aggregations of precursors give unstable germ nuclei; some of these embryos become large enough to be stable nuclei; and spontaneous deposition of more Al and Si complexes on such nuclei results in larger crystalline zeolite. The factors affecting the synthesis of zeolite are the factors affecting the procedures of nucleation and crystal growth.

The precursors existing in zeolite synthesis are Al(OH)₄⁻ and silicate monomer, dimer and larger oligomer anions. Harris and Newman (1977) indicated that in solutions containing 8M KOH, 3M SiO₂ and 0.02M Cr³⁺, the presence of five major species of silicate anions were at the following concentrations:
Monomer 1.45M  
Dimer 0.22M  
Cyclic trimer 0.16M  
Substituted cyclic trimer 0.08M  
Linear trimer 0.07M  
Linear tetramer 0.03M

When a stable aluminosilicate solution is mixed with a stable silicate solution, no nucleation occurs unless the metastability of the system is increased by decreasing the temperature and condensing the concentration of Al and Si species. The rates of nucleation of the system rise with the extent of undercooling and the increase in viscosity. The formed nuclei may build up in size until some reach the critical size needed for spontaneous further growth. The deposition rate on a seed or stable nucleus is proportional to the extent of supersaturation and undercooling. Apart from temperature, alkalinity (pH), composition of the reaction mixtures and cations are also the major factors affecting the synthesis of zeolite.

2.3.2.1 Alkalinity (pH) and composition of reaction mixtures

Within the stability field of a given zeolite, increasing alkalinity at constant temperature influences the kinetics, likewise increasing temperature at constant alkalinity. It decreases the nucleation time and enhances the rate of crystal growth of zeolite. Such effect of increase in alkalinity is believed to be attributed at least in part to the much greater concentrations of dissolved Al and Si species (Barrer, 1982), since the higher concentrations of Al and Si species help nuclei to develop more quickly from the more numerous encounters between precursor species in solution. Similarly, the greater concentration of precursors accelerates surface nucleation and reaction at the crystal solution interface. Other important effects of OH⁻ that have been observed are that starting with silica-rich mixtures, the greater the concentration of OH⁻ the more closely the ratio of SiO₂/Al₂O₃ approaches 2 (Lowenstein, 1954). This is also seen in Figure 2.9 (Barrer and Mainwaring, 1972) for some parent compositions K₂O·Al₂O₃·nSiO₂ + excess KOH + aq. The final products were the zeolite chabazite type K-G and the edingtonite type K-F. When the ratio of
SiO$_2$/Al$_2$O$_3$ is two the Al and Si should locate as far as possible alternately throughout the tetrahedral framework according to the Al-O-Al avoidance rule (Lowenstein, 1954). Thus, by increasing the OH$^-$ concentration the tendency of Al and Si to be ordered in the tetrahedral sites is increased.

When the concentration of OH$^-$ (as KOH) was kept constant, but the absolute amount is increased by increasing the volume of KOH solution added, the yields of crystals declined as shown in Figure 2.10 (Barrer and Mainwaring, 1972). The two solutions are 1M and 6M and K-G and K-F types of zeolite are yielded respectively. Thus the extra added KOH solution remains unreacted but dissolves more Al and Si species. The zeolites accordingly appear to dissolve in their alkaline mother liquor, as the ratio of liquid to solid is increased and the ratio of Si/Al in the “equilibrium” solution therefore, approaches more closely to that in the crystals. Such effect makes the side reactions such as selective extraction of Al less significant.

Generally, it is found that when zeolites form from aqueous, alkaline, silica-rich mixtures the zeolites usually have lower SiO$_2$/Al$_2$O$_3$ ratios than the parent mixtures. If the reaction mixture is highly aluminous (SiO$_2$/Al$_2$O$_3$<2) the zeolite formed may have a SiO$_2$/Al$_2$O$_3$ ratio equal to or more than 2, which is regarded as more siliceous than the parent mixture (Barrer, 1982). Thus, it is noted that in zeolite synthesis, the formed gel usually presents a certain SiO$_2$/Al$_2$O$_3$ ratio which is either lower than its silica-rich parent mixture or higher than its aluminium-rich mother liquor. However, within the range of SiO$_2$/Al$_2$O$_3$ ratio from 2 to 8 in reaction mixtures, an increase in concentration of OH$^-$ and amount of OH$^-$ will result in zeolite products with better ordering as well as possessing the SiO$_2$/Al$_2$O$_3$ ratio close to its mother solution.

2.3.2.2 Cations

Gabelica et al. (1983) observed that small alkali metal cations produce the highest rates of zeolite nucleation. They also noted that this trend parallels the ability of such cations to order water molecules. The attraction between a positive charge centre and the oxygen of the water molecule can serve to enhance the tendency of water to form a transient network. Large cations, however, do not fit well into such networks and so produce disorder among the water molecules. For these reasons, small cations
(inorganic cations) are referred to as “structure-producing” whereas large cations (Tetraalkylammonium TAA cations) are referred to as “structure-breaking”. Gabelica et al. (1983) proposed that as with water, small alkali metal cations are effective in producing ordered arrays of silicate tetrahedra which can then bond together to form a nucleus for zeolite synthesis. The primary role of cations suggested by Gabelica et al. (1983) and Barrer (1982) is also to order the silicate species, thereby facilitating their condensation. However, other authors (McCormick et al., 1988) have proposed a different role for cations. They indicate that Coulombic interactions between cations and silicate (or aluminosilicate) anions lead to a selective stabilisation of particular structures relative to others.

The distribution of silicate anions is a function of cation size as well as silicate ratio. Trimethylsilation/chromatography (Ray and Plaisted, 1983), Raman spectroscopy (Dutta and Shieh, 1985) and NMR spectroscopy (McCormick et al., 1988) have shown that the distribution of silicate anions shifts toward large species as the cation size increases. The observed trend can be ascribed to the formation of cation-anion pairs. Direct evidence for the formation of such pairs has been obtained by McCormick et al. (1989a) from NMR spectra of alkali metal cations. The extent of pairing is found to depend on both cation and anion size. For small anions (monomer), the extent of ion pairing decreases with increasing cation size. For large anions, preferential pairing occurs with the larger cations due to high polarisability of such ions. It has also been proposed that these counterbalancing trends can account for the increase in the concentration of large silicate anions with increasing cation size (McCormick et al., 1989a; Ray and Plaisted, 1983; Dutta and Shieh, 1985).

The exchange between silicate anions, monomer, dimer and trimer in high pH alkaline solution can be expressed as the following two reactions:

\[
\text{Monomer (M) + Monomer (M) } \rightleftharpoons \text{ Dimer (D)} \quad (2.3)
\]

\[
\text{Monomer (M) + Dimer (D) } \rightleftharpoons \text{ Cyclic trimer (C-T)} \quad (2.4)
\]

McCormick et al. (1989b) found that the rate coefficients for reactions 2.3 and 2.4 are dependent on cation size and that the rate coefficient for reaction 2.3 is greater for K⁺
and that the rate coefficient for reaction 2.4 is greater for Na⁺. These effects of cations on the dynamics of Si species exchange are attributed to the formation of cation-anion pairs (McCormick 1989c). A more detailed exchange mechanism involving a range of silicate anions has been discussed by Kinrade and Swaddle (1986) with results showing that Na⁺ better stabilises the monomer and K⁺ increases the amount of dimer and trimer. By means of ²⁹Si NMR exchange spectroscopy (EXSY), Knight et al. (1988) noted that the cyclic trimer appeared to be rather labile, undergoing rapid ring opening and closing. Therefore in silicate alkaline solutions, K⁺ is supposed to increase the extent of polymerisation between Si anions more than Na⁺.

During the study of synthesis of zeolite, ²⁷Al NMR has revealed that an increase in the silicate ratio increases the extent of reaction between silicate and aluminate species (Dent Glasser and Harvey, 1984a; 1984b; Muller et al., 1981; McCormick et al., 1986). Since the degree of oligomerisation increases with increasing silicate ratio, the observed trend suggests that large oligomers react more readily with aluminate anions than smaller silicate oligomers do (McCormick and Bell, 1989). Cation size also influences the condensation of silicate and aluminate anions with larger cations increasing the extent of condensation (McCormick and Bell, 1989).

In summary, cations influence the polymerisation of silicate as well as aluminosilicate by directing water molecules and selectively stabilising the silicate anions. In particular, alkali metal cations affect the condensation of aluminosilicate by ion pairing reactions.

2.4 GEOPOLYMERISATION

2.4.1 Early geopolymerisation

The earliest published paper on geopolymer and geopolymerisation can be traced back to 1979 (Davidovits, 1979). Davidovits, a French scientist, invented and first used the terms geopolymerisation and geopolymer on the basis that geopolymers consist of Al and Si which are both essential geological structural elements (Davidovits, 1991; 1994). In his works, Davidovits stated that kaolinite was used as
reactant and the reactions were in a hot NaOH aqueous environment. After
thermosetting at 150 °C, the resultant products were named as geopolymers
(Davidovits, 1991). During the period of 1979 to 1995, about 50 journal papers and
patents (see Bibliography) were published on the subjects of geopolymers and
geco-polymerisation. Some of those researches contain similar concepts, but with
different titles, for instance, the inorganic aluminosilicate polymers used by Haack
and Randel (1994) and the low-temperature inorganic aluminosilicate polymers
mentioned by Neuschaeffer et al. (1985), Huang et al. (1990) and Mahler (1980).
Among these 50 publications, 26 (52 %) are done by Davidovits and his team and 30
(60 %) are published as patents. In particular 13 (43.3 %) out of 30 are patented by
Davidovits or his team.

A first detailed introduction on geco-polymerisation, geco-polymeric products and their
properties and structures was presented by Davidovits (1991) based on his studies
which covered geco-polymeric matrices, resins and composite materials. According to
Davidovits (1991; 1994), the chemical designation of geopolymers is poly-sialate.
Sialate is an abbreviation for silicon-oxo-aluminate. The sialate network consists of
SiO₄ and AlO₄ tetrahedra linked alternately by sharing all the oxygens. Positive ions
(Na⁺, K⁺, Li⁺, Ca²⁺, Ba²⁺, NH₄⁺ and H₂O⁺) must be present in the framework cavities
to balance the negative charge of Al³⁺ in IV-fold coordination. Poly-sialate has this
empirical formula:

\[ M_n \{-(\text{SiO}_2)_z\text{-AlO}_2\}_n \cdot w\text{H}_2\text{O} \]  \hfill (2.5)

Where M is a cation such as sodium, potassium or calcium, and 'n' is the degree of
geco-polycondensation; 'z' is 1, 2 or 3. Poly-sialates are chain and ring polymers with Si⁴⁺
and Al³⁺ in IV-fold coordination with oxygen and range from amorphous to semi-
crystalline. Apart from poly-sialate (-Si-O-Al-O-), poly-sialate-siloxo (-Si-O-Al-O-Si-
O-) and poly-sialate-disiloxo (-Si-O-Al-O-Si-O-Si-O-) are also possible structural
units for geopolymers when the amount of silicate reactants increases in the reaction
system.
Geopolymerisation is exothermic and is schematised by Davidovits (1991; 1994) as follows:

$$\text{NaOH/KOH}$$

$$\begin{align*}
(Si_2O_5, Al_2O_2)_n + 3nH_2O & \rightarrow n(\text{OH})_3 - \text{Si-O-Al}^-(\text{OH})_3 \\
& \text{ (Orthosialate)} \\
\text{NaOH/KOH} & \text{ (Na, K)-(Si-O-Al}^-(\text{OH})_3) \\
\text{O} & \text{O} \\
& \text{(Na, K)-poly(sialate)}
\end{align*}$$

$$\text{NaOH/KOH}$$

$$\begin{align*}
(Si_2O_5, Al_2O_2)_n + n2SiO_2 + 4nH_2O & \rightarrow n(\text{OH})_3 - \text{Si-O-Al}^-(\text{OH})_3 \\
& \text{ (Ortho(sialate-siloxo))}
\end{align*}$$

$$\text{NaOH/KOH}$$

$$\begin{align*}
n(\text{OH})_3 - \text{Si-O-Al}^-(\text{OH})_3 & \rightarrow (\text{Na, K)-(Si-O-Al}^-(\text{OH})_3) \\
& \text{ (Na, K)-poly(sialate-siloxo)}
\end{align*}$$

It is also assumed by Davidovits (1991; 1994) that the syntheses are carried out through oligomers (dimer, trimer) which provide the actual unit structure of the three dimensional macromolecular edifice. When geopolymeric polymerisation is carried out at ambient temperature, amorphous or semi-crystalline structures are formed. However, when the geopolymers are synthesised at a hydro-thermal setting and hardening temperature in the 150 -180 °C range, the geopolymeric products are crystalline in structure (Davidovits, 1991; 1994). The coordination of Si and Al in geopolymers detected from NMR is IV fold and the X-ray diffraction of geopolymer binder is amorphous with no crystalline peak detectable. The difference between a geopolymer binder and a geopolymeric product is that the geopolymer binder is synthesised from precursor (Si$_2$O$_5$•Al$_2$O$_2$) (calcined kaolinite) at ambient environment. However, geopolymeric products or industrial applications are different from the binder, because other materials or metals are involved in the system as an
aggregator or reinforcement, for example: sand, SiC, and carbon fibre (Davidovits, 1991; 1994). The applied geopolymeric products invented by Davidovits include reinforced plastics/composite, panel, tiles and thermal insulated foam geopolymeric products, tooling materials, decorated ceramic geopolymers, Mo, Fo-type refractory coating and geopolymeric cement and concrete (Davidovits and Cordi, 1979; Davidovits, 1983; Davidovits and Davidovits, 1988; Davidovits et al., 1990; Davidovits et al., 1991a; b; c; Davidovits and Davidovits, 1991; Davidovits et al., 1992; Davidovits et al., 1994;).

Weiss (1987) published a geopolymeric product, trolit, in 1987 using SiO₂ and Al₂O₃ reacted in an aqueous alkaline medium with resultant products possessing a three dimensional network of aluminosilicate. The structure of the three dimensional network is a zeolite or feldspar like structure but amorphous or partially crystalline. It could be said that the products obtained by Weiss are geopolymers in terms of their properties as well as their method of synthesis.

Kokai (1989) patented the technique of manufacturing geopolymer composite with kaolin, wollastonite or fly ash as reactants. The composites are prepared in alkaline metal silicate (Na silicate, K silicate and Li silicate). Also, an anionic surfactant is added for stable air entraining and the mixture resulted therefore is foamed and hardened to obtain a final product. Also, organic or inorganic fillers as the dispersive phase are added.

Laney (1993; 1994) and Laney et al., (1993; 1995) invented geopolymer-modified gypsum-based construction material for wallboard having improved strength and fire and water resistance and their manufacture. Also Fouche patented his research results (1993) for composition of geopolymeric binder materials upon being mixed with water. Vestecka obtained his patent (1993) for geopolymer gypsum-free Portland cements. Haack (Haack and Randel, 1994) received his patent on lightweight inorganic composite thermal insulators, and process and apparatus for their manufacture.

Apart from all those industrial applications published as patents, Palomo et al. (1992a; b) and Huang et al. (1990) have characterised geopolymeric binders and products.
Also, applications of geopolymerisation to immobilise wastes have been studied by Comrie and Davidovits (1988), Comrie et al. (1989) and Khalil and Merz (1992; 1994) with positive results showing that geopolymerisation can successfully immobilise or encapsulate a wide range of wastes such as Sr, Cs and Mo into geopolymers.

It is noticed that during the early study of geopolymerisation and geopolymeric products, Davidovits has made a remarkable contribution to both research and industrial application. Moreover, an emphasis on industrial application from the very beginning of inventions of geopolymerisation and geopolymers has indicated the prospective potential of this technique.

2.4.2 Recent study of geopolymerisation

From 1996 onwards, about 41 journal and patent publications as well as one conference proceedings (Geopolymer '99) have been published in dealing with geopolymeric products and geopolymerisation (see Bibliography). Eleven out of those forty one (24.4%) works are conducted by Van Deventer and his team (Phair and Van Deventer, 2000; 2001; Xu and Van Deventer, 2000a; b; 2001; Van Jaarsveld and Van Deventer, 1999 a; b; Van Jaarsveld, et al., 1997; 1999; 2000; Van Deventer, 2000). These works cover the field of geopolymerisation of natural minerals, fly ash and immobilisation of toxic metals in fly ash based geopolymers that has greatly widened the fundamental knowledge of geopolymerisation. A comparison between studies conducted before and after 1996 (Table 2.6) shows a drop from 60 % to 31.7 % for patent works and a decrease from 52 % to 9.8 % for publications contributed by Davidovits and his team. This reflects an increase in fundamental research in geopolymerisation, and furthermore that Van Deventer together with his team has become a new research centre on geopolymeric reactions.

A geopolymeric composite with better fire and heat resistance and higher mechanical strength is still the main objective of industrial application (Beer, et al., 1998; Bertin and Boivinet, 1997; Davidovits, 1996; 1999; Davidovits et al., 1996; 1998; Foden, et al., 1996; 1997; Laurent and Paillet, 1996; Lyon, et al., 1996; 1997;). In addition, the immobilisation of toxic metals in geopolymers has received substantial attention. Van

The development of geopolymerisation and geopolymeric products has changed the meaning of terminology specified initially by Davidovits. For instance, geopolymer, which was defined in 1978, originally meant geopolymeric binder according to Davidovits (1991; 1994). A geopolymeric binder is a specific kind of geopolymer which is synthesised by complete transformation of reactants (calcined kaolinite) from the solid phase to gel phase. Such geopolymer has a certain stoichiometric composition, (poly-sialate, poly-(sialate-siloxo), or poly-(sialate-disiloxo)) and possesses amorphous to semi-crystalline structure. However, along with the widening of source materials used for geopolymerisation, the meaning of geopolymer nowadays has deviated from the meaning of geopolymeric binder with a certain formula (poly-sialate, poly-(sialate-siloxo) and poly-(sialate-disiloxo)) to indicate a geopolymeric mixture comprising geopolymeric gel and solid source materials. The structure of a geopolymer, therefore, is a mixture of amorphous to semi-crystalline gel phase and crystalline source materials. An ambient condition combined with a thermal setting and hardening at a temperature lower than 50°C is applied for most geopolymerisations conducted recently (Phair and Van Deventer, 2000; 2001; Xu and van Deventer, 2000a; b; 2001; Van Jaarsveld et al. 1997; Van Jaarsveld et al. 1999; Van Jaarsveld and Van Deventer, 1999 a; b; Van Jaarsveld, et al., 2000; Van Deventer, 2000). Equation 2.10 describes the differences between the geopolymerisations nowadays and that defined by Davidovits in 1991 (Eq. 2.6 to 2.9).

\[
\text{Al-Si materials (s) + nMOH (aq.) + } M_2\text{SiO}_3 \text{ (s or l) + aggregates (s)} \quad \text{↓mixing} \quad \text{↓}
\]
T°C \text{\underline{setting and hardening}}

\text{Geopolymeric gel + Al-Si particles (remained) + aggregates (s) (2.10)}

(Geopolymer or geopolymeric products)

Figure 2.11 is the SEM image of a geopolymer synthesised from fly ash, kaolinite and Na-feldspar. It is observed that the geopolymer presented in Figure 2.11 is a mixture of geopolymeric gel ("C"), fly ash ("A") and Na-feldspar ("B") particles.

2.4.3 \textit{Chemistry involved in geopolymerisation}

Geopolymerisation has been regarded as the analogue of synthesis of zeolite (Davidovits, 1991; 1994). The chemistry involved in geopolymerisation is close to that in synthesis of zeolite, although the resultant products are different in composition and structure. Table 2.7 lists the comparison between synthesis of zeolite and geopolymerisation. Zeolite products have certain stoichiometric compositions and crystalline structures. Geopolymeric products, however, do not have stoichiometric composition and comprise mixtures of amorphous to semi-crystalline structure and crystalline Al-Si particles. The process of zeolite synthesis consists of prenucleation, nucleation and crystal growth. In contrast, geopolymerisation comprises leaching, diffusing, condensation and hardening steps.

When solid Al-Si source materials come in contact with alkaline solution, leaching of both Al and Si species starts. The extents of leaching for both Al and Si are dependent on concentration of the alkaline solution, alkali metal cation in alkaline solution, stirring speed, leaching period as well as the structure and composition of Al-Si source materials. Of all these stated factors, the properties of the Al-Si source materials and the concentration of alkaline solutions are believed to be dominant.

After being leached from the surface of Al-Si particles, Al and Si species diffuse into the gel phase, which reduces the concentrations of Al and Si species at the Al-Si particle surfaces and therefore stimulates the further leaching of Al and Si. During the diffusion step, the time and intensity of stirring are dominant factors. Longer leaching period and a more intense stirring can maximally remove dissolved Al and Si
complexes from the surface and kinetically break the barrier between the Al-Si particle surface and the gel phase so as to accelerate diffusion of Al and Si complexes.

One of the essential reactants in geopolymerisation is added silicates (whether solid or liquid), which makes Si complexes more amenable to polymerisation with aluminate once Al leaches from the Al-Si surface. Since the activation energy for forming an Al-O-Si linkage is lower than forming a Si-O-Si linkage (Barrer, 1982), polymerisation between Al complexes and Si complexes takes preference to the polymerisation between Si complexes. Therefore, a simultaneous condensation between Al and Si complexes occurs along with leaching and diffusion of Al and Si complexes from Al-Si materials. Factors affecting the polymerisation between Al and Si complexes will affect the condensation of Al and Si complexes during geopolymerisation. It has been discussed in section 2.3.2 that temperature, pH and cations are the three major factors to affect synthesis of zeolite. It is believed that these three factors affect geopolymerisation greatly as well. A higher temperature, higher pH (or higher concentration of alkaline solution) and alkali metal cation with a larger atomic size stimulate the condensation step and so promote the geopolymerisation to a complete stage.

The hardening step is a particular process occurring in geopolymerisation, which differs from the drying and hardening steps in zeolite synthesis. During the drying and hardening step of zeolite synthesis, no chemical reaction is involved, but only evaporation of water. However, during the hardening of geopolymerisation, although there is no obvious movement of particles at this stage, leaching and diffusion between particle surfaces and the gel phase may still occur and a slight movement of paste in capillary pores may also take place. Temperature and air circulation are two main factors determining whether geopolymeric products have higher mechanical strength or possess cracks.

2.4.4 Analytical methods used in geopolymerisation

Davidovits (1991; 1994) applied X-ray diffraction and $^{27}$Al and $^{29}$Si MAS-NMR techniques in the analysis of geopolymeric products. The results of X-ray diffraction analysis on geopolymers showed that only an amorphous phase exists in
geopolymeric binders synthesised by Davidovits and his team (Davidovits, 1991). By using $^{27}$Al and $^{29}$Si MAS-NMR, Al and Si are found to possess four fold coordination irrespective of the coordination of Al in the starting Al-Si materials (Davidovits, 1991; 1994). During the early studies of geopolymerisation, a complete conversion of Al-Si reactants from the solid phase to an amorphous geopolymeric binder has been assumed, so that the composition of geopolymeric binder can be simply obtained from the composition of reactants and the stoichiometry of the geopolymeric reactions (Davidovits, 1991; 1994). Therefore, with the assumption that all Al-Si starting materials have been geopolymerised and transferred into geopolymers, the characterisation of the geopolymeric products is simplified. X-ray diffraction technique can be used for detecting any crystal structure of the geopolymer and MAS-NMR analysis shows the coordination of Al and Si atoms in the three dimensional structure. Also, the composition of geopolymer can be obtained easily from the compositions of reactants and the stoichiometry of geopolymeric reactions.

For geopolymers comprising both amorphous gel phase and crystalline Al-Si resource materials, the characterisation becomes complicated and more techniques, as a result, will be applied. It has been mentioned in section 2.4.3 that geopolymerisation includes leaching, diffusion, condensation and hardening steps. Therefore, in this thesis ICP, XRF, XRD, SEM, TEM, HREM and compressive strength tests are used to analyse and characterise the reactants as well as geopolymeric products.

ICP technique is used for the analysis of leaching extent of the Al-Si reactants. It is believed that a higher leaching extent of the starting Al-Si materials will generate a condensed gel phase faster so as to have a higher extent of geopolymerisation. For the Al-Si minerals studied in this thesis, including fifteen natural Al-Si minerals, three industrial minerals, i.e. kaolinite, Na-feldspar and K-feldspar, their leaching behaviour is investigated prior to the study of their geopolymerisation.

XRD is a powerful tool for detecting the crystalline phases comprised in both Al-Si reactants and in formed geopolymers. $^{27}$Al and $^{29}$Si MAS NMR spectra can be used to interpret the coordination of Al and Si in either Al-Si reactants or geopolymers. So XRD or $^{27}$Al and $^{29}$Si MAS NMR or the combination of both has been applied in the
thesis for the structural composition analysis of the geopolymers as well as the identification of the Al-Si reactants.

XRF analysis has been conducted for all the Al-Si minerals investigated in the thesis in order to obtain their chemical composition. For geopolymers synthesised, their gel phases are analysed by SEM/EDX or TEM/EDX techniques for the composition or the molar ratio of Si/Al.

Throughout this thesis, the compressive strength of geopolymers is used as the measurement for successful geopolymers with higher MPa values and failed geopolymers with lower MPa values. However, there are no absolute standard MPa values that have been set for good or bad geopolymerisations. The discussion in the following chapters is presented on the base of the comparison of geopolymers with different compressive strength obtained from the different conditions.

2.5 NOVELTY OF THE THESIS

As indicated in formula 2.10, theoretically, any Al-Si containing materials might become the source for geopolymerisation. Natural Al-Si minerals, which consist of more than 75% of the earth shell, are certainly the largest Al-Si source existing in the world. However, there are no studies conducted on these potential materials until 1998, when the author of this thesis started a systematic investigation. The research conducted in this thesis covers not only the geopolymerisation of natural Al-Si minerals, but also other fundamental aspects, such as sample characterisation, factors affecting the geopolymerisation and the quantum modelling of dissolution. The novelty of this thesis can be summarised as:

1) It is the first time that natural Al-Si minerals and alkali-feldspars are used as the main Al-Si source for geopolymerisation. The obtained positive results indicate that natural Al-Si minerals and alkali-feldspars have a high potential to be applied in the geopolymer industry.

2) The relationship between the leachability of the Al-Si minerals and their ability to undergo geopolymerisation is established. Geopolymerisation starts
from the leaching of the Al-Si reactants. The higher the leaching ability of the Al-Si reactants, the thicker the gel generated, hence a higher extent of the geopolymerisation will be obtained. Despite such a phenomenon being noticed by previous researchers (Van Jaarsveld et al., 1999), the direct linkage between leaching and geopolymerisation is first applied in this thesis.

3) The factors that affect the geopolymerisation of Al-Si minerals are studied in detail. Van Jaarsveld and Van Deventer (1999a) have investigated the effect of alkali metal cations on fly ash based geopolymers. In addition to the factors of alkali metal cations, the alkalinity, setting pressure and sample preparing procedure are investigated in this thesis.

4) It is the first attempt to interpret the mechanisms involved in leaching and geopolymerisation by the cation-anion ion pair theory. Before 1997, there were no researches carried out on the mechanisms involved in geopolymerisation. Van Jaarsveld and Van Deventer (1999a) indicated that alkali cations influenced the geopolymerisation of fly ash by directing water molecules. The work conducted in this thesis shows that the cation-anion ion pair theory can better explain the observations obtained from both leaching and geopolymerisation.

5) It is the first attempt to look at the effect of alkali metals structured in the Al-Si minerals on the geopolymerisation. The researches done previously by Van Jaarsveld and Van Deventer (1999a) and recently by the author (Xu and Van Deventer, 2000a) indicate that alkali metal cations affect the geopolymerisation significantly. The alkali metals are also found to be structured in most natural Al-Si minerals. So an investigation on the interaction between alkali metal cations in alkaline solutions and the alkali metals structured in Al-Si minerals will aid the further understanding of the geopolymerisation of Al-Si minerals, which will benefit the design of geopolymeric reactions and the prediction of the properties for geopolymers produced.

6) The techniques of XRD, XRF, MAS NMR, SEM/EDX, TEM/EDX and HREM are combined to semi-quantitatively characterise the Al-Si reactants as well as the geopolymers. Davidovits (1991; 1994) has characterised the geopolymeric binder products by using XRD and MAS NMR techniques. Polomo together with his team (1992a, 1992b) conducted the characterisation
on geopolymers by DTA and SEM analyses. However, neither the work done by Davidovits, nor the characterisation carried out by Polomo's team does aim at the semi-quantitative characterisation of the geopolymers whose structure comprises both amorphous gel phase and crystalline reactant particles. The characterising method established in this thesis can also be applied in related research, such as cement and concrete.

7) Quantum chemical calculations are first applied to model the dissolution of the framework structured Al-Si mineral, stilbite. Geopolymerisation consists of dissolution, transportation, condensation and hardening steps as indicated by Davidovits as disaggregation, digestion, geopolymerisation and setting (Davidovits, et al. 1994). The formed geopolymers are the mixtures of amorphous gel phase and undissolved crystalline reactant particles. Due to the uncertainties and complexities involved in both geopolymerisation and geopolymers, modelling of geopolymerisation has not been conducted previously. The first step of the geopolymerisation, i.e. dissolution, is successfully modelled with an initial attempt of modelling geopolymerisation at a quantum calculation grade. Quantum chemical calculations are applied in this thesis to study the geopolymeric precursors formation energies and to verify the ion pair theory as well.

This thesis establishes an understanding of the geopolymerisation of natural Al-Si minerals, which is significant for the potential commercialisation of the geopolymerisation technique. It proposes systematic analytical methods for reactants and formed geopolymers that will benefit all kinds of geopolymerisation studies. The quantum chemical calculations conducted in the thesis provide a powerful tool for the theoretical modelling of this complicated polymerisation system.
Table 2.1. The structural and physical properties of selected alumino-silicate minerals (Deer et al., 1992; Nickel and Nichols, 1991; Dunn et al., 1978; Passaglia and Gottardi, 1973)

<table>
<thead>
<tr>
<th>Ortho- and ring</th>
<th>Formula</th>
<th>Average density (g/cm³)</th>
<th>Average hardness (Mohs)</th>
<th>Al-O* bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Almandine</td>
<td>Fe₂Al₂(SiO₄)₃</td>
<td>4.3</td>
<td>7.0</td>
<td>O</td>
</tr>
<tr>
<td>Grossular</td>
<td>Ca₂Al₂(SiO₄)₃</td>
<td>3.55</td>
<td>7.0</td>
<td>O</td>
</tr>
<tr>
<td>Pumpellyite-Fe³⁺</td>
<td>Ca₃Fe⁺³Al₂(SiO₄(Si₂O₇)(OH₂O)₂•H₂O</td>
<td>3.35</td>
<td>5.5</td>
<td>O</td>
</tr>
<tr>
<td>Sillimanite</td>
<td>Al₂SiO₅</td>
<td>3.25</td>
<td>7</td>
<td>T + O</td>
</tr>
<tr>
<td>Mullite</td>
<td>Al₆Si₂O₁₃</td>
<td>3.18</td>
<td>6.5</td>
<td>O</td>
</tr>
<tr>
<td>Andalusite</td>
<td>Al₂SiO₅</td>
<td>3.15</td>
<td>7</td>
<td>O</td>
</tr>
<tr>
<td>Kyanite</td>
<td>Al₂SiO₅</td>
<td>3.59</td>
<td>6.3</td>
<td>O</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>3.48</td>
<td>6.6</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chain</th>
<th>Formula</th>
<th>Average density (g/cm³)</th>
<th>Average hardness (Mohs)</th>
<th>Al-O* bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Augite</td>
<td>(Ca,Mg,Fe)₂(Si,Al)₂O₆</td>
<td>3.3</td>
<td>5.7</td>
<td>T</td>
</tr>
<tr>
<td>Spodumene</td>
<td>LiAl₂Si₂O₆</td>
<td>3.1</td>
<td>6.7</td>
<td>T</td>
</tr>
<tr>
<td>Sapphirine-2M</td>
<td>Mg₇Al₁₈Si₃O₄₀</td>
<td>3.45</td>
<td>7.5</td>
<td>T + O</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>3.28</td>
<td>6.6</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sheet</th>
<th>Formula</th>
<th>Average density (g/cm³)</th>
<th>Average hardness (Mohs)</th>
<th>Al-O* bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lepidolite-M</td>
<td>K(Li,Al)₂(Si,Al)₂O₆(F₂OH)₂</td>
<td>2.84</td>
<td>3.2</td>
<td>T</td>
</tr>
<tr>
<td>Lithiophane</td>
<td>(K₂H₂O)Al₂(Si₃Al)O₁₀(H₂O₂OH)₂</td>
<td>2.7</td>
<td>1.5</td>
<td>T</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₂Si₂O₅(OH)₄</td>
<td>2.62</td>
<td>2.3</td>
<td>O</td>
</tr>
<tr>
<td>Muscovite-1M</td>
<td>KAl₂(Si₃Al)O₁₀(OH,F)₂</td>
<td>2.8</td>
<td>2.7</td>
<td>T</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>2.74</td>
<td>2.4</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Frameworks</th>
<th>Formula</th>
<th>Average density (g/cm³)</th>
<th>Average hardness (Mohs)</th>
<th>Al-O* bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Celsian</td>
<td>BaAl₂Si₂O₆</td>
<td>3.38</td>
<td>6.25</td>
<td>T</td>
</tr>
<tr>
<td>Sodalite</td>
<td>Na₆(Si₃Al₃)O₁₂Cl</td>
<td>2.25</td>
<td>5.7</td>
<td>T</td>
</tr>
<tr>
<td>Stilbite</td>
<td>Na₁Ca₁(Si₂Al₄)O₇₂•H₂O</td>
<td>2.2</td>
<td>3.7</td>
<td>T</td>
</tr>
<tr>
<td>Heulandite</td>
<td>(Na₆K₆Ca₆Sr₆Ba₆)(Al₂Si₁₇)O₇₂•26H₂O</td>
<td>2.2</td>
<td>3.7</td>
<td>T</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>KCa₂Si₂O₂₀(OH,F)·8H₂O</td>
<td>2.36</td>
<td>4.75</td>
<td>T</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl₂Si₂O₈</td>
<td>2.76</td>
<td>6.25</td>
<td>T</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td>2.53</td>
<td>5.1</td>
<td></td>
</tr>
</tbody>
</table>

*: "T" refers to tetrahedrally structured Al-O and "O" represents octahedrally structured Al-O.
Table 2.2 Equilibrium reactions for various silicate species at 25°C (Lindsay, 1979)

<table>
<thead>
<tr>
<th>Equilibrium Reaction</th>
<th>log ( K^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2) Minerals</td>
<td></td>
</tr>
<tr>
<td>SiO(_2) (silica glass) + 2H(_2)O ⇄ H(_4)SiO(_4)^\circ)</td>
<td>-2.71</td>
</tr>
<tr>
<td>SiO(_2) (amorph) + 2H(_2)O ⇄ H(_4)SiO(_4)^\circ)</td>
<td>-2.74</td>
</tr>
<tr>
<td>SiO(_2) (coesite) + 2H(_2)O ⇄ H(_4)SiO(_4)^\circ)</td>
<td>-3.05</td>
</tr>
<tr>
<td>SiO(_2) (soil) + 2H(_2)O ⇄ H(_4)SiO(_4)^\circ)</td>
<td>-3.10</td>
</tr>
<tr>
<td>α-SiO(_2) (tridymite) + 2H(_2)O ⇄ H(_4)SiO(_4)^\circ)</td>
<td>-3.76</td>
</tr>
<tr>
<td>α-SiO(_2) (cristobalite) + 2H(_2)O ⇄ H(_4)SiO(_4)^\circ)</td>
<td>-3.94</td>
</tr>
<tr>
<td>α-SiO(_2) (quartz) + 2H(_2)O ⇄ H(_4)SiO(_4)^\circ)</td>
<td>-4.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Silicate ions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_4)SiO(_4)^\circ) ⇄ H(_3)SiO(_4)^\circ + H(^+)</td>
<td>-9.71</td>
</tr>
<tr>
<td>H(_4)SiO(_4)^\circ) ⇄ H(_3)SiO(_4)^(^+) + 2H(^+)</td>
<td>-22.98</td>
</tr>
<tr>
<td>H(_4)SiO(_4)^\circ) ⇄ HSiO(_4)^(^+) + 3H(^+)</td>
<td>-32.85</td>
</tr>
<tr>
<td>H(_4)SiO(_4)^\circ) ⇄ SiO(_4)^(^+) + 4H(^+)</td>
<td>-45.95</td>
</tr>
<tr>
<td>4H(_4)SiO(_4)^\circ) ⇄ H(_6)Si(<em>6)O(</em>{12})^(^2+) + 2H(^+) + 4H(_2)O</td>
<td>-13.32</td>
</tr>
</tbody>
</table>

\( K^\circ \) represents equilibrium in terms of activity.
H\(_4\)SiO\(_4\)^\circ\) represents aqueous state with no charge.
Table 2.3 Equilibrium reactions of aluminium minerals and complexes at 25°C  
(Lindsay, 1979)

<table>
<thead>
<tr>
<th>Equilibrium reaction</th>
<th>log $K^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides and hydroxides</td>
<td></td>
</tr>
<tr>
<td>0.5$\gamma$-Al$_2$O$_3$ (c) + 3H$^+$ ⇌ Al$^{3+}$ + 1.5H$_2$O</td>
<td>11.49</td>
</tr>
<tr>
<td>0.5$\alpha$-Al$_2$O$_3$ (corundum) + 3H$^+$ ⇌ Al$^{3+}$ + 1.5H$_2$O</td>
<td>9.73</td>
</tr>
<tr>
<td>Al(OH)$_3$ (amorph) + 3H$^+$ ⇌ Al$^{3+}$ + 3H$_2$O</td>
<td>9.66</td>
</tr>
<tr>
<td>$\alpha$-Al(OH)$_3$ (bayerite) + 3H$^+$ ⇌ Al$^{3+}$ + 3H$_2$O</td>
<td>8.51</td>
</tr>
<tr>
<td>$\gamma$-AlOOH (boehmite) + 3H$^+$ ⇌ Al$^{3+}$ + 2H$_2$O</td>
<td>8.13</td>
</tr>
<tr>
<td>Al(OH)$_3$ (norstrandite) + 3H$^+$ ⇌ Al$^{3+}$ + 3H$_2$O</td>
<td>8.13</td>
</tr>
<tr>
<td>$\gamma$-Al(OH)$_3$ (gibbsite) + 3H$^+$ ⇌ Al$^{3+}$ + 3H$_2$O</td>
<td>8.04</td>
</tr>
<tr>
<td>$\alpha$-AlOOH (diaspore) + 3H$^+$ ⇌ Al$^{3+}$ + 2H$_2$O</td>
<td>7.92</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td></td>
</tr>
<tr>
<td>Al$^{3+}$ + H$_2$O ⇌ AlOH$^{2+}$ + H$^+$</td>
<td>-5.02</td>
</tr>
<tr>
<td>Al$^{3+}$ + 2H$_2$O ⇌ Al(OH)$_2^{2+}$ + 2H$^+$</td>
<td>-9.3</td>
</tr>
<tr>
<td>Al$^{3+}$ + 3H$_2$O ⇌ Al(OH)$_3^{3+}$ + 3H$^+$</td>
<td>-14.99</td>
</tr>
<tr>
<td>Al$^{3+}$ + 4H$_2$O ⇌ Al(OH)$_4^{4+}$ + 4H$^+$</td>
<td>-23.33</td>
</tr>
<tr>
<td>Al$^{3+}$ + 5H$_2$O ⇌ Al(OH)$_5^{5+}$ + 5H$^+$</td>
<td>-34.24</td>
</tr>
<tr>
<td>2Al$^{3+}$ + 2H$_2$O ⇌ Al$_2$(OH)$_4^{2+}$ + 2H$^+$</td>
<td>-7.69</td>
</tr>
</tbody>
</table>

$K^\circ$ represents equilibrium in terms of activity.  
Al(OH)$_3^\circ$ represents aqueous state with no charge.

Table 2.4 Equilibrium reactions of selected aluminosilicates at 25 °C  
(Lindsay, 1979)

<table>
<thead>
<tr>
<th>Equilibrium reaction</th>
<th>log $K^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$SiO$_5$ (sillimanite) + 6H$^+$ ⇌ 2Al$^{3+}$ + H$_2$SiO$_4^\circ$ + H$_2$O</td>
<td>15.45</td>
</tr>
<tr>
<td>Al$_2$SiO$_5$ (kyanite) + 6H$^+$ ⇌ 2Al$^{3+}$ + H$_2$SiO$_4^\circ$ + H$_2$O</td>
<td>15.12</td>
</tr>
<tr>
<td>Al$_2$SiO$_5$ (andalusite) + 6H$^+$ ⇌ 2Al$^{3+}$ + H$_2$SiO$_4^\circ$ + H$_2$O</td>
<td>14.48</td>
</tr>
<tr>
<td>Al$_2$Si$_2$O$_5$ (OH)$_4$ (halloysite) + 6H$^+$ ⇌ 2Al$^{3+}$ + 2H$_2$SiO$_4^\circ$ + H$_2$O</td>
<td>8.72</td>
</tr>
<tr>
<td>Al$_2$Si$_2$O$_5$ (OH)$_4$ (dickite) + 6H$^+$ ⇌ 2Al$^{3+}$ + 2H$_2$SiO$_4^\circ$ + H$_2$O</td>
<td>5.95</td>
</tr>
<tr>
<td>Al$_2$Si$_2$O$_5$ (OH)$_4$ (kaolinite) + 6H$^+$ ⇌ 2Al$^{3+}$ + 2H$_2$SiO$_4^\circ$ + H$_2$O</td>
<td>5.45</td>
</tr>
</tbody>
</table>

$K^\circ$ represents equilibrium in terms of activity.  
H$_2$SiO$_4^\circ$ represents aqueous state with no charge.
Table 2.5 Conditions of curves A, B, C, D, E and F in Figure 2.7

<table>
<thead>
<tr>
<th>Curve</th>
<th>Temperature (°C)</th>
<th>SiO₂:Na₂O</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>90</td>
<td>97</td>
<td>8.8-9.7</td>
</tr>
<tr>
<td>B</td>
<td>90</td>
<td>186</td>
<td>7.9-9.7</td>
</tr>
<tr>
<td>C</td>
<td>90</td>
<td>470</td>
<td>7.1-8.1</td>
</tr>
<tr>
<td>D</td>
<td>50</td>
<td>97</td>
<td>8.8-9.0</td>
</tr>
<tr>
<td>E</td>
<td>50</td>
<td>186</td>
<td>7.9-8.4</td>
</tr>
<tr>
<td>F</td>
<td>50</td>
<td>470</td>
<td>7.1-7.5</td>
</tr>
</tbody>
</table>

Table 2.6 Analysis of publications on geopolymerisation and geopolymeric products

<table>
<thead>
<tr>
<th>Time period</th>
<th>Total</th>
<th>Journal %</th>
<th>Patent %</th>
<th>Davidovits (France)%</th>
<th>Van Deventer (Australia) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1979-1995</td>
<td>50</td>
<td>40</td>
<td>60</td>
<td>52</td>
<td>0</td>
</tr>
<tr>
<td>1996-2001</td>
<td>41</td>
<td>68.3</td>
<td>31.7</td>
<td>9.8</td>
<td>24.4</td>
</tr>
</tbody>
</table>
### Table 2.7 The comparison between synthesis of zeolite and geopolymerisation

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Synthesis of zeolite</th>
<th>Geopolymerisation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al complexes solution + Si complexes solution</td>
<td>Al-Si solid source material + Alkaline solution + silicates (solid or liquid)</td>
</tr>
<tr>
<td>Early stage of reaction</td>
<td>Nucleation in solution</td>
<td>Leaching of Al-Si solid into paste</td>
</tr>
<tr>
<td>Later stage of reaction</td>
<td>Crystal growth in solution</td>
<td>Diffusion and condensation of leached Al and Si complexes in paste</td>
</tr>
<tr>
<td>Temperature</td>
<td>90 –300 °C</td>
<td>Ambient</td>
</tr>
<tr>
<td>pH</td>
<td>6-11</td>
<td>14</td>
</tr>
<tr>
<td>Product</td>
<td>Crystalline Zeolite</td>
<td>Mixture of gel and Al-Si solid source materials</td>
</tr>
<tr>
<td>Composition</td>
<td>Certain stoichiometric formula</td>
<td>No certain stoichiometric composition</td>
</tr>
<tr>
<td>Structure</td>
<td>Unique crystal</td>
<td>Mixture of amorphous to semi-crystalline gel phase and crystalline Al-Si source materials</td>
</tr>
<tr>
<td>Mechanical strength</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>
Figure 2.1 Projection of idealised kaolinite layer on (001) (Deer, et al. 1992).
Figure 2.2 The structure of kaolinite as viewed along $y$ and $x$ axes showing the stacking of layers in the $x$ and $y$ directions respectively (Deer et al., 1992).
Figure 2.3 Idealised illustrations of the feldspar “chain” (Deer, et al. 1992).
Figure 2.4 The framework of tetrahedral groups in the structure of sodalite (Deer, et al. 1992).
Figure 2.5 The solubility of selected aluminosilicate minerals compared to Al(OH)$_3$
(Iler, 1979)
Figure 2.6 The effect of pH on the gelling of silica sols. Curve ABC is in the absence of sodium salts; curve DEF is in the presence of sodium salts (Iler, 1979)
Figure 2.7 Rate of growth of silica particles at 50 °C and 90 °C and different pH values. The conditions of A, B, C, D, E and F are listed in Table 2.5. (Iler, 1979)
Figure 2.8 Possible bonding between silica particles through coordination with flocculating metal cations. (a) Hydroxyl ion transfers negative charge to water layer hydrogen-bonded to silanol groups on particle surface; equivalent to adsorption of a hydroxyl ion; (b) hydrated sodium ion is adsorbed at negative site forming neutral complex; (c) collision with uncharged area of a second particle permits sodium ion to coordinate with oxygens of silanol and surface-bonded water, forming a coordination linkage between particles. Note: circles represent oxygen atoms (Iler, 1979).
Figure 2.9 Effect of concentration of KOH solution upon the ratio SiO$_2$/Al$_2$O$_3$ in the resultant crystals. The products are primarily chabazite type K-G and edingtonite type K-F (Barrer and Mainwaring, 1972).
Figure 2.10 Effect of the volume of KOH solution of constant concentration upon the yield of crystallisation products from metakaolinite. ○, 1M KOH, giving chabazite type K-G; △, 6M KOH, giving edingtonite type K-F (Barrer and Mainwaring, 1972).
Figure 2.11 The SEM image of geopolymer synthesised from fly ash, kaolinite and Na-feldspar at mass ratio of 4:1:2. “A” represents fly ash particles, “B” represents Na-feldspar particles and “C” represents gel.
CHAPTER THREE

MATERIALS AND EXPERIMENTAL METHODS

The Al-Si minerals investigated in this thesis include natural Al-Si minerals (pieces of rocks) and industrial Al-Si minerals, i.e. kaolinite, Na-feldspar and K-feldspar (powder samples in 25kg/bag). The methods used to characterise andanalyse these Al-Si minerals as well as geopolymers include leaching, compressive strength testing, Brunauer-Emmett-Teller surface area (BET), particle size analysis, X-ray diffractogram (XRD), X-ray fluorescence (XRF), inductively coupled plasma (ICP), magic angle spinning nuclear magnetic resonance (MAS NMR), Fourier Transform Infrared spectra (FT-IR), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). This chapter will give a detailed discussion on materials, instruments and methodologies applied in both geopolymerisation and analysis conducted in this thesis.

3.1 MATERIALS

3.1.1 Al-Si minerals

Fifteen natural Al-Si minerals, i.e. almandine, grossular, sillimanite, andalusite, kyanite, pumpellyite, spodumene, augite, lepidolite, illite, celsian, sodalite, stilbite, heulandite and anorthite have been bought from “Geological Specimen Supplies”, Turramurra, NSW, Australia at a rough size of 5cm × 5cm × 5cm. After being crushed, the natural Al-Si minerals are picked by hand to avoid undesirable paragenesis and then ground and sieved to −212 μm.

Kaolinite, grade HR1/F, has been purchased from Commercial Minerals, Australia and has a particle size of 50% less than 0.5 μm and 1% greater than 38 μm. Soda and potash feldspars are obtained from Minerals Corporation Ltd., Broken Hill, NSW, Australia. Both Na-feldspar and K-feldspar have a particle size of 100% less than 53
μm. The chemical composition of kaolinite, Na-feldspar and K-feldspar is listed in Table 3.1.

### 3.1.2 Chemicals

Sodium silicate (Vitrosol N40) and potassium silicate (Kasil 2236) solutions are supplied by PQ Australia Pty. Ltd., Victoria, Australia. The average composition, density and viscosity of sodium silicate and potassium silicate are presented in Table 3.2. Analytical grade chemicals and distilled water are used throughout the geopolymerisation and chemical analyses.

### 3.1.3 Moulds

There are two kinds of moulds used during the geopolymerisation carried out in this thesis. Due to the difficulties to obtain a large quantity of natural Al-Si minerals with satisfactory homogeneous properties, a small cubic stainless steel mould, measuring as 20mm × 20mm × 20mm, is used during the geopolymerisation of those fifteen natural Al-Si minerals. A polyvinyl chloride (PVC) cylinder mould with 50mm (diameter) × 100mm (height) is used to cast the geopolymers synthesised from kaolinite, Na-feldspar and K-feldspar.

### 3.2 EXPERIMENTAL METHODS

#### 3.2.1 Leaching

A specified mass of Al-Si minerals (± 0.01) is mixed with NaOH or KOH solution in a polypropylene beaker (100ml or 150ml) at room temperature for certain hours using a magnetic stirrer (Teflon covered octagon stirring bar measured as 3/2 × 5/16 inches). After centrifuging, the clear liquid part of the solution (about 5 to 10ml) is diluted to 0.1 or 0.2 M alkaline concentrations and neutralised by condensed HCl to pH < 1. A Perkin-Elmer Optima 3000 ICP-OES is used to analyse for concentrations of silicon and aluminium leached into the alkaline solution. Scandium is used as an internal standard for ICP analysis during the tests of fifteen natural Al-Si minerals.
Since a comparing trial on the leaching samples with and without Sc shows the results to be very close, Sc is not used in the ICP analysis for the other Al-Si minerals (kaolinite, Na-feldspar and K-feldspar).

3.2.2 Geopolymerisation

Two or three Al-Si minerals are dry mixed at specified mass ratios for 5 to 10 minutes in a container by hand or by a FRITSCH Vibratory Shaker before the addition of MOH and M$_2$SiO$_3$ solution (where M = Na and/or K). The subsequent mixture is shaken by a FRITSCH Vibratory Shaker for another 3 to 5 minutes. The resulting paste is then transferred to a mould and left in an oven for setting at 35°C, 40°C or 45°C for 24 or 48 hours. After being removed from the mould, the sample is left in the oven for further setting and hardening at 35°C, 40°C or 45°C for 3 or 7 or 28 days. After this time, the compressive strength of each sample is tested using a Tinus Tolsen or an Amsler FM 2750 Compressive Strength testing machine. Two or three samples of each condition are tested, with average compressive strength values reported as the results.

3.3 ANALYTICAL TECHNIQUES

3.3.1 X-ray fluorescence spectroscopy (XRF)

X-ray fluorescence spectrometry is used for elemental analysis of Al-Si minerals. The Siemens SRS 3000 sequential X-ray fluorescence spectrophotometer driven by dedicated hardware and software is used in this thesis. X-rays of the machine are generated by a Ph-anode tube with diffraction of LiF100, LiF110, OVO55 and PET crystals being applied. Either or both scintillation or argon flow counter detectors installed are used to collect the signals. The equipment is capable of measuring elements above atomic number 8 with a detection limit typically of the order of 5 ppm. Both major and trace elements are analysed on a single sample powder fused bead. Each element analysis is fully corrected for line interference and matrix effects of all the other analysed elements.
3.3.1.1 Sample preparation and analysis for XRF

Dry Al-Si minerals powder (3 to 4 grams) is heated in a porcelain crucible at 105 °C overnight. After cooling to room temperature, 1.00000 (±0.00001 gram) gram of sample powder is weighted into a vial with 5.00000 (±0.00001 gram) gram of pure lithium metaborate (LiBO₂) powder. The LiBO₂ powder must be pre-dried overnight in a furnace at 500 °C. Approximately 0.2 to 0.4 grams ammonium nitrate (for oxidisation of sulphur) are added into the vial and homogenised by rolling the vial. Using tongs, the platinum crucible is placed in a preheated furnace (600 °C) for 5 to 10 minutes until all brown vapours from ammonium nitrite are expelled. Then the furnace is turned up to 999 °C to melt the sample for 10 to 15 minutes.

The sample is removed from the furnace to a Meke burner to expel the bubbles by rolling the crucible gently. Then the sample is re-melted in the furnace at 999 °C for 5 to 10 minutes before it is brought to the Meke burner again. The melted sample is then poured vigorously into a graphite mould. After 20 minutes, the sample is dumped out of its mould and left on a hotplate for annealing overnight.

The glass disc for XRF analysis is prepared by using a steel file to file off excess glass from the rims. Then the disc will be washed with ethanol and pad dried with tissue paper before it can be put into the steel sample holder and subjected to XRF analysis.

In every routine analytical run, one sample is chosen at random for every 20 samples and analysed in duplicate. This provides a measure of the reproducibility or precision or the analytical procedure. Machine drift is monitored, and corrected, by the routine running of a commercial monitor sample containing appropriate levels of all elements of interest. Accuracy is estimated by the analysis of a well characterised in-house sample of a composition which most closely approximates the unknown samples.

3.3.2 Powder X-ray diffraction (XRD)

Fifteen natural Al-Si minerals, three industrial Al-Si minerals and some selected geopolymers have been analysed by XRD for the identification of their crystalline
phases. The Phillips PW1800 has a fully integrated Automatic Powder Diffraction System that consists of a high speed, high precision goniometer, high efficiency generator and automatic sample loading facility. X-rays are generated by a copper anode tube. The system of XRD is fitted with a graphite monochromator. 0.5 to 1.0 gram of sample is packed into a specially modified sample holder. The Al-Si minerals discussed in this thesis are analysed by Cu Kα radiation and scanned at the rate of 0.02° 2θ/sec. from 5 to 70° with step of 0.5 and counting time of 2 seconds. The obtained spectra were characterised using XPLOT™ and identified by comparing diffraction patterns to JCPDS (Joint Committee on Powder Diffraction Standards) data.

3.3.3 Magic angle spinning nuclear magnetic resonance (MAS NMR)

The ²⁹Si and ²⁷Al MAS NMR responses are used to detect the structural environment for Al and Si in both Al-Si minerals and geopolymers. The ²⁹Si and ²⁷Al spectra are recorded at 59.61 and 18.18 MHz on a Varian 300/solid-state spectrometer that employs magic angle spinning at 6.9 kHz. The obtained NMR peaks are fitted using Gaussian lines. The powdered samples are prepared by packing a certain amount of powder into a 7 mm zirconium rotor.

3.3.4 Fourier Transform Infrared spectra (FTIR)

The infrared spectra of the ground samples are recorded as the photoacoustic spectra on a Bio-Rad FTS-60A FTIR spectrometer with scan speed selected as 2.5 kHz. The applied aperture is 2 cm⁻¹ for all the tests. Well crystallised carbon is used as the background and 256 scans and 4500 points are collected for a single spectrum.

3.3.5 Differential scanning calorimeter (DSC)

A TA Instruments 2920 Modulated DSC is utilised to gain DSC thermograms in conjunction with the Thermal Solution software. The powdered samples are placed inside aluminium hermetic pans and scanned from −50 to 250 or 300 °C, respectively.
3.3.6 Transmission electron microscopy (TEM), energy dispersive X-ray microanalyser (TEM/EDX) and High resolution transmission electron microscopy (HREM)

Geopolymers are the mixtures of amorphous gel phase and crystalline particles in which the gel phase cannot be separated from the particles and so as to be analysed by traditional experimental methods. Hence TEM, TEM/EDX and HREM techniques are applied in the thesis for identification of crystalline particles as well as the elemental analysis of the gel phases in geopolymers.

Sample preparation for TEM and HRTEM analysis consists of grinding bulk specimens and depositing fine particles from an alcohol suspension on carbon-covered copper grids. The size range of particles analysed is 500 to 1000 nm so that the adsorption of fluorescence and X-ray from specimen can be neglected.

TEM and TEM/EDX analyses are conducted on a Phillips EM 420 electron transmission microscopy at the accelerating voltage of 100 kV. The diameter of the electron beam and the probe current are varied to give a machine dead time of approximately 30%. The X-ray counts are obtained by integrating Kα X-ray peaks using an EDAX PV 9900 energy dispersive X-ray microanalyser. Background subtraction is effected by manually selecting one background level close to the peak in question and subtracting this value from each channel integrated. The spectra are accumulated for 100 seconds to decrease the errors arising from the counting statistics. The results are processed following principles first proposed by Cliff and Lorimer (1975). The accuracy of the system is tested with kaolinite (CMS KGa-1, obtained from the Department of Geology, University of Missouri, Columbia, Missouri, U.S.A) and the systematic error is found to be less than 5% compared to the ideal composition of the kaolinite (CMS KGa-1).

A JEOL LEM-400EX high resolution electron transmission microscopy is used to observe the micro structure of geopolymers at lattice grade. The accelerating voltage of 300 kV and the bright current of lower than 95.1 μA are employed throughout the investigation.
3.3.7 Scanning electron microscopy (SEM), energy dispersive X-ray microanalyser (SEM/EDX) and field emission gun scanning electron microscopy (FEG SEM)

SEM and SEM/EDX analyses are the key tools for investigation of fractured surfaces of geopolymers. They are also handy and powerful for the elemental analysis of the gel phases in geopolymers.

Sample preparation for SEM, SEM/EDX and FEG SEM analyses follows the same procedure. The samples are placed on the sample holders that are supported by carbon conductive paint, and then undergo 1 minute sputter coating of gold (for image analysis) or carbon (for elemental analysis) to make the sample surface conductive.

A JEOL JSM-840 microscope with Tracor Northern EDAX system is used for SEM/EDX analysis at the accelerating voltage of 20 kV. A JEOL JSM-6300 Field Emission Gun Scanning Electron Microscope is used for image observation of the samples at the accelerating voltage of 5 kV. A Phillips XL30 SEM coupled with an Oxford energy dispersive spectrometer is also used for SEM and BEM (back scattered electron microscopy) images as well as elemental analysis at the accelerating voltage of 20 kV.

3.3.8 Inductively coupled plasma spectroscopy (ICP OES)

The leaching solutions of Al-Si minerals are analysed by a Perkin Elmer Optima 3000 inductively coupled plasma spectrometer (ICP OES). Spectral lines used are Si: 288.158 nm and Al 309.271 nm. All samples tested contain Si lower than the maximum solubility of amorphous silica about 500 ppm (Barrer, 1982), so that no gelling occurred during the ICP analysis.

3.3.9 Specific surface area

The Brunauer-Emmett-Teller (BET) surface area for kaolinite and stilbite is determined using a Micromeritics Flowsoorb ASAP 2020 apparatus with a computer interface running an MS DOS™ control program. A 30/70 mixture of N₂ and H₂ is
used as the adsorbing gas and adsorption is assumed as representative of a type I isotherm. Samples are placed in a glass tube and degassed at 95 °C for 18 hours until reaching a vacuum of around 35 mmHg. The specific surface area is determined by counting the weight loss resulting from the degassing.

3.3.10 Particle size analysis

The particle size distributions of kaolinite and stilbite are analysed by a Coulter LS 130 optical particle size analyser. Samples are added into distilled water to form a suspension with a rough concentration of 1% particle by mass. The particle sizes are measured after a sonic vibration of 5 minutes.

3.3.11 Compressive strength test

A Tinius Tolsen compressive strength testing machine is used to determine the compressive strength for the geopolymers cast by the cubic moulds (20mm ×20mm ×20mm). For geopolymers formed in cylindrical moulds (50mm diameter × 100mm height), an Amsler FM 2750 compressive strength testing apparatus is used and all the samples tested are capped one side with a thin layer of dental CaSiO₃ powder to create an accurate perpendicular surface.

3.4 SUMMARY

During the geopolymerisation conducted in this thesis, the Al-Si reactants are fine powdered materials containing both Al and Si. The ratio of solid Al-Si reactants (gram) and the mixture of alkaline and silicate solutions (ml) varies from 2.7 to 4.0. Such a high solid/liquid ratio generates a paste when the solid particles are mixed with the liquid phase. This high ratio also increases the difficulty for analysis of the formed geopolymers, because the paste contains both amorphous gel phase and the undissolved crystalline reactants. However, a combination of techniques, for instance, XRD, XRF, ICP and compressive strength test, is established in this thesis to give an understanding of the ability of Al-Si minerals to undergo geopolymerisation. Moreover, the application of the combination of XRD, XRF, MAS NMR, SEM/EDX,
TEM/EDX and HREM is found to be successful for the characterisation of both Al-Si reactants and formed geopolymers. More details on specific experimental condition are provided in each of the subsequent chapter discussing results.
Table 3.1 Mass composition of kaolinite, Na-feldspar and K-feldspar detected by XRF analysis

<table>
<thead>
<tr>
<th>Element as oxide</th>
<th>Na-Feldspar</th>
<th>K-Feldspar</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>70.9</td>
<td>67.1</td>
<td>54.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17</td>
<td>17.6</td>
<td>29.4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>9.75</td>
<td>3.16</td>
<td>0.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.43</td>
<td>10.6</td>
<td>0.2</td>
</tr>
<tr>
<td>CaO</td>
<td>0.31</td>
<td>0.18</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.07</td>
<td>0.21</td>
<td>1.4</td>
</tr>
<tr>
<td>MgO</td>
<td>0.04</td>
<td>0.04</td>
<td>0.2</td>
</tr>
<tr>
<td>MnO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>-</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.14</td>
<td>0.26</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.045</td>
<td>0.01</td>
<td>2.8</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>0.75</td>
<td>0.62</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 3.2 The composition, density and viscosity of sodium silicate and potassium silicate solutions

<table>
<thead>
<tr>
<th>Composition wt%</th>
<th>Na₂SiO₃ (Vitrosol N40)</th>
<th>K₂SiO₃ (Kasil 2236)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>8.7-9.1</td>
<td>10.8-11.2</td>
</tr>
<tr>
<td>K₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>28.4-28.9</td>
<td>24.2-24.8</td>
</tr>
<tr>
<td>Solids</td>
<td>37.1-38.0</td>
<td>35.0-36.0</td>
</tr>
<tr>
<td>Density (g/ml) at 20°C</td>
<td>1.37-1.40</td>
<td>1.31-1.33</td>
</tr>
<tr>
<td>Viscosity (Brookfield) at 20°C</td>
<td>180</td>
<td>100</td>
</tr>
</tbody>
</table>
CHAPTER FOUR

GEOPOLYMERISATION OF FIFTEEN SELECTED ALUMINOSILICATE MINERALS

This chapter is based on the publication: The geopolymerisation of alumino-silicate minerals, Int. J. Miner. Process., 59 (2000), 247-266.

Geopolymers are similar to zeolites in chemical composition, but reveal an amorphous microstructure. They form by the co-polymerisation of individual aluminate and silicate species, which originate from the dissolution of silicon and aluminium containing source materials at a high pH in the presence of soluble alkali metal silicates. It has been shown before that geopolymerisation can transform a wide range of waste aluminosilicate materials into building and mining materials with excellent chemical and physical properties, such as fire and acid resistance (Davidovits, 1991; 1994; Forss, 1987). The geopolymerisation of fifteen natural occurring Al-Si minerals has been investigated in this chapter with the aim to determine the effect of mineral properties on the compressive strength of the synthesised geopolymer and to understand the mechanisms involved in geopolymerisation.

4.1 BACKGROUND

4.1.1 Introduction

Davidovits has developed amorphous to semi-crystalline three-dimensional aluminosilicate materials, which he called "geopolymers" in 1978 (Comrie and Davidovits, 1988; Davidovits and Davidovits, 1988; Davidovits et al., 1990; Davidovits, 1991, 1994; Davidovits et al., 1994). Geopolymerisation involves a chemical reaction between various aluminosilicate oxides (Al$^{3+}$ in IV-V fold coordination) with silicates under highly alkaline conditions, yielding polymeric Si-O-Al-O bonds, which can be presented schematically as follows:
\[
\begin{align*}
n(Si_2O_5Al_2O_2) + 2nSiO_2 + 4nH_2O + NaOH \text{ or (KOH)} \quad & \quad \downarrow \\
(Si-Al \text{ materials}) \quad & \quad \downarrow \\
Na^+,K^+ + n(OH)_3-Si-O-Al^-O-Si-(OH)_3 \quad & \quad \downarrow \\
(\text{Geopolymer precursor}) \quad & \quad (OH)_2 \\
(4.1) \\
\end{align*}
\]

\[
\begin{align*}
n(OH)_3-Si-O-Al^-O-Si-(OH)_3 + NaOH \text{ or (KOH)} \\
(\text{OH})_2 \\
\downarrow \\
(Na^+,K^+)-(Si-O-Al^-O-Si-O) + 4nH_2O \\
O \quad O \quad O \\
(\text{Geopolymer backbone}) \\
(4.2)
\end{align*}
\]

The above two reaction paths indicate that any Si-Al materials might become sources of geopolymerisation (Van Jaarsveld et al., 1997). According to Davidovits (1994) geopolymeric binders are the synthetic analogues of natural zeolites and require similar hydrothermal synthesis conditions. Reaction times, however, are substantially faster, which results in amorphous to semi-crystalline matrices compared with the highly crystalline and regular zeolitic structures. The electron diffraction analysis conducted by Van Jaarsveld et al. (1999) showed that the structure of geopolymers is amorphous to semi-crystalline. The exact mechanism by which geopolymer setting and hardening occur is not fully understood. Most proposed mechanisms consist of dissolution, transportation or orientation, as well as a precipitation (polycondensation) step (Davidovits, 1991; 1994; Van Jaarsveld et al., 1997). It appears that an alkali metal salt and/or hydroxide is required for dissolution of silica and alumina to proceed, as well as for the catalysis of the condensation reaction. In aluminosilicate structures silicon is always 4 co-ordinated, while aluminium ions can be 4 or 6 co-ordinated. It is possible that the co-ordination number of aluminium in the starting materials will have an effect on its ability to undergo geopolymerisation. A highly reactive intermediate gel phase is believed to form by co-polymerisation of individual
aluminate and silicate species. Little is known about the behaviour of this gel phase and the extent to which the nature of the starting materials and the actual concentrations in solution are affecting the formation and setting of this gel phase. A major experimental problem is that the gel phase cannot be "frozen" and then analysed to observe the evolution of its composition and texture.

It is well known that the synthetic analogues of natural zeolite materials, called geopolymers, possess excellent mechanical properties, fire resistance and acid resistance (Davidovits and Davidovics, 1988; Palomo et al., 1992b). These properties make geopolymers a potential construction material, which has attracted a great deal of attention internationally in the past twenty years (Davidovits et al., 1994; Laney, 1993; Malone et al., 1986; Van Jaarsveld et al., 1997). Although commercial applications of geopolymers are limited at present, a recent increase in research and development activity could facilitate the wider acceptance of these materials. In previous papers many Al-Si containing source materials such as building residues, fly ash, furnace slag, pozzolan and kaolinite and metakaolinite have been studied (Davidovits, 1991; 1994; Van Jaarsveld et al., 1997; 1999a; 1999b). In fact, some research results have already been applied successfully in industry to substitute traditional cement. Nevertheless, most of these studies have used the source materials on an arbitrary basis without consideration of the structure, mineralogy and paragenesis of the individual minerals. This means that no generic knowledge is available on the propensity of Al-Si minerals to geopolymerise, despite the availability of some data on the solubility of selected minerals in alkaline medium. Usually the interrelationship between mineralogy and reactivity of individual minerals is extremely complex, and this is the reason why previous studies have focused on the geopolymerisation of selected materials that are widely available (for example, kaolinite and metakaolinite). More than 75 % of the crust of the earth consists of Al-Si materials, so that it is most useful to understand how individual Al-Si minerals will geopolymerise. Such information will also enhance the commercialisation of this promising new technology.

The primary aim of this chapter is to demonstrate that a wide range of Al-Si minerals could form geopolymers. Secondly, an attempt is made to relate the composition, physical properties, mineralogy, structure and paragenesis of these minerals to the
compressive strengths of the final synthesised matrices. A mechanism of
gopolymerisation will also be proposed. Fifteen natural Al-Si minerals, which cover
the ring, chain, sheet and framework crystal structure groups, as well as the garnet,
mica, clay, feldspar, sodalite and zeolite mineral groups, were investigated. It will be
shown that all these minerals produced acceptable matrices.

4.1.2 Materials and methods

Fifteen natural occurring Al-Si minerals with particle sizes of -212μm have been
analysed by XRF and XRD respectively. Table 4.1 lists the elemental composition
and the approximate formula of each of these minerals. The hardness and density
which are obtained from Nickel and Nichols (1991) are presented in Table 4.1 as well.

The extent of dissolution of the fifteen minerals in alkaline medium is determined by
mixing 0.50g ± 0.002g of each mineral with 20ml of alkaline solution (2N, 5N and
10N of NaOH or KOH) at room temperature for 5 hours using a magnetic stirrer.
After filtration the solution part is diluted to 0.2 N alkaline concentration and
neutralised by 36% HCl. During the ICP analysis of these solutions, 1 ppm scandium
is used as an internal standard.

In real geopolymeric reactions, the mass ratio of aluminosilicate powder to alkaline
solution is about 3.0, which causes the alkaline solution to form a thick gel
instantaneously upon mixing with the minerals. At that stage the dissolution reaction
proceeds simultaneously with the gel formation and polycondensation (setting)
reactions, so that the dissolution reaction cannot be isolated. As the gel phase cannot
be separated or analysed in-situ, a dissolution procedure with lower solid/solution
ratio has been chosen to investigate the dissolution behaviour of minerals. At 10N
NaOH it becomes impractical to use filtration as a means of separating the dissolving
solids from the alkaline solution at solid/solution ratios higher than 0.25. Moreover, in
both NaOH and KOH solutions it is found that the concentration of Al or Si after a
certain time is linearly dependent on the solid/solution ratio. Consequently, the extent
of dissolution of these fifteen minerals at low solid/solution ratios could be used to
predict their performance at high solid/solution ratios.

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In order to achieve homogeneously mixed geopolymers and in view of the restricted availability of some mineral samples, very small samples are prepared. In all tests 10.0 gram of mineral and 5.0 gram of kaolinite are dry mixed for 10 minutes, followed by the addition of 0.9 gram of sodium silicate solution (with [Si] = 0.74 M) and 5.0 ml of 10N KOH or NaOH solution, followed by a further 2 minutes of mixing by hand. The resulting slurry is then transferred to steel moulds measuring 20 × 20 × 20mm, which is followed by a gel setting and hardening stage at 35°C for 72 hours. After being analysed by XRD to ensure that all samples are dried, the resulting compressive strength of each geopolymer is tested. It should be noted that such small samples are well below the minimum required in standard testing specifications, so that the obtained MPa values should not be interpreted in absolute but rather in relative terms. It should also be realised that such compressive strengths could be substantially higher when the reacting minerals occur in combination with filling or aggregate material of a suitable particle size distribution, similar to what happens in concrete.

The concentration of the silicate solution used in this research is [Si] = 0.74 M. The aim of adding sodium-silicate solution is to enhance the formation of geopolymer precursors upon contact between a mineral and the solution. In view of the different extents of dissolution displayed by the various minerals, it is necessary to optimise the concentration of the sodium silicate solution in each case, as this concentration affects the properties of the ultimate geopolymer. Owing to the limited supply of mineral samples, such an optimisation is conducted only for stilbite by keeping all other conditions constant and using sodium-silicate concentrations ranging from [Si] = 0.72 M to 3.7 M. It is found that [Si] = 0.74 M yielded optimal compressive strengths for both NaOH and KOH conditions in the case of stilbite. This concentration is then applied in the case of all other minerals without further optimisation. The concentration of sodium-silicate used by other researchers ranges from [Si] = 0.72 M to 3.96 M (Van Jaarsveld et al., 1997; 1999a; 1999b; Palomo et al., 1992b).

Kaolinite and metakaolinite are a relatively inexpensive aluminosilicates which have been used in most previous studies on geopolymerisation (Comrie and Davidovits,
1988; Van Jaarsveld et al., 1997; 1999a; 1999b; Palomo et al., 1992b; Rahier et al., 1996a; 1996b; 1997). Many of these studies have utilised kaolinite or metakaolinite as a secondary source of soluble Si and Al in addition to waste or natural aluminosilicate materials to synthesise geopolymers. Often the rate of dissolution of Al from the waste or natural aluminosilicates is insufficient to produce a gel of the desired composition. In such cases the addition of kaolinite is necessary. However, if only kaolinite is used without the presence of other aluminosilicates a weak structure is formed, so that the synergy between different aluminosilicates seems to be important. This is an aspect that requires considerable further research. In the present study it has been found that some of the natural aluminosilicate minerals such as stilbite and sodalite could form geopolymers on their own accord, while other weakly reactive minerals could not form acceptable bonds without the presence of kaolinite. Consequently, it has been decided to add the same amount of kaolinite to each of the minerals in order to allow a more reasonable comparison between minerals and also to allow comparison with previously published results.

4.2 CHARACTERISATION OF AL-SI MINERALS

4.2.1 Composition

These 15 natural Al-Si minerals comprise four crystal structure groups (Ortho-, di- and ring silicates, chain silicates, sheet silicates and framework silicates) and six mineral groups (garnet, mica, feldspars, clay, sodalite and zeolite). They all contain SiO₂ and Al₂O₃, with the SiO₂ content varying from 27.57 wt% in sodalite to 64.38 wt% in heulandite and Al₂O₃ content varies from 1.59 wt% in grossular to 57.78 wt% in sillimanite.

The main metallic elements contained in the 15 natural minerals are Fe, Ca, Mg, K and Na. There are nine minerals, almandine, grossular, kyanite, pumpellyite, spodumene, augite, illite, heulandite and anorthite, containing some iron. Of them, almandine pumpellyite and augite contain iron in their chemical formula, while the others contained iron by paragenesis. It is known in the cement industry that Fe₂O₃ as one of five main components (Al₂O₃, SiO₂, SiO₃, CaO, Fe₂O₃) contributes to the
strength development of Portland cement at later ages (Popovics, 1992). In
geopolymisation it is still an open question whether iron has any effect on strength
development.

Nine minerals, grossular, andalusite, pumpellyite, augite, celsian, sodalite, stilbite,
heulandite and anorthite, contain calcium with the CaO content varying from 2.25
wt% in heulandite to 25.41 wt% in grossular. The calcium content is an important
factor affecting the quick setting and final strength in concrete (Popovics, 1992), and
there are indications that it may also affect the properties of geopolymers (Davidovits,
1994; Van Jaarsveld et al., 1999). The minerals almandine, grossular, kyanite,
pumpellyite, spodumene, augite, illite and anorthite contain MgO, with kyanite, augite
and anorthite having a relatively high content. It is undesirable for cement to contain
more than 5 wt% MgO, but it is still unknown what effect MgO has on
geopolymerisation.

Five minerals, andalusite, kyanite, spodumene, lepidolite and illite, show a substantial
content of K2O. The minerals sodalite and heulandite contain a significant amount of
Na2O. In concrete it is undesirable to have a substantial content of alkali metals owing
to alkali activation which causes subsequent stresses. In geopolymerisation the
dissolution reaction and polycondensation steps involve alkali metals, which implies
that the alkali metal content of reacting minerals could have a significant effect on
strength development.

4.2.2 Structure

XRD patterns of the minerals listed in Table 4.1 show varying degrees of
crystallisation and contamination. The minerals sillimanite, spodumene and stilbite
have clear patterns with well matched peak positions and peak intensities which
means they are pure and highly crystallised minerals (Figures 4.1 to 4.3). The XRD
patterns of the almandine, lepidolite and sodalite samples showed well crystallised
minerals, but there were also some weak unknown peaks caused by impurities
(Figures 4.4 to 4.6). The crystallised grossular and kyanite samples showed
paragenesis of andradite, quartz and anandite respectively (Figures 4.7 and 4.8). The
XRD patterns of andalusite, illite and heulandite had some noise which indicates that
these samples were partly polycrystallised and, moreover, andalusite is the
paragenesis of zinnwaldite and quartz, while illite and heulandite are the paragenesis
of quartz (Figures 4.9 to 4.11). A high degree of noise was present in the XRD
patterns of celsian, pumpellyite, augite and anorthite, which were partly amorphous
and impure (Figures 4.12 to 4.15). Pumpellyite is the paragenesis of sepiolite, with
augite containing natrolite and anorthite containing augite.

4.3 LEACHING

The behaviour of aluminosilicate materials in alkaline solution has been researched
extensively (Antonić et al., 1993 & 1994; Dent Glasser, 1982; Dent Glasser and
Harvey, 1984 a&b; Devidal et al., 1994; Gasteiger et al., 1992; Hendricks et al.,
1991; McCormick et al., 1989a,b&c; Swaddle et al, 1994). However, all these studies
dealt with either pure aluminates, silicates or aluminosilicates and were mostly related
to the synthesis of zeolite. There have been some studies on the dissolution and
gelatinisation of natural Al-Si minerals in acid or weak alkaline medium (Deer et al.,
1992). In contrast, little has been done on the reactivity of natural minerals in highly
alkaline medium, mainly as a result of their comparatively lower solubility in alkaline
medium than in acid medium.

As stated before, the process of geopolymerisation starts with the dissolution of Al
and Si from Al-Si materials in alkaline solution as hydrated reaction products with
NaOH or KOH, hence forming the \([M_n(AIO_2)_y(SiO_2)_z \cdot nMOH \cdot mH_2O]\) gel.
Subsequently, after a short time setting proceeds, with the gel hardening into
gleopolymers. Consequently, an understanding of the extent of dissolution of natural
Al-Si minerals is imperative for an understanding of geopolymerisation reactions.

Table 4.2 gives the extent of dissolution of all fifteen minerals in terms of the
concentration of Al or Si in 20 ml of solution after 5 hours of contact with 0.50 gram
of mineral. The alkaline solutions contained NaOH or KOH at concentrations of 2N,
5N and 10N. The following general trends can be observed from Table 4.2:
1) Minerals have a higher extent of dissolution with increasing concentrations of alkaline solution.

2) Minerals show a higher extent of dissolution in the NaOH than in the KOH solution, except for sodalite;

3) The concentrations of Si are higher than the corresponding Al, which could be caused partly by the higher content of Si than Al in the minerals, but also by the higher intrinsic extent of dissolution of Si than Al.

4) Si and Al appear to have synchro-dissolution behaviour in alkaline solution, which means that Si and Al could dissolve from the mineral surface in some linked form.

5) Minerals with framework structure possess a higher extent of dissolution than di-, ortho, -ring, chain and sheet structures in both NaOH and KOH solutions.

Normally, the possible chemical process for the dissolution of Al-Si minerals and silicates under strongly alkaline conditions can be expressed as the following reaction schemes (McCormick et al., 1989b; Babushkin et al., 1985) (M represents the Na and/or K).

\[
\text{Al-Si solid particle + OH}^- (aq) \rightleftharpoons \text{Al(OH)}_4^- + \text{^1OSi(OH)}_3 \text{ monomer monomer} \quad (4.3)
\]

\[
\text{^1OSi(OH)}_3 + \text{OH}^- \rightleftharpoons \text{^1OSi(OH)}_2 \text{O}^- + \text{H}_2 \text{O} \quad (4.4)
\]

\[
\begin{align*}
\text{O}^- & \\
\text{^1OSi(OH)}_2 \text{O}^- + \text{OH}^- & \rightleftharpoons \text{^1OSi(OH)}_3 \text{O}^- + \text{H}_2 \text{O} \quad (4.5)
\end{align*}
\]

\[
\text{M}^+ + \text{^1OSi(OH)}_3 \text{ monomer} \rightleftharpoons \text{M}^+\text{OSi(OH)}_3 \text{ monomer} \quad (4.6)
\]

\[
\begin{align*}
2\text{M}^+ + \text{^1OSi(OH)}_2 \text{O}^- & \rightleftharpoons \text{M}^+\text{OSi(OH)}_2 \text{O}^+ \text{M} \text{ monomer monomer} \quad (4.7)
\end{align*}
\]

\[
\begin{align*}
\text{O}^- & \\
3\text{M}^+ + \text{^1OSi(OH)}_3 \text{O}^- & \rightleftharpoons \text{M}^+\text{OSi(OH)}_3 \text{O}^+ \text{M} \text{ monomer monomer} \quad (4.8)
\end{align*}
\]
\[
M^+ + \text{Al(OH)}_4^- + \text{OH}^- \rightleftharpoons M^{+\circ}\text{Al(OH)}_2^+ + \text{H}_2\text{O} \\
\text{monomer} \quad \text{monomer}
\]

\[
\text{O}^\cdot\text{Si(OH)}_3^+ + M^{+\circ}\text{Si(OH)}_3^+ \rightleftharpoons M^{+\circ}\text{Si(OH)}_2^\circ\text{O-Si(OH)}_3^+ + \text{MOH} \\
\text{monomer} \quad \text{monomer} \quad \text{dimer}
\]

\[
\text{O}^\cdot\text{Si(OH)}_2^\circ\text{O}^\cdot + M^{+\circ}\text{Si(OH)}_3^+ \rightleftharpoons M^{+\circ}\text{Si(OH)}_2^\circ\text{O-Si(OH)}_2^\circ\text{O}^\cdot + \text{MOH} \\
\text{monomer} \quad \text{monomer} \quad \text{dimer}
\]

\[
\text{O}^\cdot\text{Si(OH)O}^\cdot + M^{+\circ}\text{Si(OH)}_3^+ \rightleftharpoons M^{+\circ}\text{Si(OH)} -\text{O-Si(OH)}_2^\circ\text{O}^\cdot + \text{MOH} \\
\text{monomer} \quad \text{monomer} \quad \text{dimer}
\]

\[
2\text{Silicate monomer} + 2\text{Silicate dimer} + 2M^+ \rightleftharpoons M^+\text{cyclic trimer} + M^2\text{linear trimer} \\
+ 2\text{MOH} \\
\]

As the concentrations of Al and Si in the present study are quite low, mainly these eleven reactions occurred (McCormick et al., 1989b; Babushkin et al., 1985). With concentrated silicate anion addition, the tetramer, pentamer, hexamer, octamer, nonamer and their compounds will appear (Hendricks et al., 1991). The dissolution reaction 4.3, for a fixed particle size, is a function of MOH concentration, the structure and the surface properties of the minerals. As the minerals chosen here covered a wide range of structures, compositions and paragenesis, the factors, which are expected to affect reaction 4.3, are very complex. In a simplified conceptualisation only the effect of MOH concentration will be discussed below.

From the eleven reactions given above it can be seen that increasing the concentration of alkaline solution favours all reactions 4.3 to 4.9 shifting to the right hand side. Equations 4.3 to 4.5 are chemical hydration reactions, where the OH\textsuperscript{-} anions react with the Al-Si solid surface to form Al(OH)\textsubscript{4}\textsuperscript{+}, OSi(OH)\textsubscript{3}, divalent orthosilicic acid and trivalent orthosilicic acid ions. Reactions 4.6 to 4.9 are physical electrostatic reactions, where the alkali metal cation M\textsuperscript{+} reacts with Al(OH)\textsubscript{4}\textsuperscript{+}, OSi(OH)\textsubscript{3}, divalent orthosilicic acid and trivalent orthosilicic acid ions to balance Coulombic electrostatic repulsion. Reactions 4.10 to 4.13 are cation-
anion pair condensation interactions based on Coulombic electrostatic attraction. In reactions 4.9 to 4.13 the M⁺ cation reacts with Al(OH)₄⁻ and species of orthosilicic acid ions to form ion pairs of M⁺Al(OH)₄ monomer and silicate monomer, dimer and trimer ions, which reduce the amount of free Al(OH)₄⁻ and the species of orthosilicic acid ions, therefore shifting reactions 4.3 to 4.5 to the right hand side. According to Dent Glasser and Harvey (1984a) there is no cation-anion pair reaction directly on Al(OH)₄⁻ tetrahedra, which limits the dissolution of Al, so that the concentration of Al is always lower than the corresponding concentration of Si.

Reactions 4.6 to 4.13 suggest that the alkali-metal cation affects the extent of dissolution of an alumino-silicate. As Na⁺ and K⁺ have the same electric charge, their different effects are a result of their different ionic sizes. It has been shown that cation-anion pair interaction becomes less significant as the cation size increases. The cation with the smaller size favours the ion-pair reaction with the smaller silicate oligomers, such as silicate monomers, dimers and trimers (Swaddle et al., 1994; McCormick et al., 1989a; Hendricks et al., 1991). Thus we can expect that Na⁺ with the smaller size will be more active in reactions 4.6 to 4.13 than K⁺ which should result in a higher extent of dissolution of minerals in the NaOH solution (as shown by Table 4.2). The fact that the sodalite structure is stabilised by sodium but not by potassium may be the reason why sodalite, in contrast with the other minerals, shows a higher extent of dissolution in KOH than in NaOH solution.

A one way analysis of variance (ANOVA) is conducted on the extent of dissolution data in Table 4.2 for the different mineral structures in order to determine whether symmetry and structure have a statistically significant effect. Tables 4.3 and 4.4 show that the framework structure has a higher extent of dissolution than other structures for both Si and Al, with chain structures being the next highest. The order of the extent of dissolution of the other structures is less clear. The calculated correlation coefficient between the extent of dissolution of Si and Al is 0.93, which suggests that Si and Al are synchro-dissolving from the solid surface.
4.4 GEOPOLYMERISATION

Table 4.5 gives the compressive strength of the geopolymers formed from natural Al-Si minerals in NaOH and KOH conditions. A comparison of Tables 4.2 and 4.5 shows that some minerals with a higher extent of dissolution such as sodalite and stilbite developed higher than average compressive strength after geopolymerisation. Minerals with a low extent of dissolution, such as grossular and sillimanite do not reveal this relationship, which is indicative of the complexity of these reactions. It is significant that all fifteen minerals demonstrate higher compressive strengths after geopolymerisation in KOH than in NaOH, despite the higher extent of dissolution in NaOH than in KOH. When KOH was used the mean compressive strength of all minerals was 11MPa, which was 42% higher than for NaOH.

It can be expected that the compressive strength developed after geopolymerisation is a highly non-linear function of numerous variables. In order to identify such variables and to quantify the relative importance of these variables, a linear multi-variable regression analysis is performed using the following variables: (a) The %SiO₂, %Al₂O₃, %CaO, %K₂O, %MgO, %Na₂O and molar Si/Al in the original mineral, the Mohs hardness, the density (g/cm³) according to Table 4.1; (b) Crystallographic symmetry, where Cubic = 3, Monoclinic = 2, Orthorhombic = 1, Triclinic = 0; (c) Type of alkali, where NaOH = 1 and KαOH = 2; (d) Extent of dissolution of Si and Al in 10N alkaline solution (ppm); (e) Molar Si/Al ratio in a 10N alkaline solution during dissolution tests. The correlation coefficients between these factors and the compressive strength are shown in Table 4.6. Despite the fact that a linear correlation is inappropriate as an accurate predictor, it at least provides some guidance to the interpretation of this complex system.

Evidently, factors such as the %CaO, %K₂O and the molar Si/Al in the original mineral, the type of alkali, the extent of dissolution of Si and the molar Si/Al ratio in solution during dissolution tests have a significant correlation with compressive strength. Of these factors, the %CaO, the molar Si/Al in the original mineral, the use of KOH, the extent of dissolution of Si and the molar Si/Al ratio in solution show a positive correlation, while the %K₂O and the use of NaOH correlate negatively with
strength. It is worth noting that the hardness of the original minerals, which gives an indication of the original strength, has a positive correlation with the ultimate strength, but it is not as significant as the other variables mentioned above. This suggests that the geopolymeric matrices were not merely the products of different mineral particles acting as fillers or aggregate in a stabilised gel formed from the dissolution of kaolinite in the presence of sodium silicate. Instead, the significance of the molar Si/Al ratio during the alkaline dissolution of the individual minerals indicates that compressive strength is the result of complex reactions between the mineral surface, kaolinite and the concentrated alkaline sodium silicate solution. After geopolymerisation the undissolved particles remain bonded in the matrix, so that the hardness of the minerals correlates positively with final compressive strength, as expected. By “forward selection”, the following three factors were identified as having a significant effect on strength: the type of alkali, %K₂O in the mineral and ppm Si in solution. All three these predictors are at the 95% level of significance. Since it has already been demonstrated above that the mineral structure affects the extent of dissolution of Si, it can be argued that structure affects strength indirectly as well. Equation 4.14 gives the regression expression.

Comp. Strength (MPa) = 14.1 – 3.29 alkaline used – 0.573 K₂O + 0.00937 Si ppm

(4.14)

Tables 4.7 and 4.8 give a statistical analysis and ANOVA on the regression equation. It becomes apparent that compressive strength cannot be expressed as a simplified function of these variables.

4.5 MECHANISTIC CONSIDERATIONS

In geopolymerisation the weight ratio of aluminosilicate powder to alkaline solution is very high, usually between 3.0-5.5 (Palomo et al., 1992a; b; Van Jaarsveld et al., 1999). Once the aluminosilicate powder is mixed with alkaline solution, it forms which quickly transforms into hard geopolymers. In such a situation, there is not sufficient time and space for the gel or paste to grow into a well crystallised structure, which is the fundamental difference between zeolites and geopolymers.
Figures 4.3 and 4.12 show the XRD patterns of unreacted stilbite and celsian respectively. Figures 4.16 and 4.17 show the XRD patterns of geopolymeric matrices formed by stilbite/kaolinite and celsian/kaolinite respectively. A comparison of Figures 4.3 and 4.16, and 4.12 and 4.17, shows that after geopolymerisation all main characteristic peaks of both Al-Si minerals and kaolinite still remained, but decreased in intensities. This suggests that the stilbite, celsian and kaolinite did not dissolve totally into the gel phase. However, there were no new peaks, which means that no new major crystalline phases formed. Similar to the observation by Van Jaarsveld et al. (1999), the baseline broadened between 20 and 40 degrees 2θ, which is indicative of an increased amorphicity. Although not shown here, electron diffraction analysis has shown that the formed geopolymer indeed consists of a number of amorphous and poly-crystalline phases.

With the shorter setting and hardening time, geopolymers are formed with tightly packed polycrystalline structure so as to give better mechanical properties than zeolite which have lower density and cage-like crystalline structure. By taking these differences between zeolites and geopolymers into account the following reaction scheme is proposed for the polycondensation process of geopolymerisation from minerals:

$$\text{Al-Si materials (s) } + \text{MOH (aq) } + \text{Na}_2\text{SiO}_3 \text{ (s or aq) }$$

$$\downarrow$$

$$\text{Al-Si material (s) } + \left[\text{M}_4\text{(AlO}_2\text{)}_4\text{(SiO}_2\text{)}_b\text{•nMOH•m H}_2\text{O}\right]_{\text{gel}}$$

$$\downarrow$$

$$\text{Al-Si material (s)•}\left[\text{M}_4\text{(AlO}_2\text{)}_4\text{(SiO}_2\text{)}_b\text{•nMOH•m H}_2\text{O}\right]$$

Geopolymers with amorphous structure

In reactions 4.15 and 4.16, the amount of Al-Si material (s) used depends on the particle size, the extent of dissolution of Al-Si materials and the concentration of the alkaline solution. With finer particle sizes (< 0.5μm) and hence higher extent of dissolution, comparatively lower ratios of aluminosilicate powder/alkaline solution could be used, as most aluminosilicate particles could then be dissolved as a gel. In
most cases, however, aluminosilicate particles cannot be converted totally from the solid phase to the gel phase. Undissolved aluminosilicate solids contained in a geopolymer can behave as reinforcement of the matrix (Palomo et al., 1992b). In the present research neither of the fifteen minerals dissolved extensively, because their characteristic crystalline peaks could still be detected by XRD after geopolymerisation.

The formation of \([M_2(AlO_2)\times(SiO_2)_y\cdot MOH\cdot H_2O] gel\), which essentially relies on the extent of dissolution of aluminosilicate materials, is a dominant step in geopolymerisation. Aluminosilicate solids react with MOH solution and form a gel layer on their surfaces. It is proposed that the gel then diffuses outward from the particle surface into larger interstitial spaces between the particles with precipitation of gel and concurrent dissolution of new solid. When the gel phase hardens, the separate aluminosilicate particles are therefore bound together by the gel which acts as a binder.

The gel phase is formed by dissolution from the surfaces of the aluminosilicate minerals listed in Table 4.1 as well as the added kaolinite. For the purpose of this discussion, the gel is classified in terms of its origin as gel(kao) and gel(Al-Si). It is proposed that the ratio of gel(kao)/gel(Al-Si) depends on the relative extent of dissolution of kaolinite and the Al-Si minerals. Although kaolinite has a much finer particle size (70% < 2.0μm) than the other Al-Si minerals, the contribution of the Al-Si minerals to the gel phase is still important. A separate experiment (Section 6.3.2) was conducted on the composition of the gel phase for the stilbite-kaolinite system with the result showing gel(kao)/gel(stilbite) \(\approx 1 : 1.33\). This significant contribution by stilbite to the gel phase could be due to recondensation of the gel, which stimulates further dissolution of the Al-Si minerals. When the gel(kao)/gel(Al-Si) ratio becomes very low, it has been observed that the resulting geopolymers appear cracked, which indicates that the gel formed mainly from dissolution of the Al-Si mineral, but that this gel is not a sufficiently strong binder. On the other hand, if the gel(kao)/gel(Al-Si) ratio is very high, such as for the mineral lepidolite, which has a low extent of dissolution and hence low gel formation, the resulting geopolymer demonstrates low
compressive strength. A possible reason for this is the poor wettability between the gel(kao) and the lepidolite solid surface.

In geopolymerisation high concentrations of silicate are used, especially when sodium silicate is added. Hence, stronger ion-pair formation is expected, which will result in more long chain silicate oligomers as well as Al-O-Si complexes, i.e. geopolymer precursors (McCormick et al., 1989c). In a concentrated alkaline solution of Al and Si, all lengths of silicate could potentially form Al-O-Si complexes. Whereas Al(OH)$_4^-$ does not combine readily with small highly charged silicate oligomers, such as silicate monomers (Dent Glasser and Harvey, 1984a), the more long chain silicate oligomers exist, the more readily the geopolymer precursors form. This is why the addition of extra Na$_2$SiO$_3$ is essential (reaction 4.15), as most Al-Si materials cannot supply sufficient Si in alkaline solution to start the geopolymerisation. Na$^+$, with its smaller size than K$^+$, displays strong pair formation with the smaller silicate oligomers (such as monomers). Such pairs in turn do not readily pair with another silicate anion (Hendricks et al., 1991), which hinders the further formation of large silicate oligomers. The larger K$^+$ favours the formation of larger silicate oligomers with which Al(OH)$_4^-$ prefers to bind. Therefore in KOH solutions more geopolymer precursors exist which result in better setting and stronger compressive strength of the geopolymers than in the case of NaOH.

4.6 THEORETICAL MODELLING

As stated earlier (4.5), Na$^+$ and K$^+$ stabilise the silicate smaller oligomers (monomer and dimer) and larger oligomers (trimer tetramer et al.) better respectively because of their specific sizes. This conclusion is also drawn by other researchers based on the Na$^+$ and K$^+$ NMR spectra obtained in silicate solutions (McCormick et al., 1989a). In order to further verify this observation as well as to gain proof of the assumption that K$^+$ preferentially forms geopolymer precursors, an ab initio quantum calculation is designed by modelling ion pairing and geopolymer precursor forming reactions. A Gaussian 94 software package (Frisch et al., 1994) is used to conduct the calculation on an Ormond supercomputer (OSF) Cray. A Restricted Hartree-Fock (RHF) theory and a 6-31G basis set are used throughout the calculations.
According to Davidovits (1991; 1994), the geopolymer precursors are sialate $[\text{SiO}_4\cdot\text{AlO}_4]$, sialate-siloxo $[\text{SiO}_4\cdot\text{AlO}_4\cdot\text{SiO}_4]$ and sialate-disiloxo $[\text{SiO}_4\cdot\text{AlO}_4\cdot\text{SiO}_4\cdot\text{SiO}_4]$. Equations 4.18 to 4.23 describe the forming reactions of them in NaOH or KOH solution.

\[
\text{Al}(\text{OH})_4 + \text{Si(OH)}_3\text{Na} \Rightarrow \text{Na(OH)}_2\text{OSi-O-Al(OH)}_3 \quad \text{(Na-sialate)} \\
(4.18)
\]

\[
\text{Al}(\text{OH})_4 + \text{Si(OH)}_3\text{K} \Rightarrow K(\text{OH})_2\text{OSi-O-Al(OH)}_3 \quad \text{(K-sialate)} \\
(4.19)
\]

\[
\text{Na(OH)}_2\text{OSi-O-Al(OH)}_3 + \text{Si(OH)}_4 \Rightarrow \text{Na(OH)}_2\text{OSi-O-Al(OH)}_2\cdot\text{OSi(OH)}_3 \quad \text{(Na-sialate-siloxo)} \\
(4.20)
\]

\[
K(\text{OH})_2\text{OSi-O-Al(OH)}_3 + \text{Si(OH)}_4 \Rightarrow K(\text{OH})_2\text{OSi-O-Al(OH)}_2\cdot\text{OSi(OH)}_3 \quad \text{(K-sialate-siloxo)} \\
(4.21)
\]

\[
\text{Na(OH)}_2\text{OSi-O-Al(OH)}_2\cdot\text{OSi(OH)}_3 + \text{Si(OH)}_4 \Rightarrow \Rightarrow \text{Na(OH)}_2\text{OSi-O-Al(OH)}_2\cdot\text{Si(OH)}_2\cdot\text{Si(OH)}_3 \quad \text{(Na-sialate-disiloxo)} \\
(4.22)
\]

\[
K(\text{OH})_2\text{OSi-O-Al(OH)}_2\cdot\text{OSi(OH)}_3 + \text{Si(OH)}_4 \Rightarrow \Rightarrow K(\text{OH})_2\text{OSi-O-Al(OH)}_2\cdot\text{OSi(OH)}_2\cdot\text{Si(OH)}_3 \quad \text{(K-sialate-disiloxo)} \\
(4.23)
\]

The energies of ion pairing reactions are calculated for both Na$^+$ and K$^+$ cases based on the equations 4.10 and 4.13. For equation 4.13, formation of linear trimer and cyclic trimer is calculated separately. Table 4.9 gives the calculated reaction energies. It is found from Table 4.9 that K$^+$ favours linear and cyclic silicate trimer forming by releasing more enthalpy. However, Na$^+$ shows to benefit the forming of silicate dimer. This finding agrees very well with the experimental observations obtained by McCormick et al. (1989a) and Dent Glasser and Harvey (1984a; 1984b). This also verifies the fact that Na$^+$ can leach more Al and Si.

During the geopolymerisations conducted in this chapter, an addition of concentrated silicate solution not only increases the concentration of the silicate complexes greatly, but also increases the probability of forming geopolymeric precursors sialate-siloxo and sialate-disiloxo. It is noticed in Table 4.9 that reaction between K$^+$ and sialate-
siloxo or sialate–disiloxo results in much more exothermal enthalpy. This indicates that a more stable sialate-siloxo or sialate-disiloxo is achieved when K⁺ rather than Na⁺ is present. In other words, geopolymers formed in KOH are stronger and possess higher compressive strength as observed in Table 4.5.

4.7 SUMMARY

The geopolymerisation behaviour of fifteen natural Al-Si minerals has been investigated. These minerals are all to some extent soluble in concentrated alkaline solution with a higher extent of dissolution in NaOH than in KOH, except in the case of sodalite. The framework structure shows a higher extent of dissolution than other structures for both Si and Al, with chain structures being the next most soluble. The order of the extent of dissolution of the other structures such as sheet and ring structures is less evident. Silicon and aluminium appear to be synchro-dissolving from the surface of the minerals, as their extents of dissolution for the different minerals have a high correlation coefficient. Ion pair theory could be used to explain the differences in the extent of dissolution in NaOH and KOH solutions, as well as the increased compressive strength of the geopolymers synthesised in the presence of KOH.

Factors such as the %CaO, %K₂O and the molar Si/Al in the original mineral, the type of alkali, the extent of dissolution of Si and the molar Si/Al ratio in solution have a significant correlation with compressive strength. Stilbite in the presence of KOH shows the highest compressive strength at 18 MPa.

The geopolymerisation results show that natural Al-Si minerals could be a source material for geopolymers. However, it is evident that the reaction mechanisms involved in the dissolution, gel formation, setting and hardening phases are extremely complex and a further study on factors affecting the leaching, gel forming and geopolymerisation is required.
Table 4.1. Elemental composition and physical properties of selected alumino-silicate minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Stoichiometry</th>
<th>Composition, wt% (XRF)</th>
<th>Hardness</th>
<th>Den.</th>
<th>Contaminant (XRD)</th>
<th>Molar Si/Al ratio based on XRF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>M₁⁺</td>
<td>M₂⁺</td>
<td>M₃⁺</td>
<td>Mohs&lt;sup&gt;abh&lt;/sup&gt;</td>
</tr>
<tr>
<td>Almandine</td>
<td>Fe₃Al₃(SiO₄)₃</td>
<td>38.57</td>
<td>20.09</td>
<td>Fe₂O₃ 36.71</td>
<td>MnO 4.06</td>
<td>MgO 2.25</td>
</tr>
<tr>
<td>Grossular</td>
<td>Ca₃Al₂(SiO₄)₃</td>
<td>48.53</td>
<td>1.59</td>
<td>Fe₂O₃ 9.68</td>
<td>CaO 25.41</td>
<td>MgO 1.26</td>
</tr>
<tr>
<td>Garnet Group</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sillimanite</td>
<td>Al₂SiO₅</td>
<td>40.8</td>
<td>57.78</td>
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<tr>
<td>Andalusite</td>
<td>Al₂SiO₅</td>
<td>39.87</td>
<td>43.63</td>
<td>K₂O 4.32</td>
<td>CaO 4.05</td>
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<tr>
<td>Kyanite</td>
<td>Al₂SiO₅</td>
<td>38.97</td>
<td>44.68</td>
<td>Fe₂O₃ 4.76</td>
<td>K₂O 3.90</td>
<td>MgO 4.9</td>
</tr>
<tr>
<td>Pumpellyte-(Fe&lt;sup&gt;2+&lt;/sup&gt;)</td>
<td>Ca₃Fe³⁺Al₃(SiO₄)₉Si₂O₇(OH,F,OH)·H₂O</td>
<td>46.83</td>
<td>15.28</td>
<td>Fe₂O₃ 10.95</td>
<td>CaO 12.59</td>
<td>MgO 6.31</td>
</tr>
<tr>
<td>CHAIN SILICATE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spodumene</td>
<td>LiAlSi₃O₆</td>
<td>62.84</td>
<td>26.58</td>
<td>Fe₂O₃ 1.85</td>
<td>K₂O 1.51</td>
<td>MgO 0.58</td>
</tr>
<tr>
<td>Augite</td>
<td>(Ca,Mg,Fe&lt;sub&gt;3&lt;/sub&gt;Si₃Al₂O₆)</td>
<td>44.47</td>
<td>14.92</td>
<td>Fe₂O₃ 12.4</td>
<td>CaO 6.68</td>
<td>MgO 10.23</td>
</tr>
<tr>
<td>SHEET SILICATE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lepidolite</td>
<td>K(Li,Al)₂(Si,Al)₃O₆(F,OH)₂</td>
<td>49.55</td>
<td>28.58</td>
<td>K₂O 9.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mica Group</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>(K₂H₃O)Al₃(Si,Al)₃O₆(H₂O,OH)₃</td>
<td>58.01</td>
<td>20.14</td>
<td>Fe₂O₃ 4.93</td>
<td>K₂O 6.04</td>
<td>MgO 2.54</td>
</tr>
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</table>
Table 4.1. Elemental composition and physical properties of selected aluminosilicate minerals
(continued)

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Ideal Stoichiometry</th>
<th>Composition, wt% (XRF)</th>
<th>Hardness</th>
<th>Den.(ab)</th>
<th>Contaminant (XRD)</th>
<th>Molar Si/Al ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>M₁*</td>
<td>M₂*</td>
<td>M₃*</td>
</tr>
<tr>
<td>Clay Group</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Celsian</td>
<td>BaAl₂Si₂O₈</td>
<td>46.29</td>
<td>25.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feldspar Group</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anorthite</td>
<td>Ca₂Al₂Si₂O₈</td>
<td>46.38</td>
<td>14.87</td>
<td>Fe₂O₃, 11.81</td>
<td>CaO 6.58</td>
<td>MgO 9.88</td>
</tr>
<tr>
<td>Sodalite Group</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodalite</td>
<td>Na₄(Si₂Al₅)O₉Cl</td>
<td>27.57</td>
<td>21.51</td>
<td>CaO 10.76</td>
<td>Cl 4674 ppm</td>
<td>Na₂O 11.53</td>
</tr>
<tr>
<td>Heulandite</td>
<td>(Na,K,Ca,Str.Ba)₆(Al₂Si₇)O₂₀·26H₂O</td>
<td>64.38</td>
<td>12.6</td>
<td>Fe₂O₃ 6.93</td>
<td>CaO 2.25</td>
<td>Na₂O 3.63</td>
</tr>
<tr>
<td>Zeolite Group</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stilbite</td>
<td>NaCa₃(Si₇Al₃)O₉·30H₂O</td>
<td>58.47</td>
<td>15.04</td>
<td>CaO 7.61</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a)Nickel and Nichols (1991)  (b) Deer et al. (1992)
(c)Experimental XRF results.  (d) Experimental XRD results.

* Main metal oxides contained in minerals.
<table>
<thead>
<tr>
<th>Mineral</th>
<th>2N NaOH</th>
<th>2N KOH</th>
<th>5N NaOH</th>
<th>5N KOH</th>
<th>10N NaOH</th>
<th>10N KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si ppm</td>
<td>Al ppm</td>
<td>Si ppm</td>
<td>Al ppm</td>
<td>Si ppm</td>
<td>Al ppm</td>
</tr>
<tr>
<td>Almandine</td>
<td>59.2</td>
<td>39.6</td>
<td>62.3</td>
<td>39.8</td>
<td>51</td>
<td>34.2</td>
</tr>
<tr>
<td>Grossular</td>
<td>60.6</td>
<td>1.5</td>
<td>50.1</td>
<td>1.82</td>
<td>66</td>
<td>2.02</td>
</tr>
<tr>
<td>Sillimanite</td>
<td>21.1</td>
<td>27.4</td>
<td>17</td>
<td>23.4</td>
<td>23.4</td>
<td>28.4</td>
</tr>
<tr>
<td>Andalusite</td>
<td>31.5</td>
<td>33.3</td>
<td>30.2</td>
<td>32.6</td>
<td>31.2</td>
<td>33.2</td>
</tr>
<tr>
<td>Kyanite</td>
<td>22.6</td>
<td>20.9</td>
<td>21.1</td>
<td>20.3</td>
<td>26.4</td>
<td>24.4</td>
</tr>
<tr>
<td>Pumpellyite</td>
<td>30.6</td>
<td>14.9</td>
<td>31.1</td>
<td>14.5</td>
<td>19.8</td>
<td>11</td>
</tr>
<tr>
<td>Spodumene</td>
<td>34.2</td>
<td>20.2</td>
<td>29.6</td>
<td>17.5</td>
<td>39.4</td>
<td>23.2</td>
</tr>
<tr>
<td>Augite</td>
<td>59.3</td>
<td>19.8</td>
<td>53.1</td>
<td>20.9</td>
<td>164.8</td>
<td>74.4</td>
</tr>
<tr>
<td>Lepidolite</td>
<td>36.8</td>
<td>25.1</td>
<td>32.5</td>
<td>22.5</td>
<td>34.4</td>
<td>24.4</td>
</tr>
<tr>
<td>Illite</td>
<td>42.2</td>
<td>19.8</td>
<td>42</td>
<td>15.8</td>
<td>52</td>
<td>23.4</td>
</tr>
<tr>
<td>Celsian</td>
<td>78</td>
<td>62.7</td>
<td>65.8</td>
<td>56.6</td>
<td>78.8</td>
<td>68.2</td>
</tr>
<tr>
<td>Sodalite</td>
<td>68.5</td>
<td>13.6</td>
<td>82.1</td>
<td>38</td>
<td>101</td>
<td>37.2</td>
</tr>
<tr>
<td>Stilbite</td>
<td>116</td>
<td>45.9</td>
<td>98.7</td>
<td>32.9</td>
<td>122.8</td>
<td>44.4</td>
</tr>
<tr>
<td>Heulandite</td>
<td>127</td>
<td>45.8</td>
<td>94.8</td>
<td>35</td>
<td>141.4</td>
<td>51.6</td>
</tr>
<tr>
<td>Anorthite</td>
<td>86.2</td>
<td>36.2</td>
<td>69.5</td>
<td>29</td>
<td>79.6</td>
<td>36.6</td>
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</tbody>
</table>
Table 4.3. ANOVA for Si concentration in solution versus %SiO₂ in minerals

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>3</td>
<td>90.28</td>
<td>30.09</td>
<td>5.67</td>
<td>0.004</td>
</tr>
<tr>
<td>Error</td>
<td>26</td>
<td>138</td>
<td>5.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>29</td>
<td>228.29</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Level</th>
<th>N</th>
<th>Mean</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (orth, di, ring)</td>
<td>12</td>
<td>1.604</td>
<td>1.331</td>
</tr>
<tr>
<td>2 (chain)</td>
<td>4</td>
<td>2.937</td>
<td>2.385</td>
</tr>
<tr>
<td>3 (sheet)</td>
<td>4</td>
<td>1.041</td>
<td>0.28</td>
</tr>
<tr>
<td>4 (framework)</td>
<td>10</td>
<td>5.273</td>
<td>3.329</td>
</tr>
</tbody>
</table>

Pool. St. Dev = 2.304

Individual 95% Confidence Intervals for mean based on pooled St. Dev.

SS = Sum of squares
MS = Mean squares
DF = Degrees of freedom
P-value = Error probability
F = F-statistic
Table 4.4. ANOVA for Al concentration in solution versus %Al₂O₃ in minerals

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>3</td>
<td>226.98</td>
<td>75.66</td>
<td>10.8</td>
<td>0.0001</td>
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<tr>
<td>Error</td>
<td>26</td>
<td>182.1</td>
<td></td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>29</td>
<td>409.08</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Level</th>
<th>N</th>
<th>Mean</th>
<th>St. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (orth,di,ring)</td>
<td>12</td>
<td>1.263</td>
<td>0.629</td>
</tr>
<tr>
<td>2 (chain)</td>
<td>4</td>
<td>5.042</td>
<td>4.57</td>
</tr>
<tr>
<td>3 (sheet)</td>
<td>4</td>
<td>1.233</td>
<td>0.289</td>
</tr>
<tr>
<td>4 (framework)</td>
<td>10</td>
<td>7.225</td>
<td>3.572</td>
</tr>
</tbody>
</table>

Individual 95% Confidence Intervals for mean based on pooled St.Dev.

Poooled St.Dev. = 2.646

SS = Sum of squares
MS = Mean of squares
DF = Degrees of freedom
P-value = Error probability
F = F-statistic
Table 4.5. The compressive strength of geopolymers formed from Al-Si minerals

<table>
<thead>
<tr>
<th>Minerals</th>
<th>Compressive strength (MPa)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali</td>
<td>KOH</td>
<td>NaOH</td>
</tr>
<tr>
<td>Almandine</td>
<td>10.3</td>
<td>8.5</td>
</tr>
<tr>
<td>Grossular</td>
<td>16.7</td>
<td>14.5</td>
</tr>
<tr>
<td>Sillimanite</td>
<td>12.7</td>
<td>6.5</td>
</tr>
<tr>
<td>Andalusite</td>
<td>11.1</td>
<td>8.8</td>
</tr>
<tr>
<td>Kyanite</td>
<td>6.8</td>
<td>6.3</td>
</tr>
<tr>
<td>Pumpellyte</td>
<td>10.8</td>
<td>8.8</td>
</tr>
<tr>
<td>Spodumene</td>
<td>13.1</td>
<td>5</td>
</tr>
<tr>
<td>Augite</td>
<td>6.7</td>
<td>5</td>
</tr>
<tr>
<td>Lepidolite</td>
<td>4.3</td>
<td>2.5</td>
</tr>
<tr>
<td>Illite</td>
<td>7.1</td>
<td>5.8</td>
</tr>
<tr>
<td>Celsian</td>
<td>9.7</td>
<td>8.7</td>
</tr>
<tr>
<td>Sodalite</td>
<td>15</td>
<td>10.3</td>
</tr>
<tr>
<td>Stilbite</td>
<td>18.9</td>
<td>14.2</td>
</tr>
<tr>
<td>Heulandite</td>
<td>7.4</td>
<td>5.6</td>
</tr>
<tr>
<td>Anorthite</td>
<td>14.4</td>
<td>6</td>
</tr>
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</table>
Table 4.6. Correlation coefficients for a linear multi-variable regression analysis between various factors and compressive strength

<table>
<thead>
<tr>
<th>Factors</th>
<th>SiO$_2$(s)</th>
<th>Al$_2$O$_3$ (s)</th>
<th>CaO (s)</th>
<th>K$_2$O (s)</th>
<th>MgO (s)</th>
<th>Na$_2$O (s)</th>
<th>Hardness</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPA</td>
<td>-0.084328</td>
<td>-0.25619</td>
<td>0.48249</td>
<td>-0.53044</td>
<td>-0.17557</td>
<td>0.14615</td>
<td>0.26578</td>
<td>-0.10059</td>
</tr>
<tr>
<td>Factors</td>
<td>Symmetry</td>
<td>Molar Si/Al (s)</td>
<td>NaOH</td>
<td>KOH</td>
<td>Si ppm</td>
<td>Al ppm</td>
<td>Molar Si/Al (l)</td>
<td></td>
</tr>
<tr>
<td>MPA</td>
<td>-0.192612</td>
<td>0.42003</td>
<td>-0.40639</td>
<td>0.40639</td>
<td>0.47473</td>
<td>0.26965</td>
<td>0.41295</td>
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</tr>
</tbody>
</table>

Table 4.7. Statistical analysis on coefficients in regression equation (4.14)

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Coeff.</th>
<th>St. Dev.</th>
<th>T</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>14.131</td>
<td>1.858</td>
<td>7.61</td>
<td>0</td>
</tr>
<tr>
<td>Alkaline used</td>
<td>-3.289</td>
<td>1.063</td>
<td>-3.1</td>
<td>0.005</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>-0.5734</td>
<td>0.2064</td>
<td>-2.78</td>
<td>0.01</td>
</tr>
<tr>
<td>Si</td>
<td>0.009366</td>
<td>0.004167</td>
<td>2.25</td>
<td>0.033</td>
</tr>
</tbody>
</table>

S = 2.909 \quad R(Sq) = 53.7\% \quad \text{R}(Sq)_{adj} = 48.3\%

P = \text{Error probability}, \quad T = \text{T-statistic}
Table 4.8. ANOVA on coefficients in regression equation (4.14)

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
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<td>Regression</td>
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<td>254.742</td>
<td>84.914</td>
<td>10.03</td>
<td>0</td>
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<tr>
<td>Residual Error</td>
<td>26</td>
<td>220.019</td>
<td>8.462</td>
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<td></td>
</tr>
<tr>
<td>Total</td>
<td>29</td>
<td>474.762</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

DF = Degrees of freedom  
SS = Sum of squares  
MS = Mean of squares  
P-value = Error probability  
F = F-statistic

Table 4.9 The reaction energies calculated by ab initio quantum calculation

<table>
<thead>
<tr>
<th>Ion pair reaction</th>
<th>$\Delta E$, kJ/Mol</th>
<th>Precursor forming reaction</th>
<th>$\Delta E$, kJ/Mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimer, Na</td>
<td>-96.7</td>
<td>Na-sialate</td>
<td>-68.38</td>
</tr>
<tr>
<td>Dimer, K</td>
<td>-67.34</td>
<td>K-sialate</td>
<td>-32.45</td>
</tr>
<tr>
<td>Linear trimer, Na</td>
<td>-71.54</td>
<td>Na-sialate-siloxo</td>
<td>-83.72</td>
</tr>
<tr>
<td>Linear trimer, K</td>
<td>-71.93</td>
<td>K-sialate-siloxo</td>
<td>-187.71</td>
</tr>
<tr>
<td>Cyclic trimer, Na</td>
<td>-16.88</td>
<td>Na-sialate-disiloxo</td>
<td>-43.88</td>
</tr>
<tr>
<td>Cyclic trimer, K</td>
<td>-75.71</td>
<td>K-sialate-disiloxo</td>
<td>-62.09</td>
</tr>
</tbody>
</table>
Figure 4.1 XRD pattern of sillimanite
Figure 4.2 XRD pattern of spodumene
Figure 4.3 XRD pattern of stilbite
Figure 4.4 XRD pattern of almandine
Figure 4.5 XRD pattern of lepidolite
Figure 4.6 XRD pattern of sodalite
Figure 4.7 XRD pattern of grossular
Figure 4.8 XRD pattern of kyanite
Figure 4.9 XRD pattern of andalusite
Figure 4.10 XRD pattern of illite
Figure 4.11 XRD pattern of heulandite
Figure 4.12 XRD pattern of celsian
Figure 4.13 XRD pattern of pumpellyite
Figure 4.14 XRD pattern of augite
Figure 4.15 XRD pattern of anorthite
Figure 4.16 XRD pattern of geopolymer synthesised from stilbite and kaolinite
Figure 4.17 XRD pattern of geopolymer synthesised from celsian and kaolinite
CHAPTER FIVE

FACTORS AFFECTING THE GEOPOLYMERISATION OF STILBITE


As found in chapter 4, stilbite is a naturally occurring aluminosilicate mineral which has a high potential to undergo geopolymerisation. This chapter uses stilbite as a case study to investigate the effect of various factors on the extent of geopolymerisation and the compressive strength of resultant geopolymers.

5.1 BACKGROUND

5.1.1 Introduction

A brief introduction on geopolymers and geopolymerisation has been given in chapter 4 with an emphasis on reactants used in geopolymerisation. However, it is necessary to place the work in this chapter in the context of the existing literature.

Over the past 20 years, Davidovits and his team have conducted extensive research on geopolymers and the geopolymerisation process (Davidovits, 1988a; 1988b; 1991; 1994; Davidovits, et al., 1990). In particular, Davidovits has improved the chemical and mechanical characteristics of geopolymeric products and has identified a variety of industrial applications for these products. Davidovits primarily used kaolinite and calcined kaolinite (metakaolin) as the source of aluminosilicate oxides. However, certain kinds of minerals (Davidovits, 1984) and blast furnace slag (Davidovits and Sawyer, 1985) were also investigated by Davidovits during the 80’s. Helfferich and Shook (1984) and Neuschaeffer et al. (1985) published separate patents on the synthesis of amorphous aluminosilicate polymers in 1984 and 1985 respectively. These aluminosilicate polymers described are similar in chemical and mechanical properties as well as in preparation procedures to the geopolymer materials proposed.

During the late 90’s, Van Jaarsveld and Van Deventer (Van Jaarsveld et al., 1997; 1999; Van Jaarsveld and Van Deventer, 1999a; 1999b;) conducted research on the ability to form geopolymers using waste such as fly ash. The focus of the work by Van Jaarsveld and Van Deventer was on the industrial application of fly ash based geopolymeric materials, including the immobilisation of toxic metals. Silverstrim et al. (1996) and Khalil and Merz (1994) also investigated fly ash containing cementitious material for the immobilisation of industrial waste. It should be mentioned that besides professor Davidovits, only Rahier et al. (1996a; 1996b; 1997) have conducted detailed research on stoichiometry, rheological properties, compositions of the silicate solution and structure of the aluminosilicate polymers. It is important to note that Rahier named his products as “Low-temperature synthesised aluminosilicate glasses”.

Xu and Van Deventer (2000a) studied the ability of fifteen natural aluminosilicate minerals to undergo geopolymerisation. Each of these minerals has a different crystal structure, chemical composition, density, hardness and degrees of the paragenesis. It was found that various natural aluminosilicate minerals behaved significantly differently due to their individual properties. In particular, it was observed by Xu and Van Deventer that stilbite, one of the zeolite minerals, possessed a high reactivity in geopolymeric reactions.

As noticed from the previous study, although various methods and reactants have been used in geopolymerisation, the factors that affect geopolymerisation have not been investigated yet except for the work done by Van Jaarsveld and Van Deventer (1999a), who researched the effect of alkali metal activator on the geopolymerisation of fly ash. In this chapter, alkalinity, alkali metals, the amount of added silicates, setting pressure and sample preparation have been studied using stilbite as a case
study with the compressive strength of the resulting geopolymers as a performance indicator.

5.1.2 Experimental section

5.1.2.1 Leaching

The elemental composition of stilbite and kaolinite detected by XRF analysis is listed in Table 5.1. A specified mass of stilbite and kaolinite (with accuracy of ± 0.01g) is mixed with 10ml MOH solution (where M = Na and/or K) at room temperature for 18 hours using a magnetic stirrer. After centrifuging, the clear liquid part of the solution is diluted to 0.2M alkaline concentration and neutralised by concentrated HCl before it is tested by ICP. The leaching results of stilbite and kaolinite for three alkaline concentrations 2M, 5M and 10M (corresponding to M₂O/H₂O ratios of 0.018, 0.045 and 0.09, respectively) are presented in Table 5.2 and Figures 5.1 to 5.4.

5.1.2.2 Geopolymerisation

15 grams stilbite are dry mixed with 7.5 grams kaolinite for 10 minutes prior to the addition of sodium silicate and MOH solution (where M = Na and/or K). The subsequent mixture is mixed by hand for a further 5 minutes. The resulting slurry is then transferred to a steel mould measuring 20 × 20 × 20mm and left in an oven at 35°C for 24 hours. The sample is then removed from the mould, and kept in the oven for another 2 days at 35°C. After this time, the compressive strength of each sample is tested using a Tinus Tolsen Compressive Strength Testing Machine. Three samples of each geopolymer mixture are tested, with average compressive strength values listed in Table 5.3. In Table 5.3, samples 4-6 and 12-14 are prepared in the same manner as described above except for an additional 3 days of hardening at 35°C in the oven. Samples 7, 8, 15 and 16 are prepared by mixing 70 grams of stilbite and 35 grams of kaolinite for 10 minutes by hand, followed by 10 minutes using a FRITSCH Vibratory Shaker. MOH and Na₂SiO₃ solutions are then added to the dry mixture. The obtained paste is then shaken by the FRITSCH Vibratory Shaker for another 10 minutes before the paste is poured into a steel cylinder mould measuring 27 mm (diameter) × 54 mm
(height) and set under a specific pressure for 30 minutes at room temperature. After being removed from the mould, the sample is left in the oven for further setting and hardening at 35°C for 3 days. It is observed that after the pressurised setting, the height of samples 7, 8, 15 and 16 is less than 54mm. The maximum decrease of 15mm in height is observed for sample 16. Consequently, the height/diameter ratio for these four samples is between 1.4 and 1.9, rather than the standardised 2.0. This means that the obtained compressive strength values shown in Table 5.3 for these four samples should be slightly higher than the true values. Unless otherwise specified, for the M_2O/H_2O and SiO_2/M_2O molar ratios specified in the present investigation, M_2O is contributed by both MOH solution and Na_2SiO_3 solution, while SiO_2 and H_2O are calculated only from the Na_2SiO_3 and MOH solutions respectively.

5.2 FACTORS AFFECTING THE GEOPOLYMERISATION OF STILBITE

5.2.1 Effect of M_2O/H_2O ratio (where M = Na and/or K)

Although not clearly stated in the published literature, the geopolymerisation process involves four main steps. These steps include: (a) the dissolution of solid aluminosilicate oxides in MOH solution; (b) the diffusion or transportation of dissolved Al and Si complexes from particle surfaces to the inter-particle space; (c) the formation of a gel phase resulting from the polymerisation between added silicate solution and Al and Si complexes, and (d) hardening of the gel phase by the expulsion of spare water to form a monolithic geopolymeric product. Due to the difficulties existing in practical experimental techniques, it is hard to distinguish between the dissolved Al and Si complexes, the gel phase and the spare water. As a consequence, a quantitative research investigation on the geopolymerisation process can only be conducted on the dissolution step. Three M_2O/H_2O ratios of 0.018, 0.054 and 0.09 have been investigated in both leaching of Al and Si species and the extent of geopolymerisation for the purpose of elucidating the relationship between the dissolution of stilbite and kaolinite and the final compressive strength of the formed geopolymers.
Figures 5.1 to 5.4 express the concentrations of leached Al (ppm) and Si (ppm) from stilbite and kaolinite using either NaOH or KOH solutions. The solid (g)/liquid (ml) ratio (S/L) varies from 0.1 to 0.5 and 0.1 to 0.7, respectively. For both kaolinite and stilbite, the concentrations of leached Al and Si increase with increasing M₂O/H₂O ratio. It is also shown that NaOH solution has a greater propensity to leach more Al and Si than KOH solution. Despite kaolinite having a finer particle size, it is found for each M₂O/H₂O ratio (0.018, 0.045 or 0.09), that its concentrations of leached Al and Si are lower than stilbite in both NaOH and KOH solutions. This implies that during geopolymerisation, stilbite will contribute more dissolved Al and Si complexes than kaolinite into the gel phase. The dissolution procedures of kaolinite and stilbite in alkaline solution can be described as:

\[
\begin{align*}
\text{Dissolution} & \quad \text{Kaolinite (s)} & \rightarrow & \quad (\text{Al + Si}) \text{ complexes} \\
\text{Precipitation} & \\
\text{Dissolution} & \quad \text{Stilbite (s)} & \rightarrow & \quad (\text{Al + Si}) \text{ complexes} \\
\text{Precipitation}
\end{align*}
\] (5.1) (5.2)

When the S/L ratio changes from 0.1 to 0.3 and 0.1 to 0.4 respectively for kaolinite and stilbite, the concentrations of leached Al and Si increase linearly. With a further increase in the S/L ratio, a decrease in the leached Al and Si is observed and the equilibrium is obtained for S/L ratios of 0.5 and 0.7 for kaolinite and stilbite respectively. These results suggest that a certain layer of kaolinite and stilbite is rapidly dissolved and that the dissolution equilibrium shown by Equations 5.1 and 5.2 should be satisfied at the S/L ratios of 0.5 and 0.7 respectively.

In the case that one gram of stilbite or kaolinite has been added to 10ml MOH solution, the dissolution of the certain layers of the surface of the mineral is completed after 18 hours mixing. When the S/L ratio increases from 0.1 to 0.3 and 0.1 to 0.4 for kaolinite and stilbite respectively, the surface area available for dissolution
increases, which results in the linear increase in the concentrations of leached Al and Si complexes. A decrease in the leaching of Al and Si from kaolinite and stilbite is observed for S/L ratios greater than 0.35 and 0.45 respectively. It is proposed that this observed decrease is due to the high concentrations of Al and Si complexes in the solution, which hinder the further dissolution of Al and Si from the solid phase. At S/L ratios of 0.5 and 0.7 for kaolinite and stilbite respectively, the dissolution of Al and Si from the mineral surfaces of all particles occurs simultaneously. The concentrations of Al and Si, therefore, increase rapidly and the dissolution equilibria represented by Equations 5.1 and 5.2 are obtained. Along with a further increase in S/L ratio for kaolinite or stilbite, the concentrations of leached Al and Si complexes are found to remain almost constant. Consequently, it is assumed that the initial concentrations of Al and Si in the geopolymerisation are the same as the values observed at the S/L ratios of 0.5 and 0.7 for kaolinite and stilbite, respectively.

It is often expected that an increase in the dissolution of the aluminosilicate oxide source corresponds to an increase in the extent of geopolymerisation and hence to a higher compressive strength of the geopolymer product. In view of the above discussion, the greater M₂O/H₂O ratio and the Na⁺ cation should favour the geopolymerisation of the stilbite and kaolinite system. However, the results presented in Table 5.3 indicate that the compressive strength of the samples 1 to 3 and 9 to 11 decreases with an increase in the M₂O/H₂O ratio from 0.035 to 0.062 and then increases when the M₂O/H₂O ratio is varied from 0.062 to 0.107. It is also noted that the Na⁺ alkali metal cation, compared with K⁺, shows a significant negative influence on the compressive strength of the samples. Table 5.3 shows that for samples left in the oven for additional two days at a temperature of 35°C (samples 4 to 6 and 12 to 14), the compressive strength increased progressively as the M₂O/H₂O ratio is increased. This suggests that the difference in the compressive strength caused by different hardening times in the oven may be due to the viscosity as well as the M₂O/H₂O ratio. A longer hardening time may be required for samples with a higher M₂O/H₂O ratio to exclude an equivalent amount of spare water than for the lower M₂O/H₂O ratio. It is observed in the present work that two-day hardening in the oven at 35°C is satisfactory for a M₂O/H₂O ratio of 0.035, but five days are better for the 0.062 and 0.107 cases.
In summary, the present investigation shows that with increasing $M_2O/H_2O$ ratio, an increase in the dissolution of Al and Si is observed for both kaolinite and stilbite and this corresponds to an increase in the compressive strength of the formed geopolymer. This observation agrees well with the results presented in chapter 4. Alkali metal cations ($Na^+$ and $K^+$) are found to affect the dissolution and polymerisation steps. A separate and detailed discussion of their effects will be given later in this chapter.

5.2.2 Effect of $SiO_2/M_2O$ (where $M = Na$ and/or $K$)

Table 5.3 shows that the compressive strengths of samples 3, 11, and 17 to 20 increase with increasing $SiO_2/M_2O$ ratio. However, samples 18 and 20 (which are prepared without addition of $Na_2SiO_3$ solution) are found to exhibit significantly lower compressive strengths compared to the other samples tested. It has been reported previously by Davodovits (1991; 1994) that the addition of silicates or silicate solution is one of the essential conditions for geopolymerisation. The lower compressive strength of samples 18 and 20 is, therefore, expected because the geopolymeric gel phase formed by the dissolution of only kaolinite and stilbite is proposed to be too weak to bind the remaining undissolved Al-Si particles and resulting in a well formed geopolymer.

Table 5.3 also shows that increasing the $SiO_2/M_2O$ ratio from 0.18 to 0.26 results in an increase in the compressive strength of the geopolymers from 8.5 to 15.5 MPa and 18.9 to 25.1 MPa for NaOH and KOH cases, respectively (samples 3, 17, 11 and 19). A $SiO_2/M_2O$ ratio of greater than 0.26 has been tested in the study, but no significant increase is observed by using either NaOH or KOH solutions. It is worth noting that by addition of $Na_2SiO_3$ solution, the compressive strength of the resultant geopolymers increased significantly. This implies that some kind of mechanism must involve the $Na_2SiO_3$ species in geopolymeric reactions. The leaching results presented in Figures 5.1 to 5.4 and Table 5.2 show that the maximum condensed gel phase formed by the dissolution of kaolinite and stilbite in 10 M NaOH solution ($Na_2O/H_2O = 0.09$) is composed of $[(6.25 \times 10^{-2})_{kaolinite} + (4.4 \times 10^{-1})_{stilbite}] [SiO_2]$ and $[(1.75 \times 10^{-2})_{kaolinite} + (6.5 \times 10^{-2})_{stilbite}] [Al_2O_3]$. This composition is significantly lower than the minimum gel-polymerisation concentrations quoted by Barrer (1982) and so this
could be a reason for the lower compressive strength of samples 18 and 20. The compressive strength of geopolymers is believed to be derived from a combination of factors, including: (a) gel phase strength, (b) the ratio of the gel phase/undissolved Al-Si particles, (c) the distribution and the hardness of the undissolved Al-Si particle sizes, and (d) the surface reaction between the gel phase and the undissolved Al-Si particles. By adding the Na$_2$SiO$_3$ solution into geopolymer mix, an improvement in at least one, if not all, of the above listed factors is expected. In order to gain a qualitative insight into the gel phase behaviour of samples produced with and without addition of the Na$_2$SiO$_3$ solution, XRD and MAS-NMR techniques have been applied. These techniques enable an interpretation of the gel phase behaviour, which is impossible to be gained by conventional practical experiments.

XRD experiments are conducted on geopolymer samples having a Na$_2$O/H$_2$O ratio of 0.107 and a kaolinite/stilbite mass ratio varying from 9.0 to 0.1. The XRD patterns for stilbite, kaolinite and geopolymers formed using a kaolinite(g)/stilbite(g) ratio equal to 6.5 and different SiO$_2$/Na$_2$O ratios are presented in Figure 5.5. It is observed from patterns “c” and “d” that stilbite and kaolinite show lower intensities of their characteristic peaks when the SiO$_2$/Na$_2$O ratio is increased from 0.0 to 0.18. This means that the crystalline structure of stilbite and kaolinite decreases as the SiO$_2$/Na$_2$O ratio is increased, with the subsequent formation of an amorphous gel phase which is not detected by XRD. It is also noted that in XRD pattern “e”, the characteristic peak “A” for stilbite is not present. This suggests that nearly all crystalline stilbite, or at least some of its crystal planes, is leached into the gel phase when the SiO$_2$/Na$_2$O ratio is greater than or equal to 0.26. Therefore, it can be concluded that increasing the Na$_2$SiO$_3$ ratio in geopolymerisation (by addition of Na$_2$SiO$_3$ solution) results in a higher extent of geopolymerisation because a greater amount of kaolinite and stilbite is dissolved into the gel phase.

The $^{29}$Si and $^{27}$Al chemical shifts observed from MAS-NMR analyses on stilbite (Lippmaa et al., 1981), kaolinite (Madani et al., 1990) and geopolymers formed by stilbite and kaolinite are presented in Table 5.4. It is important to mention that kaolinite and stilbite have different $^{29}$Si NMR spectra and so the interpretation of $^{29}$Si NMR spectra of geopolymers from kaolinite and stilbite is possible. Geopolymer (1) listed in Table 5.4 is prepared by using a mass ratio of kaolinite/stilbite equal to 6.5
and a SiO$_2$/Na$_2$O and Na$_2$O/H$_2$O ratio of 0.0 and 0.107, respectively. According to Davydovits (1991; 1994) and Lippmaa et al. (1986) the $^{27}$Al chemical shifts of 63.5ppm and 1.7ppm observed for geopolymer (1) can be attributed to the tetrahedral framework structure of stilbite and the octahedral layer structure of kaolinite, respectively. Characteristic $^{29}$Si chemical shifts for both stilbite and kaolinite are detected in geopolymer (1), which means that the majority of stilbite and kaolinite still exist as their original crystalline structures. When the SiO$_2$/Na$_2$O ratio is increased to 0.26 (geopolymer (2)), three main differences for the $^{29}$Si and $^{27}$Al chemical shifts appear in the MAS-NMR spectra. The first two differences are the disappearance of the characteristic $^{29}$Si and $^{27}$Al chemical shifts at −98ppm and 63.5ppm for stilbite. This result is important because it implies that an increase in the SiO$_2$/Na$_2$O ratio results in stilbite being totally transferred into the geopolymeric gel phase. The third difference in the MAS-NMR spectrum for geopolymer (2) is that the $^{27}$Al chemical shifts are observed at 70.1ppm and 9.9ppm. This can be attributed to the gel phase and undissolved kaolinite particles. In conclusion, the $^{29}$Si and $^{27}$Al MAS-NMR analyses have shown that increasing the SiO$_2$/Na$_2$O ratio results in an increase in the dissolution of stilbite and kaolinite, with a corresponding increase in the amount of aluminosilicate particles that dissolve into the gel phase. This increases the density of the geopolymeric gel phase and as a consequence an improvement in the compressive strength of the geopolymer is observed because the gel phase/undissolved Al-Si particle ratio is increased.

The reasons why or how the SiO$_2$/M$_2$O ratio can have such a significant influence on geopolymeric reactions still remain unclear. At this stage, the other possible effects of the SiO$_2$/M$_2$O ratio on size distribution of undissolved Al-Si particles and the surface reactions between the gel phase and undissolved Al-Si particles in geopolymerisation are not well understood due to the restriction of proper experimental techniques.

In general, it is well accepted that in highly alkaline solution (pH ≈ 14), Al and Si complexes exist as Al(OH)$_4^−$, (OH)$_2$SiO$_2^{2−}$, (OH)SiO$_3^{2−}$ and other silicate oligomer anions (Barrer, 1982; Harvey and Dent Glasser, 1989; Caulet and Guth, 1989; Harris et al. 1982; Iler, 1982; Marsmann and Vongehr, 1982; Andersson et al. 1982; Dent Glasser and Lachowski, 1980; McCormick et al., 1989a; 1989b; 1989c; Hendrick, et
al. 1991). Without the addition of Na₂SiO₃ solution, the Al and Si complexes leached from stilbite and kaolinite in the present investigation are: Al(OH)₄⁺, (OH)₂SiO₂²⁻, (OH)SiO₃³⁻ and the silicate dimer (McCormick, et al., 1989a; Gasteiger, et al., 1992). The concentrations of these complexes are lower than required for polymerisation to occur between Al(OH)₄⁺ and silicate complexes (Barrer, 1982). Barrer (1982), Harvey and Dnet Glasser (1989), Caullet and Guth (1989), Andersson et al (1982) and McCormick et al., (1989a) have discovered previously by using ²⁹Si NMR that increasing the SiO₂/M₂O ratio promotes the formation of larger silicate oligomers, e.g. trimer, tetramer, hexamer and octamer. Furthermore, these studies have shown that the reaction rate between silicate oligomers and Al(OH)₄⁺ increases substantially under high pH conditions, which has been attributed to the Al(OH)₄⁺ complex having a greater ability to polymerise with larger silicate oligomers. This could possibly be the reason why in geopolymerisation an addition of silicate solids or condensed silicate solution is required. Caullet and Guth (1989) stated that the most stable polymerised species in highly alkaline aluminosilicate solution is that containing the highest number of Al atoms. Caullet and Guth (1989) have also indicated that the greater the amount of free Al(OH)₄⁺ existing in the solution, the more polymerisation of amorphous aluminosilicate gels can occur. Andersson et al (1982) proposed that Al-Si polymerisation occurs predominantly between Al(OH)₄⁺ and larger silicate oligomers, because he found that after such polymerisation, the amount of smaller silicate species (e.g. monomer and dimer species) remained constant while the amount of larger silicate species decreased. The observations of Caullet and Guth (1989) and Andersson et al (1982) implies that the aluminosilicate polymeric reaction takes place predominantly between Al(OH)₄⁺ and larger silicate oligomers. Therefore, it is expected that a simultaneous polymerisation between Al(OH)₄⁺ and larger silicate oligomers occurs along with the addition of silicate solids or solution. This polymerisation decreases the concentration of Al(OH)₄⁺ complexes in solution, thereby promoting the further dissolution of Al-Si particles from stilbite or kaolinite. This also suggests that the optimum SiO₂/M₂O ratio in geopolymerisation is a function of all the factors that affect the solubility of the Al-Si oxides sources used, such as the crystal structure, reaction time and also the particle size distribution.
5.2.3 Effect of Alkali Metal Cations (Na⁺ and K⁺)

In geopolymerisation, positively charged alkali metal cations are needed principally for balancing the negative charges caused by Al substitution for Si in the tetrahedral aluminosilicate framework structure (Davidovits, 1991; 1994). However, it has been shown previously that metal cations affect each step of the geopolymerisation process, including the dissolution of Al-Si oxides sources, polymerisation of the dissolved Al(OH)₄⁻ and silicate complexes, and also setting and hardening (Davidovits, 1991; 1994; Xu and Van Deventer, 2000a; Van Jaarsveld and Van Deventer, 1999a). Van Jaarsveld and Van Deventer (1999a) investigated the effect of the alkali metal activator on fly ash based geopolymers and concluded that the alkali metal cation affects the dissolution, gel hardening and eventual crystal formation processes by ordering H₂O and dissolved Al and Si complexes in solution. They also proposed that the alkali metal cations played a structure-directing role during geopolymerisation (Van Jaarsveld and Van Deventer, 1999a). Xu and Van Deventer (2000a) indicated that alkali metal cations affected the leaching and geopolymerisation by cation-anion ion pairing reaction.

Barrer (1982) and McCormic and Bell (1989) have proposed the structure-directing role of metal cations in zeolite nucleation as well as crystal growth processes. Gabelica et al. (1983) have suggested in their work on the synthesis of zeolite ZSM-5 that alkali metal cations simultaneously order water molecules and play a structure directing role as well. However, it should be noted that the conclusions drawn by Gabelica et al. (1983) are based on conditions of acidic nucleating and gelling, followed by weakly basic (pH ≈ 9, i.e [NaOH] ≈ 0.007 M) crystal growth. It is well accepted that alkali metal cations in acidic solution will order water molecules by the attraction between their positive charge centres and the oxygen of water through hydrogen bonds. In contrast, in highly alkaline solution positively charged alkali metal cations have an increasing probability to form ionic bonds with OH⁻ anion. This difference in bonding will result in less ordering as well as structure directing effects.

Geopolymers are often considered as the synthetic analogues of zeolites because of the similar hydrothermal reaction conditions as well as reactants involved
(Davidovits, 1991; 1994). This means that the results and conclusions drawn from zeolite research could be used to aid in the understanding of the phenomena observed in geopolymerisation. The essential difference between geopolymers and zeolites is that the former are synthesised in highly alkaline conditions while the latter are synthesised with a combination of acidic and basic conditions. Geopolymer products possess an amorphous to semi-crystalline structure while zeolites have highly ordered and readily identifiable crystal units. Therefore, it is possible to predict the bulk properties of zeolites from their crystal structure unit and also their chemical and physical properties from the structural precursors used to produce them. In contrast, similar properties for geopolymers are difficult to predict because of the uncertainties associated with the gel composition, gel structure, particle size distribution of undissolved Al-Si particles as well as the ratio of undissolved Al-Si particles and gel. In the present work, the geopolymers synthesised are a mixture of an amorphous gel phase and undissolved crystalline Al-Si particles. Accordingly, it should be realised that only in the dissolution and in early gelling stages geopolymerisation is similar to the synthesis of zeolites. After the gelling stage, the chemical and physical mechanisms involved in geopolymerisation and zeolite synthesis are different and as a result substantially different products are obtained. It should also be noted that these chemical and physical mechanisms are well understood in zeolite synthesis but unknown in geopolymerisation.

As discussed in chapter 4 and in previous research conducted by other researchers (Barrer, 1982; Harvey and Dent Glasser, 1989; Caulet and Guth, 1989; Harris et al. 1982; Iler, 1982; Marsmann and Vongehr, 1982; Andersson et al. 1982; Dent Glasser and Lachowski, 1980; McCormick et al., 1989a; 1989b; 1989c; Hendrick, et al. 1991), in highly alkaline solution, Na\(^+\) has a greater ability to stabilise silicate monomers and K\(^+\) favours forming larger silicate oligomers.

It is observed in chapter 4 and in the present work that more Al and Si can be leached from Al-Si oxide sources using NaOH solution rather than KOH solution. But the compressive strength of the geopolymers obtained shows significantly higher values when KOH solution is used. It is expected that upon the addition of silicate solids or silicate solution (e.g Na\(_2\)SiO\(_3\) or K\(_2\)SiO\(_3\)) into the geopolymer mix, the concentration of larger silicate oligomer anions is increased. These larger silicate oligomer anions
are ion-paired by the K$^+$ cation in preference to the Na$^+$ cation, thereby reducing the negative charge and also stabilising the larger silicate oligomer anions. Therefore, KOH solution contains not only a greater amount of larger silicate oligomers at any given time, but also a higher ratio of larger silicate oligomers/smaller oligomers than NaOH solution does. As a result, the polymerisation between Al(OH)$_4^-$ and larger silicate oligomers or larger polymerised particles is expected to occur faster in KOH solution. This directly results in faster setting and larger internal surface area as found by Van Jaarsveld and Van Deventer (1999a). Despite the fact that the K$^+$ cation can increase the rate of polymerisation between Al(OH)$_4^-$ and larger silicate oligomers, it has not been established to what degree K$^+$ is able to increase the extent of polymerisation, to improve the gel-phase composition, or to change the distribution between gel phase and undissolved Al-Si particles. This is important because it is believed that these factors affect the final compressive strength of geopolymers. Due to experimental restrictions, a direct investigation of the extent of geopolymerisation, the composition of gel phase and the distribution between gel phase and undissolved Al-Si particles cannot be conducted. However, through the application of XRD techniques, some important qualitative results can be obtained.

Figure 5.6 shows XRD patterns of geopolymers formed by stilbite and kaolinite using NaOH and KOH solutions and also for kaolinite/stilbite mass ratios 6.5/1 and 1/6.5 respectively. It is shown by Figure 5.6 that the characteristic peak for stilbite (labelled “A”) is not present in the XRD pattern labelled “a” but this peak is detected in pattern labelled ‘b’.

The difference between these XRD patterns is the type of metal cation used during the dissolution of stilbite. This result suggests that for a constant kaolinite/stilbite mass ratio of 6.5/1, the Na$^+$ cation promotes the formation of an amorphous gel phase with a corresponding decrease in the crystallinity of stilbite (as noted by the absence of the characteristic peak for stilbite in pattern “a”). In contrast, it is shown by the lower intensity of the characteristic peak for kaolinite (labelled “B”) in pattern “c” compared with “d” that the K$^+$ cation promotes the dissolution of kaolinite into the gel phase. This suggests that for a constant kaolinite/stilbite mass ratio of 1/6.5, the Si/Al molar ratio in the K$^+$-gel phase is lower than that in the Na$^+$-gel phase because kaolinite has a lower SiO$_2$/Al$_2$O$_3$ molar (Table 5.1) ratio than stilbite (i.e. SiO$_2$/Al$_2$O$_3$ kaolinite = 3.15, SiO$_2$/Al$_2$O$_3$ stilbite = 6.81). Although only qualitatively described, the results obtained using XRD have determined the effect of
metal cations on gel phase composition. This is an important result because the gel phase composition directly influences the final compressive strength of the geopolymer. As stated earlier, kaolinite has a much smaller particle size (1% >38 μm) than stilbite (25% >38 μm) and so kaolinite possesses a much larger surface area. Consequently this will result in less surface area left behind if the same amount of kaolinite is being transferred into the gel phase as in the case of stilbite. Therefore the type of metal cation (either Na⁺ or K⁺) could not only affect the gel phase composition but also change the ratio of gel/(undissolved Al-Si particles’ surface area), with K⁺ favouring a higher gel/(undissolved Al-Si particles’ surface area) ratio than the Na⁺ cation.

In conclusion, the present work has shown that the metal cations Na⁺ and K⁺ have a two-fold effect on geopolymerisation. They are ion pairing and preferentially leaching minerals. Na⁺ is found to increase the dissolution of Al-Si oxides, which has a beneficial effect on polymerisation and gelling steps in the geopolymerisation process. However, K⁺ cation is able to stabilise larger silicate oligomers and so acts as an accelerator in the condensation step of the geopolymerisation process. The results of the present work also show that K⁺ changes the gel phase composition and also increases the extent of polymerisation. Although the dissolution of Al and Si species is essential in initiating geopolymerisation, the polymerisation step appears to have a more significant effect on the final compressive strength of the geopolymer. This means that K⁺ rather than Na⁺ plays a more important role in geopolymerisation.

5.2.4  Effect of Setting Pressure and Mixing Procedure

Table 5.3 shows that setting pressure significantly increases the compressive strength of geopolymers formed in both NaOH and KOH cases. It is observed during the pressurised setting of samples 7, 8, 15 and 16 that solution is squeezed out of the joints in the sample mould. Consequently, it is believed that pressurised setting can exclude spare solution contained in the gel phase and result in an increase in the gel density. In addition, pressured setting will also cause the gel to evenly coat on undissolved Al-Si particles, thereby narrowing the inter-particle space which occurs
due to the evaporation of water. It is proposed that these two factors result in an increase in the compressive strength of the geopolymer.

The effect of different mixing procedure on the final compressive strength of geopolymer is shown by samples 3, 6 and 21 to 24 in Table 5.3. Samples 21 and 23 are prepared by first mixing MOH solution with Al-Si solid, followed by the addition of Na$_2$SiO$_3$ solution. In contrast, samples 22 and 24 are prepared by mixing the Al-Si solid with Na$_2$SiO$_3$ solution followed by the addition of MOH solution. Table 5.3 shows that both mixing procedures, “b” (samples 21 and 23) and “c” (samples 22 and 24), result in a geopolymer of lower compressive strength than the geopolymer formed by using mixing procedure “a”. Mixing procedure “a” involved the mixing of MOH and Na$_2$SiO$_3$ solutions, followed by the gradual addition of Al-Si solid source. These results suggest that MOH and Na$_2$SiO$_3$ solutions play a joint role, rather than separate roles, in geopolymerisation as recommended by Davidovits (1994). This observation is consistent with earlier results presented in this chapter. It is possible that due to the high viscosity of Na$_2$SiO$_3$ solution, whether mixing solid Al-Si oxide sources first with MOH solution (procedure “b”) or first with Na$_2$SiO$_3$ solution (procedure “c”), neither mixing procedure is able to produce a paste which is as homogeneously mixed as procedure “a”. Therefore, only a certain part of solid Al-Si particles takes part in geopolymerisation, which results in a large sacrifice in compressive strength.

5.3 SUMMARY

A series of geopolymerisations have been conducted by utilising stilbite as the main source of Al-Si oxides to investigate the different factors which affect the final compressive strength of geopolymers. The results obtained show that M$_2$O/H$_2$O molar ratio affects the solubility of stilbite and kaolinite as well as final compressive strength of the geopolymer. It has been found that increasing the M$_2$O/H$_2$O molar ratio results in an increase in dissolution of Al and Si species and also an increase in final compressive strength.

The ratio of added silicate solution and alkalinity SiO$_2$/M$_2$O is found to catalyse the geopolymerisation. Without the addition of silicate solution, there is no
geopolymerisation found to occur. The stilbite and kaolinite dissolve in the alkaline solution and precipitate onto the particle surface along with the evaporation of the water. Nearly no mechanical strength can be obtained when the stilbite/kaolinite matrix is geopolymerised in alkaline solutions without silicate addition.

A high SiO₂/M₂O molar ratio is assumed to result in the formation of predominantly larger silicate oligomers in solution. These larger silicate oligomers initiate the polymerisation with Al(OH)₄⁻ species and cause a decrease in the concentration of both Al and Si species in solution. Consequently, further dissolution of Al and Si species from the Al-Si solid occurs due to the shift in the dissolution equilibrium. The optimum SiO₂/M₂O ratio of 0.26 is determined in this study (M₂O/H₂O = 0.107). Under these conditions, a compressive strength of the resultant geopolymers is 15.5 MPa and 25.1 MPa respectively for the NaOH and KOH cases.

Pressurised setting has been shown to significantly improve the compressive strength of geopolymers formed by using NaOH and KOH solutions. The improvement in compressive strength, as setting pressure is increased, has been attributed to a reduction in internal spare space and more effective coating of the gel phase on undissolved Al-Si particles. It is found that a substantial improvement in compressive strength is achieved when MOH and sodium silicate solution is mixed prior to the addition of the Al-Si solid. The other mixing procedures investigated are proposed not to be able to produce a homogeneously mixed paste and so to result in a geopolymer with high compressive strength. It has been established that the metal cations, Na⁺ and K⁺, have multiple effects on the dissolution and polymerisation steps, with Na⁺ leading to a higher extent of dissolution and K⁺ resulting in a better compressive strength.

The possible chemical mechanisms involved in dissolution as well as in polymerisation can be explained by an ion-pair effect. However, other mechanisms, which have not yet been investigated, must also be involved in the dissolution and polymerisation steps, because it has been observed that K⁺ increases the dissolution of kaolinite, while Na⁺ increases the leaching of stilbite. A further study is needed to characterise the gel phase and to model the leaching and geopolymerisation processes.
Table 5.1 Composition of kaolinite and stilbite as determined by XRF analysis

(Mass %)

<table>
<thead>
<tr>
<th>Element as oxide</th>
<th>Kaolinite HR1/F</th>
<th>Stilbite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>54.5</td>
<td>59.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>29.4</td>
<td>14.8</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2</td>
<td>0.07</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.4</td>
<td>0.23</td>
</tr>
<tr>
<td>CaO</td>
<td>0.2</td>
<td>7.65</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.2</td>
<td>0.03</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.2</td>
<td>0.18</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.8</td>
<td>0.03</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>11</td>
<td>15.87</td>
</tr>
</tbody>
</table>

Table 5.2 Aluminium and silicon leached from kaolinite and stilbite in 10M MOH (10ml) solutions, calculated as [Al] ppm, [Si] ppm and [Al₂O₃], [SiO₂] molar concentrations respectively

<table>
<thead>
<tr>
<th>Kaolinite (g)</th>
<th>Stilbite (g)</th>
<th>Na₂O/H₂O ppm</th>
<th>K₂O/H₂O ppm</th>
<th>[Al] ppm</th>
<th>[Si] ppm</th>
<th>[Al₂O₃] (M)</th>
<th>[SiO₂] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.09</td>
<td>945</td>
<td>1750</td>
<td>1.75 × 10⁻²</td>
<td>6.25 × 10⁻²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.09</td>
<td>995</td>
<td>1709</td>
<td>1.84 × 10⁻²</td>
<td>6.1 × 10⁻²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.09</td>
<td>3510</td>
<td>12320</td>
<td>6.5 × 10⁻²</td>
<td>4.4 × 10⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.09</td>
<td>1200</td>
<td>4900</td>
<td>2.22 × 10⁻²</td>
<td>1.75 × 10⁻¹</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.3 Compressive strength of geopolymers formed by stilbite

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Na$_2$O/ H$_2$O</th>
<th>K$_2$O/H$_2$O</th>
<th>M$_2$O/H$_2$O (M=Na and/or K)</th>
<th>SiO$_2$/M$_2$O (M=Na and/or K)</th>
<th>Setting Pressure (lb/cm$^2$)</th>
<th>Mixing Procedure</th>
<th>MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.035</td>
<td>0.035</td>
<td>0.74</td>
<td>0</td>
<td>0</td>
<td>a</td>
<td>10.4</td>
</tr>
<tr>
<td>2</td>
<td>0.062</td>
<td>0.062</td>
<td>0.34</td>
<td>0</td>
<td>0</td>
<td>a</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>0.107</td>
<td>0.107</td>
<td>0.18</td>
<td>0</td>
<td>0</td>
<td>a</td>
<td>8.5</td>
</tr>
<tr>
<td>4</td>
<td>0.035</td>
<td>0.035</td>
<td>0.74</td>
<td>0</td>
<td>0</td>
<td>a</td>
<td>10.1*</td>
</tr>
<tr>
<td>5</td>
<td>0.062</td>
<td>0.062</td>
<td>0.34</td>
<td>0</td>
<td>0</td>
<td>a</td>
<td>11.5*</td>
</tr>
<tr>
<td>6</td>
<td>0.107</td>
<td>0.107</td>
<td>0.18</td>
<td>0</td>
<td>0</td>
<td>a</td>
<td>12.7*</td>
</tr>
<tr>
<td>7</td>
<td>0.107</td>
<td>0.107</td>
<td>0.18</td>
<td>5</td>
<td>a</td>
<td>15.1</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.107</td>
<td>0.107</td>
<td>0.18</td>
<td>20</td>
<td>a</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.017</td>
<td>0.018</td>
<td>0.035</td>
<td>0.74</td>
<td>0</td>
<td>a</td>
<td>19.2</td>
</tr>
<tr>
<td>10</td>
<td>0.017</td>
<td>0.045</td>
<td>0.062</td>
<td>0.34</td>
<td>0</td>
<td>a</td>
<td>16.3</td>
</tr>
<tr>
<td>11</td>
<td>0.017</td>
<td>0.09</td>
<td>0.107</td>
<td>0.18</td>
<td>0</td>
<td>a</td>
<td>18.9</td>
</tr>
<tr>
<td>12</td>
<td>0.017</td>
<td>0.018</td>
<td>0.035</td>
<td>0.74</td>
<td>0</td>
<td>a</td>
<td>18.9*</td>
</tr>
<tr>
<td>13</td>
<td>0.017</td>
<td>0.045</td>
<td>0.062</td>
<td>0.34</td>
<td>0</td>
<td>a</td>
<td>20.3*</td>
</tr>
<tr>
<td>14</td>
<td>0.017</td>
<td>0.09</td>
<td>0.107</td>
<td>0.18</td>
<td>0</td>
<td>a</td>
<td>23.8*</td>
</tr>
<tr>
<td>15</td>
<td>0.017</td>
<td>0.09</td>
<td>0.107</td>
<td>0.18</td>
<td>5</td>
<td>a</td>
<td>33.3</td>
</tr>
<tr>
<td>16</td>
<td>0.017</td>
<td>0.09</td>
<td>0.107</td>
<td>0.18</td>
<td>20</td>
<td>a</td>
<td>59.7</td>
</tr>
<tr>
<td>17</td>
<td>0.107</td>
<td>0.107</td>
<td>0.26</td>
<td>0</td>
<td>a</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>0.107</td>
<td>0.107</td>
<td>0.00</td>
<td>0</td>
<td>a</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>0.017</td>
<td>0.09</td>
<td>0.107</td>
<td>0.26</td>
<td>0</td>
<td>a</td>
<td>25.1</td>
</tr>
<tr>
<td>20</td>
<td>0.017</td>
<td>0.09</td>
<td>0.107</td>
<td>0.00</td>
<td>0</td>
<td>a</td>
<td>3.5</td>
</tr>
<tr>
<td>21</td>
<td>0.107</td>
<td>0.107</td>
<td>0.18</td>
<td>0</td>
<td>b</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>0.107</td>
<td>0.107</td>
<td>0.18</td>
<td>0</td>
<td>c</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.017</td>
<td>0.09</td>
<td>0.107</td>
<td>0.18</td>
<td>0</td>
<td>b</td>
<td>5.1</td>
</tr>
<tr>
<td>24</td>
<td>0.017</td>
<td>0.09</td>
<td>0.107</td>
<td>0.18</td>
<td>0</td>
<td>c</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Where “a” represents the mixing of MOH and Na$_2$SiO$_3$ solutions before the addition of solid sample.

“b” represents the mixing of MOH solution with solid sample first, followed by the addition of Na$_2$SiO$_3$ solution.

“c” represents the mixing of solid sample with Na$_2$SiO$_3$ solution, followed by the addition of MOH solution.

Data with “**” are treated by 5 days hardening in oven at 35°C.
Table 5.4 $^{27}$Al and $^{29}$Si MAS-NMR chemical shifts (ppm) of stilbite, kaolinite and geopolymers formed by stilbite and kaolinite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si(4Al)$^a$</th>
<th>Si(3Al)$^a$</th>
<th>Si(2Al)$^a$</th>
<th>Si(1Al)$^a$</th>
<th>Si(0Al)$^a$</th>
<th>Al(4Si)$^e$</th>
<th>Al(3Si)$^a$</th>
<th>Al$^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stilbite</td>
<td></td>
<td></td>
<td>-98$^b$</td>
<td>-101.5$^b$</td>
<td>-108$^b$, -111.3</td>
<td>59.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-91.5$^c$</td>
<td></td>
<td>-100.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0 , 2.3</td>
</tr>
<tr>
<td>Geopolymer</td>
<td>-92.4</td>
<td>-98.8</td>
<td>-104.7</td>
<td>-114.2</td>
<td>63.5</td>
<td></td>
<td></td>
<td>1.7</td>
</tr>
<tr>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Geopolymer</td>
<td>-90.03</td>
<td></td>
<td>-101.1</td>
<td>-106.6</td>
<td>70.1</td>
<td></td>
<td></td>
<td>9.9</td>
</tr>
<tr>
<td>(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a*: Si(nAl) and Al(nSi) designate the SiO$_4$ and AlO$_4$ tetrahedrons connected each other through shared oxygen atoms.

*b*: Data referred from Lippmaa et al. 1981.

*c*: Values cited from Madani et al. 1990.

*d*: Al associates with octahedral Al.

Geopolymer (1): Geopolymer formed by kaolinite/stilbite mass ratio = 6.5, Na$_2$O/H$_2$O = 0.107, SiO$_2$/Na$_2$O = 0.0,

Geopolymer (2): Geopolymer formed by kaolinite/stilbite mass ratio = 6.5, Na$_2$O/H$_2$O = 0.107, SiO$_2$/Na$_2$O = 0.26.
Figure 5.1. Leached [Si] (ppm) of kaolinite in 2M, 5M and 10M MOH (M = Na and/or K) solutions.

Figure 5.2 Leached [Al] (ppm) of kaolinite in 2M, 5M and 10M MOH (M = Na and/or K) solutions.
Figure 5.3 Leached [Si] (ppm) of stilbite in 2M, 5M and 10M MOH (M = Na and/or K) solutions.

Figure 4 Leached [Al] (ppm) of stilbite in 2M, 5M and 10M MOH (M = Na and/or K) solutions.
Figure 5.5. XRD patterns of stilbite, kaolinite and geopolymers formed by stilbite and kaolinite at kaolinite/stilbite mass ratio of 6.5, Na$_2$O/H$_2$O ratio of 0.107 and SiO$_2$/Na$_2$O ratio of 0.0, 0.18 and 0.26 respectively.
Figure 5.6. XRD patterns of geopolymers formed by stilbite and kaolinite at $\text{M}_2\text{O}/\text{H}_2\text{O}$ ratio of 0.107, SiO$_2$/M$_2$O ratio of 0.26, kaolinite/stilbite mass ratio of 6.5 and stilbite/kaolinite mass ratio of 6.5 in NaOH and KOH solutions respectively.
CHAPTER SIX

MICROSTRUCTURAL CHARACTERISATION OF GEOPOLYMERS SYNTHESISED FROM STILBITE/KAOLINITE MIXTURES USING XRD, MAS-NMR, SEM/EDX, TEM/EDX AND HREM

This chapter is based on a manuscript submitted to Cem. Concr. Res. 2001.

From the discussion in chapters 4 and 5, it has been found that geopolymers contain crystalline particles and amorphous gel as part of their structure. This particular structure makes the characterisation of geopolymers difficult, because the crystalline particles cannot be separated from the amorphous gel phase. On the other hand, the characterisation of geopolymers is essential to the study of geopolymerisation and improvement of the geopolymers produced. This chapter establishes a method using XRD, MAS-NMR, SEM/EDX, TEM/EDX and HREM techniques to successfully characterise the geopolymers synthesised from stilbite/kaolinite mixtures. The method developed in this chapter is also applicable to other geopolymeric systems as well as other related materials such as cement and concrete.

6.1 BACKGROUND

6.1.1 Introduction

Davidovits (1994) reported the structural characterisation of geopolymeric binders by XRD and MAS-NMR in 1994. It is noted that the geopolymeric binders (Poly-sialate, Poly-sialate-siloxo and Poly-sialate-disiloxo) characterised by Davidovits (1994) are evenly dispersed amorphous to semi-crystalline products synthesised at a temperature higher than 100°C and a pressure higher than atmosphere using kaolinite, yet at a temperature lower than 100°C and ambient atmosphere with calcined kaolinite as the sole aluminosilicate source. In contrast, most geopolymers synthesised from different starting materials are mixtures of crystalline aluminosilicate particles, semi-crystalline
and amorphous aluminosilicate gel, as discussed in chapters 4 and 5. Due to the complex composition of such geopolymers and the difficulties of separating the crystalline aluminosilicate particles from the semi-crystalline and amorphous gel phases, the characterisation of the structural composition of geopolymers has not been conducted so far.

As a mixture of amorphous to semi-crystalline phases, the mechanical strength of a geopolymer should be the result of both the amorphous gel phase as binder and the crystalline aluminosilicate particles as filler. Hence, an understanding of the structural composition as well as the gel phase of a geopolymer will aid in the development of improved geopolymers.

XRD, MAS-NMR, SEM/EDX and TEM/EDX techniques have been used previously to characterise cement, concrete, fly ash, zeolites and clay (Gao, et al., 1999; Davies and Oberholster, 1988; Iob, et al., 1993; Nagy, et al., 1989; Shigemoto, et al., 1995; Enders, 1995; Gomes, et al., 1999; Gomes and François, 2000; Velde, 1984). However, most of the work has involved qualitative or semi-quantitative analysis of crystalline materials (Gao, et al., 1999; Iob et al., 1993; Shigemoto, et al., 1995; Gomes, et al., 1999; Gomes and François, 2000). By using SEM/EDX, Davies and Oberholster (1988) carried out a semi-quantitative analysis of both the crystalline and amorphous phases for the surfaces of concrete and mortar specimens. Also, Enders (1995) characterised separate glassy and anhydrite fly ash particles by combining AEM and EDX techniques. Nevertheless, it has been noted that neither Davies and Oberholster's (1988) nor Ender's (1995) work is aimed at characterising the bulk structural composition with respect to the crystalline and amorphous phases.

The objective of this chapter is to develop an approach to semi-quantitative characterisation of the geopolymeric materials possessing both crystalline and amorphous phases. XRD, MAS-NMR, SEM/EDX, TEM/EDX and HREM techniques have been applied to analyse the structure of the geopolymers synthesised from stilbite/kaolinitite mixtures. The effect of the structural composition on the mechanical strength of geopolymers has also been considered.
6.1.2 Materials and experiments

Table 6.1 lists the composition, the average density, hardness and the mean particle size for kaolinite and stilbite. Clay (CMS KGa-1) is a well-crystallised kaolinite from Georgia, USA and obtained from the Source Clay Repository, Department of Geology, University of Missouri, Columbia, Missouri, U.S.A.

A total of 21 grams of kaolinite and stilbite powder are dry mixed at a kaolinite/stilbite mass ratio of 6.5 (G1), 0.5 (G2) and 0.1 (G3) for 10 minutes before the addition of 1.3 ml of sodium silicate and 6ml of 5M NaOH solutions. Each of the subsequent mixtures is mixed by hand for a further 5 minutes and then transferred to a steel mould measuring 20x20x20mm. After being left in an oven for 3 days at 35°C, the compressive strengths for these three samples are tested using the Tinus Tolsen Compressive Strength Testing Machine.

Geopolymers synthesised from the kaolinite/stilbite mixtures show differences in mechanical strength when different kaolinite/stilbite mass ratios are applied. It is assumed that a higher strength geopolymer is associated with a more desirable internal microstructure. A series of samples with kaolinite/stilbite mass ratios changing from 9.0 to 0.1 were investigated. An incremental increase in mechanical strength is observed as the kaolinite/stilbite mass ratio decreased. However, the geopolymer obtained at the kaolinite/stilbite mass ratio of “0” shows a lower compressive strength than that synthesised at the kaolinite/stilbite mass ratio of 0.1 (G3). Therefore, three geopolymers synthesised at kaolinite/stilbite mass ratios of 6.5 (G1), 0.5 (G2) and 0.1 (G3) are selected for investigation in the present work, with compressive strength given in Table 6.2. These compositions and matrices have not been selected to give optimal strengths, but rather to demonstrate the process principles involved.

XRD is used to detect the crystalline phases in geopolymers. As the kaolinite characteristic and stilbite characteristic peaks are found to be located at less than 30 degrees (2θ), the XRD patterns (Figures 6.1, 6.2 and 6.3) recorded for kaolinite, stilbite and the geopolymers synthesised from kaolinite/stilbite mixtures are shown
from 5 to 30 degree (2θ). The $^{29}$Si and $^{27}$Al MAS-NMR spectra are applied to analyse the co-ordinations of Al in kaolinite, stilbite as well as geopolymers G1, G2 and G3. SEM and SEM/EDX techniques are used to obtain the images and elemental composition for kaolinite, stilbite and geopolymers G1, G2 and G3. TEM and TEM/EDX analyses are conducted to obtain both images and elemental composition. A comparison between SEM/EDX and TEM/EDX is discussed. The accuracy of the TEM/EDX is tested with kaolinite (CMS KGa-1) and the systematic error is found to be less than 5% compared to the ideal composition of the kaolinite (CMS KGa-1). A HREM is used to observe the micro-structure of geopolymers G1 and G3.

6.2 STRUCTURAL CHARACTERISATION

6.2.1 XRD characterisation

Figures 6.1 to 6.3 show the powder X-ray diffraction patterns of kaolinite, stilbite and geopolymers synthesised at the kaolinite/stilbite mass ratios of 0.5, 6.5 and 0.1, respectively. It is found from Figure 6.1 that for the geopolymer synthesised at a kaolinite/stilbite mass ratio of 0.5 (G2), both the stilbite (020) peak “A” and the kaolinite (001) peak “B” are detectable, despite these two peaks being significantly lower in intensity after the geopolymerisation. This observation means that G2 contains both crystalline kaolinite and stilbite particles. It is also worthy to note that no new crystalline peak can be detected in any XRD patterns recorded for geopolymers G1, G2 and G3. Consequently, the gel phases formed during the geopolymerisation of the kaolinite and stilbite are probably amorphous to semi-crystalline in structure. The reason that the typical amorphous halo shape has not been observed in Figures 6.1(a), 6.2 and 6.3 could be attributed to the extraordinarily high intensity of the stilbite peak (thousands higher in intensity) which depresses the relative value of the amorphous signals. Moreover, a comparatively small amount of the gel phase embodied in the bulk geopolymers (G1, G2 and G3) could be another reason for the gel phase to be observed as the increased background, rather than an obvious halo shape. Nevertheless, when the most intensive peak (020) of the stilbite is removed from the XRD pattern (Figure 6.1(b)), an obviously increased background in
Figure 6.1(b) indicates that G2 comprises crystalline kaolinite and stilbite particles and amorphous to semi-crystalline gel phase.

Figure 6.2 shows the XRD pattern of the geopolymer synthesised at a kaolinite/stilbite mass ratio of 6.5 (G1). An XRD pattern for the powder mixture of kaolinite and stilbite before geopolymerisation at the same mass ratio of 6.5 is also given in Figure 6.2. It is noted that no stilbite characteristic peak “A” is observed for the geopolymer so that a complete transfer of stilbite particles from the crystalline phase to the amorphous gel phase is assumed to occur in the geopolymerisation of G1. For the geopolymer synthesised at a kaolinite/stilbite mass ratio of 0.1 (G3), the corresponding XRD pattern (Figure 6.3) contains only stilbite characteristic peaks. The disappearance of the kaolinite characteristic peak “B” in Figure 6.3 implies a complete dissolution of crystalline kaolinite particles during the geopolymerisation of G3.

Consequently, different structural compositions are observed for G1, G2 and G3, of which G1 consists of crystalline kaolinite particles and amorphous gel, G2 possesses both crystalline kaolinite and stilbite particles as well as gel phase, and G3 is composed of crystalline stilbite particles and gel phase. It is also noteworthy that there are no new peaks found in the XRD patterns recorded for G1, G2 and G3, which demonstrates that there are no new crystalline phases formed during the geopolymerisation of G1, G2 and G3.

6.2.2 MAS-NMR characterisation

Table 6.3 and Figure 6.4 describe the chemical shifts of $^{27}$Al and $^{29}$Si MAS-NMR for kaolinite, stilbite, G1, G2 and G3. It is observed that the $^{27}$Al and $^{29}$Si MAS-NMR signals for kaolinite and stilbite are different. In particular, kaolinite is structured by tetrahedral Si and octahedral Al atoms, while in stilbite both Si and Al atoms are tetrahedrally combined. The corresponding chemical shifts of $^{27}$Al MAS-NMR for kaolinite and stilbite are therefore found at 2.3 and 59.1 ppm respectively (Figure 6.4). The substantial difference between the chemical shifts of $^{27}$Al and $^{29}$Si MAS-NMR for kaolinite and stilbite also suggests that the technique of $^{27}$Al and $^{29}$Si MAS-NMR is useful for the characterisation of G1, G2 and G3.
NMR can be used for interpreting the microstructure of the geopolymers synthesised from kaolinite/stilbite mixtures.

From Figure 6.4, it is noted that the chemical shifts of $^{27}\text{Al}$ MAS-NMR obtained for G1 show both tetrahedral and octahedral Al atoms, of which the octahedral Al atom (9.9 ppm) can be interpreted as derived from kaolinite. The tetrahedral Al atom (70.1 ppm) observed in G1 is attributed to the Al atom structured in a three dimensional Si-O-Al block of the gel phase. The chemical shift of $^{29}\text{Si}$ MAS-NMR found in G1 also represents the Si atom (-90 ppm) present in kaolinite (Table 6.3).

In contrast with G1, G3 gives only tetrahedral $^{27}\text{Al}$ MAS-NMR signals at 57.9 ppm (Figure 6.4) despite the background showing an increase compared with the unreacted kaolinite or stilbite. The $^{27}\text{Al}$ MAS-NMR signals at 57.9 ppm can be assigned to the undissolved stilbite particles. The $^{27}\text{Al}$ MAS-NMR signals of G3 (Figure 6.4) show that no kaolinite particles can be detected in G3, because kaolinite will create characteristically an octahedral $^{27}\text{Al}$ MAS-NMR signal in the range of 0 to 10 ppm. The $^{27}\text{Al}$ MAS-NMR signals observed for G2 show both kaolinite and stilbite characteristic signals at 1.8 and 58.7 ppm respectively, which indicates both kaolinite and stilbite remaining in G2.

However, it is worthy to indicate that the $^{27}\text{Al}$ and $^{29}\text{Si}$ MAS-NMR signals corresponding to the gel phase are not clearly detected in the geopolymers synthesised from kaolinite/stilbite matrices (Figure 6.4). The possible reasons for this phenomenon could be as follows:

1. The formed gel phase is not abundant enough to show an identifiable peak as observed in G1 and G2 (Figure 6.4); it appears as the background instead.

2. With the addition of $\text{Na}_2\text{SiO}_3$ and due to the higher SiO$_2$ than Al$_2$O$_3$ contained in both kaolinite and stilbite (Table 6.1), the Si/Al ratio in the formed gel phase is expected to be higher than 2. This higher Si/Al ratio in the gel phase means that the $^{29}\text{Si}$ MAS-NMR signals of the gel may appear only as a halo ranging from Si(2Al) to Si(Al) and to Si(0Al). Since both kaolinite and stilbite have comparatively stronger signals appearing in the same range (Table 6.3), the signals created by the gel phase cannot be detected clearly.
In summary, the structural insight obtained from $^{27}$Al and $^{29}$Si MAS-NMR analyses for G1, G2 and G3 is in good agreement with the conclusions drawn from XRD analyses. G1 is a mixture of kaolinite particles and gel, G2 possesses both kaolinite and stilbite particles and gel, and G3 contains stilbite particles and gel. Such agreement demonstrates that both XRD and $^{27}$Al and $^{29}$Si MAS-NMR are reliable techniques for analysis of the structural composition in the present work.

6.3 GEL PHASE CHARACTERISATION

6.3.1 SEM and SEM/EDX characterisation

Figures 6.5 and 6.6 are images of kaolinite and stilbite powder taken by the JSM-6300F FEG scanning electron microscope. Kaolinite powder (Figure 6.5) shows a layered hexagonal shape with a particle size mostly smaller than 5 μm. Stilbite powder displays fourlings and triangle shapes (Gottardi and Galli, 1985) with a particle size mostly larger than 5 μm. During the geopolymerisation, the kaolinite and stilbite particles will partly dissolve and reduce in size, but they will not change their characteristic crystalline shapes. Therefore, the difference in appearance between the crystalline kaolinite and stilbite particles could be used for distinguishing the kaolinite and stilbite particles during SEM and TEM investigations of G1, G2 and G3.

As mentioned earlier, geopolymers are often mixtures of aluminosilicate particles and gel phase. Such mixtures can also be observed from the SEM images of G1, G2 and G3. Figures 6.7 to 6.9 are SEM images of the fractured surfaces of G1, G2 and G3 in which kaolinite particles ('A') are detected under the gel layer on the broken surface of G1 (Figure 6.7), while stilbite particles ('C') as well as gel are found on the broken surface of G3 (Figure 6.9). For G2 (Figure 6.8), both kaolinite ('A') and stilbite ('B') particles are observed with the gel on the fractured surface. It is also noticed from Figures 6.7 to 6.9 that G1 broke in the gel phase, while G2 and G3 fractured at the places where there was a deficiency of gel between particles. The observed difference between the broken surfaces of G1, G2 and G3 may suggest that G1 has a weaker gel than G2 and G3. The different amounts of the gel phase contained in G1, G2 and G3 may be another factor.
SEM/EDX analyses for the gel phases of G1, G2 and G3 were conducted at a magnification of 2000 at 15 different points in the gel phase. Table 6.4 lists the SEM/EDX results for the mean compositions of the gel phases of G1, G2 and G3. It is found from Table 6.4 that for G1 and G2, which started at the different kaolinite/stilbite mass ratios of 6.5 and 0.5 respectively, the mean concentrations of Al₂O₃ wt % and SiO₂ wt % in the corresponding gels are very close to each other. This phenomenon suggests that an equilibrium of Al₂O₃ wt % and SiO₂ wt % may exist in the gel phases of G1 and G2. As the kaolinite and stilbite have different Al₂O₃ wt % and SiO₂ wt % contents, the different starting mass ratio (6.5 and 0.5) will, consequently, transfer different amounts of Al and Si species from kaolinite and stilbite into the gel phases to form gels with different Al₂O₃ wt % and SiO₂ wt % concentrations. Since similar Al₂O₃ wt % and SiO₂ wt % are observed in the gel phases of G1 and G2, it is assumed that a kind of equilibrium between Al₂O₃ wt % and SiO₂ wt % may affect the formation of the gel phases.

However, it is also noticed that the mean Al₂O₃ wt % detected from the gel phase of G3 (Table 6.4) is significantly lower than that contained in the gel phases of G1 and G2. As the geopolymerisation of G3 is started at the kaolinite/stilbite mass ratio of 0.1, the lower mean Al₂O₃ wt % contained in the gel phase of G3 might be due to the lower content of Al₂O₃ wt % contained in stilbite (Table 6.1). The XRD and ⁷⁷Al and ²⁹Si MAS-NMR results showed that kaolinite was completely transferred into the gel phase of G3. Therefore, it can be deduced that an equilibrium is established between the Al₂O₃ wt % and SiO₂ wt % in the gel phase, but such an equilibrium is based on certain conditions. In particular, one such condition may be that both Al₂O₃ and SiO₂ rich aluminosilicate sources should be available throughout the geopolymerisation. In the geopolymerisation of kaolinite and stilbite, kaolinite should be treated as an Al₂O₃ rich source and stilbite as a SiO₂ rich source. The complete dissolution of kaolinite particles during the geopolymerisation of G3 made the Al₂O₃ wt % rich aluminosilicate source unavailable at some stage of the reaction, so that the Al₂O₃ wt % contained in the gel of G3 was lower than the equilibrium Al₂O₃ wt % observed in G1 and G2.

Another observation from Table 6.4 is that the mean CaO wt % contained in the gel phase increased along with a decrease in the kaolinite/stilbite mass ratio in the
geopolymerisation of G1, G2 and G3. From Table 6.1, kaolinite and stilbite are found to contain 0.2 wt % and 7.65 wt % of CaO respectively so that stilbite is the dominant mineral to dissolve CaO into the corresponding gel during geopolymerisation. In other words, the more stilbite involved in the geopolymerisation, the higher the CaO wt % observed in the corresponding gel. The CaO content of a source mineral was observed to enhance the mechanical strength of the resultant geopolymer (Xu and van Deventer, 2000a) although the exact mechanism is not known. No cement related calcium silica hydrate phases were found in XRD analysis (Figures 6.1 to 6.3), so that it can be assumed that the calcium forms part of the amorphous phase. G1 was observed to fracture in its gel phase at lower MPa values, which may imply that the gel phase of G1 comprised of lower CaO wt % is weaker than the gel phases of G2 and G3. It is also noticed (Table 6.4) that the Na₂O wt % in the gel phases of G1, G2 and G3 is 4.24, 1.53 and 9.27, respectively. The effect of Na₂O wt % contained in the gel phases on the compressive strength of the geopolymers or on the formation of gel phases is not clear yet.

It should be noticed that the SD (standard deviation) of SEM/EDX analyses for G1, G2 and G3 shown in Table 6.4 is up to 7.09. The observation of these high SD values can be attributed to the rough fractured surfaces of the samples. Usually SEM/EDX analysis is conducted on polished surfaces. However, G1, G2 and G3 are porous products that are hard to be polished without rubbing off of the particles from their surfaces and embedding of the grinding particles (SiC and/or Al₂O₃) in the surfaces. Furthermore, G1, G2 and G3 have soluble aluminates and silicates on their surfaces that will be contaminated by washing water during the cutting and polishing procedures. Thus, for geopolymers G1, G2 and G3, the SEM/EDX analyses were conducted on their rough fractured surfaces, which inevitably gave errors originating from the false reading of micro holes and/or micro crystalline particles on their surfaces.

6.3.2 TEM and TEM/EDX characterisation

Figures 6.10 and 6.11 depict the TEM image and diffraction pattern (DP) respectively of kaolinite powder taken by the Phillips EM 420 transmission electron microscope. The triclinic hexahedral shapes and hexahedral DP are observed from Figures 6.10
and 6.11, respectively. The obtained DP (Figure 6.11 (b)) from a kaolinite single crystal matches well with the theoretically simulated DP of kaolinite (Figure 6.11 (a)).

Figures 6.12 and 6.13 show the stilbite TEM image and diffraction pattern, respectively. Stilbite has triangular and fourlings shapes. The DP of stilbite (Figure 6.13 (b)) was observed to match the theoretically simulated DP (Figure 6.13 (a)) as well.

Figures 6.14 and 6.15 are TEM images of G1 and G3, respectively. Figures 6.10, 6.12, 6.14 and 6.15 show that TEM images offer an opportunity to view, select and analyse particles on a micro scale. A kaolinite particle (Figure 6.14 “A”) and stilbite particles (Figure 6.15 “A”) are identified in Figures 6.14 and 6.15, respectively. This corresponds with the previous XRD, NMR and SEM results. Also, gel particles with irregular shapes can be found in Figures 6.14 and 6.15.

Figures 6.16 and 6.17 show the diffraction patterns of gel particles. The DP with a dotted ring shape (Figure 6.16) is interpreted as a poly-crystallised particle and the DP with a cloudy ring (Figure 6.17) shape is produced by an amorphous particle.

TEM/EDX analyses for the gel phases of G1 and G3 were carried out as follows:
1) Find a gel particle with irregular shape at 12.7k magnification.
2) Perform an electronic diffraction on the selected particle to see whether it is amorphous or not.
3) After identifying the particle as an amorphous gel particle, perform an EDX analysis.
4) Repeat the above procedures (1) to (3) fifteen times to determine the variability of results.

Table 6.5 shows the mean results obtained from the TEM/EDX analyses for G1 and G3. During the analysis of TEM/EDX, the Cliff-Lorimer factor $K_{\text{sial}}$ has been calculated by using the stoichiometry of kaolinite (CMS KGa-1). Thus only Al$_2$O$_3$ and SiO$_2$ values calculated from the Al and Si counts are reported in Table 6.5. The values of Al$_2$O$_3$ wt % and SiO$_2$ wt % for G1 and G3 listed in Table 6.5 are close to the values shown in Table 6.4. It is noteworthy that the values of SD are lower in Table 6.5 than in Table 6.4. Consequently, it is observed that both SEM/EDX and
TEM/EDX are reliable techniques for semi-quantitative analysis of the gel compositions of G1 and G3, but TEM/EDX has a higher reproducibility and can be considered more accurate. The reason why TEM/EDX is more accurate than SEM/EDX for the analysis of gel is that the TEM/EDX technique can analyse individual particles after the identification of the amorphous gel phase, which avoids false readings from any other crystalline phases or micro holes.

The investigation results obtained from XRD and $^{27}$Al and $^{29}$Si MAS-NMR suggest that stilbite particles are completely dissolved during the geopolymerisation of G1 and kaolinite particles are totally transferred into the gel of G3. Therefore, a calculation for the structural compositions of G1 and G3 can be conducted based on the assumptions that there are no new crystalline products and precipitates formed during the geopolymerisation of G1 and G3, and the added sodium silicate stays in the gel phase. Equation (1) listed below schematically describes the geopolymerisation from kaolinite/stilbite mixtures:

$$\text{Kaolinite (s) + Stilbite (s) + Sodium silicate solution + NaOH solution}$$

\[ \downarrow \]

\[ \downarrow \]

Geopolymer

(undissolved solid particles + gel phase )

(6.1)

The $\text{Al}_2\text{O}_3$ and $\text{SiO}_2$ contained in the gel can be expressed as equations 2 and 3, respectively.

$$\text{SiO}_2 \text{ (K)} + \text{SiO}_2 \text{ (St)} + \text{SiO}_2 \text{ (So)} = \text{SiO}_2 \text{ (Gel)}$$

(6.2)

$$\text{Al}_2\text{O}_3 \text{ (K)} + \text{Al}_2\text{O}_3 \text{ (St)} = \text{Al}_2\text{O}_3 \text{ (Gel)}$$

(6.3)

where $\text{SiO}_2 \text{ (K)}$ represents $\text{SiO}_2$ dissolved from kaolinite powder, $\text{SiO}_2 \text{ (St)}$ represents $\text{SiO}_2$ dissolved from stilbite particles, $\text{SiO}_2 \text{ (So)}$ represents $\text{SiO}_2$ added from sodium silicate solution, $\text{SiO}_2 \text{ (Gel)}$ represents $\text{SiO}_2$ contained in gel phase, $\text{Al}_2\text{O}_3 \text{ (K)}$ represents $\text{Al}_2\text{O}_3$ dissolved from kaolinite powder, $\text{Al}_2\text{O}_3 \text{ (St)}$ represents $\text{Al}_2\text{O}_3$
dissolved from stilbite particles and Al₂O₃ (Gel) represents Al₂O₃ contained in the gel phase. The weight percentages of Al₂O₃ and SiO₂ in kaolinite, stilbite and gel phases of G1 and G3 can be obtained from Tables 6.1 and 6.5, respectively. The added SiO₂ (So) is calculated as 1.3 ml × 1.385 (g/ml) × 28.65 wt %, which gives 0.516 (g) of SiO₂ (So).

The total start solid mixture weighs 21 grams and the kaolinite/stilbite mass ratios for G1 and G3 are 6.5 and 0.1, respectively, so that 2.8 grams of stilbite and 1.91 grams of kaolinite have been transferred respectively into the gel phases of G1 and G3. Thus equations (2) and (3) can be expressed for the case of G1 as:

\[2.8 \times 59.2 \% + X \times 54.5 \% + 0.516 = Y \times 64.7 \%\]  \hspace{1cm} (6.4)
\[2.8 \times 14.8 \% + X \times 29.4 \% = Y \times 25.96 \%\]  \hspace{1cm} (6.5)

and for the case of G3 as:

\[1.91 \times 54.5\% + Z \times 59.2 \% + 0.516 = W \times 62.75 \%\]  \hspace{1cm} (6.6)
\[1.91 \times 29.4 \% + Z \times 14.8 \% = W \times 19.22 \%\]  \hspace{1cm} (6.7)

where X represents the grams of kaolinite dissolved into the gel phase of G1, Y represents the total grams of the gel phase of G1, Z represents the grams of stilbite dissolved in the gel phase of G3, and W represents the total grams of the gel phase of G3.

When (6.4) and (6.5) or (6.6) and (6.7) are combined, X and Z can be solved as:

\[X = 6.1 \text{ (g)}\]  \hspace{1cm} (6.8)
\[Z = 2.5 \text{ (g)}\]  \hspace{1cm} (6.9)

So the dissolved kaolinite and stilbite in the geopolymerisations of G1 and G3 are 6.1 and 2.5 grams, respectively. The structural composition of G1 is 12.1 grams of kaolinite particles and 8.5 grams of gel. In other words, G1 is composed of 58.7 wt % of crystalline particles and 41.3 wt % of amorphous gel. G3 consists of 77 wt % of
crystalline stilbite particles and 23 wt % of amorphous gel phase. It has been noted that G1 contains more gel phase than G3. However, G1 also showed lower compressive strength than G3 (Table 6.2), which suggests that other factors such as the ratio of (average surface area)/gel, CaO wt % in the gel and the interwoveness of crystalline particles with gel may also affect the final mechanical strengths of G1 and G3.

The calculated average surface areas of the particles contained in G1 and G3 by using average particle sizes and densities of kaolinite and stilbite are $6.82 \times 10^4$ (cm$^2$) and $2.35 \times 10^4$ (cm$^2$), respectively. It is noticed that the surface area of the particles contained in G1 is 2.9 times the surface area of the particles in G3. Also, the calculated ratio of (average surface area)/gel in G1 is found to be 1.64 times that in G3. Hence, it is found that although G1 contains more gel phase than G3, it has a higher ratio of (average surface area)/gel as well. A higher ratio of (average surface area)/gel means on average a thinner gel layer between the undissolved particles in G1. Therefore, the reasons why G1 shows lower compressive strength than G2 and G3 may be not only the weaker gel phase but also the higher ratio of (average surface area)/gel. Besides the lower CaO wt % contained in the gel and the higher ratio of (average surface area)/gel in G1, the lower hardness (2.5 Mohs.) of the remaining kaolinite particles may also negatively affect the mechanical strength of G1.

However, it has to be stated that the analyses of SEM/EDX and TEM/EDX conducted in this chapter are only at a semi-quantitative level, as the analyses cover only a very small part of the corresponding bulk geopolymer. Considering that other practical techniques cannot distinguish the crystalline phases from the amorphous gel, such a semi-quantitative method is satisfactory for providing some insight into the structural composition of geopolymers. The interpretation of the results obtained from semi-quantitative SEM/EDX and TEM/EDX analyses can also aid in the understanding of the factors affecting the final compressive strength of a geopolymer. The method developed in the present work is also applicable to other related materials such as cement and concrete.
6.3.3 HREM characterisation

Figures 6.18 and 6.19 are the images of G1 and G3 taken by High Resolution Transmission Electron Microscopy (HREM). It has been observed that both G1 and G3 are composed of amorphous gel and crystalline particles. The crystal lattice of kaolinite can be observed ("A") in Figure 6.18, while only a distorted crystal lattice of stilbite is found in Figure 6.19 ("B"). A quick shift from a regular crystal lattice image to a disordered amorphous image is observed throughout the HREM investigations for both kaolinite and stilbite particles. In particular, the crystalline stilbite is found to have a quicker shift than that of kaolinite, which is also the reason why only an image of a distorted crystal lattice was recorded for stilbite. The phenomenon of the shifts of crystal lattice suggests that beam damage happened for both kaolinite and stilbite during the HREM studies. The shifts of crystal lattice observed during HREM analyses also suggest that the energy gaps between crystalline kaolinite or stilbite and their amorphous structures are not large, which may be the reason why these two minerals have high reactivity in geopolymerisation. In spite of beam damage which will transfer part of the crystalline kaolinite and stilbite particles into the amorphous phase, the HREM studies of G1 and G3 have proven at the micro-crystal level that only amorphous and kaolinite or stilbite characteristic crystal lattices are observed in G1 and G3 respectively.

6.4 SUMMARY

When an excess of stilbite is present in a mixture of stilbite and kaolinite, a fraction of the stilbite remains as a crystalline phase interspersed in a continuous amorphous geopolymeric phase. When the stilbite is deficient, the kaolinite remains partially dissolved in the gel phase. XRD and $^{29}$Si and $^{27}$Al MAS-NMR were used to show the characteristic diffraction patterns and chemical shifts respectively for the remaining crystalline phase. TEM electron diffraction and HREM were used to establish the amorphous nature of the formed continuous gel phase. SEM, TEM and HREM could also be used to identify the undissolved mineral phases. TEM/EDX was shown to give a more reliable micro-analysis of the composition of the gel phase than SEM/EDX. The mean composition of the continuous gel phase was used in a simple mass balance
equation to calculate the quantity of gel formed and the associated amount of partially reacted mineral, if it was assumed that one mineral in a binary system dissolved completely. For example, a geopolymer synthesised at the kaolinite/stilbite mass ratio of 6.5 was found to contain 58.7 wt % of crystalline kaolinite particles and 41.3 wt % of gel phase. At the kaolinite/stilbite mass ratio of 0.1, the produced geopolymer was composed of 77 wt % of crystalline stilbite particles and 23 wt % of gel phase. It was also found that the compressive strength of a geopolymer increased as a higher CaO wt % was present in its gel, a lower ratio of (average surface area)/mass of gel was developed, and where the remaining crystalline particles had a higher hardness. These observations will provide the basis for an improved understanding of geopolymer technology and the characterisation of source materials. The method developed in this chapter could also be used in other related materials such as conventional concrete.
Table 6.1 Composition, density, hardness and mean particle size of kaolinite and stilbite

<table>
<thead>
<tr>
<th>Element as oxide</th>
<th>Kaolinite HR1/F</th>
<th>Stilbite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>54.5</td>
<td>59.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>29.4</td>
<td>14.8</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2</td>
<td>0.07</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.4</td>
<td>0.23</td>
</tr>
<tr>
<td>CaO</td>
<td>0.2</td>
<td>7.65</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.2</td>
<td>0.03</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.2</td>
<td>0.18</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.8</td>
<td>0.03</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>11</td>
<td>15.87</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Density g/cm³³</th>
<th>2.62</th>
<th>2.21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (Mhos)*</td>
<td>2.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

| Mean particle size | 5.8 µm | 23.05 µm |

*: Cited from Nichol and Nichols, 1991

Table 6.2 Compressive strength of geopolymers synthesised from kaolinite/stilbite matrix

<table>
<thead>
<tr>
<th>Geopolymer</th>
<th>Kaolinite/stilbite (mass ratio)</th>
<th>MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>6.5</td>
<td>2.3</td>
</tr>
<tr>
<td>G2</td>
<td>0.5</td>
<td>7.8</td>
</tr>
<tr>
<td>G3</td>
<td>0.1</td>
<td>9.5</td>
</tr>
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</table>
Table 6.3 $^{27}$Al and $^{29}$Si MAS-NMR chemical shifts (ppm) of stilbite, kaolinite and geopolymers synthesised from kaolinite/stilbite mixtures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si(3Al)$^a$</th>
<th>Si(2Al)$^a$</th>
<th>Si(1Al)$^a$</th>
<th>Si(0Al)$^a$</th>
<th>Al(4Si)$^a$</th>
<th>Al(3Si)$^a$</th>
<th>Al$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stilbite</td>
<td>-98</td>
<td>-101.5</td>
<td>-111.3</td>
<td>59.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kaolinite</td>
<td>-91.6</td>
<td>-100.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.3</td>
</tr>
<tr>
<td>G1</td>
<td>-90</td>
<td>-101.1</td>
<td>-106.6</td>
<td>70.1</td>
<td>9.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G2</td>
<td>-92.4</td>
<td>-98.8</td>
<td>-102.3</td>
<td>-114.9</td>
<td>58.7</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>G3</td>
<td>-98.2</td>
<td>-102.1</td>
<td>-110.7</td>
<td>57.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a: Si(nAl) and Al(nSi) designate the SiO$_4$ and AlO$_4$ tetrahedrons connected to each other through shared oxygen atoms.

b: Al associates with octahedral Al.

G1: Geopolymer synthesised at the kaolinite/stilbite mass ratio of 6.5.
G2: Geopolymer synthesised at the kaolinite/stilbite mass ratio of 0.5.
G3: Geopolymer synthesised at the kaolinite/stilbite mass ratio of 0.1.

Table 6.4. Composition of gel phase in geopolymers (G1, G2 and G3) detected by SEM/EDX

<table>
<thead>
<tr>
<th>Element as oxide wt %</th>
<th>G1</th>
<th>G2</th>
<th>G3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
<td>Mean</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>27.25</td>
<td>6.96</td>
<td>28.18</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>63.13</td>
<td>5.97</td>
<td>60.08</td>
</tr>
<tr>
<td>CaO</td>
<td>2.83</td>
<td>2.19</td>
<td>7.7</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>4.24</td>
<td>2.56</td>
<td>1.53</td>
</tr>
<tr>
<td>FeO</td>
<td>0.85</td>
<td>0.6</td>
<td>0.41</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.76</td>
<td>1.55</td>
<td>2.14</td>
</tr>
</tbody>
</table>

SD: Represents the standard deviation.
Table 6.5 Composition of gel phase in geopolymers (G1 and G3) obtained from TEM/EDX analyses

<table>
<thead>
<tr>
<th>Element as oxide wt %</th>
<th>G1</th>
<th></th>
<th>G3</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>25.96</td>
<td>2.79</td>
<td>19.22</td>
<td>2.71</td>
</tr>
<tr>
<td>SiO₂</td>
<td>64.7</td>
<td>3.59</td>
<td>62.75</td>
<td>1.8</td>
</tr>
</tbody>
</table>

SD: Represents the standard deviation.
Figure 6.1. XRD patterns, (a) geopolymer and powder mixture of kaolinite and stilbite at the mass ratio of 0.5 ($2\theta = 5 - 30$), (b) geopolymer of kaolinite and stilbite at the mass ratio of 0.5 ($2\theta = 15 - 30$).
Figure 6.2. XRD patterns of geopolymer with kaolinite/stilbite mass ratio of 6.5 and the powder mixture of kaolinite and stilbite with the same mass ratio.
Figure 6.3. XRD patterns of geopolymer with kaolinite/stilbite mass ratio of 0.1 and the powder mixture of kaolinite and stilbite with the same ratio.
Figure 6.4. The chemical shifts of $^{27}$Al NMR recorded for stilbite, kaolinite and geopolymers synthesised at the kaolinite/stilbite mass ratio of 6.5 (G1), 0.5(G2) and 0.1 (G3), respectively.
Figure 6.5. SEM image of kaolinite powder

Figure 6.6. SEM image of stilbite powder
Figure 6.7. SEM image of G1 with ‘A’ showing kaolinite particles

Figure 6.8. SEM image of G2, with ‘A’ showing kaolinite particle and ‘B’ showing stilbite particle
Figure 6.9. SEM image of G3 with ‘C’ showing stilbite particle

Figure 6.10 TEM image of kaolinite
(a) Simulated DP of kaolinite

(b) DP of kaolinite

Figure 6.11. Simulated and real Dp of kaolinite particle
Figure 6.12. TEM image of stilbite
(a) Simulated DP of stilbite

(b) DP of stilbite

Figure 6.13. Simulated and real Dp of stilbite particle
Figure 6.14. TEM image of G1 with 'A' showing kaolinite particle

Figure 6.15. TEM image of G3 with 'A' showing stilbite particle
Figure 6.16. DP of semi-crystallised geopolymer formed by kaolinite/stilbite matrix

Figure 6.17. DP of amorphous geopolymer formed by kaolinite/stilbite matrix
Figure 6.18. HREM image of G1 with 'A' showing kaolinite crystal particle

Figure 6.19. HREM image of G3
CHAPTER SEVEN

MODELLING OF STILBITE USING AB INITIO CALCULATION

This chapter is based on the publication: Ab initio calculations on the five-membered aluminosilicate framework rings model: implications for dissolution in alkaline solutions, Computers and Chemistry 24 (2000), 391-404.

It has been discussed in chapter 4 that the crystal structure of Al-Si minerals has a significant influence on their ability to undergo geopolymerisation. It has also been found that framework structured Al-Si minerals show the highest ability to undergo geopolymerisation. Chapters 4 to 6 have discussed the factors affecting geopolymerisation, the mechanisms involved in leaching and geopolymerisation, and characterisation of geopolymers. However, how the crystal structure of Al-Si minerals affects their leaching and geopolymerisation has not been studied so far. Since the natural Al-Si minerals possess a large variation in crystal structure, such a study has to be simplified and limited to certain models. Due to its higher ability to undergo geopolymerisation, stilbite, which possesses a framework structure, has been modelled in this chapter. The geopolymerisation of stilbite involves silicates, alkaline solution, kaolinite and stilbite which makes the system too complex to be modelled by the ab initio method, so that only the dissolution step is calculated in this chapter. Kaolinite, which is very important in geopolymerisation, has been studied by the ab initio method previously (Hobbs et al., 1997) so that no calculation is conducted on it in this thesis.

7.1 BACKGROUND

7.1.1 Introduction

Geopolymers are amorphous to semi-crystalline three dimensional aluminosilicate materials. The primary structural building units of geopolymers are the tetrahedral $\text{TO}_4$, where T is Si or Al. Under strongly alkaline conditions aluminosilicate oxides ($\text{Al}^{2+}$ in IV or VI fold coordination) and silicates are dissolved into solution to form
tetrahedral T(OH)$_4$ units. If water is gradually split out in a polycondensation reaction
the T(OH)$_4$ units are linked irregularly to yield polymeric (SiO$_4$)$\bullet$(AlO$_4$),
(SiO$_4$)$\bullet$(AlO$_4$)$\bullet$(SiO$_4$) and (SiO$_4$)$\bullet$(AlO$_4$)$\bullet$(SiO$_4$)$\bullet$(SiO$_4$) precursors by sharing nearly
all oxygen between two tetrahedral TO$_4$ units, and thereby forming amorphous to
semi-crystalline Al-Si geopolymer (Davidovits, 1991, 1994).

The kinetics and mechanisms of dissolution of silicate and aluminosilicates have been
researched extensively by both practical and theoretical scientists (Dibble and Tiller,
1981; Knauss and Wolery, 1988; Casey et al., 1988; Casey et al., 1989; Casey and
Bunker, 1990; Casey, 1991; Casey and Westrich, 1992; Casey et al., 1993; Casey and
Ludwig, 1995; Dove and Crerar, 1990; Dove and Elston, 1992; Brady and Walther,
1989, 1990; Gratz and Bird, 1993a,b; Xiao and Lasaga, 1994; Kubicki et al., 1993;
1996; Kubicki and Sykes, 1993; 1995; Antonic et al., 1993, 1994; Dent Glasser, 1982;
Dent Glasser and Harvey, 1984a,b; Devidal et al., 1994; Gasteiger et al., 1992;
Hendricks et al., 1991; McCormick et al., 1989a,b,c; Swaddle et al., 1994; Babushkin
et al., 1985). In all those theoretical studies it is essential to postulate a molecular
structure to enable an analysis of the kinetics and mechanism of silicate dissolution.
The selection of an energy-optimised geometry is an essential starting step for an
eventual understanding of the chemical bonding occurring on the mineral surface.

High level ab initio calculations have been shown to be successful in predicting the
structures and physical properties of minerals (Hobbs, et al., 1997). By far the most
important conclusion from this work is that the major structures and energetics of
silicates, oxides and aluminosilicates can be accounted for by short-range directional
forces, or "covalent" bonding in the traditional sense (Lasaga and Gibbs, 1988). As a
result, finite molecular clusters can be used to simulate the local environment and
provide significant insights into the atomic forces and bonding pictures of minerals.
With the vast increase in computational power, it is feasible to calculate high level ab
initio potential surfaces that incorporate bonding breaking and bonding forming
processes. In particular, the reaction pathways and energetics of surface reactions
involving silicates and aluminosilicates can be studied from the atomic point of view
with these techniques (Lasaga and Gibbs, 1988; Casey et al., 1990; Kubicki et al.,
1993).
Stilbite \([\text{NaCa}_4(\text{Si}_{27}\text{Al}_9)\text{O}_{72} \cdot 30\text{H}_2\text{O}]\) is an aluminosilicate mineral with a 5-membered framework ring structure. In geopolymerisation experiments stilbite shows a relatively high extent of dissolution under strongly alkaline solutions and is highly reactive in geopolymerisation reactions (Xu and Van Deventer, 2000a). Stilbite could be considered as a representative aluminosilicate mineral with potential to be a source material for geopolymers. In order to understand the behaviour of such aluminosilicate minerals in the dissolution process an ab initio Hartree-Fock calculation utilising the standard 6-31G basis set is carried out to study the atomic interactions responsible for the role of local and alkaline environment. This chapter will aim to answer the following questions:

1. In an energy-optimised 5-membered framework ring model containing a total of 10 T sites, which T site is the most favourable site for Al substitution of Si, and which T site is the least favourable site?

2. Under local environment, which T\((Q^3)\) centre is the most favourable T site for ring breakage to release T\((\text{OH})_4\) tetrahedra, and which is responsible for the effect of the local environment?

3. Under a highly alkaline environment, how do Na\(^+\) and K\(^+\) cations affect the broken ring structures as well as dissolved Al and Si species after releasing T centres as HOT\((\text{OM})_3\) tetrahedra, in terms of their different sizes (Where M represents Na and K)?

4. A brief explanation will also be given for the dissolution mechanism of a 5-membered framework ring in highly alkaline solutions, and how such dissolution relates to the formation of geopolymers.

7.1.2 Structural modelling

The ab initio calculations are carried out using Gaussian 94 (Frisch et al., 1994) on an Cray Ormond supercomputer (OSF). For the calculation of electronic structure a Restricted Hartree-Fock (RHF) theory is employed. A semi-empirical calculation PM3 is used to determine fully optimised geometries for all stationary points, except the cluster containing Na or K atoms. The atomic structure and the total energies are calculated at HF level with a basis set of 6-31G. The geometry of clusters containing
Na or K is fully optimised for all stationary points at the level of HF with a 6-31G basis set.

An important requisite of ab initio studies of minerals is to choose suitable molecular clusters to simulate the bulk solid or solid surface, which enables quantum calculations to be carried out. Of primary concern is the size of the cluster and the basis set being used in such calculations. This is because the computing time increases dramatically with an increase in the size of the cluster as well as the basis set. On the one hand both the chosen cluster as well as the basis set should be sufficiently large to accurately mimic the local environment of the structure of the mineral, while on the other hand the cluster and basis set should be sufficiently small to ensure computational feasibility.

Figures 7.1(a), 7.1(b) and 7.1(c) show the infinite structure of three minerals (all from the heulandite group) stilbite, heulandite and brewsterite respectively with nodes substituting the tetrahedral centres and linkages substituting the oxygen bridges (Gottardi and Galli, 1985). It can be seen that these three minerals have the same structural unit, which is called the heulandite unit or 4-4-1-1 unit (Gottardi and Galli, 1985) as shown in Figure 7.1(d).

The heulandite unit consists of two 5-membered rings and possesses C2/m symmetry. In previous molecular orbital studies on 3-membered and 4-membered framework rings the potential energy minima, force constant and vibrational frequencies have been calculated using a single ring cluster model (Chakoumakos et al., 1981; Kubicki and Sykes, 1993,1995; Sykes and Kubicki, et al. 1996). The 5-membered rings are uncommon in either silicates or siloxanes, consequently few theoretical calculations have been conducted for this structure, especially for the cluster containing two connected 5-membered rings (Chakoumakos et al., 1981). A study of the two connected 5-membered rings with symmetry of C2/m will give a more accurate representation of the heulandite group minerals because it models the heulandite 4-4-1-1 unit. In order to minimise the model size this cluster with all suspended bonds terminated by OH groups is selected in MO (Molecular Orbital) calculations. Figure 7.2 depicts the energy-optimised structure of the 4-4-1-1 cluster with all T sites occupied by Si atoms.
7.2 AB INITIO STUDY OF ALUMINIUM SUBSTITUTION

The stoichiometric formula of stilbite, NaCa4(Si27Al9)O72•30H2O, indicates that the total atomic ratio of Si/Al in stilbite is 3. As the cluster calculated contains 10 T sites, the real distribution of Al and Si atoms in the cluster will be the combination of the cluster with 8 Si atoms and 2 Al atoms, and the cluster with 7 Si atoms and 3 Al atoms. The cluster with 7 Si atoms and 3 Al atoms will be studied in detail in this chapter, because the ratio of 7/3 = 2.333 is closer to 3 than the value of 8/2 = 4 for the cluster with 8 Si atoms and 2 Al atoms.

A semi-empirical calculation PM3 is used to calculate fully optimised geometries for all T sites substituted by 1 Al, 2 Al and 3 Al atoms. This is followed by an RHF single point calculation at a 6-31G basis set for the total energies as well as substitution energies. Table 7.1 lists the HF (a.u) values and the energies of replacing silicon by aluminium in a total of 10 T sites of the cluster. Figure 7.3 gives the numbering scheme for the cluster with 7 Si atoms and 3 Al atoms. On the basis of the substitution energies given in Table 7.1 it can be concluded that the T6 site is the most favourable site for one Al atom replacing a Si atom, followed by the T1 site being the most favourable site for a second Al atom replacing a Si atom. The most favourable T site for the third Al atom replacing Si is the T9 site. The least favourable sites for one Al atom replacing Si atoms are T7 and T10, with substitution energies of 66.4 kJ/mol. and 63.3 kJ/mol. respectively.

It is worth noting that the T6 site is neighboured by one Si(Q2) and two Si(Q3) centres. Both Si(Q2) sites, i.e. T7 and T10, are the least favourable sites, which implies that in the 5-membered aluminosilicate rings model Al prefers to be neighboured by more Si atoms, and locates at the Q3 position, excluding the restrained T2, T3, T5 and T8 sites. For substitution of a Si atom by the second Al atom the least favourable sites are T10, T5 and T3 with substitution energies of 173.0 kJ/mol., 119.6 kJ/mol. and 117.3 kJ/mol. respectively. T10 is the Si(Q2) site as well as the neighbouring site of T6. Both T5 and T3 are neighbouring sites of T6 as well. It is obvious that the Al atom prefers the site which is maximally neighboured by Si atoms as well as non-neighboured by Al atoms, which is consistent with the Lowenstein rule (Lowenstein, 1954). Besides the
The substitution energies for the third Al atom substituting a Si atom are all higher than 72.5 kJ/mol except the T₄ site, which is the only site that can satisfy both the symmetry and non-neighbouring Al atom rule.

The average substitution energy ΔE for the first Al atom replacing a Si atom is 8.4 kJ/mol for all T sites excluding the Q² centres. For substitution by the second Al atom the average ΔE is 26.4 kJ/mol excluding Al neighboured T sites. The sites for substitution of the third Al atom are limited by the non-neighbouring Al atom rule, which means that only the T₄ and T₀ sites are appropriate with an average ΔE of 5.3 kJ/mol. It can be concluded from these ΔE values that the first Al atom substituting for a Si atom is a comparatively easy step, because there is little symmetry restriction involved and the substitution is controlled merely by the T(Q³) centre rule. In contrast, the second Al atom replacing a Si atom is a more energy intensive step, which is controlled by the non-neighbouring Al atom rule, the T(Q³) centre rule as well as the maximised symmetry factor. Of all 10 T sites only the T₄ and T₀ sites will allow exchange of a third Si atom by an Al atom and still obey the non-neighbouring Al atom rule as well as the maximised symmetry rule. This causes the difference in substitution energy between T₄ and T₀ to be only 5.3 kJ/mol.

Table 7.2 gives the average bond lengths and angles for the 10 T sites in a 4-4-1-1 cluster model in comparison with previous experimental and MO calculated values (Smith and Bailey, 1963; Sykes and Kubicki, 1996; Chakoumakos et al., 1981). Clearly the calculated bond lengths and angles compare well with previous work. However, it should be noted that the values observed by Smith and Bailey (1963) as listed in column “a”, are mean bond lengths for aluminosilicate framework minerals excluding the heulandite group. The allowed errors for Si-O and Al-O are ±0.02 and ±0.03 respectively. In view of the lack of data on a 5-membered ring cluster in the literature, column “b” of Table 7.2 shows comparative values calculated at the 3-21G basis set for a 4-membered single ring cluster (H₈Si₃AlO₁₂)⁺ (Sykes and Kubicki, 1996). Column “c” of Table 7.2 lists the observed mean bond angle of a 5-membered silicate ring with values ranging from 143 to 155 degrees (Chakoumakos et al., 1981). Figures 7.4 and 7.5 depict the various bond lengths and angles for one to three T sites occupied by Al atoms. Evidently, the bond lengths of the cluster stretch with more T
sites occupied by Al atoms. The effect of substituting more Al at the T sites on the bond angle is more convoluted, with all T-O(br)-T angles sharpening except in the case of Si(Q^3)-O(br)-Si(Q^3) and three O(br)-T-O(br) angles. The changes in bond lengths and angles with increasing Al substitution of Si atoms manifest a more relaxed structure with O(br) atoms moving outwards and all T sites moving inwards to form a distorted 5-membered framework ring. As the bond angles of Si(Q^3)-O(br)-Si(Q^3) increase with more Al replacing Si, the actual changes of Si atoms on the T_{2,5} and T_{5} sites are combinations of relaxation and contraction.

### 7.3 AB INITIO STUDY OF DISSOLUTION ENERGY

#### 7.3.1 Ab initio study of dissolution energy in local environment

Based on the energy-optimised 5-membered rings model with 7 Si atoms and 3 Al atoms (4-4-1-1 unit), a dissolution process is modelled phenomenologically for ring breakage and releasing of T(OH)_4 tetrahedra as follows:

\[
\begin{align*}
\equiv (TO)_3 \equiv SiOH + 3H_2O & \Rightarrow \equiv TOH + Si(OH)_4 \quad \Delta E_1 \quad (7.1) \\
\equiv (TO)_3 \equiv Al^{+}OH + 3H_2O & \Rightarrow \equiv TOH + Al^{+}(OH)_4 \quad \Delta E_2 \quad (7.2)
\end{align*}
\]

It should be noted that the Si(Q^3) centre involves less water molecules, so that it results in a significant difference in energy compared with the other Q^3 centres, therefore only Q^3 centres have been studied in this work. Xiao and Lasaga (1994) and Kubicki et al. (1993) studied the mechanism of silicate dissolution in acid and local environment by conducting calculations on both transition state and dissolution enthalpy for linear clusters not larger than five T sites. The current work deals with much larger clusters (10 T sites) and with a structure of two connected 5-membered rings, for which it is nearly impossible to calculate the transition state without the help of the detailed dissolution information. In this study, a direct PM3 has been carried out on the energy-optimised geometry for all 10 T sites, followed by a single point RHF calculation of total energy at the 6-31G basis set for the dissolution energies \(\Delta E_1\) and \(\Delta E_2\).
Table 7.3 lists reaction energies (ΔE) as well as the bond lengths and angles for the broken ring cluster. Figures 7.6 and 7.7 depict the geometries of the broken 5-membered ring cluster after releasing Al(OH)₄ and Si(OH)₄ tetrahedra respectively. It is noteworthy that in comparison with Si(Q⁵) centres, the Al(Q⁵) centres show strongly exothermic reaction enthalpies for the proposed dissolution reactions. The T(Al) site most susceptible to the dissolution reaction is T₉, while the least favourable T(Si) site is T₄ apart from the two Si(Q⁵) centres. The difference in the reaction energies between the most reactive Al(Q⁵) centre (T₉) and the most reactive Si(Q⁵) centre (T₃) is 300.3kJ/mol., which suggests that Al dissolves in preference to Si in local environment in the case of a two connected 5-membered Al-Si framework rings structure.

Figures 7.8 and 7.9 show the changes in bond lengths and angles after T₉ (Al) and T₃ (Si) centres have been released from the ring to form T(OH)₄ tetrahedra (data listed in Table 7.3). The T-O_br and T-O_hbr bond lengths for release of the T₉ site from the ring are shorter than those of the T₃ site being released from the ring. However, the T-O-T angles show a correspondingly widening trend, except for Si(Q⁵)-O-Si(Q⁵). Consequently, the structure reveals more T-O overlap and less repulsive force between two neighbouring T sites after the release of the T₉(Al) site compared with the release of the T₃(Si) site. It should be noted that the difference in energy between the release of the T₉(Al) and T₃(Si) sites is caused mainly by a re-combination of the chemical bonds, whereas the difference in the resultant structures plays only a minor part.

7.3.2  *Ab initio study of dissolution energy in highly alkaline solution*

As mentioned in the introduction, the dissolution of Al-Si minerals in highly alkaline solutions is important in geopolymerisation as the starting step as well as the gel-forming step. The purpose of this study is to gain insight into the dissolution mechanism of Al-Si minerals with 5-membered ring structure in alkaline solutions. Based on the energy-optimised 5-membered rings with 7 Si atoms and 3 Al atoms (4-4-1-1 unit), the dissolution processes in NaOH and KOH solutions are modelled as given below (T represents Al or Si tetrahedra):
\[(\text{TO})_3\text{Si-OH} + 3\text{NaOH} \Rightarrow 3 \equiv \text{TOH} + \text{HO-Si}(\text{ONa})_3 \quad \Delta E_3 \quad (7.3)\]

\[(\text{TO})_3\text{Si-OH} + 3\text{KOH} \Rightarrow 3 \equiv \text{TOH} + \text{HO-Si}(\text{OK})_3 \quad \Delta E_4 \quad (7.4)\]

\[(\text{TO})_3\text{Si-OH} + 4\text{NaOH} \Rightarrow 2 \equiv \text{TOH} + \equiv \text{T-ONa} + \text{HO-Si}(\text{ONa})_3 + \text{H}_2\text{O} \quad \Delta E_5 \quad (7.5)\]

\[(\text{TO})_3\text{Si-OH} + 4\text{KOH} \Rightarrow 2 \equiv \text{TOH} + \equiv \text{T-OK} + \text{HO-Si}(\text{OK})_3 + \text{H}_2\text{O} \quad \Delta E_6 \quad (7.6)\]

\[(\text{TO})_3\text{Al}^-\text{OH} + 3\text{NaOH} \Rightarrow 3 \equiv \text{TOH} + \text{HO-Al}(\text{ONa})_3 \quad \Delta E_7 \quad (7.7)\]

\[(\text{TO})_3\text{Al}^-\text{OH} + 3\text{KOH} \Rightarrow 3 \equiv \text{TOH} + \text{HO-Al}(\text{OK})_3 \quad \Delta E_8 \quad (7.8)\]

\[(\text{TO})_3\text{Al}^-\text{OH} + 4\text{NaOH} \Rightarrow 2\equiv \text{TOH} + \equiv \text{T-ONa} + \text{HO-Al}(\text{ONa})_3 + \text{H}_2\text{O} \quad \Delta E_9 \quad (7.9)\]

\[(\text{TO})_3\text{Al}^-\text{OH} + 4\text{KOH} \Rightarrow 2 \equiv \text{TOH} + \equiv \text{T-OK} + \text{HO-Al}(\text{OK})_3 + \text{H}_2\text{O} \quad \Delta E_{10} \quad (7.10)\]

In highly alkaline geopolymerisation (pH > 14), more than 97.47% of Si(OH)$_4$ orthosilicic acid exists as HOSiO$_3$* (Babushkin et al., 1985) anion which will participate in an ion-pairing reaction with alkali metal cations Na$^+$ and K$^+$ to form HOSi(ONa)$_3$ and HOSi(OK)$_3$ species respectively (McCormick et al., 1989a,b,c; Swaddle et al., 1994; Kinrade and Pole, 1992; and Hendricks et al., 1991). In a comparison of reaction energies between the T(Al) and T(Si) centres it is assumed that Al$^-$(OH)$_4$ tetrahedra exist as HOAl$^-$ (OM)$_3$ species in MOH solutions as well.

The effect of alkaline solutions NaOH and KOH on the dissolution process of the 5-membered rings model is threefold: (1) Ring breakage for releasing Al or Si atoms; (2) The dissolved Al and Si atoms forming HO-T(OM)$_3$ species, and (3) An interaction between the remaining broken ring cluster and NaOH or KOH. Equations 7.3, 7.4, 7.7 and 7.8 represent the ring breakage as well as formation of HO-T(OM)$_3$ species with the remaining broken ring cluster similar to that in local environment (equations 7.1 and 7.2). Equations 7.5, 7.6, 7.9 and 7.10 include not only the ring breakage and the formation of HO-T(OM)$_3$ species, but also interactions between the
remaining broken ring cluster and MOH. Therefore the values of ($\Delta E5 - \Delta E3$), ($\Delta E6 - \Delta E4$), ($\Delta E9 - \Delta E7$) and ($\Delta E10 - \Delta E8$) actually embody the interaction between MOH solution and the remaining broken ring cluster.

The HOT(OM)$_3$ and $\equiv$T-OM clusters are optimised directly by RHF at 6-31G basis set. Because the optimisation is cumbersome, only $T_1$ and $T_2$ sites have been calculated. Table 7.4 lists the calculated reaction energies for equations 1 to 10. Figures 7.10 – 7.13 show the energy-optimised geometries of the remaining broken ring clusters $\equiv$ T-OK and $\equiv$ T-ONa after the $T_1$ (Al) and $T_2$ (Si) centres have been released in KOH and NaOH solutions respectively. From Table 7.4 the following observations could be made.

Alkaline solutions will dramatically increase the soluble extent of the 5-membered rings model with much higher exothermal dissolution energies for both $T_1$(Al) and $T_2$(Si) centres than that in local environment ($|\Delta E5| >> |\Delta E1|, |\Delta E6| >> |\Delta E1|, |\Delta E9| >> |\Delta E2|, |\Delta E10| >> |\Delta E2|)$. Both $T_1$(Al) and $T_2$(Si) display higher exothermicity when dissolved in NaOH than in KOH solution ($|\Delta E3| > |\Delta E4|, |\Delta E5| > |\Delta E6|, |\Delta E7| > |\Delta E8|, |\Delta E9| > |\Delta E10|$), which means that NaOH solution favours the dissolution of the 5-membered Al-Si framework rings model. This result agrees well with our laboratory experiments (chapter 4) in which both heulandite and stilbite minerals show higher soluble extent in NaOH than in KOH solution at 2N, 5N and 10N.

$|\Delta E3|$ and $|\Delta E7|$ are higher than the corresponding $|\Delta E4|$ and $|\Delta E8|$, which indicates that a stronger ion-pairing reaction takes place between HOSiO$_3$" and the Na$^+$ cation, and a stronger interaction occurs between H$\alpha$AlO$_3$" and the Na$^+$ cation as well. This proves the observation gained by McCormick et al. (1989a,b,c) and Swaddle et al. (1994) that in alkaline solution, alkali metal cations of smaller size favour ion-pairing reactions with silicate monomer species.

The difference between $\Delta E10$ and $\Delta E9$ is 149.5 kJ/mol., while the difference between ($\Delta E9 - \Delta E7$) and ($\Delta E10 - \Delta E8$) is only 1.5 kJ/mol., which means that NaOH solution favours the dissolution of $T_1$(Al) centre. Therefore, the dissolution of this $T$ centre is
mainly a result of stronger interaction between the Na\(^+\) cation and HOAl'\(\text{O}_3\)\(^-\) anion than that between the K\(^+\) cation and HOAl'\(\text{O}_3\)\(^-\) anion.

The difference in energy between \(\Delta E5\) and \(\Delta E6\) is 31.2 kJ/mol., which is the sum of 21.0 kJ/mol. (\(\Delta E4\) - \(\Delta E3\)) and 10.2 kJ/mol.[(\(\Delta E6\) - \(\Delta E4\)) - (\(\Delta E5\) - \(\Delta E3\))]. In other words, 67.2% of the difference in the dissolution energy for the \(T_2(\text{Si})\) centre dissolving in NaOH and KOH solutions is contributed by stronger ion-pairing reaction between the Na\(^+\) cation and HOSiO\(_3\)\(^-\) anion (\(\Delta E4\) - \(\Delta E3\)), while 32.8% comes from the interaction between the remaining broken ring cluster (≡SiOH) and NaOH [(\(\Delta E6\) - \(\Delta E4\)) - (\(\Delta E5\) - \(\Delta E3\))].

It can be concluded that the dissolution mechanism of the stilbite model in alkaline solutions consists of an ion-pairing reaction and an interaction between the remaining broken ring cluster ≡TOH and MOH. It is these two steps that enable the stilbite model to show a higher soluble extent in both NaOH and KOH solutions than in local environment. As the interaction between HOTO\(_3\)\(^-\) anion and Na\(^+\) cation is stronger than that between HOTO\(_3\)\(^-\) anion and K\(^+\) cation, the proposed soluble extent for the stilbite model will be higher in NaOH than in KOH solution. The interaction between the remaining broken ring cluster ≡TOH and MOH plays an important role in the dissolution process, however, it acts differently after the \(T_1(\text{Al})\) and \(T_2(\text{Si})\) centres have been released. For the remaining broken ring cluster after release of the \(T_1(\text{Al})\) centre, the reaction energy between ≡TOH and NaOH is \(-563.6\) kJ/mol., which is 1.5 kJ/mol. less than that between ≡TOH and KOH. This means that both Na and K atoms can stabilise the remaining broken ring cluster with the K atom being slightly better. In contrast, the reaction energy between the remaining broken ring cluster after release of the \(T_2(\text{Si})\) centre and NaOH is 10.2 kJ/mol. higher than that between ≡TOH and KOH, which shows that the Na atom is more able to minimise the remaining broken ring cluster than the K atom. With regard to geopolymerisation it can be concluded that NaOH solution will give higher extents of dissolution of Al-Si minerals with the 5-membered framework rings structure and result in a better initialisation and gel formation reactions.
7.4 SUMMARY

By utilising the standard 6-31G basis set, ab initio Restricted Hartree-Fock calculations are performed for PM3 optimised geometries for the stilbite model (a five-membered aluminosilicate framework rings cluster) on all ten T sites. The study has shown that the most favourable sites for 1Al, 2Al and 3Al substitution are the T₆, T₁ and T₉ sites respectively.

Based on the optimised stilbite model, a further ab initio RHF calculation has been conducted on ring breakage for releasing Al(Q₃) and Si(Q₃) centres to form T(OH)₄ and HOT(OM)₃ tetrahedra under local and high alkaline environment respectively. The obtained results suggest that Al(Q₃) centres compared with Si(Q₃) break more readily so as to dissolve in preference to Si in local environment. The dissolution mechanism of the stilbite model in highly alkaline solution has been revealed to consist of an ion-pairing reaction and an interaction between the remaining broken ring cluster ≡TOH and MOH. The Na⁺ cation gives a stronger ion-pairing effect, which results in a higher exothermal dissolution energy when the 5-membered rings structure dissolves in NaOH solution compared with KOH solution. The interaction between the remaining broken ring cluster ≡TOH and NaOH is obviously stronger than that between ≡TOH and KOH after the T₂(Si) centre has dissolved, which shows that the Na atom can better stabilise the remaining broken ring cluster than the K atom. Consequently, in geopolymerisation NaOH solution is expected to give a higher extent of dissolution of Al-Si minerals with 5-membered rings structure and supply a better initialisation as well as faster gel formation.

It is worth noting that only two T centres have been researched for the dissolution in alkaline solution which may offer an incomplete explanation of the dissolution mechanism of the 5-membered Al-Si rings model in alkaline solution. However, the results have corresponded well with experimental data and have enhanced our understanding of dissolution mechanisms of Al-Si minerals in highly alkaline solutions, which is especially relevant to geopolymerisation.
Table 7.1 HF energy values and the energies of replacing silicon by aluminium

<table>
<thead>
<tr>
<th>$T_{\text{site}}^d$</th>
<th>HF (a.u.) $\Delta E_{(kJ/mol.)}^b$</th>
<th>$T_{\text{sites}}^c$</th>
<th>HF (a.u.) $\Delta E_{(kJ/mol.)}^d$</th>
<th>$T_{\text{sites}}^e$</th>
<th>HF (a.u.) $\Delta E_{(kJ/mol.)}^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$</td>
<td>-4796.465</td>
<td>8.5</td>
<td>$T_{1,6}$</td>
<td>-4749.685</td>
<td>0</td>
</tr>
<tr>
<td>$T_2$</td>
<td>-4796.466</td>
<td>5.7</td>
<td>$T_{2,6}$</td>
<td>-4749.679</td>
<td>13.4</td>
</tr>
<tr>
<td>$T_3$</td>
<td>-4796.467</td>
<td>1.3</td>
<td>$T_{3,6}$</td>
<td>-4749.65</td>
<td>117.3</td>
</tr>
<tr>
<td>$T_4$</td>
<td>-4796.465</td>
<td>8.3</td>
<td>$T_{4,6}$</td>
<td>-4749.671</td>
<td>35.3</td>
</tr>
<tr>
<td>$T_5$</td>
<td>-4796.464</td>
<td>9.4</td>
<td>$T_{5,6}$</td>
<td>-4749.652</td>
<td>119.6</td>
</tr>
<tr>
<td>$T_6$</td>
<td>-4796.468</td>
<td>0</td>
<td>$T_{7,6}$</td>
<td>-4749.676</td>
<td>45.3</td>
</tr>
<tr>
<td>$T_7$</td>
<td>-4796.443</td>
<td>66.4</td>
<td>$T_{8,6}$</td>
<td>-4749.68</td>
<td>13.1</td>
</tr>
<tr>
<td>$T_8$</td>
<td>-4796.463</td>
<td>12.5</td>
<td>$T_{9,6}$</td>
<td>-4749.674</td>
<td>24.9</td>
</tr>
<tr>
<td>$T_9$</td>
<td>-4796.463</td>
<td>13.3</td>
<td>$T_{10,6}$</td>
<td>-4749.632</td>
<td>173</td>
</tr>
<tr>
<td>$T_{10}$</td>
<td>-4796.444</td>
<td>63.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

"a": $T$ site which is occupied by Al atom, with remaining $T$ sites being Si atoms.

"b": $\Delta E = E_{T1} - E_{T6}$, $T_i = T_1 - T_5$ and $T_7 - T_{10}$.

"c", "e": $T$ sites which are occupied by Al atoms, with remaining $T$ sites being Si atoms.

"d": $\Delta E = E_{T_{ij}} - E_{T_{1,6}}$, $T_{ij} = T_{2,6} - T_{10,6}$.

"f": $\Delta E = E_{T_{ij,k}} - E_{T_{1,6,7}}$, $T_{ij,k} = T_{1,6,2} - T_{1,6,7}$ and $T_{1,6,10}$. 

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Table 7.2 Average bond lengths and bond angles for the 10T sites in the 4-4-1-1 cluster model

<table>
<thead>
<tr>
<th></th>
<th>I(^a)</th>
<th>II(^b)</th>
<th>III(^c)</th>
<th>A(^d)</th>
<th>B(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond Length (Angstrom)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-O(_{br})</td>
<td>1.782</td>
<td>1.781</td>
<td>1.784</td>
<td>1.77</td>
<td>1.747</td>
</tr>
<tr>
<td>Al-O(_{nbr})</td>
<td>1.784</td>
<td>1.794</td>
<td>1.808</td>
<td></td>
<td>1.747</td>
</tr>
<tr>
<td>Si(Q(^3))-O(_{br})</td>
<td>1.652</td>
<td>1.657</td>
<td>1.662</td>
<td></td>
<td>1.62</td>
</tr>
<tr>
<td>Si(Q(^3))-O(_{nbr})</td>
<td>1.709</td>
<td>1.715</td>
<td>1.731</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(Q(^2))-O(_{br})</td>
<td>1.643</td>
<td>1.651</td>
<td>1.655</td>
<td></td>
<td>1.614</td>
</tr>
<tr>
<td>Si(Q(^3))-O(_{nbr})</td>
<td>1.704</td>
<td>1.714</td>
<td>1.724</td>
<td></td>
<td>1.633</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th>C(^d)</th>
<th>B(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(<em>{br})-Si(Q(^3))-O(</em>{br})</td>
<td>112.91</td>
<td>108.05</td>
<td>115.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(<em>{br})-Si(Q(^3))-O(</em>{br})</td>
<td>117.08</td>
<td>119.75</td>
<td>122.08</td>
<td></td>
<td>111.01</td>
</tr>
<tr>
<td>O(<em>{br})-Al(Q(^3))-O(</em>{br})</td>
<td>107.62</td>
<td>109.21</td>
<td>110.46</td>
<td></td>
<td>109.34</td>
</tr>
<tr>
<td>O(<em>{br})-Si(Q(^3))-O(</em>{nbr})</td>
<td>105.66</td>
<td>103.94</td>
<td>102.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(<em>{br})-Si(Q(^2))-O(</em>{nbr})</td>
<td>108.58</td>
<td>108.25</td>
<td>107.99</td>
<td></td>
<td>108.86</td>
</tr>
<tr>
<td>O(<em>{nbr})-Si(Q(^3))-O(</em>{nbr})</td>
<td>104.08</td>
<td>102.24</td>
<td>100.34</td>
<td></td>
<td>110.21</td>
</tr>
<tr>
<td>O(<em>{br})-Al(Q(^3))-O(</em>{nbr})</td>
<td>111.29</td>
<td>109.7</td>
<td>108.47</td>
<td></td>
<td>108.31</td>
</tr>
<tr>
<td>Si(Q(^3))-O(_{br})-Si(Q(^3))</td>
<td>142.88</td>
<td>145.26</td>
<td>145.5</td>
<td>147</td>
<td></td>
</tr>
<tr>
<td>Si(Q(^3))-O(_{br})-Al(Q(^3))</td>
<td>150.45</td>
<td>153.01</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si(Q(^3))-O(_{br})-Si(Q(^3))</td>
<td>141.58</td>
<td>134.89</td>
<td>132.51</td>
<td></td>
<td>141.79</td>
</tr>
<tr>
<td>Si(Q(^3))-O(_{br})-Al(Q(^3))</td>
<td>162.91</td>
<td>157.09</td>
<td>153.63</td>
<td></td>
<td>137.79</td>
</tr>
</tbody>
</table>

\(^{a}\) (I) \(T_6\) one site occupied by Al atom in a total of ten sites.

\(^{b}\) (II) \(T_1\) and \(T_6\) two sites occupied by Al atoms in a total ten \(T\) sites.

\(^{c}\) (III) \(T_1\), \(T_6\), and \(T_9\) three sites occupied by Al atoms in a total ten sites.

\(^{d}\) Refs. (A) Smith and Bailey (1963); (B) Sykes and Kubicki (1996), data based on four-membered ring \((H_6\text{Si}_3\text{AlO}_{12})^+\) and (C) Chakournakos *et al.*, (1981).
Table 7.3 Reaction energies, average bond lengths (Angstrom) and bond angles (degree)

<table>
<thead>
<tr>
<th>T site</th>
<th>HF (a.u.)</th>
<th>ΔE (kJ/mol)^a</th>
<th>Bond length</th>
<th>III^b</th>
<th>IV^c</th>
<th>V^d</th>
<th>Bond angle</th>
<th>III^b</th>
<th>IV^c</th>
<th>V^d</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_1</td>
<td>-4386.775</td>
<td>-306.9</td>
<td>Al-O_{tr}</td>
<td>1.784</td>
<td>1.784</td>
<td>1.778</td>
<td>O_{tr}-Si(Q^3)-O_{tr}</td>
<td>115.07</td>
<td>114.55</td>
<td>114.14</td>
</tr>
<tr>
<td>T_2</td>
<td>-4339.785</td>
<td>-3.8</td>
<td>Al-O_{nbr}</td>
<td>1.808</td>
<td>1.806</td>
<td>1.792</td>
<td>O_{tr}-Si(Q^3)-O_{tr}</td>
<td>122.08</td>
<td>120.9</td>
<td>120.37</td>
</tr>
<tr>
<td>T_3</td>
<td>-4339.796</td>
<td>-33.8</td>
<td>Si(Q^3)-O_{tr}</td>
<td>1.662</td>
<td>1.658</td>
<td>1.656</td>
<td>O_{tr}-Al(Q^3)-O_{tr}</td>
<td>110.46</td>
<td>111.09</td>
<td>109.05</td>
</tr>
<tr>
<td>T_4</td>
<td>-4339.778</td>
<td>14.8</td>
<td>Si(Q^3)-O_{nbr}</td>
<td>1.731</td>
<td>1.732</td>
<td>1.712</td>
<td>O_{tr}-Al(Q^3)-O_{tr}</td>
<td>109.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T_5</td>
<td>-4339.791</td>
<td>-20.1</td>
<td>Si(Q^3)-O_{tr}</td>
<td>1.655</td>
<td>1.649</td>
<td>1.647</td>
<td>O_{tr}-Si(Q^3)-O_{nbr}</td>
<td>102.89</td>
<td>103.64</td>
<td>104.13</td>
</tr>
<tr>
<td>T_6</td>
<td>-4386.799</td>
<td>-244.4</td>
<td>Si(Q^3)-O_{nbr}</td>
<td>1.724</td>
<td>1.72</td>
<td>1.712</td>
<td>O_{tr}-Si(Q^3)-O_{nbr}</td>
<td>107.99</td>
<td>108.06</td>
<td>107.58</td>
</tr>
<tr>
<td>T_7</td>
<td>-4339.785</td>
<td>-4.2</td>
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<td></td>
<td></td>
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<td>O_{tr}-Al(Q^3)-O_{nbr}</td>
<td>108.47</td>
<td>107.75</td>
<td>109.91</td>
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<tr>
<td>T_9</td>
<td>-4386.81</td>
<td>-334.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Si(Q^3)-O_{tr}-Si(Q^3)</td>
<td>145.5</td>
<td>151.3</td>
<td>145.19</td>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Si(Q^3)-O_{tr}-Al(Q^3)</td>
<td>150</td>
<td>151.3</td>
<td>155.57</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>Si(Q^3)-O_{nbr}-Si(Q^3)</td>
<td>132.51</td>
<td>136.91</td>
<td>143.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Si(Q^3)-O_{nbr}-Al(Q^3)</td>
<td>153.63</td>
<td>159.16</td>
<td>162.31</td>
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<td></td>
<td></td>
<td>Si(Q^3)-O_{tr}-Al(Q^3)</td>
<td>167.22</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Si(Q^3)-O_{nbr}-Al(Q^3)</td>
<td>166.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Al(Q^3)-O_{tr}-Si(Q^3)</td>
<td>167.84</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^a^: ΔE represents ΔE3 and ΔE4.

^b^: Cluster with T_1, T_6 and T_7 sites occupied by Al atoms, other seven T sites occupied by Si atoms.

^c^: Cluster after releasing Si atom on T_1 site.

^d^: Cluster after releasing Al atom on T_9 site.
<table>
<thead>
<tr>
<th>T site</th>
<th>$\Delta E_1$(kJ/mol)</th>
<th>$\Delta E_3$(kJ/mol)</th>
<th>$\Delta E_4$(kJ/mol)</th>
<th>$\Delta E_5$(kJ/mol)</th>
<th>$\Delta E_6$(kJ/mol)</th>
<th>$\Delta E_5 - \Delta E_3$</th>
<th>$\Delta E_6 - \Delta E_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_2$(Si)</td>
<td>-3.8</td>
<td>-255.4</td>
<td>-234.4</td>
<td>-729.6</td>
<td>-698.4</td>
<td>-474.1</td>
<td>-463.9</td>
</tr>
<tr>
<td>$T_1$(Al)</td>
<td>-306.9</td>
<td>-231.9</td>
<td>-80.9</td>
<td>-795.5</td>
<td>-646</td>
<td>-563.6</td>
<td>-565.1</td>
</tr>
</tbody>
</table>
Figure 7.1 The infinite structures of heulandite group minerals with some nodes free for connections to other sheets through the mirror plane. (a) Stilbite. (b) Heulandite. (c) Brewsterite. (d) The 4-4-1-1 structural unit of the heulandite group.
Figure 7.2 The energy-optimised structure of the 4-4-1-1 cluster with all T sites occupied by Si atoms.
Figure 7.3 The numbering scheme for the cluster with seven Si atoms and three Al atoms.
Figure 7.4 Bond lengths (Angstrom) of two connected five-membered clusters. I: Cluster with T₆ site occupied by Al atom. II: Cluster with T₆ and T₁ sites occupied by Al atoms. III: Cluster with T₆, T₁ and T₅ occupied by Al atoms.
Figure 7.5 Bond angles (degree) of two connected five-membered rings cluster. I: Cluster with T₆ site occupied by Al atom. II: Cluster with T₆ and T₁ sites occupied by Al atoms. III: Cluster with T₆, T₁ and T₉ occupied by Al atoms.
Figure 7.6 Energy-optimised geometry of reaction product for ring breakage and release of $T_9(Al)$ centre as $Al(OH)_4^-$ tetrahedron in local environment.
Figure 7.7 Energy-optimised geometry of reaction product for ring breakage and release of T₃(Si) centre as Si(OH)₄ tetrahedron in local environment.
Figure 7.8 Bond lengths (Angstrom) before and after release of $T_3$ (Si) and $T_9$ (Al) centre from ring. III: Cluster before T centre is released from ring. IV: Cluster after $T_3$ (Si) centre has been released from ring. V: Cluster after $T_9$ (Al) centre has been released from ring.
Figure 7.9 Bond angles (degree) before and after release of $T_3$(Si) and $T_9$ (Al) centre from ring. III: Cluster before T centre is released from ring. IV: Cluster after $T_3$ (Si) centre has been released from ring. V: Cluster after $T_9$(Al) centre has been released from ring.
Figure 7.10 Energy-optimised geometry of remaining broken ring cluster after dissolution of the $T_1(\text{Al})$ centre as $\text{HOAl}^-(\text{ONa})_3$ tetrahedron in NaOH solution.
Figure 7.11 Energy-optimised geometry of remaining broken ring cluster after dissolution of the $T_1(Al)$ centre as $\text{HOAl}(\text{OK})_3$ tetrahedron in KOH solution.
Figure 7.12 Energy-optimised geometry of remaining broken ring cluster after dissolution of the T$_2$(Si) centre as HOSi(ONa)$_3$ tetrahedron in NaOH solution.
Figure 7.13 Energy-optimised geometry of remaining broken ring cluster after dissolution of the $\text{T}_2(\text{Si})$ centre as $\text{HOSi(OK)}_3$ tetrahedron in KOH solution.
CHAPTER EIGHT

FURTHER MODELLING OF FIVE MEMBERED RING

This chapter is based on a manuscript submitted to the Journal of Physical Chemistry, 2001.

A double five membered aluminosilicate framework ring structure has been modelled for stilbite (chapter 7). It is found that such a model can well explain the dissolution of stilbite in both local and alkaline environments, and represents the structure of zeolite minerals comprised in the heulandite group very well (Gottardi and Galli, 1985). However, a five membered ring is found existing not only in the structures of zeolite minerals but also other minerals (Deer et al., 1992). Those minerals could possess either ortho- and ring or sheet and framework structures (Deer et al., 1992). Therefore, regardless of the connections between a five membered ring and its structural environment in real Al-Si minerals, the study of a single five membered ring model is expected to provide a more general insight into the dissolution of any natural Al-Si mineral whose structure embodies the single five membered ring. Moreover, despite good agreement of calculated bond lengths and angles with the data published (Tables 7.2 and 7.3), physical verification of IR or Raman spectra has not been applied to the model studied in Chapter 7. The reason is that the higher level Density Functional Theory (DFT) cannot be successfully applied to the model with such a size to calculate the vibrational frequencies. Consequently, a further simplified model with a single 5 membered ring is used in this chapter to study the dissolution energies, molecular structure, charge distribution, thermodynamic properties and the vibrational spectra of the model.

8.1 THEORETICAL APPROACH AND COMPUTATIONAL DETAILS

The calculations presented in this chapter are performed applying the Hartree-Fock (HF) and density functional theory (DFT) levels of calculation. The DFT calculations utilised the B3LYP functional (Becke, 1993). The geometry optimisations are performed
applying the standard 6-31G basis set (Hehre et al., 1972; Franel et al., 1982). No symmetry constraints are imposed during the optimisation process. Vibrational frequencies and thermodynamic properties of the studied complexes are calculated applying the ideal gas, rigid rotor, and harmonic oscillator approximations (Davidson, 1962). The single point calculations at HF and DFT levels of theory are performed within the 6-31G basis set supplemented by p polarisation functions on hydrogens and d polarisation functions on heavy atoms (denoted as 6-31G(d,p)) (Hariharran and Pople, 1973). The calculations are carried out using the Gaussian 94 code (Frisch et al., 1994).

8.2 STRUCTURES AND ENERGETICS OF 5 MEMBERED RING AND ITS DISSOLUTION

The initial 5-membered ring is extracted from the crystal structure of stilbite. The Si-O-Si bridges connecting rings are replaced by SiOH (the extended model, Figure 8.1) or SiH (Figure 8.2) units. The skeleton of the crystal imposes the rigidity on the ring allowing only small structural changes upon the reaction of dissolution. The model ring without stiffening Si-O-Si linkages has more freedom to form various topological forms. The optimisation of geometry has been performed by taking caution that convergence to non-physical structures is not allowed. The main obstacle in the gas phase optimisation of the ring is the possible formation of hydrogen bonds which are not present in the crystal environment. The termination of the inter ring linkages by the –SiH group prevents the formation of such bonds within the 5-membered framework rings. In the case of an extended model the replacement of Si-O-Si by SiOH may lead to non-physical hydrogen bonds. However, the carefully optimised structure of Si₅O₅H₁₀ and its dissolution product obtained in this work represent the physically appropriate framework (Figure 8.1a,b).

The dissolution of silicate and aluminosilicate material is modelled by reaction (8.1):

\[ \text{Si}_{5+}\text{Al}_1\text{O}_5\text{H}_{10}^{+} + \text{H}_2\text{O} + \text{OH}^- = \text{Si}_{4+}\text{Al}_1\text{O}_5\text{H}_{10}^{+} + \text{OSi(OH)H}_2^- \]  

(8.1)
The studied 5-membered complexes include the silicate ring (Figures 8.1 and 8.2a) and its aluminium derivatives. Two aluminium derivatives complying with the "Loewenstein rule" (Loewenstein, 1954) are considered (Figures 8.2b,c). The possible products after the elimination of the OSi(OH)H$_2^-$ (OSi(OH)$_3^-$ in the case of the extended model) anion are Si$_4$O$_3$H$_{10}$ (Figure 8.3a), isomers of Si$_3$AlO$_3$H$_{10}^-$ (Figures 8.3b1, 8.3b2), and Si$_2$Al$_2$O$_5$H$_{10}^{2-}$ (Figure 8.3c). The reason for OSi(OH)H$_2^-$ rather than OAl(OH)H$_2^-$ being selected to be the dissolved fragment is that this study focuses on the vibrational calculations of the model which includes both Al and Si atoms in its structure.

The average distances in the studied complexes agree well with those found from the crystallographic data in Table 8.1 (Galli, 1971). The data listed in Table 8.1 are also found to match the experimental results better than those showed in Chapter 7 (Table 7.2). This means that the model optimised in this chapter better represents the real structures in aluminosilicates. Interestingly, the average distance between two nearest oxygen atoms in the ring is comparable to the O-O bond in the water dimer (Odutola and Dyke, 1980). It indicates the favourable conditions for the formation of hydrogen bonds without large structural changes. The 4-membered complexes, products of the dissolution reactions, are formed without significant structural distortions and are stabilised by hydrogen bonds. Their structures reasonably represent the situation found in the real crystal. In agreement with experimental data (Galli, 1971; Bish, 1993) the Al-O distances are found to be longer than Si-O distances.

The atomic charges calculated according to the Mulliken population analysis scheme indicate the uniform electronic density distribution within the ring (Table 8.2). Atomic charges on different oxygen atoms inside rings are almost the same with little impact from neighbouring atoms. The bonding with OH groups in the case of the extended model increases charges on the Si atoms by 0.58 electron. This increase, however, has little impact on other atoms present in the ring. In both models considered, atomic charges on oxygen inside the ring as well as on the OH...O hydrogen bond skeleton are almost the same. In the first order approximation, atomic charges may be considered additive. More importantly, the choice of the model has little influence on the electron
density distribution within the ring. The Al atom substituting Si possesses lower positive charge. The same observation is also valid for Al and Si atoms spanning hydrogen bonds. In all cases studied the hydrogen bonds are formed following the Si-OH...O-Al scheme.

The energies and enthalpies of dissolution reactions are studied using the Hartree-Fock reference optimised geometries. Single point energies are also calculated in the extended basis set (6-31G(d,p)) with the inclusion of correlation energy (DFT level). As expected, energies of dissolution are sensitive to the basis set choice and to the level of theory applied (Table 8.3). However, regardless of the method applied the differences between dissolution energies for different reactions are similar. The replacement of the single Si atom by Al increases the enthalpy of dissolution of Si, which matches the experimental observations (Barrer, 1982). This increase is similar for both possible isomeric products. In the case of the double Al/Si exchange, the energy of the reaction changes a little compared to the dissolution of the pure silicate ring. Such a behaviour indicates that the energetics of dissolution is a complex function of many factors such as the hydrogen bond formation, the stability of 5-membered substrate, and the stabilisation of 4-membered products. The calculated enthalpies of dissolution reactions closely follow the same pattern as revealed for the energies.

8.3 VIBRATIONAL PROPERTIES

The calculations of frequencies are performed for optimised structures of reactants and products of the reaction (8.1). The vibrational modes corresponding to Si-O-Si structural fragments are similar in different complexes (Table 8.4). This also applies to the Si-O-Al fragments. In both cases these vibrations are found to be IR active and Raman inactive. The substitution of Si by Al atoms leads to lower vibrational frequencies in agreement with the experimental data. These fragments when preserved in dissolution products possess similar vibrational properties.

The dissolution reaction leads to the formation of hydrogen bonds and free OH groups. The measured stretching vibrations in the hydrogen bond well match the calculated
values (Table 8.4). The calculated frequencies of free OH groups compare well with those found in materials which possess OH groups in a similar environment. These materials have non-hydrogen bonded surface silanol groups (Fripiat, 1982) and Al⁺ in the tetrahedral coordination on the surface (Knözinger and Ratnasamy, 1978). The calculated Si-OH frequencies agree reasonably with those measured by Mysen (Mysen et al., 1980). The Raman intensities are significant for vibrations associated with the OH fragment. The good agreement between the calculated frequencies and the experimental results indicates that the model studied in this chapter can be used to represent the aluminosilicate minerals that contain the five membered ring (single or double) in their structures, such as stilbite.

8.4 SUMMARY

The single 5-membered ring which terminates by SiOH or SiH groups has been modelled in this chapter. The properties of such a model and the products of its dissolution are studied theoretically (HF and DFT). The optimised structure of rings closely reproduces bond distances found in real crystals. Despite the lack of oxygen bridges stiffening the crystal skeleton, model rings are optimised to the structure closely resembling that found in the crystal.

The calculated atomic charges indicate the uniform electronic density distribution within the ring. The replacement of Si by Al lowers the charge on such a centre. The electrostatic forces due to charge distribution lead to the preferred SiOH…OAl hydrogen bond scheme.

The exchange of Si for Al atom significantly influences the enthalpy of the dissolution. When the single Si atom is replaced by Al, the enthalpy of dissolution of Si increases from 2 kcal/mol. to 7.4 kcal/mol. dependent on the basis set. In contrast, after two Si atoms are exchanged for Al, the enthalpy of dissolution of the Si atom is lowered except for the basis set of 6-31G. This result suggests that the five membered ring model with two Al atoms substituted for Si would display a faster and a higher extent of dissolution.
in alkaline solutions. This result is also important for aiding the design of geopolymerisation reaction in terms of the selection of natural Al-Si minerals.

The vibrational properties calculated for model systems reasonably agree with experimental frequencies found in real structures possessing such a model. All the properties studied for the model structures show the local character, which indicates that these properties are determined by the short-range directional interactions.
Table 8.1. Averaged distances in aluminosilicate complexes and their products of dissolution (distances “R” in Angstrom and angles in degrees).

<table>
<thead>
<tr>
<th>Complex</th>
<th>R(Si-O)</th>
<th>R(Al-O)</th>
<th>R(O-O)</th>
<th>Hydrogen bond parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O-O</td>
</tr>
<tr>
<td>Si₅O₅H₁₅</td>
<td>1.640⁶</td>
<td></td>
<td>2.663⁴</td>
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</tr>
<tr>
<td>Si₄O₅H₁₃</td>
<td>1.641</td>
<td></td>
<td>2.722</td>
<td>0.960</td>
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<tr>
<td>Si₅O₅H₅</td>
<td>1.664</td>
<td></td>
<td>2.746</td>
<td></td>
</tr>
<tr>
<td>Si₄O₅H₅</td>
<td>1.665</td>
<td></td>
<td>2.754</td>
<td>0.957</td>
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<tr>
<td>Si₄AlO₅H₅⁻</td>
<td>1.659</td>
<td>1.771⁵</td>
<td>2.793</td>
<td></td>
</tr>
<tr>
<td>Si₃AlO₅H₅⁻⁻</td>
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<td>1.790</td>
<td>2.577</td>
<td>0.991</td>
</tr>
<tr>
<td>Si₃AlO₅H₅⁻⁻⁻</td>
<td>1.665</td>
<td>1.784</td>
<td>2.687</td>
<td>0.976</td>
</tr>
<tr>
<td>Si₃Al₂O₅H₅⁻⁻⁻</td>
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<td>1.763</td>
<td>2.852</td>
<td></td>
</tr>
<tr>
<td>Si₂Al₂O₅H₅⁻⁻⁻</td>
<td>1.657</td>
<td>1.759</td>
<td>2.684</td>
<td>0.975</td>
</tr>
</tbody>
</table>

a) Isomer a, Figure 8.3b1,
b) Isomer b, Figure 8.3b2,
c) Averaged experimental values: Si-O 1.64 Å, O-O 2.68 Å, (Galli, 1971),
d) The O-O distance in the water dimer: 2.98 Å, (Odutola and Dyke, 1980),
e) Averaged experimental value in kaolinite: 1.908 Å, (Bish, 1993).
Table 8.2. Averaged atomic charges on ring atoms and atomic charges on atoms involved in the hydrogen bond formation SiOH...OX (X=Si, Al) (charges in electron).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ring atoms</th>
<th>Hydrogen bond and vicinity&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
<td>Al</td>
</tr>
<tr>
<td>Si&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;13&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>2.29</td>
<td>-1.24</td>
</tr>
<tr>
<td>Si&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;13&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>2.30</td>
<td>-1.24</td>
</tr>
<tr>
<td>Si&lt;sub&gt;5&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>1.72</td>
<td>-1.25</td>
</tr>
<tr>
<td>Si&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>1.72</td>
<td>-1.25</td>
</tr>
<tr>
<td>Si&lt;sub&gt;4&lt;/sub&gt;AlO&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>1.71</td>
<td>1.40</td>
</tr>
<tr>
<td>Si&lt;sub&gt;3&lt;/sub&gt;AlO&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.72</td>
<td>-1.25</td>
</tr>
<tr>
<td>Si&lt;sub&gt;3&lt;/sub&gt;AlO&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.70</td>
<td>-1.25</td>
</tr>
<tr>
<td>Si&lt;sub&gt;3&lt;/sub&gt;Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.72</td>
<td>1.41</td>
</tr>
<tr>
<td>Si&lt;sub&gt;2&lt;/sub&gt;Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.71</td>
<td>1.41</td>
</tr>
</tbody>
</table>

<sup>a</sup>Isomer a, Figure 8.3b1,
<sup>b</sup>Isomer b, Figure 8.3b2,
<sup>c</sup>Figures 8.3a-c.
Table 8.3. The energies (\(\Delta E\)) and enthalpies (\(\Delta H\)) of the model dissolution reaction (8.1) (energies in kcal/mol).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Method</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HF 6-31G</td>
</tr>
<tr>
<td>Si(<em>5)O(</em>{13})H(_{10})</td>
<td>Si(<em>4)O(</em>{13})H(_{10})</td>
<td>(\Delta E)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta H)</td>
</tr>
<tr>
<td>Si(_3)O(<em>3)H(</em>{10})</td>
<td>Si(_4)O(<em>2)H(</em>{10})</td>
<td>(\Delta E)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta H)</td>
</tr>
<tr>
<td>Si(_4)AlO(<em>3)H(</em>{10})(^{-})</td>
<td>Si(_3)AlO(<em>3)H(</em>{10})(^{a})</td>
<td>(\Delta E)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta H)</td>
</tr>
<tr>
<td>Si(_4)AlO(<em>3)H(</em>{10})(^{-})</td>
<td>Si(_3)AlO(<em>3)H(</em>{10})(^{b})</td>
<td>(\Delta E)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta H)</td>
</tr>
<tr>
<td>Si(_3)Al(_2)O(<em>5)H(</em>{10})(^{-})</td>
<td>Si(_2)Al(_2)O(<em>5)H(</em>{10})(^{-})</td>
<td>(\Delta E)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(\Delta H)</td>
</tr>
</tbody>
</table>

\(^{a}\)Isomer a, figure 8.3b1,

\(^{b}\)Isomer b, figure 8.3b2,
Table 8.4. Calculated and experimental vibrational frequencies (values given in parentheses are scaled by 0.89) for different structural fragments of studied complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molecular fragment</th>
<th>Frequency</th>
<th>IR intensity</th>
<th>Raman</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cm⁻¹</td>
<td>Km/mol</td>
<td>Å²/mol</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>Si₅O₁₅H₁₀</td>
<td>Si-O-Si</td>
<td>1224(1093)</td>
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<td>0</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>1282(1141)</td>
<td>210</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1283(1142)</td>
<td>1181</td>
<td>0</td>
<td>1150ᵃ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1285(1144)</td>
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<td>0</td>
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<td></td>
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<td>602</td>
<td>0</td>
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<tr>
<td>Si₅O₂H₁₀</td>
<td>Si-O-Si</td>
<td>1211(1078)</td>
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<td></td>
<td>1216(1082)</td>
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<td>0</td>
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<td></td>
<td>1217(1083)</td>
<td>129</td>
<td>0</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>1233(1097)</td>
<td>1040</td>
<td>0</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>1233(1097)</td>
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<td>0</td>
<td>1150ᵃ</td>
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<tr>
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<td>Si-O-Si</td>
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<td>917</td>
<td>2</td>
<td>1150ᵃ</td>
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<td></td>
<td>1215(1081)</td>
<td>610</td>
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<td></td>
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<td>Al-O-Si</td>
<td>1165(1040)</td>
<td>442</td>
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<td></td>
<td></td>
<td>1181(1054)</td>
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<td>3</td>
<td></td>
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<td>1142(1016)</td>
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<td></td>
<td></td>
<td>1177(1047)</td>
<td>329</td>
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<td>1286(1144)</td>
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- 193 -
Table 8.4. Calculated and experimental vibrational frequencies (values given in parentheses are scaled by 0.89) for different structural fragments of studied complexes (continued).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molecular fragment</th>
<th>Frequency</th>
<th>IR intensity</th>
<th>Raman</th>
<th>Experimental data</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cm⁻¹</td>
<td>Km/mol</td>
<td>Å⁴/mol</td>
<td>cm⁻¹</td>
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<tr>
<td>OH...O (b)</td>
<td>1177(1047)</td>
<td>35</td>
<td>3</td>
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<tr>
<td>OH...O (s)</td>
<td>3858(3434)</td>
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<tr>
<td>OH (free)</td>
<td>4140(3684)</td>
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<td>76</td>
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<td>3740ᵇ</td>
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<td>Si₄O₅H₁₀</td>
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<td>1226(1091)</td>
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<tr>
<td>Si-OH</td>
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<td>10</td>
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<td>OH...O (b)</td>
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<td>OH...O (s)</td>
<td>3886(3458)</td>
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<td>129</td>
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<td>3438ᵃ</td>
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<tr>
<td>OH (free)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Si-OH</td>
<td>888(790)</td>
<td>512</td>
<td>29</td>
<td>880ᵈ</td>
<td></td>
</tr>
<tr>
<td>OH...O (b)</td>
<td>1377(1226)</td>
<td>118</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH...O (s)</td>
<td>3517(3130)</td>
<td>1149</td>
<td>145</td>
<td>3740ᵇ</td>
<td></td>
</tr>
<tr>
<td>OH (free)</td>
<td>3987(3548)</td>
<td>350</td>
<td>74</td>
<td>3740ᵇ</td>
<td></td>
</tr>
<tr>
<td>Si₂Al₂O₅H₁₀</td>
<td>Si-O-Si</td>
<td>1157(1030)</td>
<td>291</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>
Table 8.4. Calculated and experimental vibrational frequencies (values given in parentheses are scaled by 0.89) for different structural fragments of studied complexes (continued).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molecular fragment</th>
<th>Frequency</th>
<th>IR intensity</th>
<th>Raman</th>
<th>Experimental data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>cm⁻¹</td>
<td>Km/mol</td>
<td>Å²/mol</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>Al-O-Si</td>
<td>1122(998)</td>
<td>303</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1180(1050)</td>
<td>1007</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-OH</td>
<td>900(801)</td>
<td>51</td>
<td>10</td>
<td></td>
<td>880d</td>
</tr>
<tr>
<td>OH…O (b)</td>
<td>1147(1021)</td>
<td>118</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH…O (s)</td>
<td>3544(3154)</td>
<td>1340</td>
<td>155</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH (free)</td>
<td>4086(3636)</td>
<td>8</td>
<td>86</td>
<td></td>
<td>3760-3780⁹</td>
</tr>
</tbody>
</table>

a) Authors’ experimental data,
b) (Fripiat, 1982),
c) (Knözinger and ratnasamy, 1978),
d) (Mysen et al., 1980).
Figure 8.1 The optimised structures of 5-membered silicate ring (a) and the product of its dissolution (b). The inter ring Si-O-Si linkages are replaced by –SiOH groups (the extended model).
Figure 8.2 The optimised structures of (a) 5-membered silicate ring and (b) aluminosilicate ring with a single Al atom. The inter ring Si-O-Si linkages are replaced by –SH groups.
Figure 8.2 (c) The optimised structure of 5-membered aluminosilicate ring with two Al toms. The inter ring linkages are replaced by –SH groups.
Figure 8.3. The optimized structures of dissolution products (a) and (b1) for complexes presented in Figure 8.2.
Figure 8.3. The optimized structures of dissolution products (b2) and (c) for complexes presented in Figure 8.2.
CHAPTER NINE

GEOPOLYMERISATION OF ALKALI-FELDSPARS

Part of this chapter has been submitted to Minerals and Metallurgical Processing, 2001.

Chapters 4 to 8 discussed a series of aspects centred on the geopolymerisation of natural Al-Si minerals. They include the ability of fifteen natural Al-Si minerals to undergo geopolymerisation (chapter 4), factors which significantly affect geopolymerisations (chapter 5), characterising methods for both Al-Si minerals and formed geopolymers (chapter 6) and the theoretical modelling of the dissolution of stibnite (chapters 7 and 8). These discussions (chapters 4 to 8), present a significant understanding of the geopolymerisation of natural Al-Si minerals.

However, due to the limited availability of most of the natural Al-Si mineral samples, the studies conducted in chapters 4 to 6 are based on small geopolymer samples (20 × 20 × 20 mm). This makes the comparison between the results obtained in chapters 4 to 6 and those published by other investigators (Van Jaarsveld and Van Deventer, 1999a; b) difficult. Moreover, KOH is found (chapter 4) to increase the extent of geopolymerisation for all the fifteen natural Al-Si minerals with the geopolymers formed possessing a higher compressive strength, while the K₂O wt % content in the Al-Si minerals shows a negative effect on the geopolymerisation. This significantly different influence between the alkali metal cations in alkaline solution and the alkali metals structured in the Al-Si minerals implies that some sort of interactions between them may affect the geopolymerisation.

This chapter selects alkali-feldspars, which are available in abundant quantity and possess homogeneous properties, to study the effects of both alkali metal cations contained in solution and the alkali metals structured in feldspars, on geopolymerisation.

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# 9.1 BACKGROUND

## 9.1.1 Introduction

The previous work (Xu and Van Deventer, 2000a) reveals that natural Al-Si minerals with a framework structure have a higher reactivity than many other structures in geopolymeration. It is also observed (Xu and Van Deventer 2000a) that an increase in compressive strength of a synthesised geopolymer is achieved when KOH rather than NaOH solution is used. The CaO content of an Al-Si mineral is found to significantly enhance the compressive strength of the geopolymer synthesised (Xu and Van Deventer 2000a). However, the content of K$_2$O shows a negative effect on the compressive strength of the geopolymers formed in KOH. Moreover, sodalite (Na$_4$(Si$_3$Al$_2$)O$_{12}$Cl) with a higher content of Na$_2$O (11.53 wt%) is observed to leach less in NaOH than in KOH solution, which is in contrast with the general trend found for most of the other minerals investigated (Xu and Van Deventer 2000a).

Alkali metals are the most common metals contained in natural Al-Si minerals and NaOH and/or KOH are essential reactants for geopolymerisation. In spite of previous studies on the effect of NaOH and KOH on geopolymerisation (Van Jaarsveld and Van Deventer, 1999a; Xu et al., 2001) an understanding of the interactions between alkali metals contained in Al-Si minerals and NaOH and/or KOH solutions during geopolymerisation has not been established yet.

Feldspar is a large group of naturally occurring framework structured Al-Si minerals, which is also a group of common industrial minerals possessing homogeneous properties. The alkali-feldspars albite (NaAlSi$_3$O$_8$) and microcline (KAlSi$_3$O$_8$) have the same linked four-members ring structure (Figure 2.3). The chemical compositions of albite and microcline, as determined by XRF, are listed in Table 9.1. They are found to be very close to each other, except for the type of alkali metals. Thus, albite and microcline (Na-feldspar and K-feldspar) have been selected in the present work for the purpose of exploring the effect of alkali metals contained in framework structured Al-Si minerals on
geopolymerisation. An attempt is also made to predict the ability of naturally occurring Al-Si minerals containing alkali metals to undergo geopolymerisation. The effect of the mass ratio of alkali-feldspar/kaolinite on compressive strength of the geopolymers synthesised has been studied as well.

9.1.2 Materials and methods

The chemical composition, average hardness and density of kaolinite, Na-feldspar and K-feldspar are listed in Table 9.1.

A specified mass of M-feldspars or kaolinite is leached in 20 ml MOH solution (where M = Na and/or K) at room temperature for 18 hours for 2M, 5M and 7.5M concentrations. The leached Al and Si, as determined by ICP, are depicted in Figures 9.1 to 9.8.

A total 950 grams of kaolinite and Na-feldspar and/or K-feldspar are mixed for 10 minutes before an addition of 32 ml of sodium silicate and 245 ml of MOH solutions (where M = Na and/or K). The subsequent mixture is shaken by a FRITSCH Vibratory Shaker for another 3 minutes. The resulting paste is then transferred to a polyvinyl chloride (PVC) cylinder mould measuring 50 mm (diameter) × 100 mm (height) and left in an oven for setting at 45 °C for 24 hours. After being removed from the mould, the sample is left in the oven for further setting and hardening at 45 °C for 27 days. After this time, the compressive strength of each sample is tested using a Tinus Tolsen Compressive Strength testing machine. Two samples of each geopolymer mixture are tested, with the average compressive strength values depicted in Figures 9.10-9.13.

9.2 LEACHING

9.2.1 Leaching of kaolinite

The dissolution of natural Al-Si minerals in MOH solutions has been investigated in chapters 4 and 5 with results showing that NaOH compared with KOH is able to leach
more Al and Si. The concentrations of Al and Si are found to increase significantly when the concentration of MOH (where M = Na and/or K) increased from 2M to 5M and further to 10M (Xu and Van Deventer, 2000a).

Figures 9.1 and 9.2 depict the concentrations of Al and Si leached from kaolinite in NaOH and KOH solutions respectively. It is noted that the concentrations of Al and Si increased greatly along with an increase in the concentrations of NaOH and KOH solutions, which is consistent with the general trend discovered from the study of other Al-Si minerals (Xu and Van Deventer, 2000a). Nevertheless, kaolinite is found to leach more Si complex in NaOH than in KOH solution for concentrations of 2M, 5M and 7.5M respectively. However, contrary to the observations made previously (Xu and Van Deventer, 2000a), kaolinite shows a lower concentration of leached Al complex in NaOH than in KOH solution, especially when the molar concentration of MOH (where M = Na or K) changed from 5M to 7.5M. The observation of the dissolution of kaolinite in NaOH and KOH solutions implies that NaOH and KOH do preferentially affect the dissolution of Si and Al respectively. The preferential effect of KOH on the geopolymerisation of kaolinite in the mixture of stilbite/kaolinite has been observed previously (Xu et al., 2001) However, the fact that KOH dissolves more Al complex from kaolinite than NaOH is noted firstly in the present work.

9.2.2 Leaching of Na-feldspar

Figures 9.3 and 9.4 show the leaching results of Na-feldspar in NaOH and KOH solutions respectively. In agreement with the observations made on other Al-Si minerals (Xu and Van Deventer, 2000a), NaOH leaches more Al and Si complexes into solution than KOH for the three concentrations 2M, 5M and 7.5M. A significant increase in the concentrations of Al and Si is observed when the concentration of NaOH increased from 2M to 5M. The extent of such an increase dropped when the concentration of NaOH increased further to 7.5M. Furthermore, it is observed in Figure 9.4 that a large increase of leached Al and Si occurred with an increase in the concentration of KOH from 2M to 5M, beyond which the leached Al and Si slightly decreased when the concentration of
KOH further changed to 7.5M. The difference between Na-feldspar and the other Al-Si minerals investigated (Xu and Van Deventer, 2000a) during their dissolution suggests that an effect of inhibition exists in the dissolution of Na-feldspar when the concentration of MOH (where $M = Na$ and $K$) solution rises from 5M to 7.5M.

### 9.2.3 Leaching of K-feldspar

For K-feldspar, NaOH is observed to leach more Al and Si complexes than KOH at all three concentrations (2M, 5M and 7.5M) (see Figures 9.5 and 9.6). Similar to the dissolution of Na-feldspar discussed above, K-feldspar leached significantly more Al and Si complexes when the concentrations of MOH (where $M = Na$ and $K$) increased from 2M to 5M. However, a decrease and a slight increase in concentrations of Al and Si complexes are observed respectively along with a further increase in the concentrations of NaOH and KOH to 7.5M. Therefore the inhibition effect as noted occurs not only on the dissolution of Na-feldspar but also on that of K-feldspar when the concentration of MOH (where $M = Na$ and/or $K$) is increased to 7.5M. It is also interesting to note that K-feldspar is able to leach more Al and Si complexes into the MOH solution (where $M = Na$ and/or $K$) than Na-feldspar.

### 9.2.4 Leaching of mixture of Na-feldspar/K-feldspar at mass ratio of 1

Figures 9.7 and 9.8 describe the leaching results of Na-feldspar and K-feldspar at a mass ratio of 1 in the NaOH and KOH solutions. As noted, the dissolution behaviour of the mixture of Na-feldspar/K-feldspar at the mass ratio of 1 is very similar to that of K-feldspar. Such an analogy between K-feldspar and the mixture of Na-feldspar/K-feldspar at the mass ratio of 1 could suggest that K-feldspar in comparison with Na-feldspar dominates the dissolution of the mixture of Na-feldspar/K-feldspar in the NaOH and KOH solutions.

Consequently, the study of the dissolution of kaolinite, Na-feldspar and K-feldspar reveals that NaOH leaches more Al and Si complexes than KOH solution at all the three
concentrations of 2M, 5M and 7.5M, except that KOH dissolves more Al complex from kaolinite than NaOH. A significant increase of leached Al and Si complexes is observed in the dissolution of kaolinite, Na-feldspar and K-feldspar when the concentration of MOH (where M = Na and/or K) is increased from 2M to 5M. Then the dissolution of Na-feldspar and K-feldspar is inhibited when the concentration of MOH (where M = Na and/or K) is further changed to 7.5M. For the mixture of Na-feldspar/K-feldspar at the mass ratio of 1, the dissolution trend follows that of K-feldspar at all the three concentrations of 2M, 5M and 7.5M.

9.2.5 Mechanisms involved in leaching

The mechanisms involved in the dissolution of Al-Si minerals in highly alkaline solutions have been investigated in chapters 4 and 5 (Xu and Van Deventer, 2000a). The results obtained show that the anion/cation ion pair theory could be applied to explain why NaOH dissolves more Al and Si complexes from Al-Si minerals than KOH does. The observed higher concentrations of Al and Si leached from Na-feldspar and K-feldspar in NaOH than in KOH solution can also be attributed to the ion pair reactions.

The dissolution of kaolinite, Na-feldspar and K-feldspar in alkaline solution can be schematically described below (where M = Na and/or K):

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{H}_2\text{O} + 4\text{MOH} \iff 2\text{Al(OH)}_4^- + 2\text{OSi(OH)}_3 + 4\text{M}^+ \quad (9.1)
\]
(Kaolinite)

\[
\text{NaAlSi}_3\text{O}_8 + 5\text{H}_2\text{O} + 3\text{Na}^+ + 3\text{OH}^- \iff \text{Al(OH)}_4^- + 3\text{OSi(OH)}_3 + 4\text{Na}^+ \quad (9.2)
\]
(Na-Feldspar)

\[
\text{NaAlSi}_3\text{O}_8 + 5\text{H}_2\text{O} + 3\text{K}^+ + 3\text{OH}^- \iff \text{Al(OH)}_4^- + 3\text{OSi(OH)}_3 + \text{Na}^+ + 3\text{K}^+ \quad (9.3)
\]
(Na-Feldspar)
KAISi$_3$O$_8$ + 5H$_2$O + 3Na$^+$ + 3OH$^- \Leftrightarrow$ Al(OH)$_4^-$ + 3'OSi(OH)$_3$ + 3Na$^+$ + K$^+$ \hfill (9.4)
(K-Feldspar)

KAISi$_3$O$_8$ + 5H$_2$O + 3K$^+$ + 3OH$^- \Leftrightarrow$ Al(OH)$_4^-$ + 3'OSi(OH)$_3$ + 4K$^+$ \hfill (9.5)
(K-Feldspar)

An increase in the concentration of MOH will shift the reactions 9.1 to 9.5 towards the right hand side. As observed in experiments, the concentrations of Al and Si complexes leached from kaolinitite, Na-feldspar and K-feldspar in MOH solutions increase along with an increase in the concentration of MOH from 2M to 5M. Equations 9.1 to 9.5 also indicate that the dissolution of kaolinitite in alkaline solutions is affected by Na$^+$ and K$^+$ contained in the alkaline solution. However, the dissolution of Na-feldspar and K-feldspar in alkaline solutions is affected not only by Na$^+$ and K$^+$ contained in the alkaline solution but also by Na and K structured in the feldspars.

It is noted from Equation 9.2 that along with an increase in NaOH from 5M to 7.5M, a probability for the Equation to move back to the left hand side is increased. Because Na$^+$ is one of the reactants of the dissolution (Equation 9.2, left hand side to the right hand side), it is also one of the reactants of the potential precipitation (Equation 9.2, right hand side to the left hand side). A quick shift of Equation 9.2 to the right hand side derived from an increase in [OH$^-$] increases the concentrations of Al, Si and Na$^+$ greatly, and in return, some kind of sodium aluminosilicate precipitation is, hence, stimulated. Although the natural Al-Si minerals normally take a long time to reach the equilibrium at ambient temperature, the precipitation or deposition is always found to coexist with the dissolution (Lindsay, 1979). In the case of Equation 9.2, the precipitates could be sodium aluminates, sodium silicates or simply Na$_x$Al$_y$Si$_z$•H$_2$O$_w$ complexes. Of them, the probability of forming Na-feldspar should be at the top of all the other possibilities, as the undissolved Na-feldspar particles in the suspension can serve as nuclei for Na-feldspar to deposit. So the ultimate values of Al and Si in the solution are the competitive results of two effects, i. e. dissolution and precipitation. This could be the reason why the increase in leached Al and Si is slowed down for Na-feldspar in 7.5M NaOH solution.
From the right hand sides of the Equations 9.3 and 9.4, it is noticed that the same chemical species, \( \text{Al(OH)}_4^- \), \( \text{OSi(OH)}_3 \), \( \text{Na}^+ \) and \( \text{K}^+ \) are formed from the dissolution of \( \text{NaAlSi}_2\text{O}_5 \) and \( \text{KAlSi}_3\text{O}_8 \) in KOH and NaOH solutions, respectively. This means that the possible precipitates could extend to hydrated sodium aluminosilicates, hydrated potassium aluminosilicates and hydrated sodium and potassium aluminosilicates. Of them, both Na-feldspar and K-feldspar are regarded as the most possible precipitates, because they have the same crystal structure and the undissoled particles in the solution, either Na-feldspar or K-feldspar, could act as nuclei. So along with an increase in KOH from 5M to 7.5M, the leached \( \text{Al(OH)}_4^- \) and \( \text{OSi(OH)}_3 \) species from Na-feldspar could combine with either \( \text{Na}^+ \) or \( \text{K}^+ \) or both to deposit on the solid particles. This eventually makes the concentrations of Al and Si in the 7.5M solution lower than in 5M solution. The analogous inhibiting phenomena occurring in the dissolution of K-feldspar are due to the same mechanisms discussed here.

Figure 9.9 depicts the PAS FT IR (photoacoustic FT IR) spectra recorded for Na-feldspar and K-feldspar powders before and after leaching in 7.5M NaOH and KOH solutions. Due to the similar framework structure, Na-feldspar and K-feldspar generate similar IR absorbance in Figure 9.9, as also observed previously by other researchers (Zhang et al., 1996; Zhang et al., 1997). The major difference between the IR absorbance of Na-Feldspar and K-feldspar is located at the wavenumber ws ranging from 700 to 1200 (Zhang et al., 1996), as indicated by the dashed boxes “A” and “B”, respectively (Figure 9.9). It is noted that after the leaching, the surfaces of Na-feldspar and K-feldspar display a substantially higher degree of the Al-Si disorder with peaks becoming broader (Zhang et al., 1997). This phenomenon suggests that during the leaching, some kind of Al-Si precipitates formed on the surfaces of Na-feldspar and K-feldspar particles. In addition, such precipitates are more in the amorphous phase despite being similar to the Na-feldspar and K-feldspar in bulk structure. The new peaks appearing in the spectra of 2 and 3 (indicated as “C” in Figure 9.9) could be assigned as the Si-O stretching derived from the disordered hydrated surfaces (Ying and Benziger, 1993). Interestingly, only leaching residues (both Na-feldspar and K-feldspar) from the NaOH solution show this particular absorbance. Nevertheless, all four leached samples (1, 2, 3 and 4 in Figure 9.9)
are found to have an absorbance at about 1390 cm\(^{-1}\). The absorbance of 1390 cm\(^{-1}\) was observed previously (Basila, 1962) and assigned as the Al-O vibration (Basila, 1962). Thus, the new peaks at 1390 cm\(^{-1}\) ("D") and 900 cm\(^{-1}\) ("C") might imply that some kind of Al-O precipitates and Na\(^+\) related Si-O precipitates were formed in addition to the disordered Na-feldspar and K-feldspar during the leaching. This observation verifies the assumption made in the discussion of the last paragraph that both dissolution and precipitation reactions exist in the leaching process. However, clear evidence for the precipitates of Na-feldspar and K-feldspar on the surfaces of K-feldspar and Na-feldspar during the leaching of K-feldspar and Na-feldspar in NaOH and KOH solutions, respectively, cannot be identified from Figure 9.9. The reasons can be stated as follows:

1. The FAS FT-IR absorbances of Na-feldspar and K-feldspar are very close to each other, in particular after the leaching, which makes the identification of Na-feldspar and K-feldspar harder.

2. The amount of the precipitates has not been enough to give strong signals. The undissolved Na-feldspar and k-feldspar particles together with the precipitates will display combined signals.

3. The disordered Na-feldspar and K-feldspar precipitates broaden the signals and overlap the differences.

Consequently, it could be the precipitating reactions that cause Na-feldspar and K-feldspar to dissolve less in the concentrated MOH solutions. When the alkali metal structured in the alkali-feldspar is different from the alkali metal cation present in the alkaline solution, such inhibition effect becomes more significant. As previously observed (Xu and Van Deventer, 2000a), sodalite ((Na\(_4\)(Si\(_3\)Al\(_3\))O\(_{12}\)Cl), structured with 4 Na atoms in its molecule, shows a lower dissolution extent in NaOH than in KOH solution. This could be due to the precipitation of some kind of hydrated sodium aluminosilicate as well. A higher tendency of sodalite-like material to precipitate is expected when the concentration of Na\(^+\) (NaOH) rather than K\(^+\) (KOH) is increased.
K-feldspar has been observed to dissolve more Al and Si complexes than Na-feldspar in MOH solutions (Figures 9.3 to 9.6). This could be due to the different chemical equilibrium constants, dissolution rate constants and apparent activation energies. Most dissolution equilibria for alkali-feldspars studied previously are in an acid environment (Lindsay, 1979). However, Chou and Wollast (1985), Hellmann (1994), Gérard et al. (1998) and Blum and Stillings (1995) have studied the dissolution rate constants and apparent activation energies for Na-feldspar and K-feldspar in caustic solutions, as listed in Table 9.1. It is noted from Table 9.1 that K-feldspar compared with Na-feldspar possesses a slightly higher dissolution rate constant and a substantially lower apparent activity energy so that K-feldspar needs lower energy to dissolve and dissolves faster than Na-feldspar in alkaline solutions. This could be why K-feldspar leaches more Al and Si complexes within a certain given time than Na-feldspar.

For the mixture of Na-feldspar/K-feldspar at the mass ratio of 1, the dissolution trends (Figures 9.7 and 9.8) are very close to those for K-feldspar (Figures 9.5 and 9.6). During the dissolution of the mixture of Na-feldspar/K-feldspar with the mass ratio of 1, both Na-feldspar and K-feldspar leach Al and Si complexes into the leachate at their specific rates. With a higher dissolution rate constant, K-feldspar is able to dissolve more Al and Si complexes than Na-feldspar in any unit of time, hence the ultimate concentrations of Al and Si complexes are more affected by K-feldspar rather than by Na-feldspar. So the observed dissolution trends for the mixture of Na-feldspar/K-feldspar at the mass ratio of 1 are found to follow the corresponding trends for K-feldspar.

9.3 GEOPOLYMERISATION OF ALKALI-FELDSPARS/KAOLINITE

The synthesis procedure for the geopolymers from the mixtures of M-feldspar/kaolinite (where M = Na and/or K) comprises three steps as follows:

(1) M-feldspar and kaolinite dissolve Al and Si complexes into MOH and silicate solutions to form a gel.

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(2) The formed gel phase becomes thicker and starts polymerising Al and Si complexes into a three dimensional amorphous and semi-crystalline polymer structured with alkali metal M to compensate the negative charges caused by Al.

(3) Along with the evaporation of the excess water in the system, the synthesised geopolymer, a mixture of a gel phase and the undissolved M-feldspar and/or kaolinite particles, becomes a piece of monolithic material with a high mechanical strength.

So factors which affect any step or steps described above will affect the geopolymerisation and consequently affect the compressive strength of the geopolymers formed. Eight factors, which are found to be involved in the geopolymerisation of M-feldspar/kaolinite, are listed below:

(1) Starting mass ratio of M-feldspar/kaolinite (where M = Na and/or K).
(2) Concentration of MOH solution.
(3) Alkali metals contained in MOH solution.
(4) Alkali metals structured in M-feldspar.
(5) Evaporation of excess water contained in a geopolymeric paste.
(6) Composition of the gel phase (or molar ratios of Al/Si and Na/K in gel phase).
(7) Mass ratio of gel phase/(undissolved M-feldspar and/or kaolinite particles).
(8) Average hardness of undissolved M-feldspar and/or kaolinite contained in a geopolymer.

Therefore, the compressive strength of a geopolymer synthesised is the bulk effect of all these factors.
9.3.1 Effect of alkaline solution on geopolymerisation of M-feldspar/kaolinite \((M = Na\) and/or \(K\))

9.3.1.1 Effect of alkaline solution on geopolymerisation of Na-feldspar/kaolinite

Figures 9.10 to 9.13 depict the compressive strength of geopolymers synthesised from the mixtures of M-feldspar/kaolinite with NaOH and KOH, respectively. The geopolymers synthesised from the mixtures of K-feldspar/kaolinite and \((\text{Na-feldspar} + \text{K-feldspar})/\text{kaolinite}\) with KOH are found to crack to various extents after setting and hardening in an oven at \(45^\circ\)C for 28 days so that no compressive strength data are reported for these samples. However, the mixtures of Na-feldspar/kaolinite are observed to produce geopolymers with acceptable mechanical strength (Figures 9.10 and 9.11) when either NaOH or KOH is applied. Interestingly, the mixtures of Na-feldspar and K-feldspar at the mass ratio of 1, as observed, show the cracking behaviour similar to the K-feldspar during geopolymerisation. This suggests that K-feldspar rather than Na-feldspar may dominate the geopolymerisation mixtures of Na-feldspar and K-feldspar.

It is noticed from Figure 9.10 that the compressive strength for the geopolymers synthesised from the mixture of Na-feldspar/kaolinite, at a mass ratio varying from 1 to 7, with NaOH shows curves with two peaks appearing at the mass ratio of 1.5 and 3.5. It is also observed that geopolymers synthesised at the concentration of 5M show the highest compressive strength followed by the geopolymers synthesised at the concentration of 2M. The concentration of 7.5M produces geopolymers with the lowest compressive strength. The dissolution behaviour of Na-feldspar in NaOH solution discussed previously (Figure 9.3) shows that the concentrations of leached Al and Si complexes are slightly higher in 7.5M solution than in 5M solution. Moreover, both 7.5M and 5M solutions leach significantly more Al and Si complexes than the 2M solution does. Generally, a higher concentration of leached Al and Si complexes in the solution will result in a geopolymer with a higher compressive strength (Xu and Van Deventer, 2000a; Xu et al., 2001). The observation that a geopolymer, synthesised at a condition associated with a higher concentration of leached Al and Si, reveals a lower compressive strength suggests that other factors must dominate the geopolymerisation.
Table 9.2 lists the viscosity data for NaOH and KOH solutions determined by a Vane Rheometer. The viscosity of NaOH solution is noted to rise significantly with an increase in concentration. A higher extent of leaching in NaOH solution at a higher concentration is expected to create a denser gel and form a geopolymer with a higher compressive strength. On the other hand, a higher viscosity of NaOH solution used may cause an inhibition on the evaporation of the excess water in the geopolymeric paste so as to soften a geopolymer and lower its compressive strength. Despite the fact that 7.5M NaOH solution can generate a denser gel than 2M NaOH solution does, its higher viscosity may eventually result in the geopolymers with lower compressive strength.

The negative effect of the viscosity of the NaOH solution has been noted before (Xu et al., 2001). A test for the geopolymerisation of Na-feldspar/kaolinite in the NaOH solution at the concentration of 7.5M has been conducted in this study to verify the effect of viscosity. Hardening in an oven at 45 °C for 7 more days is applied to all the samples and the obtained results show that an average of 40% increase in the compressive strength is observed for all the samples tested. This increase indicates that the mechanical strength of geopolymers synthesised with 7.5M NaOH is significantly affected by the amount of excess water remaining in the samples. The same tests done on the geopolymers synthesised from the Na-feldspar/kaolinite in the NaOH solution at concentrations of 2M and 5M do not show any remarkable increase in the compressive strength. The difference between these two tests reveals that it could be the viscosity that causes the lower compressive strength for the geopolymers synthesised in the NaOH solution at the concentration of 7.5M.

A separate water evaporation test (40°C) has been conducted for the geopolymers synthesised from Na-feldspar/kaolinite and K-feldspar/kaolinite with NaOH and KOH at concentrations of 2M, 5M and 7.5M, respectively (Figure 9.14). It is noted that (Figure 9.14) after being left in the oven for 12 days, geopolymers synthesised with 2M KOH solution have evaporated nearly all the excess water and stopped the geopolymeric reactions. In contrast, the geopolymerisations, taking place in the NaOH solution at the concentration of 7.5M, are found to complete the reaction after about 35 days. The 27
days setting and hardening in the oven at 45°C shows a sufficient time period for most geopolymers except for that synthesised with NaOH 7.5M solution. Specifically, the geopolymers synthesised from K-feldspar in KOH solutions (2M, 5M and 7.5M) show a quick evaporation of the excess water, which could be due to the lower viscosity of the KOH solutions (2M, 5M and 7.5M). The water evaporation test (Figure 9.14) reveals that the higher the viscosity of the MOH solution involved in the geopolymerisation of M-feldspar/kaolinite, the longer the hardening time needed. This result verifies the conclusion drawn in the previous paragraph that geopolymers synthesised from Na-feldspar/kaolinite in 7.5M NaOH solution need 7 more days hardening in the oven to gain their strength.

The 5M NaOH solution has a lower viscosity than the 7.5M NaOH, and leaches far more Al and Si complexes than the 2M one does, so produces geopolymers with higher compressive strength (Figure 9.10).

Figure 9.11 shows the compressive strength of the geopolymers synthesised from the mixture of Na-feldspar/kaolinite in the KOH solution at concentrations of 2M, 5M and 7.5M. The geopolymers synthesised with 5M KOH possess the highest compressive strength, followed by those synthesised with 7.5M KOH. This is in contrast with the results for NaOH. The geopolymers produced with KOH at the concentration of 2M show the lowest compressive strength. As noted, the dissolution of Na-feldspar in the KOH solution (Figure 9.4) shows the order of 5M> 7.5M> 2M as well. The correspondence between the trends in the compressive strength of the geopolymers and the extent of dissolution suggests that the leaching extent is the dominant factor which affects the final mechanical strength of the geopolymers.

In summary, Na-feldspar has a higher extent of geopolymerisation in KOH solution. The higher viscosity of the concentrated NaOH solution (7.5M) negatively affects the compressive strength of the resulting geopolymers.
9.3.1.2 Effect of alkaline solution on geopolymerisation of K-feldspar/kaolinite and Na- and K-feldspar/kaolinite

The compressive strength of geopolymers synthesised from K-feldspar/kaolinite with NaOH is depicted in Figure 9.12. It is observed from Figure 9.12 that similar to the geopolymerisation of Na-feldspar/kaolinite in the NaOH solution, the geopolymers with the highest compressive strength are obtained at the concentration of 5M. The geopolymers synthesised at the concentration of 2M show higher compressive strength than those formed at the concentration of 7.5M. Again the effect of the viscosity derived from the NaOH solution is noted in the geopolymerisation of K-feldspar/kaolinite.

The compressive strength of the geopolymers synthesised from the mixture of (Na-feldspar + K-feldspar)/kaolinite (where the mass ratio of Na-feldspar / K-feldspar is 1) with NaOH at the concentrations of 5M and 7.5M is presented in Figure 9.13. As noted, the compressive strength shows higher values when a concentration of 5M rather than 7.5M is applied. The compressive strength for the geopolymers synthesised at both concentrations is actually close to each other. The leaching ability of the mixture of (Na-feldspar + K-feldspar) in the NaOH solution, as depicted in Figure 9.7, is slightly higher at 5M than at 7.5M. Thus, unlike both Na-feldspar and K-feldspar, the mixture of (Na-feldspar + K-feldspar) undergoes geopolymerisation with NaOH showing less effect of viscosity. The leaching ability appears to be the dominant effect during geopolymerisation. This observation shows a similar trend to the results presented in the geopolymerisation of Na-feldspar in KOH solutions (Figure 9.11). Thus, some kind of the interaction between Na$^+$ and K$^+$ may affect the geopolymerisation, because better geopolymerisation occurs when the alkali metal cation in solution is different from the alkali metal structured in the feldspar (Figures 9.11, 9.12 and 9.13). For instance, Na-feldspar has better geopolymerisation in KOH solution and K-feldspar shows higher compressive strength in NaOH solution. Hence, it is assumed that a certain ratio of Na/K should be matched during the geopolymerisation of alkali-feldspars in order to turn out the geopolymers with the optimal compressive strength. This will be discussed later in this chapter.
9.3.2 The water evaporation and differential scanning calorimetry (DSC) tests

As noted from equations 2.6 to 2.9 in Chapter 2 and 4.1 to 4.2 in Chapter 4, water is one of the reactants in geopolymerisation, and it is also one of the products of geopolymerisation. Since the dissolution of Al-Si minerals consumes water, a lower extent of water loss during the early stage of geopolymerisation consequently reflects a higher extent of transformation of Al-Si minerals from their solid state to the gel phase. On the other hand, the polymerisation between Al and Si complexes produces water. So a higher extent of water loss in the later stage of geopolymerisation indicates a higher extent of the polymerisation between dissolved Al and Si species. Moreover, the extent of the ultimate water loss in geopolymerisation directly reflects the extent of the encapsulation of the added water in a geopolymer. This encapsulated water may physically or chemically bind in the network of the gel phase in geopolymers, and increase the extent of the disorder of the gel phase. From the results of the water evaporation test (Figure 9.14), a higher water loss is observed from the geopolymeric pastes of M-feldspar (M = Na and/or K) in MOH (M = Na and/or k) solution at the concentration of 2M. This is due to the lower solubilities of M-feldspar in MOH solution at the concentration of 2M. In particular, the water losses derived from the geopolymeric pastes of K-feldspar and Na-feldspar in KOH solution at the concentration of 2M are found to be the highest and the second highest, because in these two cases both the lower solubility and the lower viscosity increase the extent of the water loss. Another important observation is that the geopolymers with a higher compressive strength (Na-feldspar synthesised in 5M and 7.5M KOH solutions and K-feldspar synthesised in 5M and 7.5M NaOH solutions) associate with a higher water losses at the later stage (between 12 to 27 days) of their geopolymeric reactions. Specifically, these geopolymers also display the lower ultimate water losses compared to the geopolymers synthesised from M-feldspar in MOH (M = Na and/or K) solution at the concentration of 2M. Therefore, it is assumed that the mechanical strength of the geopolymers synthesised from M-feldspar in MOH solution can be partly attributed to the extent of the disorder in their gel phases.
Figures 9.15 to 9.20 depict the differential scanning calorimetry (DSC) results obtained from the geopolymers synthesised from M-feldspar/kaolinite (M = Na and/or K) at the mass ratio of 2.5 in either NaOH or KOH solution at the concentrations of 2M, 5M and 7.5M. It is noted from Figures 9.15 to 9.20 that all geopolymers display an endothermal peak at −49 °C. Since the glass transition temperature of a sodium silicate solution was found previously to occur at about −50 °C (Rahier et al. 1996a), the peak (−49 °C) observed here could be determined as the amorphous gel phase transition. Apart from the endothermal peak occurring at −49 °C, a big widened endothermal peak is observed at the temperature ranging from 105 to 200 °C. This peak could be interpreted as the evaporation of the physically adsorbed water, e.g. capillarylly encapsulated water, or transition of a glass phase (Bershtein, 1994).

From Figure 9.15, the temperature of the endothermal peak in cases 3, 4 and 5 is found to be located at 105, 107 and 111 °C, respectively. An increase in temperature of the endothermal peak means a stronger binding between the water and the network in the geopolymer gel phase, and it also reflects a shift of the physically adsorbed water to the chemically bonded water. Consequently the DSC results for geopolymers synthesised from Na-feldspar and kaolinite at the mass ratio of 2.5 in NaOH solution (Figure 9.15) reveal that an increase in concentration of the NaOH solution results in a geopolymer with a stronger binding in the gel phase. Three peaks at the temperatures of 135 °C in case 5, 119 °C in case 4 and 200 °C in case 3 were observed, although they are not obvious in the graph of Figure 9.15. These peaks are related to the transition of the amorphous gel phase in the geopolymers. A similar glass transition has been observed previously at the temperature of ~167 °C for polysilicic acid (Bershtein, 1994). Considering that the gel phase in a geopolymer may consist of both polysilicic acid and poly-aluminosilicate, a decrease in temperature for the transition of the gel phase to occur is expected (Bershtein, 1994).

From Figure 9.16, three wider endothermal peaks (3, 4 and 5) are observed compared to the thermograms showed in Figure 9.15. The wider an endothermal peak in DSC is, the higher the extent of the disorder in a glass phase will be (Bershtein, 1994). So the
geopolymers synthesised from Na-feldspar/kaolinite at the mass ratio of 2.5 in KOH solution probably comprise either more amorphous gel phases or a higher extent of disorder in the gel phase than those synthesised in NaOH solution. It is also noted that the temperatures of the peaks in Figure 9.16 are found to shift to higher values located at 112 °C, 141 °C and 151 °C, respectively. These three peaks are caused by the transitions of the gel phase in the geopolymers, despite two separate peaks derived from the evaporation of the free water (physically adsorbed water) appearing at the temperatures of 80 °C and 102 °C for the cases of 3 and 4, respectively. A comparison between the Figures 9.15 and 9.16 suggests that a stronger binding and a higher extent of the disorder in the gel phase may be the reason for the geopolymers synthesised in KOH solution to be mechanically stronger than those formed in NaOH solution (Figures 9.10 and 9.11).

The thermograms displayed in Figure 9.17 are similar in shape to those shown in Figure 9.15. However, the temperatures of the transition of the corresponding gel phase are increased from 105 °C to 117 °C, 119 °C to 121 °C and 135 °C to 147 °C for the cases of 3, 4 and 5, respectively. This increase in temperature implies that the geopolymers synthesised from K-feldspar/kaolinite at the mass ratio of 2.5 in NaOH solution possess a stronger binding between the water and the network in the gel phases than in the case of Na-feldspar. In other words, the gel phases in the geopolymers displayed in Figure 9.17 are stronger binders than those formed in the geopolymers shown in Figure 9.15, and this could be the reason for the former geopolymers having a higher compressive strength than the latter ones (Figures 9.10 and 9.12).

The thermograms displayed in Figure 9.18 are closer to those shown in Figure 9.16 in shape. However, the case 7 is observed to have two main endothermal peaks at 118 °C and 149 °C, respectively. This phenomenon indicates that both physically adsorbed water and chemically bonded water significantly exist in this geopolymer. The transition temperatures for the gel phases in cases of 7 and 8 appear at 149 °C and 147 °C, respectively. A comparison between the Figures 9.16 and 9.18 suggests that the geopolymers in Figure 9.18 appear to have similar gel phases to those in Figure 9.16. The reason is that both of them are more amorphous (wider peaks), and have a stronger
binding in the network of the gel phases (higher transition temperature). Despite the fact that all the geopolymers synthesised from the K-feldspar in KOH solution were found to crack after the setting and hardening in an oven for 28 days at the temperature of 45 °C, the DSC results obtained here (Figures 9.18) reveal that these geopolymers could potentially gain their mechanical strength, if they can be set and hardened at a proper temperature or environment.

Interestingly, the geopolymers synthesised from K-feldspar in NaOH solution (Figure 9.19) or synthesised from Na-feldspar in KOH solution (Figure 9.20) are observed to have a stronger binding (a higher transition temperature) in their corresponding gel phases. This could explain why these geopolymers have a higher compressive strength (Figures 9.11 and 9.12). Moreover, KOH solution is noted to increase the extent of the disorder in the gel phases of the geopolymers (Figure 9.20). According to the ion-pair theory mentioned in the previous Chapters of this thesis, K⁺ favours the polymerisation between Al complexes and Si complexes. KOH solution is expected to result in a higher extent of geopolymerisation so as to generate more and a thicker amorphous gel phase in the resulting geopolymer. Thus, the observation obtained here (Figures 9.19 and 9.20), again experimentally proves the assumption of the ion-pair theory. NaOH solution, with a higher viscosity, is found to produce geopolymers with a higher extent of the encapsulation of the added water, because the values of the absolute heat flow observed are higher in Figure 9.19 than those in Figure 9.20. This discovery agrees well with the results obtained from the water evaporation test shown in Figure 9.14. Finally, it is noted (Figures 9.19 and 9.20) that concentrated MOH solutions create geopolymers with a higher encapsulation of the added water (a higher absolute heat flow), which can be attributed to their higher viscosity.

9.3.3 Effect of the mass ratio of M-feldspar/kaolinite

Apart from the general trends of the compressive strength for the geopolymers synthesised discussed in section 9.3.1, two peaks are also observed in the curves presented in Figures 9.10 to 9.13 except for the geopolymers produced from (Na-feldspar
+ K-feldspar)/kaolinite with NaOH at the concentration of 7.5M. Figures 9.10 to 9.13 depict the compressive strength versus the mass ratio of M-feldspar/kaolinite (where M = Na and/or K). These two peaks reveal that along with an increase in the starting mass ratio of M-feldspar/kaolinite from 1.0, the compressive strength increases until it reaches the first peak. Following a drop, the compressive strength rises again till the second peak and then drops again without any further significant increase occurring afterwards. From the composition data listed in Table 9.1, it is noted that during the geopolymerisation of M-feldspar/kaolinite, kaolinite is an Al₂O₃ richer mineral and reacts as an Al₂O₃ supplier. Hence, along with the increase in the mass ratio of M-feldspar/kaolinite, less kaolinite will be involved in the geopolymerisation, consequently reducing the amount of Al₂O₃ in the geopolymeric gel phase and resulting in a gel composition with a higher molar ratio of Si/Al.

In order to understand the change occurring in the gel phases, an analysis of SEM/EDX on the molar ratio of Si/Al contained in the gel phases has been conducted. For each selected sample, 15 different points are analysed and the average results are reported in Table 9.3. As expected, the molar ratio of Si/Al in the gel phases (Table 9.3) increases along with an increase in the mass ratio of M-feldspar/kaolinite for all concentrations of NaOH or KOH. The increase in the molar ratio of Si/Al also indicates that the increase of the mass ratio in M-feldspar/kaolinite governs the change in the molar ratio of Si/Al in the gel phase. Also observed in Table 9.3, in the Na-feldspar/kaolinite, K-feldspar/kaolinite and (Na-feldspar + K-feldspar/kaolinite) systems, the highest compressive strength of the geopolymers formed always corresponds to a particular range of Si/Al molar ratio in the gel phases. The samples 1, 5, 6 and 10 (referring to the first peaks shown in Figures 9.10 to 9.13) listed in Table 9.3, whose compressive strengths are the highest under the corresponding geopolymeric conditions, possess a molar ratio of Si/Al from 2.17 to 2.38 in their gel phases. The compressive strength of a geopolymer is believed to be contributed by both the gel phase as a binder and the undissolved particles remaining in the geopolymer as fillers. It is deduced that along with an increase in the mass ratio of M-feldspar/kaolinite, the molar ratio of Si/Al contained in the
corresponding gel phases will increase to the certain value or values at which the geopolymers formed show the highest mechanical strength.

When the mass ratio of M-feldspar/kaolinite is further increased, the molar ratio of Si/Al in the corresponding gel phase increases beyond the optimal value, resulting in a drop in the compressive strength of the geopolymers formed. However, it is observed (Figures 9.10 to 9.13) that the compressive strength of the geopolymers after a drop rises again until it reaches the second peak and then drops afterwards. The presence of the second peak (Figures 9.10 to 9.13) in the compressive strength indicates that apart from the gel phase composition, other factors affect the compressive strength of the geopolymers as well. It is shown in Table 9.1 that the densities of the three minerals, Na-feldspar, K-feldspar and kaolinite are very close to each other, while the hardness of kaolinite is much lower than that for Na-feldspar and K-feldspar. The particle sizes of the three minerals are very close to each other as well. Hence the change in the mass ratio of M-feldspar/kaolinite will result in a change to the molar ratio of Si/Al contained in the gel phase as well as a change in the average hardness for the solid particles both before and after geopolymerisation. When the mass ratio of M-feldspar/kaolinite is increased, less kaolinite particles are involved in the geopolymerisation, increasing the probability that kaolinite is transferred completely into the gel phase. The synthesised geopolymers consequently comprise less kaolinite particles after the geopolymerisation. Because the undissolved particles left in a monolithic geopolymer are believed to act as fillers, the less kaolinite particles existing in the geopolymers, the higher the average hardness of the undissolved particles will be. Therefore, a formed geopolymer with a higher compressive strength is expected if no kaolinite particles remain undissolved.

Figure 9.21 presents the XRD patterns recorded for K-feldspar, kaolinite and geopolymers synthesised from the mixture of K-feldspar/kaolinite at the mass ratios of 5.0 and 6.0 respectively in the NaOH solution at the concentration of 5M. It is observed from Figure 9.21 that the kaolinite characteristic (001) peak is detectable in the geopolymer synthesised at the mass ratio of 5.0. However, no kaolinite characteristic peaks are found in the XRD pattern of the geopolymer produced at the mass ratio of 6.0.
This phenomenon implies that at the mass ratio of 6.0, kaolinite particles are completely transferred into the gel phase during the geopolymerisation. Referring to Figure 9.12, it is noted that at the mass ratio of 6.0, the compressive strength of the corresponding geopolymer reaches the second highest value. Moreover, a further extensive XRD analysis on the geopolymers synthesised from K-feldspar/kaolinite in the NaOH solution at the concentration of 5M reveals that the mass ratio of 6.0 is the lowest ratio of K-feldspar/kaolinite for the geopolymers synthesised with XRD patterns showing no kaolinite characteristic peaks. So only the lowest mass ratio of K-feldspar/kaolinite, at which kaolinite is completely transferred into the geopolymeric gel phase, will result in a significant increase in the compressive strength for the geopolymer produced. A series of XRD analysis has also been conducted separately on the geopolymers synthesised from Na-feldspar/kaolinite and (Na-feldspar + K-feldspar)/kaolinite. The obtained XRD patterns show that along with an increase in the mass ratio of Na-feldspar/kaolinite or (Na-feldspar + K-feldspar)/kaolinite, the intensity of the kaolinite characteristic (001) peak becomes lower and lower until completely undetectable. As indicated in the XRD patterns and in Figures 9.10 to 9.13, when geopolymers synthesised at a certain mass ratio show no kaolinite characteristic (001) peak in their XRD patterns, they possess the second highest compressive strengths.

Consequently, it is concluded that during the geopolymerisation of M-feldspar/kaolinite, there are two factors affecting the compressive strength of the geopolymers as the mass ratio of M-feldspar/kaolinite increases. One is the molar ratio of Si/Al contained in the geopolymeric gel phase, and the other is the average hardness of the undissolved particles remaining in the geopolymers.

9.3.4 Effect of the molar ratio of Na/K in gel phase on crack formation

Cracking has been observed for the geopolymers synthesised from K-feldspar/kaolinite and (Na-feldspar + K-feldspar)/kaolinite (where the mass ratio of Na-feldspar/K-feldspar is 1) with KOH at all three concentrations of 2M, 5M and 7.5M. It has also been found that those geopolymers that crack are synthesised from the systems with both K-feldspar
and KOH involved. The leaching results described in Figures 9.3 to 9.6 show that K-feldspar has a higher leaching tendency in both NaOH and KOH solutions than Na-feldspar. Therefore, K-feldspar will generate an initial gel phase denser and faster, and thus geopolymerise more quickly. Nevertheless, the results obtained from the previous studies (Xu and Van Deventer, 2000a; Xu et al., 2001; Van Jaarsveld and Van Deventer, 1999) indicate that the KOH solution has a positive effect on geopolymerisation with the geopolymers formed possessing a higher compressive strength. The fact that KOH favours geopolymerisation is believed (Xu and Van Deventer, 2000a; Xu et al., 2001) to be due to the ion pair effect between the \( K^+ \) cation and larger silicate oligomer anions. This effect leads to a higher geopolymerising extent and produces a geopolymer with a higher compressive strength. Therefore, it seems that geopolymerisation should benefit from involving both K-feldspar and KOH.

Geopolymerisation takes place in an alkaline solution with water being an essential reactant. The viscosity of the KOH solution, however, as showed in Table 9.2 is lower than NaOH (11, 15 and 18 m Pa.s respectively at the concentrations of 2M, 5M and 7.5M). On the one hand, both K-feldspar and KOH tend to generate a higher geopolymerising extent that needs more water to react with. On the other hand, a lower viscosity of KOH solution causes a faster evaporation of water (Figure 9.14). Generally a fast loss of water from the surface of a sample will quickly inhibit an even geopolymerisation and will yield a difference in the tension distribution in the sample, eventually causing cracking. It is assumed that the quicker the water has been evaporated, the more the added water will be removed from the samples, which may ultimately lower the extent of the geopolymerisation. Despite the DSC results (Figure 9.18) showing significant amorphous phases formed in the corresponding geopolymers, both the quick evaporation of water and the comparatively lower extent of geopolymerisation could be the reasons that the geopolymers synthesised from the K-feldspar/kaolinite and (Na-feldspar + K-feldspar)/kaolinite in the KOH solution crack. Other factors, for instance, the excess of \( K^+ \) in the gel phase, may also affect the cracking of the geopolymers in the reaction of K-feldspar/kaolinite with KOH. However, these factors or mechanisms are not clear yet.
The geopolymers synthesised from Na-feldspar/kaolinite with KOH and K-feldspar/kaolinite with NaOH are observed to demonstrate a higher compressive strength than those from other systems (see Figures 9.10 to 9.13). An SEM/EDX analysis on the gel phase reveals that the molar ratios of Na/K in the gel phase in these two systems (Na-feldspar/kaolinite + KOH and K-feldspar/kaolinite + NaOH) range from 1.5 to 77.9. Moreover, a further SEM/EDX analysis on the gel phase in the geopolymers with cracking shows that the molar ratios of Na/K in the gel phase are all lower than 0.1. So the molar ratio of Na/K in the gel phases may be the another factor to affect the geopolymerisation with regard to compressive strength and the occurrence of cracking. When the molar ratio of Na/K in the gel phase drops lower than 0.1, the geopolymers synthesised are found to crack after setting and hardening at 45 °C for 28 days. However, when the molar ratio of Na/K in the gel phase is between 1.5 and 77.9 (Table 9.3), the geopolymers obtained can reach high compressive strength. This result also implies that for the geopolymerisation of alkali-feldspars, Na and K contribute to the compressive strength of the geopolymers formed as a combined effect. The effect of the molar ratio of Na/K in the gel phase on the geopolymerisation is in agreement with the prediction made previously by Xu and Van Deventer (2000a). It has been indicated that a framework structured Al-Si mineral (e.g alkali-feldspars) with a higher content of CaO and a lower content of K_2O will have a higher ability to undergo geopolymerisation in concentrated KOH solution (Xu and Van Deventer, 2000a). K_2O contained in Al-Si minerals will increase the K in the geopolymeric gel phase, which will lower the molar ratio of Na/K in the gel phase, and raise the probability for geopolymers synthesised in KOH to crack.

9.4 SUMMARY

The dissolution and geopolymerisation of Na-feldspar and K-feldspar have been investigated in this chapter. The results show that both Na-feldspar and K-feldspar have a high dissolution tendency in alkaline solutions and have a high ability to undergo geopolymerisation in KOH and NaOH respectively. The alkali metals structured in feldspar are found to inhibit the dissolution of the feldspar in concentrated alkaline solutions. In particular, when the alkali metal (Na or K) structured in feldspar is different
from the counter alkali metal cation in the alkaline solution (NaOH or KOH), this inhibiting effect becomes greater. The mechanisms involved in the dissolution of M-feldspar (where M = Na and/or K) are well explained by the ion pair theory and the reversible dissolution and precipitation reactions.

Kaolinite, as an Al₂O₃ supplier during the geopolymerisation of M-feldspar/kaolinite, is observed to enable the geopolymeric gel phase to reach the optimal molar ratio of Si/Al, resulting in a geopolymer with the highest compressive strength. However, excessive kaolinite involved in geopolymerisation of M-feldspar/kaolinite will negatively affect the final mechanical strength because of its lower hardness.

The molar ratio of Si/Al in a geopolymeric gel phase and the average hardness of the undissolved particles remaining in a geopolymer are two critical factors affecting the ultimate compressive strength of the geopolymers. An optimal molar ratio of Si/Al in the gel phase will result in a geopolymer with the highest compressive strength. A high average hardness of the undissolved particles remaining in a geopolymer will result in a high compressive strength for the geopolymer formed.

The molar ratio of Na/K in the geopolymeric gel phase also affects the geopolymers formed. When the molar ratio of Na/K contained in gel phase is lower than 0.1, the obtained geopolymers show cracking after setting and hardening at 45 °C for 28 days. Also, it has been found that for an Al-Si mineral structured with alkali metal Na or K, a higher compressive strength of the geopolymer synthesised will be expected when the alkali metal cation in an alkaline solution differs from the counter part alkali metal contained in the Al-Si mineral.

The water evaporation test reveals that the geopolymers synthesised in the concentrated MOH solution need more days to complete the geopolymeric reaction. Specifically, when geopolymerisation takes place in the NaOH solution at the concentration of 7.5M, another 7 days are needed for the resulting geopolymers to fully gain compressive strength. However, for the geopolymerisations of K-feldspar/kaolinite in KOH solution, a
lower temperature might be applied during the setting and hardening in order to lower the fast evaporation of water caused by the lower viscosity of the KOH solution.

The DSC results indicate that the extent of the geopolymerisations is increased by an increase in the concentration of the MOH solution used. In particular, KOH solution is found to significantly increase the disorder in the gel phases of the geopolymers formed.
Table 9.1 Mass composition, density and hardness of Na-feldspar, K-feldspar and kaolinite, the dissolution rate constants and the apparent activation energy of Na-feldspar and K-feldspar

<table>
<thead>
<tr>
<th>Element as oxide</th>
<th>Na-feldspar</th>
<th>K-feldspar</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>70.9</td>
<td>67.1</td>
<td>54.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>17</td>
<td>17.6</td>
<td>29.4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>9.75</td>
<td>3.16</td>
<td>0.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.43</td>
<td>10.6</td>
<td>0.2</td>
</tr>
<tr>
<td>CaO</td>
<td>0.31</td>
<td>0.18</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.07</td>
<td>0.21</td>
<td>1.4</td>
</tr>
<tr>
<td>MgO</td>
<td>0.04</td>
<td>0.04</td>
<td>0.2</td>
</tr>
<tr>
<td>MnO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>-</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.14</td>
<td>0.26</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.045</td>
<td>0.01</td>
<td>2.8</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>0.75</td>
<td>0.62</td>
<td>11</td>
</tr>
<tr>
<td>Density (g/cm³)*</td>
<td>2.62</td>
<td>2.57</td>
<td>2.62</td>
</tr>
<tr>
<td>Hardness (Mohs.)*</td>
<td>6.5</td>
<td>6.5</td>
<td>2.3</td>
</tr>
<tr>
<td>( \log K_{\text{Na}^{0} \text{OH}^-} ) (mol cm⁻² s⁻¹) **</td>
<td>-18.3</td>
<td>-18.2</td>
<td></td>
</tr>
<tr>
<td>( E_{\text{Na}^{0} \text{OH}^-} ) (kcal mol⁻¹) ***</td>
<td>20.3</td>
<td>13.9</td>
<td></td>
</tr>
</tbody>
</table>

**: The dissolution rate constant cited from Chou and Willast (1985) and Madé (1991).
***: The apparent activation energy cited from Hellmann (1994).

Table 9.2 The viscosity of NaOH and KOH solutions detected at 20 °C by a Vane Rheometer

<table>
<thead>
<tr>
<th>NaOH (M)</th>
<th>Zero Shear Viscosity (m Pa.s)</th>
<th>KOH (M)</th>
<th>Zero Shear Viscosity (m Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>14</td>
<td>2</td>
<td>11</td>
</tr>
<tr>
<td>5</td>
<td>31</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>7.5</td>
<td>64</td>
<td>7.5</td>
<td>18</td>
</tr>
</tbody>
</table>
Table 9.3 The compressive strength and the average molar ratio of Si/Al and Na/K contained in the gel phases of the selected geopolymers detected by SEM/EDX analysis (where M = Na and/or K)

<table>
<thead>
<tr>
<th>Sample No</th>
<th>M-feldspar/kaolinite (g/g)</th>
<th>MOH (M)</th>
<th>Compressive strength MPa</th>
<th>Si/Al (molar ratio)</th>
<th>Na/K (molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na-feldspar, 1.50</td>
<td>NaOH, 5M</td>
<td>13.8</td>
<td>2.21</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Na-feldspar, 2.5</td>
<td>NaOH, 5M</td>
<td>8.6</td>
<td>3.35</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Na-feldspar, 1.0</td>
<td>KOH, 5M</td>
<td>8.8</td>
<td>1.72</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>Na-feldspar, 2.0</td>
<td>KOH, 7.5M</td>
<td>10.3</td>
<td>1.99</td>
<td>1.5</td>
</tr>
<tr>
<td>5</td>
<td>Na-feldspar, 2.5</td>
<td>KOH, 5M</td>
<td>24.4</td>
<td>2.38</td>
<td>8.3</td>
</tr>
<tr>
<td>6</td>
<td>K-feldspar, 2.0</td>
<td>NaOH, 5M</td>
<td>25.8</td>
<td>2.26</td>
<td>77.9</td>
</tr>
<tr>
<td>7</td>
<td>K-feldspar, 4.0</td>
<td>NaOH, 5M</td>
<td>12.5</td>
<td>3.75</td>
<td>55.7</td>
</tr>
<tr>
<td>8</td>
<td>K-feldspar, 6.0</td>
<td>NaOH, 5M</td>
<td>17.5</td>
<td>4.31</td>
<td>37.3</td>
</tr>
<tr>
<td>9</td>
<td>Na-f + K-f, 1.0</td>
<td>NaOH, 5M</td>
<td>12.7</td>
<td>1.81</td>
<td>218.9</td>
</tr>
<tr>
<td>10</td>
<td>Na-f + K-f, 2.0</td>
<td>NaOH, 5M</td>
<td>17.6</td>
<td>2.17</td>
<td>190.5</td>
</tr>
<tr>
<td>11</td>
<td>Na-f + K-f, 1.0</td>
<td>NaOH, 7.5M</td>
<td>4.6</td>
<td>1.67</td>
<td>318.6</td>
</tr>
<tr>
<td>12</td>
<td>Na-f + K-f, 3.0</td>
<td>NaOH, 7.5M</td>
<td>15.9</td>
<td>2.68</td>
<td>529.2</td>
</tr>
</tbody>
</table>
Figure 9.1. Leached [Si] (ppm) of kaolinite in 2M, 5M and 7.5M MOH (M = Na or KOH) solutions.

Figure 9.2. Leached [Al] (ppm) of kaolinite in 2M, 5M and 7.5M MOH (M = Na or K) solutions.
Figure 9.3. Leached [Si] (ppm) and [Al] (ppm) of Na-feldspar in 2M, 5M and 7.5M NaOH solutions.

Figure 9.4. Leached [Si] (ppm) and [Al] (ppm) of Na-feldspar in 2M, 5M and 7.5M KOH solutions.
Figure 9.5. Leached [Si] (ppm) and [Al] (ppm) of K-feldspar in 2M, 5M and 7.5M NaOH solutions.

Figure 9.6. Leached [Si] (ppm) and [Al] (ppm) of K-feldspar in 2M, 5M and 7.5M KOH solutions.
Figure 9.7. Leached [Si] (ppm) and [Al] (ppm) of Na-feldspar and K-feldspar in 2M, 5M and 7.5M NaOH solutions.

Figure 9.8. Leached [Si] (ppm) and [Al] (ppm) of Na-feldspar and K-feldspar in 2M, 5M and 7.5M KOH solutions.
Figure 9.9 FAS FT-IR spectra of Na-feldspar and K-feldspar before and after leaching in NaOH and KOH solutions at the concentration of 7.5M.
Figure 9.10. The compressive strength of geopolymers synthesised from a mixture of Na-feldspar and kaolinite using NaOH.

Figure 9.11. The compressive strength of geopolymers synthesised from a mixture of Na-feldspar and kaolinite using KOH.
Figure 9.12. The compressive strength of geopolymers synthesised from a mixture of K-feldspar and kaolinite using NaOH.

Figure 9.13. The compressive strength of geopolymers synthesised from a mixture of Na-feldspar, K-feldspar and kaolinite using NaOH.
Figure 9.14 The water evaporation curves (at 40 °C) of geopolymers synthesised from kaolinite and alkali-feldspars.
Figure 9.15 DSC thermograms of geopolymers synthesised from Na-feldspar/kaolinite at the mass ratio of 2.5 in NaOH solution at the concentrations of 2M, 5M and 7.5M.
Figure 9.16 DSC thermograms of geopolymers synthesised from Na-feldspar/kaolinite at the mass ratio of 2.5 in KOH solution at the concentrations of 2M, 5M and 7.5M.
Figure 9.17 DSC thermograms of geopolymers synthesised from K-feldspar/kaolinite at the mass ratio of 2.5 in NaOH solution at the concentrations of 2M, 5M and 7.5M.
Figure 9.18 DSC thermograms of geopolymers synthesised from K-feldspar/kaolinite at the mass ratio of 2.5 in KOH solution at the concentrations of 2M, 5M and 7.5M.
Figure 9.19 DSC thermograms of geopolymers synthesised from M-feldspar/kaolinite (M = Na and/or K) at the mass ratio of 2.5 in NaOH solution at the concentrations of 2M, 5M and 7.5M.
Figure 9.20 DSC thermograms of geopolymers synthesised from M-feldspar/kaolinite (M = Na and/or K) at the mass ratio of 2.5 in KOH solution at the concentrations of 2M, 5M and 7.5M.
Geopolymer synthesised from a mixture of K-feldspar/kaolinite at a mass ratio of 5.0

Geopolymer synthesised from a mixture of K-feldspar/kaolinite at a mass ratio of 6.0

Kaolinite (001) peak

K-feldspar

Kaolinite

Kaolinite (001) peak

Figure 9.21 The XRD patterns of K-feldspar, kaolinite and geopolymers synthesised from a mixture of K-feldspar/kaolinite at a mass ratio of 5.0 and 6.0 respectively
CHAPTER TEN

CONCLUSIONS

This thesis conducts a detailed study with the aim to address a wide variety of issues relating to the geopolymerisation of natural aluminosilicate minerals. Very few studies have ever been carried out previously on this particular aspect. A literature review of this field as well as the related fields, e.g. polymerisation of silicates and zeolite synthesis has been described at the beginning of the thesis. This enables readers from related research fields to understand and follow the discussions presented.

The geopolymerisation of the selected fifteen natural aluminosilicate minerals indicates that natural aluminosilicate minerals have a high potential to undergo geopolymerisation. In particular, Al-Si minerals with framework structure, high content of CaO wt % and low content of K₂O wt % show on average higher reactivity in geopolymerisation. NaOH is observed to leach more Al and Si complexes than KOH solution regardless of the structure and composition of the Al-Si minerals. KOH solution, however, is found statistically to produce geopolymers with higher compressive strength than NaOH. Stilbite, a kind of zeolite mineral, generates a geopolymer with a compressive strength of 18.9 MPa after three days setting and hardening in an oven at 35 °C.

The factors that affect geopolymerisation have been investigated by using compressive strength of geopolymers synthesised as the performance indicator. A geopolymeric matrix consisting of stilbite and kaolinite has been used as a case study. The factors studied include alkalinity, M₂O/H₂O, ratio of added silicate solution and alkalinity, SiO₂/M₂O, alkali metal cations contained in the alkaline solution, Na⁺ and K⁺, setting pressure and mixing procedures. The M₂O/H₂O, SiO₂/M₂O ratios and the setting pressure are found to positively affect the geopolymerisation with geopolymers formed showing a higher compressive strength. Moreover, the added silicate solution is observed to catalyse the geopolymerisation. Mixing alkaline solution with silicate solution prior to the
addition of solid reactants is proven to generate the best homogeneous geopolymeric paste and so to create the geopolymer with the highest compressive strength.

A combination of XRD, MAS NMR SEM/EDX, TEM/EDX and HREM techniques has been applied to characterise the geopolymers and the geopolymeric reactants at the semi-quantitative level. It is revealed that the compressive strength of geopolymers is contributed by the gel phase as the binder, the undissolved particles as the filler and the ratio of the average surface area/gel phase. The characterisation method established in this thesis can be applied in related materials, such as cement and concrete.

The mechanisms involved in leaching and geopolymerisation can be explained by the cation anion ion pair theory. Na\(^+\) with a smaller size can better stabilise the smaller silicate oligomers, such as monomer and dimer. Possessing a larger size, K\(^+\) is found to be able to lower the energies of larger silicate oligomers. During the leaching of Al-Si minerals, only silicate monomer and dimer exist and these smaller silicate oligomers are stabilised by NaOH solution and so result in a high extent of dissolution. With an addition of silicate solution, the fraction of larger silicate oligomers increases greatly. These larger silicate oligomers are preferentially pairing with the K\(^+\) cation, eventually leading to a higher extent of geopolymerisation. Ab initio calculation has been applied to verify the ion pair mechanisms in leaching and geopolymerisation. The calculated dissolution energies of stilbite in NaOH and KOH solutions show that NaOH is more exothermic than KOH solution. In other words, on a thermodynamic basis, NaOH can leach more stilbite than KOH solution. The calculated forming energies of the silicate oligomers (dimer, linear trimer and cyclic trimer) in the NaOH and KOH solutions indicate that Na\(^+\) favours the formation of dimer and K\(^+\) benefits the formation of trimer (both linear and cyclic). The results of calculations conducted on the geopolymeric precursors show that K\(^+\) statistically promotes the formation of geopolymeric precursors more than Na\(^+\) does. Consequently, the ion pair theory is found to be in good agreement with the experimental observations as well as with the theoretical calculation results.
The interaction between the alkali metals structured in the Al-Si minerals and the alkali metal cations present in the alkaline solutions has been investigated by utilising the alkali-feldspars (albite and microcline) as the main reactants. It is observed that an inhibiting reaction occurs during the dissolution of the alkali-feldspars in concentrated NaOH and KOH solutions. In particular, when the alkali metal structured in the alkali-feldspars differs from the alkali metal cations present in the alkaline solution, this inhibition becomes greater. One of the possible explanations is the reversible dissolution and precipitation reaction existing during the leaching. It is found that the geopolymers synthesised by the alkali-feldspars whose structured alkali metals are different from the alkali metal cations in the alkaline solutions have a higher compressive strength. When Na-feldspar is geopolymerised in NaOH solution rather than in KOH solution, the geopolymers formed show lower mechanical strength. Also, if geopolymerised in KOH solution, K-feldspar produces geopolymers cracking after 28 days setting and hardening in an oven at 40 °C.

The work done in this thesis shows that natural aluminosilicate minerals have a high potential to undergo geopolymerisation under certain conditions. The geopolymers synthesised from Na-feldspar and K-feldspar in 7.5M KOH and 7.5M NaOH solutions reach a compressive strength of 24.4 MPa. and 25 MPa. respectively, after 28 days setting and hardening at 45 °C.

The significance of this thesis includes the first study on geopolymerisation of natural aluminosilicate minerals, the establishment of the method to characterise geopolymers, the explanation of the experimental observations by cation anion pair theory, the theoretical verification of the ion pair theory by ab initio calculations and the study of the interaction between the alkali metals structured in the Al-Si minerals and the alkali metal cations present in the alkaline solutions. The results presented in this thesis provide a complete picture of the geopolymerisation of natural aluminosilicate minerals.
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