# Synthesis and thermal treatment of lithium- and magnesium-containing geopolymers

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A thesis submitted to the Victoria University of Wellington in partial fulfilment of the requirements for the degree of MSc in Chemistry

2009

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#### Abstract

Geopolymers are a class of cementitious aluminosilicate materials that are receiving an increasing amount of attention due to their potential applications in toxic waste remediation and as construction materials. They are composed of a network of crosslinked silicate and aluminate tetrahedra with charge-balancing alkali cations and are therefore similar in composition to alkali aluminosilicate zeolites. They are, however, x-ray amorphous.<sup>1-4</sup> They are formed by the dissolution of a solid aluminosilicate in a solution of alkali hydroxide or alkali silicate to form aluminosilicate ions which subsequently polymerise.

The effects of adding magnesium to metakaolin geopolymer systems was examined. Magnesium was added as soluble magnesium salts and as magnesium oxide and hydroxide. When added as a soluble salt, an amorphous magnesium (alumino)silicate with a lower degree of silicate polymerisation than a geopolymer is formed. When added as the oxide or hydroxide, hydrotalcite is formed. In both cases, the product is produced alongside a separate geopolymer phase. A magnesium-containing geopolymer phase was not found in either . When heated to 1200°C, geopolymers with magnesium oxide added bloated to form lightweight foams.

Lithium analogues of conventional metakaolin geopolymer systems with a range of lithium, aluminium, silicon and water contents were examined. Systems with molar ratios similar to those of commonly studied sodium and potassium metakaolin geopolymers produce self-pelletised lithium zeolites. The zeolite formed was Li-EDI, the lithium analogue of zeolite F. This is the first reported synthesis directly from metakaolin. True lithium geopolymers are found not to form in the systems examined. The zeolite bodies react to form  $\beta$ -eucryptite and  $\beta$ -spodumene at temperatures from 800 – 1350°C.

The use of aluminium hydroxide and amorphoud silica rather than aluminosilicates as raw materials for the formation of potassium geopolymers was found to produce geopolymers with embedded grains of unreacted silica and aluminium hydroxide.

## Acknowledgements

This thesis would not have been possible without the help of all those who gave me their time, effort, expertise, money and support.

Firstly I would like to thank all the people who supported my life while doing my research and writing this thesis.

In particular:

- Mum, for her constant and unwavering support for all her care parcels, phone calls and prayers.
- Dad, for his financial support throughout the last 6 years.
- Cheryl, for her love, support and endless patience. I will always be grateful for you waiting for me.

Also all of my other friends and family who helped me so much.

Secondly, I would like to thank the IRL and the Curtis-Gordon Scholarship for their invaluable financial assistance

Thirdly, I would like to thank the people who helped me in my work directly:

- All the other students and staff who were my friends, particularly Jessica Lai and the students from LB106.
- The other students in the geopolymer group, especially Nils Rahner, Matt Bolton, Jonathan Tailby and Bryan O'Leary.
- Jackie King, Teresa Gen, Alan Rennie, and Manu Pouajen-Blakiston, who always went the extra mile.
- The staff at IRL, in particular Bill Owers and Vaughan White.

And especially:

- Martin Ryan, for his help and sage advice on XRD.
- Herbert Wong, for his constantly friendly help with NMR.
- David Flynn, for his inexhaustible patience and friendliness and help with SEM.

Finally, the two people who were at VUW for me week in week out:

- Andrew Durant: My lab partner of 5 years. For every time you shared your gear, your advice, your time and your company. You were there for the good, the bad, and the HOMM3. Thanks heaps, and all the best for the future.
- Ken MacKenzie: My supervisor. For your wisdom and help inside and outside of work. For arranging scholarships, my conference trip, lab space, office space, raw materials, equipment, papers, posters and my thesis, and for being the friendly face of science. Without you I would have never come back to VUW, let alone done a Masters. Thank you.

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### Chapter 1 Literature review

#### 1.1 Geopolymer Literature Review

#### 1.1.1 History and the state of the literature

Alkali aluminosilicate geopolymers were invented by Davidovits<sup>3, 5</sup> in 1979. Davidovits coined the word 'geopolymer' to describe his new mineral binders, as the material was formed from natural (albeit thermally treated) minerals by a polymerisation reaction. The term was subsequently applied to similar products formed from industrial waste minerals such as blast furnace slag and flyash.<sup>6</sup> Various geopolymer products were patented, but geopolymers attracted comparatively little academic interest until the 1990's. Due to their potential in environmentally friendly applications, particularly for replacement of ordinary Portland cement (OPC) as a construction material and in toxic waste remediation, they are now attracting increasing research interest.<sup>4, 7-9</sup>

The literature, however, is still comparatively small and conflicting theories and experimental results are comparatively common. The geopolymerisation process contains several steps, many of which may occur simultaneously and form complex linked equilibria.<sup>9-12</sup> It is considered to be proceed under 'kinetic control', that is the products formed are metastable and are formed because of favourable kinetics of reaction intermediates rather than a strong thermodynamic preference for the product phase. Furthermore, the species responsible for the geopolymer formation reaction are difficult to study directly.<sup>11, 12</sup> This has led to characterisation of the process by describing reaction conditions and the relative concentrations of species involved, rather than a direct chemical description of the formation reaction. pH and the reaction molar composition ratios SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>/M<sub>2</sub>O, H<sub>2</sub>O/M<sub>2</sub>O and H<sub>2</sub>O/SiO<sub>2</sub> are the most commonly described reaction parameters<sup>1, 2, 13, 14</sup>, where M is a charge-balancing alkali cation, most frequently sodium or potassium. This review focuses on studies that use metakaolin materials as a raw material for geopolymerisation as metakaolinite is a reactive and comparatively pure

aluminosilicate and geopolymers made from it are therefore suitable model systems for studying the geopolymerisation process.<sup>9</sup>

Due to the complex and interlinked relationships between these ratios, pH and reaction conditions, conclusive results about the nature and optimisation of the process as a whole are difficult to make. The problem is exacerbated by the frequent use of mineral wastes as raw materials for the process which have poor composition reproducibility, and the difficulty inherent in studying the structure of x-ray amorphous inorganic phases. However, consensus is beginning to emerge on an optimal composition range for metakaolin geopolymers. In keeping with the literature, this literature review uses the molar ratio conceptual framework. The composition range  $3.3 < SiO_2/Al_2O_3 < 5$ ,  $0.6 < M_2O/Al_2O_3 < 1.4$ ,  $6 < H_2O/Na_2O < 16$  is taken as optimal for the production of strong and hard geopolymers<sup>14</sup>; compositions outside this SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> range are described as silicaceous or aluminous, and compositions outside this M<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> range as high or low alkali as appropriate. Deviation from the water content described here is rare, as insufficient water causes processing difficulties, while high water content causes rapid evaporation leaving a porous and weak material, unless SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is very high. Water acts as a solvent and a reactant in the reaction mixture, and 30 - 50% of water added is not present in the final product. As a solvent, the water present influences important reaction parameters such as pH and reactant concentrations, and the ratio H2O/Na2O is best considered a processing parameter rather than a description of the composition of a geopolymer product.

#### **1.1.2 The geopolymerisation reaction**

A geopolymer is produced when an aluminosilicate is dissolved in highly alkaline solution at ambient temperature to produce a viscous paste that hardens to form a strong cementitious material.<sup>3</sup> The solid product continues to cure for hours to days before developing full strength.<sup>11, 15, 16</sup>

The overall process is termed geopolymerisation and is complex, incorporating dissolution of the aluminosilicate, polymerisation of aluminate and silicate species present in solution, gelation of the aluminosilicate species, and drying to produce the product material. This section deals with the observed features of reactions during geopolymerisation. More information on the principles of aqueous silicate chemistry is provided in section 1.2.

Reaction begins with dissolution of an aluminosilicate. Silicon is speciated as  $H_2SiO_4^{2-}$  or a range of anionic dimers and trimers.<sup>17-19</sup> Aluminium is present as  $Al(OH)_4^{-.19}$  Few silicate oligomers are present initially, as the reaction solution has a pH around or higher than 13.<sup>19, 20</sup> As [Si]/[Al] > 1 (so that Lowenstein's Rule is obeyed), the comparatively acidic  $Al(OH)_4^{-}$  reacts quickly with one or several present silicate species to form soluble aluminosilicates.<sup>19, 21, 22</sup> These small aluminosilicate units condense to form a solid matrix.<sup>14</sup> The underlying chemistry is discussed in section 1.2.

Which, if any, silicate species undergo preferential reaction with the free aluminate is unknown.<sup>12, 22</sup> Aluminium exchange is facile in the small aluminosilicate units<sup>19, 23</sup>, and it is possible that several silicate species are involved.<sup>19, 22</sup> The mechanism of condensation between the small aluminosilicate units to form the larger units during geopolymerisation has not yet been determined.<sup>11, 12</sup> The reaction proceeds under kinetic control and the simultaneous dissolution of silicon and aluminium from the raw aluminosilicate at the same time as condensation and polymerisation is highly complex. Dissolution of silicon and aluminium occurs at different rates that change over time. Furthermore, the concentration of silicate and aluminate units may also vary with position, with higher aluminate concentrations nearer to dissolving aluminosilicate particles.<sup>24</sup>

Within the gel, polymerisation continues, causing syneresis (the expulsion of water from the gel) and hardening. A hard solid product is formed within minutes or hours, depending on reaction temperature, solution pH and composition. At 40°C, the setting time (as measured using a Vicat needle) of aluminous and high alkali geopolymers has been reported to increase from 30 minutes to 155 minutes for geopolymers with normal alkali content as  $SiO_2/Al_2O_3$  increased from 2.5 to 3.8. Increasing Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> to 1.2 caused a geopolymer with  $SiO_2/Al_2O_3 = 3.76$  to set in 58 minutes. The time needed for full strength development increased from 4 hours to more than 8 hours as  $SiO_2/Al_2O_3$  increased from 3.0 to 3.8.<sup>25</sup> Similar results have been reported elsewhere for metakaolin and flyash geopolymers. These effects were rationalised as being due to the decreased rate of dissolution of aluminium from metakaolin to form the soluble aluminosilicate units as the concentration of OH<sup>-</sup> and aluminium decreases with increasing silica content. At 35°C, Rahier *et al.* found that

potassium geopolymers with  $SiO_2/Al_2O_3 = 2.8$  and  $M_2O/Al_2O_3 = 1$  set in 95 minutes for M = Na and 205 minutes for M = K. Using potassium as the cation, an increase in temperature from 35 to 40°C caused a decrease in setting time from 205 to 121 minutes.<sup>11</sup> Davidovits and Sawyer reached similar conclusions.<sup>6</sup>

With all other reaction parameters held constant, an increase in pH is thought to increase setting time.<sup>26, 27</sup> However, in metakaolin systems, an increase in pH implies either an increase in alkali content or a decrease in water content, both of which alter other reaction parameters. Lower water content probably decreases setting time but is accompanied by an increase in viscosity, making the isolation of the pH effect difficult. An increase in alkali content is consistently shown to decrease setting time, regardless of the effect on pH.<sup>11, 25, 28</sup>

In addition, pH is the dominant factor in determining the rates of dissolution of silicon and aluminium. These rates sharply increase as pH is raised.<sup>29</sup> The influence of pH is therefore crucial but complex to study. A pH greater than 13 is necessary for complete conversion of metakaolin into geopolymer.<sup>8</sup>

#### 1.1.3 Geopolymer atomic structure

The structure of a normal geopolymer is x-ray amorphous. It is known from Magic Angle Spinning-Nuclear Magnetic Resonance (MAS NMR) that silicon and aluminium are present as silicate and aluminate tetrahedra.<sup>2</sup> Alkali cations balance the anionic charge caused by the presence of aluminate tetrahedra, and are situated in pores surrounded by a hydration shell of water molecules.

The exact structure of geopolymers has not yet been experimentally determined. Three structures have been proposed. Davidovits proposed that a random network exists, made up of polysialate, polysialate-siloxo and polysialate-disiloxo units [Figure 1-1].<sup>30</sup> Water is coordinated to both alkali cations in both phases. In potassium geopolymers with Si/Al > 3, the remaining silicon is present as an alkali polysilicate.<sup>30</sup> Small amounts of polysilicate phases have been detected by SEM.<sup>31</sup> The polysilicate and aluminosilicate make up a solid solution. An alternative proposed structure is a completely amorphous network somewhat similar to that of an alkali aluminosilicate glass, but with distorted silicate and aluminate tetrahedra and water coordinated to alkali cations in material pores.<sup>2</sup> These two definitions would be very

similar if the polymerisation of monomers in Davidovits' structure was defined to mean polymerisation similar to that of silicate ions to form amorphous silica [Section 1.2.9]. Unfortunately, Davidovits appears to conflate organic polymerisation, silica polymerisation and the formation of crystalline covalent networks, which are very distinct mechanistically. Whether a separate silicaceous phase exists at ratios Si/Al > 3 has not been examined by other authors because it is outside the range of ratios considered optimal by most authors. The existence of a separate polysilicate phase would imply an upper limit to the amount of silicon that a single aluminosilicate phase can contain, which would fit well with Davidovits' nomenclature, favouring it.

A disordered random alkali aluminosilicate network would be similar to amorphous silica with aluminate tetrahedra substituting for silicate tetrahedra. This is consistent with the observed formation of aqueous aluminosilicates which have similar chemistry to aqueous silicates. [Sections 1.2.7, 1.2.10]

Finally, a network of approximately 5 nm sized zeolite precursor crystallites bound by an aluminosilicate gel has been proposed on the basis of Transmission Electron Microscopy (TEM) evidence<sup>24</sup>, but this has been ruled out by three recent TEM studies, in which selected area electron diffraction (SAED) showed only amorphous material.<sup>32-34</sup>



Figure 1-1: Polysialate, polysialate(siloxo) and polysialate(disiloxo) units After Davidovits<sup>5</sup>

The degree of structural order depends strongly on composition and reaction conditions. A ratio  $SiO_2/Al_2O_3 < 2$  implies a breach of Lowenstein's Rule and predominantly crystalline aluminous phases are formed.<sup>13</sup> For  $2 < M_2O/Al_2O_3 < about 3 (M = K)$  or 4 (M = Na), some zeolitic phases are likely to be present, particularly if sodium is used as a cation. Similarly,  $M_2O/Al_2O_3$  much larger than 1 favours zeolite formation, especially where M = Na.<sup>28, 35</sup>

The main feature in the XRD pattern of normal and silicaceous geopolymers is a very broad symmetric peak between 20 and  $30^{\circ}$  20 due to amorphous material.<sup>2, 24</sup> However, sodium geopolymers have a significantly more ordered structure than potassium geopolymers, displaying small crystalline peaks similar to zeolites in their XRD patterns.<sup>3, 25</sup>

The difference in order between geopolymers containing sodium and potassium has been attributed to the greater preference for monomeric silicate units rather than oligomers in sodium silicate solutions than in potassium silicate solutions.<sup>35, 36</sup> However, how this affects order has not been explained. Furthermore, the differences in the overall degree of polymerisation between sodium and potassium silicates appears too small to cause such an effect [Section 1.2.5]. The greater tendency of sodium to form zeolites than the other group 1 elements, including lithium has also been cited.<sup>7</sup> Other cited reasons including the greater ion mobility of sodium than other group 1 elements due to smaller size<sup>7</sup> contradict known aqueous ion mobilities, and cannot explain the stronger zeolitisation effect of sodium than lithium.

Upon heating to 500°C, the geopolymer structure loses about 90% of its water content<sup>1, 32, 37</sup>. In a cesium geopolymer, <sup>133</sup>Cs MAS NMR showed that Cs<sup>+</sup> becomes dehydrated and is largely incorporated into the amorphous network. <sup>23</sup>Na MAS NMR showed dehydration of Na<sup>+</sup> and suggested some linkage between Na<sup>+</sup> and the network, but less than for Cs<sup>+</sup>.<sup>32</sup>

#### 1.1.4 Microstructure

Normal geopolymers tend to display a homogeneous amorphous microstructure in SEM studies.<sup>13, 14</sup> TEM studies reveal a network of aggregated spheres with diameters between 5 and 50 nm, with some limited porosity.<sup>32-34, 38</sup>

If Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 1, metakaolin geopolymers with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> > 3.3 display a completely homogeneous structure in the micron and large submicron range with a range of pore sizes ranging from the micron range to tens of nanometres.<sup>32-34, 38</sup> Macropores probably result from water loss, as in OPC, while the micropores are presumably those observed in TEM studies. As SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> increases, pore size and volume decrease. If SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> < 3.3, an increasingly heterogeneous, porous microstructure is observed which becomes completely heterogeneous at SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 2.8, with increasing amounts of aluminous crystalline phases formed. A similar effect is observed with increasing sodium content in compositions near the homogeneous-heterogeneous transition point. Microstructural change is probably responsible for the rapid decrease in strength that is observed as compositions become aluminous.<sup>14, 28</sup>

Unreacted metakaolin particles frequently remain after geopolymerisation. Their effect is currently not well understood. Substantially incomplete reaction of the metakaolin results in a weak material, but small amounts of unreacted particles have also been cited to be microaggregate that can improve mechanical properties<sup>39</sup>, and water stability in the case of highly silicaceous geopolymers.<sup>40</sup> The use of aggregates to produce concretes has resulted in diminished<sup>37, 41</sup> and improved<sup>3, 40, 42, 43</sup> properties, depending on the aggregate used. Other composites using fibrous materials display enhanced ductility.<sup>44-46</sup>

#### 1.1.5 Optimal composition

The optimal composition for producing hard geopolymers with maximum compressive strength is contested in the literature. Using metakaolin as an aluminosilicate source, cited optimal compositions include  $SiO_2/Al_2O_3 = 5.0$  with  $Na_2O/Al_2O_3 = 1.3$ ,<sup>47</sup>  $SiO_2/Al_2O_3 = 4.28$  with  $Na_2O/Al_2O_3 = 0.7$ ,<sup>25</sup>  $SiO_2/Al_2O_3 = 3.8$  with  $Na_2O/Al_2O_3 = 1.0$ ,<sup>14</sup> and  $SiO_2/Al_2O_3 = 4.0 - 4.2$  with  $K_2O/Al_2O_3 = 1.3 - 1.52$ .<sup>30</sup> Flyash geopolymers tend to be harder and stronger than metakaolin geopolymers<sup>9</sup>, but their composition optimisation is more complex.

Optimal compressive strengths of up to 80 MPa are cited<sup>35, 41, 48</sup>, although lack of comparability between different compressive strength tests makes identifying a true value difficult.

Very silicaceous geopolymers with  $SiO_2/Al_2O_3 > 24$  are flexible and fail by deformation rather than crushing. These geopolymers foam due to the rapid loss of water if heated to  $300^{\circ}C$ .<sup>13</sup> These geopolymers have a very high alkali content because of the amount of alkali needed to solubilise the silica during reaction, combined with the high  $SiO_2/Al_2O_3$  ratio. The water stability of these geopolymers is low, but the existence of unreacted raw aluminosilicate particles around 500 nm in diameter has been stated to solve this problem.<sup>40</sup>

#### 1.1.6 Stability and reactivity

Geopolymers display little reactivity towards other compounds. Little or no deterioration in their properties when exposed to sulfates, seawater or dilute sulfuric acid was found. Sulfate attack causes negligible expansion and statistically insignificant decreases in strength only. Their resistance to attack by 5% hydrochloric acid and sulfuric acid solutions was found to be superior to that of OPC.<sup>8</sup>

The thermal reactivity depends on the choice of cation. Potassium geopolymers display remarkable thermal stability, with little change in structure until  $1000^{\circ}$ C.<sup>1, 32</sup> Sodium geopolymers react to form nepheline from  $800^{\circ}$ C –  $900^{\circ}$ C. Sodium geopolymers display lower stability than potassium geopolymers at temperatures from  $30^{\circ}$ C to  $90^{\circ}$ C and high humidity, undergoing reaction to form zeolites.<sup>24, 28</sup>

Despite their lack of chemical reactivity, drying and wetting result in greatly lowered compressive strength in metakaolin geopolymers. Cracking results, probably due to water loss. The more porous matrix of flyash allows changes in water content with less microstructural damage.

#### **1.1.7** The effect of curing conditions

An increase in curing temperature accelerates the setting process, with setting rate and temperature displaying an Arrhenius-type relationship.<sup>11</sup> Generally, curing at slightly elevated temperatures ( $40 - 90^{\circ}$ C) produces a stronger material than curing at ambient temperature, at least in the early stages of curing.<sup>15</sup> However, prolonged curing at elevated temperatures causes a loss of strength in sodium geopolymers.<sup>4</sup> Zeolite formation<sup>28</sup> or drying damage<sup>4</sup> could be responsible. Curing at high relative

humidity results in lower compressive strength than curing in dry air.<sup>15</sup> In sodium geopolymers, zeolite formation has been implicated as being responsible. Potassium geopolymers have not been reported to weaken due to zeolite formation under the same conditions, and potassium has been found to be unfavourable for zeolite formation compared to sodium in zeolite syntheses.<sup>49</sup>

#### 1.1.8 Structure determination

The structure of geopolymers is primarily studied by XRD and <sup>27</sup>Al- and <sup>29</sup>Si MAS NMR. XRD has limited usefulness because geopolymers are x-ray amorphous, but can be used to detect unreacted raw materials, zeolite formation and impurity phases. The geopolymerisation process is studied using <sup>27</sup>Al- and <sup>29</sup>Si liquid-state NMR spectroscopy.<sup>2, 12, 50</sup> Unfortunately, resolution is currently too low to differentiate between different solvated aluminosilicate species with similar connectivity.<sup>12 27</sup>Al- and <sup>29</sup>Si MAS NMR may be used to examine silicon and aluminium connectivity in solidified geopolymers.<sup>1, 2, 12, 51</sup>

Unfortunately, <sup>29</sup>Si MAS NMR is currently unable to determine the connectivity of normal geopolymers. These geopolymers show one broad peak at around -90 ppm relative to TMS in their NMR spectrum. The reason for the broadness of the peak is probably the existence of silicon centres with a range of coordination environments. Q2, Q3 and Q4 silicon centres (silicon atoms with 2, 3 or 4 coordinated bridging oxygens) can all potentially form networks, and the broad peak has been attributed to the presence of all of these together, probably with distorted bond angles. A small shoulder or peak due to the presence of unreacted metakaolin at -103 ppm is often present, further complicating the identification of different silicon coordination environments is currently inadvisable, contrary to published claims, as the peak is symmetric and featureless and thus can be equally well fitted by many different combinations of Gaussian peaks.<sup>12</sup>

High alkali geopolymers show a range of narrow peaks assignable to Q1, Q2 and sometimes Q3 silicon centres after two days. The spectra of very high sodium samples ( $Na_2O/Al_2O_3 > 2$ ) display these peaks as shoulders or small peaks after 2

weeks. Slightly lower alkali samples initially display shoulders or small peaks assignable to low connectivity silicon centres after 2 days but these peaks collapse into a single broad peak after 2 weeks.<sup>12</sup>

The lower connectivity in geopolymers with excessive sodium content is indicative of less polymerisation<sup>12</sup>, probably contributing to the decreased mechanical strength of high sodium samples.<sup>25</sup> Carbonation of excess alkali has also been cited as a reason for degraded mechanical strength<sup>24</sup>, but no experimental evidence has been found for it. Zeolite formation and low connectivity are probably the main reasons for the weakness of these samples.

The <sup>27</sup>Al NMR spectrum of metakaolin shows peaks at around 10, 28 and 58 ppm, arising from 6-, 5-, and 4 coordinate aluminium respectively.<sup>12</sup> During reaction, these peaks diminish and are replaced by a narrow peak that appears near 76 ppm and moves to around 58 ppm as the geopolymer sets. Generally, the position of the main peak in the <sup>27</sup>Al spectra of geopolymers of different composition does not vary, even for poorly cured, weak products.<sup>1, 2</sup>

#### 1.1.9 Impurity elements

The presence of impurity elements causes a range of reaction behaviours and material properties, and is expected to have important effects in commercial geopolymer systems, where the mineral wastes used as raw materials contain a range of impurities.<sup>9</sup>

The addition of soluble boron and phosphorus salts leads to the inclusion of tetrahedral boron and phosphorus into the aluminosilicate network.<sup>52</sup> Boron acts as a setting retardant and has no degradative effect on mechanical strength until it makes up 10 - 13.5 wt % of the network.<sup>53</sup> Gallium appears to readily substitute for aluminium to form gallosilicate geopolymers, but germanium does not appear to substitute for silicon to any appreciable degree.<sup>54</sup>

The effect of calcium depends on what form it is in when added to the reaction mixture.<sup>51</sup> The addition of calcium oxide or soluble calcium salts (e.g. calcium chloride) results in rapid setting. Calcium carbonate and calcium phosphate remain as undissolved filler particles. Calcium hydroxide added as a suspension appears to be incorporated into the network in small amounts.<sup>51</sup> If a significant amount of calcium

hydroxide is added, a calcium silicate hydrate (CSH) gel is formed, as it is in OPC.<sup>55</sup> However, the CSH gel contains less calcium and more sodium or potassium than CSH gels formed in OPC, and cation exchange between the CSH gel and geopolymer is hypothesised to occur<sup>55</sup>. Cation exchange is proposed to occur between unreacted calcium mellilite glass particles and a geopolymer network in one patented geopolymer product.<sup>56</sup> The addition of calcium hydroxide appears to improve the durability of geopolymers in moist environments and their mechanical strength. An optimal addition level of 8 wt % has been proposed for one system.<sup>57</sup>

Data on the behaviour of added iron compounds is inconclusive. Iron added as iron (III) oxide tends to be speciated as insoluble iron oxyhydroxide phases.<sup>58</sup> The addition of 1 and 5 eq. wt % iron (III) oxide as iron (III) hydroxide to two samples caused iron enrichment of the geopolymer matrix as detected by EDS. The addition of 1 wt % eq. iron (III) nitrate caused less iron enrichment but significant sodium depletion from a geopolymer matrix phase, along with the formation of an amorphous iron silicate phase and a sodium-rich phase.<sup>59</sup> The possibility that iron is incorporated into the matrix in much the same way as calcium is therefore a distinct possibility. Notably, Mossbauer spectroscopy shows that the iron is octahedrally coordinated in all cases, thus implying that any iron in the geopolymer network is similarly octahedral.<sup>59</sup>

Arsenic is a setting accelerator, and appears to become associated with iron-rich phases in flyash geopolymers. However, it does not become associated with phases formed as a result of the addition of iron (III) oxide powder.<sup>58</sup> Lead in flyash systems forms simple silicate phases<sup>60</sup> or becomes associated with polysilicate phases, if present.<sup>31</sup> Zirconia was found to act as a filler, rather than a reactant.<sup>61</sup>

Magnesium contained in flyash geopolymers was found using EDS not to become distributed throughout the geopolymer matrix, but to form magnesium-enriched regions at the grain boundaries of flyash particles. XRD was unable to confirm whether the product was a magnesium silicate hydrate, hydrotalcite or an unreacted magnesium-containing phase from the flyash particles.<sup>62, 63</sup>.

Hydrotalcite and hydrotalcite-like phases are formed in magnesium-containing alkali activated cements.<sup>64, 65</sup> The particle size of the hydrotalcite phases ranges from about 0.5  $\mu$ m to nanoparticulate<sup>65</sup>. Hydrotalcite and hydrotalcite-like compounds are discussed in more details are discussed in sections 1.2.6 and 1.2.8.

Fluorinated geopolymers are claimed to have been synthesised by the addition of a sodium fluorosilicate to the reaction mixture. They are claimed to have extremely low thermal expansion and excellent thermal stability.<sup>66</sup>

#### 1.2 Aqueous silicate chemistry

#### **1.2.1 Introduction**

The geopolymerisation reaction is complex with several chemical processes occurring simultaneously. These processes (aluminosilicate dissolution, dissolved aluminosilicate equilibration, and geopolymer precipitation and/or gelling are not well understood) and so often little or no molecular basis for the effects of changes reaction conditions on the final products is available. Instead, trends in the properties of the solid products are ascribed to reaction conditions such as the reaction component ratios. This approach is powerful and allows products with desired characteristics to be obtained, but does not predict what will occur if a discrete variable such as the identity of the counterion is changed as in this project. To predict or rationalise observations from the synthesis of lithium- and magnesium-containing geopolymers, a knowledge of aqueous silicate chemistry is very useful.

#### 1.2.2 Silicate solution equilibria

In aqueous solutions (pH > 8), solid silica exists in equilibrium with silicic acid according to reaction 1:

Reaction 1:



 $Si(OH)_4$  has a pKa<sub>1</sub> of ~9.9 and pKa<sub>2</sub> of ~12.5, so is deprotonated in aqueous solutions of group 1 hydroxides to give an alkali silicate solution (reaction 2).



Silicate monomers are able to dimerise through reaction 3:



Further condensation between monomers, dimers and the resultant species produces a range of oligomeric species in solution. The larger silicate anions have progressively more bridging oxygen atoms than hydroxyl groups, and so approach the composition of silica (SiO<sub>2</sub>). The consequence of these reactions is very high apparent solubility of SiO<sub>2</sub> in strong aqueous bases.<sup>67, 68</sup> [Figure 1-2]

If a large amount of  $SiO_2$  is dissolved in base and then reaction conditions changed to strongly favour polymerisation by lowering pH (or removing water), solid  $SiO_2$  (or sodium silicate gels) may be produced. Kinetic control governs polymerisation and the silica produced is always amorphous, regardless of whether or not the original silica was amorphous or crystalline, and of the continuing presence of amorphous or crystalline silica. The rate and degree of dissolution of  $SiO_2$  in base depends strongly on the form of silica dissolved, however, and the crystalline forms of silica (as well as silica glasses such as fused silica) dissolve much less readily than (metastable) amorphous silica. All solid silica discussed in this section is assumed to be amorphous. The reaction conditions under which  $SiO_2$  is precipitated has profound effects on the final product form, which may range from dry powders of microspherical particles, porous gels made up of chains of nanospherical particles or sols of dispersed nanospherical particles. Aluminosilicate precipitation may be similarly affected by reaction conditions. Silica and aluminosilicate precipitation is discussed in more detail in sections 1.2.9 and 1.2.10.

Silica is soluble in solutions of alkali hydroxides or strong organic bases such as tetraalkylammonium (TAA) hydroxides, choline and guanidine.<sup>67</sup> Tetramethylammonium (TMA) hydroxide is an important reagent in zeolite synthesis. TAA hydroxides are not examined in any detail in this report.



Figure 1-2: Solubility of silica in water vs. pH. After Iler<sup>67</sup> Circles: ionic strength = 0 M, triangles: ionic strength = 1 M, inverted triangles: ionic strength = 3M.

As in silicate minerals the silicon in silicate solutions is tetrahedrally coordinated to four oxygen atoms, which may either bridge two silicon atoms, be part of a hydroxyl group or carry a negative charge<sup>69</sup>. In solution the angles between silica tetrahedra are more variable than in the solid state and a bewildering array of silicate anions of different size, shape and charge are produced<sup>69</sup>. The anions are in dynamic equilibrium with each other, undergoing reversible hydrolysis and condensation, resulting in a very complex kinetic system.<sup>19, 20</sup> The speed of hydrolysis and

condensation reactions prohibits individual silicate species from being isolated from solution. The relative amounts of the various silicate anions and colloidal particles present has a complex dependence on the amount of dissolved silica and base, what counterions, and the effect of other dissolved species. These factors are described individually below. Aluminosilicate solutions have even more complex speciation and are discussed later.

The charge on the anionic species depends strongly on the size of the anions and does not exceed -2 per silicon atom<sup>20</sup>. The average charge per silicon atom increases with decreasing anion size and pH, and the degree of protonation of the hydroxyl groups on the anions increases with decreasing connectivity and size.

#### 1.2.3 Notation

Q-notation<sup>70</sup> is used to describe the different silicate species, with a superscript denoting the number of bridging oxygen atoms and a subscript denoting total anion size, e.g.  $Q_8^3$  denotes a cubic octamer. If silicate tetrahedra within one anion have different connectivities, each connectivity type is denoted individually, e.g.  $Q_1^1 Q_1^2 Q_1^1$  denotes the linear trimer 3A. Silicon atoms that are part of or attached to a 3-ring have an additional subscript, e.g.  $Q_{\Delta}^2$  denotes the environment of the silicon atoms in the cyclic trimer, while  $Q_{\Delta}^1$  denotes the substituting  $Q_1^1$  silicon centres of the various substituted cyclic trimers.

The silicate anions may be conveniently divided into groups for describing changes in speciation. The concentrations of members of a group tend to rise or fall together as conditions are changed. The shifts of species within a group are frequently close to one another<sup>71</sup>, and in poorly resolved spectra cannot be differentiated. The groups are: monomers; dimers and cyclic trimers; larger anionic species; colloidal species. Some authors include linear trimers with dimers and cyclic trimers<sup>72</sup>, others do not<sup>72, 73</sup>.



Figure 1-3: Phase diagram for the system Na<sub>2</sub>O-SiO<sub>2</sub>-H<sub>2</sub>O. After Owusu<sup>74</sup>

#### 1.2.4 Compositions of alkali silicate systems

A phase diagram for sodium silicate solutions is given [Figure 1-3]. (Note that the axes represent content percentages by mass, not molar quantities.) The composition of commercial sodium silicates lie within region 9. They are produced by aqueous dissolution of the glasses in region 4 at elevated temperature and pressure. Excess sodium leads to the formation of alkaline precipitates (3), while insufficient water leads to useful soluble silicate powders (6), relatively inert hydrated glasses (5), unworkable semi-solids (7), or very viscous liquids (8). For any combination of base and water, the addition of excess silica results in the formation of silicaceous precipitates or gelation and solidification of the solution (11)<sup>75</sup>. Kinetically stable colloidal dispersions of silica in this composition region are commercially available but require careful synthesis and storage to prevent aggregation and gelling<sup>67</sup>. Combinations of colloidal silica with sodium and potassium silicate solutions are termed polysilicate solutions are also available and are kinetically stable.<sup>67</sup>

The composition of the solution is usually described using oxide notation (already mentioned). The molar ratio of total dissolved silica to alkali oxide is termed

R. The concentration of dissolved silica (denoted [SiO<sub>2</sub>]) and R together describes the composition of a silicate solution.

In practice, commercial sodium silicates typically have R= 2-4,  $[SiO_2] = ~7 - 8 \text{ molL}^{-1}$  and  $[Na_2O] = 2.2 - 4.5 \text{ molL}^{-1}$ .  $[H_2O]= 28 - 38 \text{ molL}^{-1}$ . Solute species make up 35 - 50% by mass. The viscosity of sodium silicates rises increasingly rapidly with  $[SiO_2]$ , and acts as a practical limit on what solutions are produced.<sup>67, 76</sup> Commercial potassium silicate solutions have similar molar ratios but are significantly less viscous.<sup>67, 76</sup>

#### 1.2.5 The effect of component concentrations on speciation

All other conditions being equal, the identity of the alkali cation  $M^+$  in alkali silicates has relatively little effect on the equilibrium speciation of alkali silicates unless it is Li<sup>+</sup>.<sup>73, 77-79</sup> In dilute solutions ([SiO<sub>2</sub>] << 1molL<sup>-1</sup>) with R near zero, the monomer is the dominant species, with a small amount of dimers and trimers. At R~1, the monomer is still the most common species, but significant amounts of dimers and trimers are now present. As [SiO<sub>2</sub>] increases to the concentrations of commercial silicate solutions, the minimum value of R required for stable solution increases to 1-2. Solutions with R lower than 1 undergo precipitation of highly alkaline silicates. Oligomeric species begin to be favoured in all stable solutions.<sup>20, 72</sup> Colloidal particles (Q<sup>4</sup>) are present in both types of solution as R approaches 3.<sup>20, 72</sup>

If the composition of an alkali silicate solution is perturbed so that colloidal species are produced and then is returned to its former state, reequilibration is slow, taking many hours.<sup>67</sup> In contrast, reequilibration amongst species when no colloidal silica is present is facile, taking only minutes<sup>80, 81</sup> (except for lithium silicates, which equilibrate slowly in both cases).<sup>67, 78, 80</sup>

No detailed study of the effect on speciation of varying  $M^+$  has been published in the literature. However, the overall degree of polymerisation in solution can be slightly affected by the counterion. Lithium silicates have increased overall degree of polymerisation relative to other alkali silicates. Kinrade observed an increase in the amount of  $Q_{8}^{3}$  at the cost of monomers and cyclic dimers/trimers in a lithium silicate solution with [SiO<sub>2</sub>] = 0.9 molL<sup>-1</sup> and Li<sub>2</sub>O = 0.45 molL<sup>-1.82</sup> The effect of other counterions has been less extensively studied, probably because the differences between the other alkali silicates are small under most conditions. <sup>73, 78, 79, 82</sup>

Lithium silicates are more easily distinguished from the other alkali silicates than they are from each other under some conditions. In particular, lithium silicates with R close to 1 form a crystalline precipitate of insoluble  $\text{Li}_2\text{SiO}_3^{78, 83}$ . On the other hand, lithium polysilicate solutions with  $\text{SiO}_2:\text{Li}_2\text{O} = 4 < x < 25$  are thermodynamically stable whereas the sodium or potassium equivalents are not. Lithium polysilicates may be synthesised directly from LiOH and amorphous SiO<sub>2</sub> and contain both dissolved silicate species and colloidal SiO<sub>2</sub> particles in equilibrium.<sup>67</sup> This is distinct from the sodium or potassium polysilicates because in those solutions equilibration between the colloidal particles and ionic species is merely strongly kinetically hindered, and equilibration leads to precipitation and gelling.

The kinetics of silica dissolution in lithium hydroxide are also somewhat different to that in the other alkali hydroxides.<sup>67</sup> The reaction of silica with the other alkali hydroxides is a simple dissolution reaction that increases with temperature. Dissolution of silica by lithium hydroxide is less than half as fast as for sodium or potassium.<sup>78</sup> During formation of lithium polysilicates, the solution initially gels to form a solid mass. At room temperature, the gel redissolves to yield a lithium polysilicate solution, whereas it remains solid at elevated temperature (e.g. 60°C). This behaviour is not observed in other alkali silicates.

The basis for the unusual behaviour of lithium silicates probably lies in the high charge density and consequent negative entropy of solvation of  $\text{Li}^+$ .  $\text{Li}^+$  has a very high charge to radius ratio, and as a result its water of hydration is held so tightly that  $\text{Li}^+$  has a negative entropy of solution. All other things being equal this results in a decrease in solubility with temperature, and a tendency to complex with silicate ions.<sup>82, 84</sup>

#### 1.2.6 Precipitated silicates

For the most part, soluble polyvalent metal ions cause rapid precipitation of amorphous metal silicate solids with varying stoichiometry. It is notable that species (aluminium and other elements discussed in section 1.2.6) that can complex with silicates to form substituted silicates when added as the oxide or oxoanion form solid precipitates if added as soluble salts in all but very dilute solutions. These do not have the characteristics of geopolymers. For instance, the product of the addition of aluminium nitrate to sodium silicate has hexacoordinated aluminium. This is due to the pH being insufficient for aluminate formation and the high concentration of sodium nitrate that would result from such a reaction [Sections 1.2.7, 1.2.9]

Calcium and magnesium silicates are not observed in the liquid phase. However, their solid silicate precipitates are important in cements and are considered here. The addition of calcium to a silicate solution causes precipitation of insoluble semicrystalline C-S-H gel. The structure of this gel has not been unambiguously characterised but is usually considered to be similar to either tobemorite (or jennite)<sup>85-<sup>87</sup>, layered single chain silicates made up of small silicate units (generally made of two, or occasionally other small numbers of silicate tetrahedra) layered with calcium oxide octahedra. The small silicate units have a strong predominance of low silicate connectivities (Q1 and Q2) at ratios of Ca/Si above 0.8, with some higher order connectivity (Q3 and Q4) at lower Ca/Si values<sup>85</sup>. Aluminium tetrahedra are able to link silicate units and are charged balanced by interlayer alkali or additional interlayer calcium.<sup>88-90</sup></sup>

The action of magnesium has been less studied. M-S-H gels may possibly form in preference to  $Mg(OH)_2$  under alkaline conditions in rather silicaceous systems. Their structure is thought to be a disordered layer structure, possibly similar to sepiolite, chrysotile or talc.<sup>91-93</sup> In highly basic systems with significant concentrations of aluminium, hydrotalcite may be formed [Section 1.2.8]

C-S-H and M-S-H gels are nearly completely immiscible, possibly due to differences in their structures.<sup>94</sup> Their relationship to geopolymer paste is not known, having only been studied using XPS elemental mapping at higher magnifications than would be required to distinguish the M-S-H and C-S-H phases.<sup>95</sup> C-S-H is known to form as a separate phase to the geopolymeric matrix when sufficient calcium is present.<sup>95</sup>

#### 1.2.7 Soluble aluminosilicates

In highly basic aqueous solutions (pH > 13), aluminium is speciated as  $Al(OH)_4^{-19}$  In silicate solutions aluminium is a good silicon scavenger and vice versa.

Soluble aluminosilicate species are formed with aluminium substituted for silicon in one or more tetrahedra. A wide range of species are probably formed, although few have been certainly assigned. For M<sup>+</sup> all but the most dilute solutions precipitate or gel over time. Both <sup>27</sup>Al<sup>19, 23, 96-103</sup> and <sup>29</sup>Si<sup>19, 23, 96, 101-103</sup> NMR have been used to detect and identify aluminosilicates but <sup>27</sup>Al NMR yields very broad resonances due to rapid chemical exchange and quadrupolar broadening<sup>100</sup> even for very dilute solutions under most conditions, so <sup>29</sup>Si NMR remains the primary tool for identification of individual species. However, careful control of pH allows well resolved <sup>27</sup>Al spectra to be obtained, and some tentative assignments made.<sup>100</sup>

The precipitation of aluminosilicates from such solutions has a complex relationship to the concentration of the reaction components. In general, in dilute solutions an increase in pH leads to an increase in gel time, but for solutions with higher dissolved  $SiO_2$  concentrations the opposite trend is observed<sup>104-106</sup>. Geopolymers display the latter behaviour, although their kinetics are complicated by the simultaneous dissolution of metakaolin.

Compared to silica, comparatively little is known about aluminosilicate precipitation and gelling. The concentrations of all species in zeolite synthesis are much lower than in geopolymer systems, and may thus be expected to have different precipitation behaviour. However, evidence is presented in this review to suggest that the silica and aluminosilicate systems may have more similar precipitation behaviour than previously expected.

#### **1.2.8 Hydrotalcite formation**

In basic aqueous systems containing magnesium and aluminium, hydrotalcite or hydrotalcite-like compounds may be formed.<sup>107</sup> Hydrotalcite has the chemical formula  $Mg_6Al_2(OH)_{16}CO_{3.4}H_2O$ , and a structure based on aluminium-substituted brucite layers and interlayer anions. The structure of brucite ( $Mg(OH)_2$ ) is made up of layers of edge-sharing octahedra of hydroxide ions around central magnesium ions. The structure of gibbsite ( $Al(OH)_3$ ) is very similar but has cation vacancies to maintain electrical neutrality. The replacement of magnesium by aluminium in brucite results in positively charged layers, which are balanced by carbonate ions. Water occupies interlayer spaces. The carbonate is exchangeable for other anions and the degree of aluminium substitution may vary from about Mg:Al = 2 - 4, resulting in hydrotalcite-like compounds. Carbonate substitution is favoured under many conditions, however there is practically no limitation to the type of anion that may be substituted, and the substitution of OH<sup>-</sup> and NO<sub>3</sub><sup>-</sup> is common. Hydrotalcite-like compounds with anions other than carbonate may be formed either directly or by ion-exchange of a pre-made hydrotalcite.

Silicate anions may be substituted into the interlayer spacings of hydrotalcite and hydrotalcite-like compounds, either by ion exchange or formation of hydrotalcite in the presence of sodium silicate.<sup>108, 109</sup> It is thought that intralayer polymerisation of the silicate anions occurs.<sup>109</sup>

#### 1.2.9 Silica precipitation and gelling

If a silicate solution is acidified, solid  $SiO_2$  is produced. This is the basis for the commercial production of a wide range of silica products. It has been studied extensively in the literature and can only be treated very briefly here, following the works of  $Iler^{67}$  and  $Bergna^{110}$  closely.

If silicic acid is present in water at concentrations above 100-200 ppm (i.e. if pH of a silicate solution drops below  $\sim 10.5$ ), the solution is saturated with Si(OH)<sub>4</sub> and it is removed by polymerisation. Polymerisation favours siloxane (Si-O-Si) bridges rather than free silanol (Si-OH) groups, so condensed ring and cage oligomer species are formed. These polymerise further until they are effectively small particles. The largest particles present grow rapidly to several nanometres in diameter by Ostwald ripening until no small particles are left. Further growth occurs by the addition of silicic acid molecules onto the particles and is slower. If the pH is from ~7 -10.5 and no dissolved salts are present in solution, the surfaces of the particles are negatively charged, preventing aggregation, and the particles grown until no silicic acid is left in solution for particle growth. Coagulating agents such as surfactants or salts (after particle growth is complete) cause aggregation and precipitation. Otherwise a stable sol (suspension) of colloidal particles is obtained. If salts are present or the pH is below 6 during particle growth, particles collide and bond to form crosslinked chains of particles (gels). By changing from one behaviour regime to another, gels made up of particles of a desired size may be obtained. [Figure 1-4] In

practice gels are usually produced at very low pH (e.g. 2 using sulfuric acid), while sols are produced by ion exchange of  $H^+$  for  $M^+$ .

Dried solid alkali silicate solutions have not been well studied. When dried, their structure depends on pH. Highly alkaline silicate solutions set into a matrix of alkali cations and small silicate anions.<sup>111</sup> The setting behaviour of less alkaline sodium silicates is less well understood, setting into structures with a <sup>29</sup>Si MAS NMR spectrum very similar to geopolymers.<sup>12, 13</sup> Dried sodium silicate forms extremely strong monolithic objects. They are soluble in water.



Figure 1-4: Polymerisation of silica under different conditions After Iler<sup>67</sup>

#### 1.2.10 Aluminosilicate precipitation and gelling

Aluminosilicates display similar behaviour. Aluminosilicate sols may readily be produced from a reactive diluted sol of specific particle size and sodium aluminate.<sup>112</sup> Aluminosilicate particles have composition MAIO<sub>2</sub>.YSiO<sub>2</sub>, where M denotes a counterion, Y is a stoichiometric coefficient and the bulk of the aluminium is tetrahedrally coordinated as in geopolymers. Purely tetrahedrally coordinated aluminium occurs in samples with compositions in the same range as geopolymers, i.e. with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> oxide ratios from 2:10. Notably, lithium may be used as the cation directly to produce these sols, while ammonium and TAA<sup>+</sup> ions may completely substitute for sodium through ion exchange. H<sup>+</sup> may replace up to 50% of the alkali cations without loss of tetrahedral coordination. Alternatively, an aluminosilicate 'skin' may be coated onto existing colloidal particles, especially of silica.<sup>113</sup> Aluminosilicate coated silica sols have been commercialised by Du Pont under the brand name Ludox AM. They have higher negative surface charge than silica and as a result both types of aluminosilicate sols may be used at pH = 6 with no loss of stability, in contrast with silica sols. They are also more resistant to coagulation by salts.<sup>67, 110</sup> This offers evidence for the possibility of using Li<sup>+</sup> and TMA<sup>+</sup> as a cation in geopolymers.

Geopolymerisation occurs under different conditions to the formation of aluminosilicate sols. In particular, no acidification is carried out, and the concentration of aluminosilicates is much higher than for the production of aluminosilicate sols, so particle growth will presumably be unrestricted. The higher negative surface charge of any polymerising aluminosilicate species will favour gel formation, while the extremely high concentrations of aluminosilicate will favour particle growth.<sup>67</sup>

TEM studies on potassium and cesium geopolymers as well as sodium geopolymers with salts added show a continuous network with some morphological structure on the 0 - 50 nm scale. This suggests that particle growth produces large particles at least after gel formation, if not before. Areas of varying darkness on the  $\sim$ 1 nm size scale are similar to that observed prior to zeolite nucleation.<sup>114</sup> The possibility of a setting mechanism similar to that of sodium silicate is suggested by the <sup>29</sup>Si MAS NMR of dried sodium silicates, which contain a geopolymer-like broad peak.<sup>111</sup> Possibly aluminium acts as a crosslinker between smaller silicate ions in geopolymers due to the thermodynamic drive for silicate-aluminate interaction.

The possibility of altering the micro- and nanostructure of geopolymers in ways analogous to silica may therefore be possible.

#### 1.3 Thermal treatment

The bulk composition of lithium geopolymers would be expected to be similar to that of lithium aluminosilicate glass-ceramics composed of a mixture of  $\beta$ -eucryptite (LiAlSiO<sub>4</sub>) and  $\beta$ -spodumene (LiAlSi<sub>2</sub>O<sub>6</sub>). These glass-ceramics are notable for their extremely low coefficients of thermal expansion, and have found a range of applications as thermal shock-proof ceramics, most notably as ceramic stovetops and cookware, but also in telescope mirrors, furnace windows, and gas turbine heat exchangers<sup>115-117</sup>. The low thermal expansion coefficients are a consequence of the low expansion coefficients of  $\beta$ -spodumene and  $\beta$ -eucryptite (average  $\alpha = 0.9 \times 10$ -6 for spodumene, -6.2 x10-6 for eucryptite from 25-1000°C)<sup>116</sup>. By controlling the relative amounts of these phases present in a ceramic body, the overall thermal expansion of the body can be tailored to match its application. Notably, an average value of zero can be obtained between 25 and 1000°C.

Lithium aluminosilicate glass-ceramics are synthesised by the production of a glass of appropriate composition, followed by thermal treatment at below 1000°C to nucleate very fine crystallites from the glass.<sup>118</sup> A nucleating agent such as TiO<sub>2</sub> or ZrO<sub>2</sub> may be added. The resulting ceramic bodies are nearly poreless, having between 90 and 99% conversion to crystalline phases. Their fine and relatively defect-free structure imparts produced bodies high flexural strength, and if tailored correctly, transparency.<sup>116</sup> The glass-ceramic process is costly due to the high temperature (1600°C) needed to refine the glass.<sup>119</sup>

Attempts to synthesise the materials at lower temperatures have had mixed success. Sol-gel techniques may be used to yield thin films of  $\beta$ -spodumene suitable for use in glass-ceramic capacitors or fibre-reinforced composites.<sup>120</sup> Attempts to synthesise the materials using conventional ceramic methods may yield local inhomogeneities due to the range of particle sizes in the green body, necessitating long sintering times.<sup>121, 122</sup> Ion-exchanging lithium for sodium in zeolites followed by firing has been attempted, but tends to produced cracked bodies, and it is difficult to remove all the sodium.<sup>121, 123</sup> Lithium geopolymers or zeolites synthesised in a sodium-free system may be suitable precursors to lithium aluminosilicate ceramic phases.

A wide range of useful magnesium (alumino)silicate ceramics, including forsterite  $(Mg_2SiO_4)^{124}$ , enstatite  $(MgSiO_3)^{125}$  and cordierite  $(Mg_2Al_4Si_5O_{18})$  exist<sup>126</sup>. The different ceramics have different properties but in general are quite refractory. Cordierite has a low thermal expansion coefficient and is used in similar applications to lithium aluminosilicate ceramics, and as a catalyst support for automotive catalytic converters. The presence of alkali is generally deleterious to the properties of these ceramics.<sup>127</sup> However, the formation of useful thermally treated cordierite-geopolymer bodies is disclosed in the patent literature<sup>128</sup>.

Magnesium and alkali metals both act as fluxes in alumino(silicate) ceramics, and therefore promote bloating, which may be desirable (e.g. for the production of lightweight ceramic foams), or undesirable (for applications demanding high strength). This is examined in section 3.3.4.

#### 1.4 Direction provided by the literature to the project design

The silicate chemistry of lithium and magnesium are highly relevant to the formation of lithium- and magnesium-containing geopolymers. It was anticipated that because lithium has a similar silicate chemistry to the other alkali metals that formation of lithium geopolymers would be possible. The slowness of dissolution of solid silica (and by extrapolation, aluminosilicate clays) and the composition region of instability were anticipated to be the main barriers to the formation of lithium geopolymers. The effect of lithium content on metahalloysite dissolution was examined and the action of silica added as different forms also examined. Thermal treatment of the resulting products were heated and the potential for lithium aluminosilicate ceramic formation assessed.

As magnesium hydroxide and magnesium silicates are insoluble, a direct synthesis of a magnesium geopolymer by the same method as an alkali metal geopolymer is impossible. Instead, magnesium compounds were considered as additives.

The action of magnesium in geopolymers would be expected to induce large changes in the reactivity of geopolymers if added to a geopolymer slurry in a reactive form (e.g. as a soluble salt), due to the dissimilarity of magnesium and alkali silicate chemistry. The effect addition of magnesium as oxides and hydroxides would depend on their degree of reactivity in the geopolymer system, and what the favoured products (e.g. brucite, hydrotalcite, magnesium silicate hydrate, magnesium-substituted geopolymer) are. The addition of magnesium in both inert and reactive forms was examined, and the reaction products examined. Exploratory thermal treatment of the resulting articles was performed.

All syntheses were constrained by the range of component molar ratios that produce well-set geopolymers. Examination of these constraints led to the synthesis of geopolymers directly from solid silica, aluminium hydroxide and potassium hydroxide, which was then examined in some detail.

# Chapter 2 Materials and Methods

#### 2.1 Synthesis methods

Potassium geopolymers were synthesised by mixing KOH and H<sub>2</sub>O in plastic containers, then adding K66 potassium silicate solution. The dissolution of both KOH and K66 in water is exothermic, and the solutions were cooled in ice before metahalloysite addition. Cooling was necessary to avoid flash setting which can occur when the (exothermic) dissolution of metahalloysite occurs too rapidly, heating the reaction mixture, causing dissolution to accelerate further, and so on. Dehydroxylated halloysite was added and stirred thoroughly.

The viscosity of the slurry was highly sensitive to the potassium hydroxide and water content, and sometimes neither a paste nor fluid formed immediately. Instead, the reaction mixture was dry and powdery. The powder would gradually dissolve over a period of 10 - 20 minutes stirring with a spatula and form a thick paste.

The slurry was a light tan colour if potassium silicate and dehydroxylated halloysite were used.

The reaction mixtures of different geopolymer syntheses may vary from dry powders to very thin fluids. In this report the term 'slurry' is used as a generic term for all the reaction mixtures, which are typically composed of water and metahalloysite particles as well as various alkaline species. To describe the viscosity, the following terms are used:

Dry paste: A very dry thick slurry that fractures on stirring rather than deforming.

Thick paste: A thick slurry that has an uneven surface when broken, and typically deforms only under strong vibration.

Medium paste: A slurry that does not deform under its own weight.

Thin paste: A slurry that deforms under its own weight but does not flow readily.

Medium fluid: A slurry that flows slowly, appears to be a viscous liquid.

Thin fluid: A slurry that flows quickly, like water or slightly more viscous.

A standard composition that was used with slight modifications throughout the entire project used 20.0 g K66, 10 g KOH, 9.0 g H<sub>2</sub>O and 30 g metahalloysite. This composition had molar ratios  $SiO_2/Al_2O_3 = 3.05$ ,  $K_2O/Al_2O_3 = 0.94$ ,  $H_2O/Al_2O_3 = 10.85$ ,  $H_2O/K_2O = 11.59$ .

All heating reactions were performed in chamber furnaces. For work below 1000°C, furnaces at Victoria University (VUW) were used. For temperatures above 1000°C, the Industrial Research Limited (IRL) Amalgams furnace was used. VUW furnaces were calibrated using a Type R standard thermocouple with cold junction compensator. The standard error was the greater of 1.5°C or 0.25%. Samples fired to temperatures above 900°C were fired in vitreous silica crucibles or on vitreous silica plates. For lower temperature work glazed porcelain crucibles were used.

#### 2.2 Sample characterisation techniques

XRD, MAS NMR and SEM were the main characterisation techniques used for this project. XRD was used to detect and analyse crystalline materials. To analyse amorphous materials, MAS NMR was used. SEM with EDS elemental mapping was used to analyse the spatial distribution of the products detected by XRD and MAS NMR. Quantitative XRD was performed using the Rietveld method in [3.2.3.3]. Qualitative tests on samples' stability in water and mechanical strength were universally used.

#### 2.2.1 Powder X-ray Diffraction (XRD)

For rapid analysis of products synthesised at VUW, XRD was performed at VUW. All other analysis was performed at IRL. Aluminium sample holders were used both at VUW and at IRL. Crystalline phases were matched using patterns from the ICDD Powder Diffraction File (PDF) Version 4+. High quality powder patterns (ICDD quality mark \* or I) were used wherever possible. Scans were typically rotated through an angular range of  $10 - 70^{\circ} 2\theta$ . A list of XRD pattern numbers is provided below, along with a description of the common amorphous phases detected by XRD.
#### IRL:

All samples were run using a Philips PW1700 series Bragg-Brentano diffractometer (IRL Diffractometer #1) with automatic divergence slits and graphite diffracted beam monochromator, using Co K $\alpha$  radiation. For Rietveld XRD, the fixed antiscatter slits were removed. Phases were assigned using Bruker Diffrac<sup>plus</sup>EVA©

#### VUW:

Samples were run using a Philips PW1730 stand alone generator, PW3170 mpd control and a PW1768/xx sample stage and a PW1050 goniometer. Cu K $\alpha$  radiation was generated from a Pw2773 Cu LFF X-ray tube, V=40kV, I=20mA. Phases were assigned using Panalytical X'Pert Highscore.

The phases most commonly encountered in this study (along with their PDF numbers and quality marks) were:

Arcanite ( $K_2SO_4$ )	01-070-1488 (*)
Bayerite	00-020-0011 (I)
Corundum	01-070-5679 (*)
Cristobalite	00-039-1425 (*)
Doyleite	00-038-0376 (I)
Forsterite	01-071-1080 (*)
Gibbsite	00-033-0018 (I)
Leucite	00-038-1423 (*)
Lithium hydroxide hydrate	00-025-0486 (C)
Lithium orthosilicate	00-037-1472 (*)
Mullite	01-074-4145 (*)
Nordstrandite	00-024-0006 (I)
Periclase	01-071-1176 (*)
Quartz	00-046-1045 (*) or 00-033-1161 (D)
Spinel	01-070-6013 (*)
Zeolite A (Na-A)	00-038-0241 (*)
Zeolite ABW (Li)	00-027-1211 (I)
Zeolite F (Li exchanged)	01-079-1893 (*)
Zeolite X (LiNa-X)	00-038-0236 (*)
β-Eucryptite	01-071-2058 (*)
β-Spodumene	00-035-0797 (*)

#### 2.2.2 Rietveld XRD

The Rietveld Method ('Rietveld XRD') is a technique used to extract quantitative data on the concentrations of crystalline phases (and particle sizes) from powder XRD scans. Using the Rietveld method, a powder XRD pattern is calculated from basic crystal structure data for each mineral phase in the sample. The patterns are summed and fitted by a least-squares refinement to a sample pattern. Mass percentages of the mineral phases are obtained by multiplying the scale factors of the peak heights by unit cell mass and volume and dividing by the Brindley absorption contrast factor to obtain mass percentages.

For all samples, long scans were used to provide the best possible signal to noise ratio. Scans were calibrated for the effect of variable slits. Background was removed by picking points manually with automatic linear interpolation. Pattern fitting was optimised ( $\chi^2$  minimised and stable). Systematic errors (i.e. missing small peaks altogether) were avoided wherever possible.

Rietveld quantitative phase analysis was performed using SIROQUANT 2.5.<sup>129</sup> SIROQUANT is a x-ray powder diffractometry software package for the quantitative analysis of mineral phases. The antiscatter slit was removed for Siroquant scans. This led to bifurcated peaks from the sample holder in many scans. These peaks were excluded from the refinement process. Some preferential orientation of brucite in geopolymer samples occurred. This was allowed for in calculations but was not prevented during sample preparation, i.e. XRD slides were not back-loaded.

# 2.2.3 Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR)

To characterise amorphous materials, <sup>29</sup>Si and <sup>27</sup>Al MAS NMR were used.

MAS NMR was performed using a Bruker Avance 500 Spectrometer.

For <sup>27</sup>Al MAS NMR, a a 4 mm Doty MAS probe and a  $Si_3N_4$  rotor spun at 10–12 kHz with. The spectrometer frequency was 130.224 MHz, with a 1 ls (p/10) pulse for solution) and a 1 s delay, spectra referenced to  $Al(H_2O)_6^{3+}$ .

For <sup>29</sup>Si-MAS NMR a 5 mm Doty MAS probe and a  $ZrO_2$  rotor spun at 3-4 kHz was used. The <sup>29</sup>Si spectrometer frequency was 99.926 MHz, with a 6 ls (p/10) pulse and a 30 s delay, spectra referenced to tetramethylsilane (TMS).

#### 2.2.4 Scanning Electron Microscopy

To prepare samples from geopolymers for SEM, samples were cut using a diamond saw into slices ~4 mm thick and soaked in an alcoholic solvent (1-propanol or 1-butanol) for at least 24 hours to remove water. They were then soaked in acetone to remove the alcoholic solvent. Samples were dried in a hot laboratory oven from 80 – 110°C to constant weight or overnight. They then mounted on half-height stubs approximately 10 mm in diameter and 5 mm high using Araldite 2 part adhesive. Carbon tape was used to earth the samples. Carbon and silver paint proved ineffective for adhering the samples to the stub and earthing. Samples were coated with between 4 and 7nm of gold or platinum. Platinum coating was preferred over gold for sample where high-magnification imaging was needed. The samples were desiccated in a large desiccator evacuated by a rotary pump. This desiccator is effective for powder samples and is widely used in SCPS (School of Chemical and Physical Sciences) but this project's samples required further desiccation in the JEOL 5300 SEM sample chamber which is evacuated by a diffusion pump and has a higher vacuum level.

Samples were generally not polished after cutting with the diamond saw. Where they were, 10µm SiC grit paper or 10µm diamond grits were used to polish the surface. Comparison of polished and unpolished samples showed that unpolished samples had much cleaner and smoother surfaces, as polishing caused particle pullout.

Imaging was performed on the VUW JEOL 6500F SEM with attached EDS (Energy Dispersive X-ray Spectroscopy) detector. All imaging was performed under EDS conditions (Accelerating voltage = 15.0 kV).

#### 2.2.5 Mechanical properties

Samples which failed to set were powder cakes which had no mechanical strength. In contrast, samples that had undergone geopolymerisation were rock-like monoliths with brittle fracture behaviour. In order to deduce what the optimal water content of lithium geopolymers was in section 5.3.3, a crude scratch and break test was carried out by hand. Force was applied to the samples by hand to flex (and thus break) them. Break tests are recorded as Y or N, where Y indicates a sample that did not break and N indicates a sample that did. The sample surface was also scratched with a fingernail. Whether a surface scratched or not was reported as either N, Y or Y!. N indicates no visible indentation in a sample after the scratch test, Y indicates a large indentation with visible particle loss from the sample, and Y! indicates a large indentation with visible particle loss along the edge of the scratch. The breaking test was *not* considered a scientific gauge of reactivity but as a simple indicator of whether a change in composition improved or degraded the mechanical properties of lithium geopolymers. See section 5.3.3.

#### 2.2.6 Water tests

Silicate bonded objects are extremely strong but dissolve in water. Distinguishing silicate bonded objects from geopolymers is often simple; silicate bonding has several distinguishing features including high sample gloss and translucency, extreme hardness, smooth fracture faces and undergoing plastic deformation or reagglomeration when ground in a mortar and pestle. However, silicate bonded objects with a high amount of filler such as metahalloysite have appearance and mechanical properties similar to those of geopolymers. Without using MAS NMR, the best way to distinguish silicate bonded objects from geopolymers was to expose them to water. Samples were either placed in beakers of cold tap water overnight or had a smooth face run under water and rubbed with a gloved finger. In the former case, silicate bonded objects spontaneously dissolve releasing filler particles, which are observed as a dust on the bottom of the beaker the next morning. In the latter case, silicate bonded objects rapidly roughen or even disintegrated. Geopolymers do not exhibit these behaviours.

### 2.3 Raw Materials

Metahalloysite preparation:

New Zealand China Clays (NZCC) Premium halloysite was weighed into porcelain crucibles and heated at 550°C overnight. This resulted in a mass loss of ~15 %, slightly higher than the suppliers stated loss on ignition (LOI) figure. This was probably due to adsorbed moisture from the air. A small amount of coarse particles ~1 mm across were removed by sieving through a 353  $\mu$ m brass mesh. These particles were hard and brittle, and probably contained crystalline impurities.

Materials:

Materials suppliers are listed. Where an purity assay was provided by the supplier it is reproduced here. For some materials levels of impurities other than hydrated species are low and purity is best gauged by a water content or loss on ignition. XRD and LOI were used where stated used to check suppliers figures.

K66 potassium silicate solution (Ineos Silicas):  $K_2O = 11.4$  wt %,  $SiO_2 = 23.4$  wt %

MgO (light): BDH LOI = 3% MgO (heavy): BDH LOI = 3% MgSO<sub>4</sub>.7H<sub>2</sub>O: May and Baker (Aust) Assay = 99.5% Magnesium carbonate (hydrated heavy): BDH LOI=65 – 68% Mg(OAc)2: BDH [OAc = Acetate] Assay = 99 % Mg(ClO<sub>4</sub>)2: BDH Water content = 16% Acros Mg(OH)<sub>2</sub>: Acros Organics, 95% Acros Al(OH)<sub>3</sub>: Acros Organics, "extra pure" - No assay given Acidic Al<sub>2</sub>O<sub>3</sub> Brockmann type 1: Amorphous activated alumina, particle size =? LOI (900°C 24 hrs = 3%): BDH RDH Al(OH)<sub>3</sub>: assay as Al<sub>2</sub>O<sub>3</sub> = 65%

Halloysite: NZCC)Premium Halloysite: Typical composition: 50.4% SiO<sub>2</sub>, 35.5 Al<sub>2</sub>O<sub>3</sub>, 0.28% Fe<sub>2</sub>O<sub>3</sub>, 0.08 TiO<sub>2</sub>, trace CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O. LOI 13.8%.

Elkem 971-U silica fume: Worst case composition: SiO<sub>2</sub> 98%, C 0.7%, Fe<sub>2</sub>O<sub>3</sub> 0.1%, Al<sub>2</sub>O<sub>3</sub> 0.3% CaO 0.3%, MgO 0.2%, K<sub>2</sub>O 0.3%, Na<sub>2</sub>O 0.2%, P<sub>2</sub>O<sub>5</sub> 0.1%, SO<sub>3</sub> 0.3%, Cl 0.1%, LOI 0.8% SA=15-30m<sup>2</sup>g<sup>-1</sup> SiO<sub>2</sub> is 98% min, all other values are max. Average diameter 0.15 μm.  $\begin{array}{l} SF98 \ Silica \ fume \ (Doral) \\ SiO_2 \ 93\%, \ ZrO_2 + HfO_2 \ 4.2\%, \ Fe_2O_3 \ 0.4\%, \ Al_2O_3 \ 0.2\%, \ P_2O_5 \ 0.25\%, \ TiO_2 \ 0.02\%, \\ CaO \ 0.01\%, \ Na_2O \ 0.01\%, \ K_2O \ 0.01\% \ LOI \ 1.0\% \ SA=15 \ m^2g^{-1} \end{array}$ 

Microsilica 600:

SiO<sub>2</sub> 87.89, A1<sub>2</sub>O<sub>3</sub> 4.31, SO<sub>3</sub> 0.13, Fe<sub>2</sub>O<sub>3</sub> 0.59, MnO 0.03, TiO<sub>2</sub> 1.16, CaO 0.32, K<sub>2</sub>O 0.49, P<sub>2</sub>O<sub>5</sub> 0.05, MgO < 0.02, Na<sub>2</sub>O 0.14, LOI 5.01%

Distilled water was used for all syntheses.

Particle sizes of raw materials in Chapters 3 and 4 were measured using laser diffraction on a Malvern Mastersizer Hydro 2000 MU. Particles were dispersed in distilled water. The manufacturers stated particle size range particle size range  $0.02 - 2000 \mu$ m, but in practice little or no volume content of any sample was found to have particle size below ~0.1  $\mu$ m.

# Chapter 3 Magnesium in geopolymer systems *3.1 Introduction*

The effect of magnesium on the geopolymer system is potentially of enormous importance. Magnesium is the eighth most abundant element in the Earth's crust<sup>83</sup> and its silicate and carbonate minerals are cheap and plentiful. Its presence in Portland cement is undesirable due to the formation of oxide (periclase) during clinker production and the tendency of the oxide to hydrate to its hydroxide (brucite) with an accompanying large volume expansion.<sup>130</sup> Despite it being a common impurity element in raw materials for geopolymerisation, its action in geopolymer systems has not been systematically studied. In addition, ceramics based on cordierite, Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>18</sub>, have low thermal expansion coefficients and find wide application as It hypothesised that thermal treatment of catalyst supports. was magnesium-containing geopolymers would produce magnesium aluminosilicate ceramics with useful properties.

It was discovered that the addition of soluble magnesium salts to geopolymer systems can have deleterious effects on the set products' mechanical properties. A preliminary study was carried out to determine the limits of potassium geopolymer composition that would yield well-setting products. This was then used to plan experiments based on the addition of soluble magnesium salts to geopolymers and rationalise the results.

It was desired to know the effect of magnesium oxide addition on geopolymers and whether or not any reaction likely to change the product properties occurs.

It was found that there were definite limits on how much of soluble magnesium salts could be added to the system, while very high levels of magnesium oxide and hydroxide (often inseparable, so both referred to as magnesium (hydr)oxide) could be incorporated into well setting bodies. Thermal treatment yielded foamed bodies rather than dense ceramics.

#### 3.2 Experimental

## 3.2.1 Constraints on syntheses: The effect of water and alkali contents

In order to gauge the effects of varying the  $K_2O/Al_2O_3$  ratio of potassium geopolymers, a series of samples with different KOH contents were prepared. Compositions were chosen to keep SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> and ratios as similar as possible while ensuring that samples with low  $K_2O/Al_2O_3$  set.

Varying amounts of KOH were added to potassium silicate solutions and geopolymer slurries made from the resulting solutions using the conventional method. Samples A1 - A5 had molar  $K_2O/Al_2O_3$  ratios higher than 1, while samples A6 - A14 had molar ratios lower than 1.

A12	3.05	8.35	0.27	30.5
A13	3.05	8.59	0.24	36.24
A14	3.05	9.42	0.2	47.07

The sample molar ratios are recorded in

Table 3-1.

A series of samples with alkali contents equal to those of series A6 - A14 but with higher water content (10 g added H<sub>2</sub>O for all samples, H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 11.3) failed to set (except sample F).

Sample	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	$K_2O/Al_2O_3$	$H_2O/K_2O$
A1	3.05	12.04	1.67	7.2
A2	3.05	11.89	1.52	7.8
A3	3.05	11.74	1.38	8.53
A4	3.05	11.6	1.23	9.43
A5	3.05	11.45	1.08	10.58
A6	3.05	11.3	0.94	12.08
A7	3.05	8.86	0.79	11.24
A8	3.05	8.95	0.64	13.95
A9	3.05	8.8	0.49	17.8
A10	3.05	8.38	0.35	24.12
A11	3.05	8.39	0.31	27.01
A12	3.05	8.35	0.27	30.5
A13	3.05	8.59	0.24	36.24
A14	3.05	9.42	0.2	47.07

Table 3-1: Molar ratios of K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> potassium geopolymers

# 3.2.2 Preparation of magnesium-containing geopolymers by addition of magnesium salts

#### **3.2.2.1 Raw materials**

Magnesium salts used were  $Mg(OAc)_2.4H_2O$ ,  $MgSO_4.7H_2O$ ,  $Mg(ClO_4)_2.xH_2O$  and basic heavy magnesium carbonate, which are described in 2.3.

#### 3.2.2.2 Synthesis method

The addition of magnesium salts to geopolymer slurries was examined. Potassium geopolymer slurries were prepared using the conventional method and solutions of magnesium sulfate, perchlorate, carbonate (in the form of hydromagnesite) and acetate added. The effects of adding different salts were compared and other studies carried out on the effects of potassium sulfate and potassium perchlorate addition.

To compare the effects of the different salts, potassium geopolymer slurries were prepared using the conventional method. Three solutions of different concentrations of magnesium acetate, magnesium sulfate, magnesium perchlorate and heavy basic magnesium carbonate were added as solutions (suspension in the case of magnesium carbonate) to a low-water content geopolymer slurry. Quantities were chosen so that compositions with nearly equal total water content were produced. In other experiments, similar levels of potassium perchlorate addition were added and attempts to purify the product made.

Solutions of  $Mg(OAc)_2.4H_2O$ ,  $Mg(ClO_4)_2$  (84%, 16%  $H_2O$ ),  $MgSO_4.7H_2O$ and basic heavy magnesium carbonate were prepared. As expected, magnesium carbonate and water formed slurries, while other magnesium salts dissolved, with heating in the case of  $MgSO_4$ .  $MgSO_4$  solutions were heated with cling film over the beaker to prevent evaporation until complete dissolution occurred.

Sample	Magnesium salt	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> / (Al <sub>2</sub> O <sub>3</sub> + MgO)	MgO/Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/ K <sub>2</sub> O	K <sub>2</sub> O/ Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/ (K <sub>2</sub> O- 2MgO)	(K <sub>2</sub> O- 2MgO)/ Al <sub>2</sub> O <sub>3</sub>
B-Control	None	3.07	9.40	3.07	0.00	9.84	0.96	9.84	0.96
B-OAc1	Mg(OAc) <sub>2</sub>	3.05	11.51	2.91	0.05	12.31	0.93	13.73	0.84
B-OAc2	Mg(OAc) <sub>2</sub>	3.05	11.73	2.78	0.10	12.53	0.94	15.83	0.74
B-OAc3	Mg(OAc) <sub>2</sub>	3.05	12.09	2.56	0.19	12.93	0.94	21.98	0.55
B-CO3-1	MgCO <sub>3</sub>	3.05	11.24	2.73	0.12	12.11	0.93	16.10	0.70
B-CO3-2	MgCO <sub>3</sub>	3.05	11.31	2.49	0.23	12.08	0.94	23.39	0.48
B-CO3-3	MgCO <sub>3</sub>	3.05	11.33	2.11	0.45	12.11	0.94	294.77	0.04
B-ClO4-1	Mg(ClO <sub>4</sub> ) <sub>2</sub>	3.05	11.38	2.93	0.04	12.16	0.94	13.30	0.86
B-ClO4-2	Mg(ClO <sub>4</sub> ) <sub>2</sub>	3.05	11.43	2.83	0.08	12.24	0.93	14.64	0.78
B-ClO4-3	$Mg(ClO_4)_2$	3.05	11.61	2.63	0.16	12.41	0.94	18.84	0.62
B-ClO4-4	$Mg(ClO_4)_2$	3.05	10.97	2.60	0.17	11.72	0.94	18.72	0.59
B-ClO4-5	Mg(ClO <sub>4</sub> ) <sub>2</sub>	3.05	11.31	2.27	0.35	12.07	0.94	46.31	0.24
BSO <sub>4</sub> -1	$MgSO_4$	3.05	11.64	2.93	0.04	12.43	0.94	13.61	0.86
BSO <sub>4</sub> -2	$MgSO_4$	3.05	15.69	2.77	0.10	16.73	0.94	21.32	0.74
BSO <sub>4</sub> -3	MgSO <sub>4</sub>	3.05	10.98	2.53	0.20	11.81	0.93	21.08	0.52
BSO <sub>4</sub> -4	MgSO <sub>4</sub>	3.05	18.20	2.39	0.28	19.40	0.94	47.39	0.38
BSO <sub>4</sub> -5	MgSO <sub>4</sub>	3.05	11.36	2.29	0.33	12.13	0.94	42.61	0.27
BSO <sub>4</sub> -6	MgSO <sub>4</sub>	3.05	11.37	2.08	0.47	12.19	0.93	-2240	-0.01

Table 3-2: Molar ratios of geopolymers containing added magnesium salts

Geopolymer slurries were prepared using the conventional method. Magnesium salt solutions were added using a plastic pasteur pipettes and stirred rapidly by hand. Two large batches of geopolymer slurry were prepared and portioned for magnesium salt addition. The resulting sample molar ratios of the samples are noted in Table 3-2.

When the magnesium sulfate and perchlorate solutions contacted the geopolymer slurries, a thin white coating immediately appeared on the surface and were mixed into the slurries. For both  $SO_4^{2^-}$  and ClO4<sup>-</sup>-containing samples, the slurries then thickened and formed lumps upon magnesium solution addition. After setting all samples chipped easily when chiselled rather than fracturing down the centre of the sample as for normal potassium geopolymers. Samples B-OAc-3, B-SO<sub>4</sub>-5, B-SO<sub>4</sub>-6, and CO<sub>3</sub>-3 set into powder cakes. All other samples set into monoliths.

Samples B-SO<sub>4</sub>-3, B-SO<sub>4</sub>-2, and B-SO<sub>4</sub>-4 were analysed using <sup>27</sup>Al- and <sup>29</sup>Si MAS NMR. Samples ClO<sub>4</sub>-4 and B-SO<sub>4</sub>-5 were analysed using SEM. [Prep methods in section 2.2.4]

#### **3.2.2.3 Boiled samples**

The geopolymers from the previous section were modified by heating them in water to remove precipitated potassium salts and produce magnesium-containing geopolymers suitable for thermal treatment. Potassium geopolymers were heated in magnesium sulfate to attempt to ion-exchange magnesium for potassium.

Two 0.5 g pieces of B-SO<sub>4</sub>-3 were cut off the main sample. The first sample was powdered. Both samples were heated in 30 g boiling water for ½ an hour. They were removed from water, filtered on a Buchner funnel in the case of the powdered sample and dried at 80°C overnight. The samples were coded C1 and C2 respectively.

A standard potassium geopolymer with molar ratios  $SiO_2/Al_2O_3 = 3.06$ ,  $H_2O/Al_2O_3 = 10.90$ ,  $K_2O/Al_2O_3 = 0.94$ , and  $H_2O/K_2O = 11.63$  was made. An 0.8 g powdered sample and an 0.7 g sample piece of the potassium geopolymer were added to the two solutions and heated to  $80 - 90^{\circ}C$ . The powdered sample was stirred with a

stir bar. The samples were coded C3 and C4 respectively. Samples were dried in a lab oven at 80°C overnight.

All four samples were examined using XRD.

## 3.2.3 Preparation of magnesium-containing geopolymers by addition of magnesium oxide and hydroxide

Samples containing magnesium oxide and hydroxide ('magnesium (hydr)oxide') were made by adding magnesium (hydr)oxide to potassium geopolymer slurries. Potassium geopolymers had standard composition [Section 1.1.5] but several different types of magnesium (hydr)oxide additives at different concentration levels were added. Sample were analysed using Rietveld XRD and SEM.

#### **3.2.3.1 Raw materials**

Three commercial raw materials were used. These were MgO (light), MgO (heavy) and Acros Organics  $Mg(OH)_2$  and are described in section 2.3 and below. A synthesised  $Mg(OH)_2$  was prepared by refluxing MgO (light) in water in a round-bottom flask for 2 days. A second  $Mg(OH)_2$  material was synthesised by the hydration of MgO (light).

MgO was prepared from MgO (light) by heating to  $450^{\circ}$ C for 24 hours [referred to as 'heated MgO (light)']. A second MgO material was prepared from Acros Mg(OH)<sub>2</sub> by heating at 550°C for 4 hours [referred to as 'heated Mg(OH)<sub>2</sub> (Acros)'.

The magnesium raw materials had XRD patterns taken at VUW. They were later analysed quantitatively by Rietveld XRD and their particle size measured using the Mastersizer. Unfortunately, by the time the raw materials were analysed, MgO (light) and Mg(OH)<sub>2</sub> (synthesised) had carbonated to form hydromagnesite.

Their composition as calculated by Rietveld XRD is recorded in Table 3-3, and their mean particle sizes in Table 3-4.

### 3.2.3.2 Synthesis method

Two series of samples were made from conventional geopolymer slurries with added magnesium (hydr)oxide. The molar ratios of the samples are described in Table 3-6. All samples were analysed using Rietveld XRD and SEM.

	Percentages by mass of total						
Raw Material	% Periclase	% Brucite	% Other crystalline	% Amorphous			
MgO (light)	64.3	14.7	18.1 (hydromagnesite)	2.9			
MgO (heavy)	79.9	20.1	0.0	0.0			
Mg(OH) <sub>2</sub> (Acros)	0.0	100.0	0.0	0.0			
$Mg(OH)_2$ (synthesised)	0.0	76.3	22.5 (hydromagnesite),	0.0			
			1.1 (calcite)				
Heated MgO (light)	65.9	0.0	0.9 (calcite)	33.2			
Heated Mg(OH) <sub>2</sub> (Acros)	82.8	2.2	0.0	15			

Table 3-3: Rietveld analysis of magnesium (hydr)oxide raw materials. Note that hydromagnesite =  $Mg_5(CO_3)_4(OH)_2.4H_2O$ , Calcite = CaCO<sub>3</sub>.

Raw material	Volume weighted mean particle size D[4,3] (µm)	Surface weighted mean particle size D[3,2] (µm)
MgO (light)	13.643	6.190
MgO (heavy)	70.912	20.842
Mg(OH) <sub>2</sub> (Acros)	16.930	2.316
$Mg(OH)_2$ (synthesised)	93.230	9.357
Heated MgO (light)	66.816	8.837
Heated Mg(OH) <sub>2</sub> (Acros)	65.490	18.201
		• •

Table 3-4: Particle sizes of magnesium (hydr)oxide raw materials

Sample	Additive	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	$H_2O/Al_2O_3$	SiO <sub>2</sub> /	MgO/Al <sub>2</sub> O	MgO/K <sub>2</sub> O	$H_2O/K_2O$	K <sub>2</sub> O/	$H_2O/K_2O$
				(Al <sub>2</sub> O <sub>3</sub> +MgO)	3			$Al_2O_3$	(Mg water
									excluded)
D1	Mg(OH) <sub>2</sub>	3.05	13.28	1.02	1.98	2.12	14.2	0.94	12.08
	(synthesised)								
D2	Mg(OH) <sub>2</sub>	3.05	16.87	0.62	3.96	4.23	18.03	0.94	13.8
	(synthesised)								
D3	MgO (light)	3.05	12.4	1.23	1.49	1.59	13.25	0.94	12.08
D4	MgO (light)	3.03	12.8	1	2.05	2.17	13.59	0.94	17.23
D5	MgO (light)	3.05	18.3	0.77	2.98	3.18	19.56	0.94	11.89
D6	Heated	3.02	11.08	0.8	2.76	2.98	11.99	0.92	11.99
	$Mg(OH)_2$								
D7	Heated MgO	3.02	11.06	0.81	2.72	2.95	11.99	0.92	11.99
D8	MgO (heavy)	3.02	10.98	0.82	2.68	2.93	11.99	0.92	11.99

Table 3-5: Molar ratios of magnesium (hydr)oxide containing geopolymers.

Ratios were calculated using the ratios of brucite and periclase provided by Rietveld analysis for MgO (light). MgO (heavy), heated MgO (light) and heated Acros Mg(OH)<sub>2</sub> are calculated as pure periclase. Synthesised Mg(OH)<sub>2</sub> is calculated as pure brucite. It was assumed that when the samples were synthesised that no carbonation had occurred.

#### **3.2.3.3 Rietveld analysis**

After sample synthesis, Rietveld XRD was performed on samples and raw materials. Pieces of set samples were ground, weighed and mixed with a known quantity of standard crystalline Al<sub>2</sub>O<sub>3</sub> (85% crystalline). Two control samples were made by grinding a normal potassium geopolymer and dry mixing with heavy MgO and adding a weighed amount of standard crystalline Al<sub>2</sub>O<sub>3</sub>. All samples were analysed with XRD at IRL and all phases indexed, then long (10 hr) scans performed. Pattern synthesis was performed using SIROQUANT as described in section 2.2.2. Minor phases were excluded from the pattern refinement process in some samples.

#### 3.2.4 Thermal treatment

#### **3.2.4.1** Synthesis of geopolymers

Two magnesium (hydr)oxide-containing geopolymer series were made by adding magnesium hydr(oxide) to geopolymer slurry during mixing.

MgO (light) and acidic  $Al_2O_3$  were added in varying amounts to portions of one slurry resulting in samples E1 - E8. Similar compositions (E9 – E16) using MgO (heavy) and  $Al_2O_3$  (calcined) were made.

The molar ratios of the samples are recorded in Table 3-6. Samples E1-E8 were fired using three different firing profiles and samples E9-E16 fired using one firing profile [Table 3-7].

Composition	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> / (Al <sub>2</sub> O <sub>3</sub> +MgO)	MgO/Al <sub>2</sub> O <sub>3</sub>	MgO/K <sub>2</sub> O	K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>
E1	3.05	8.42	3.05	0.00	0.00	0.35
E2	3.05	8.71	2.20	0.39	1.11	0.35
E3	3.05	8.99	1.72	0.77	2.22	0.35
E4	3.05	9.27	1.42	1.16	3.33	0.35
E5	2.47	6.82	2.47	0.00	0.00	0.28
E6	2.50	7.19	1.82	0.38	1.33	0.28
E7	2.47	7.37	1.41	0.75	2.66	0.28
E8	2.50	7.75	1.17	1.14	4.00	0.28
E9	3.05	8.50	3.05	0.00	0.00	1.00
E10	3.05	8.50	2.02	0.51	1.22	0.42
E11	3.05	8.50	1.51	1.02	2.43	0.42
E12	3.05	8.50	1.20	1.54	3.65	0.42
E13	2.50	6.97	2.50	0.00	0.00	0.35
E14	2.50	6.97	1.67	0.50	1.46	0.35
E15	2.50	6.97	1.25	1.01	2.92	0.35
E16	2.50	6.97	1.00	1.51	4.38	0.35

Table 3-6: Molar ratios of magnesium hydro(oxide)-containing geopolymers for thermal treatment

### **3.2.4.2** Thermal treatment

Firing was performed in the IRL Amalgams furnace under atmospheric pressure on vitreous silica plates.

The firing profiles of the different sample series are recorded in Table 3-7.

Sample Series	Firing profile
Firing 1	50/00,1300/130,1300/240, 50/3.00
Firing 2	50/00,1300/500,1300/480, 50/3.00
Firing 3	50/00,1250/510, 1250/480, 50/2.00
Firing 4	50/00,1300/130,1300/240, 50/3.00

Table 3-7: Firing profiles used for thermal treatment. xx/yy denotes temperature xx°C at the end of each step, and yy denotes the duration of the step in minutes

Samples from Firing 1 and Firing 4 were analysed using XRD.

### 3.3 Results and discussion

#### 3.3.1 Constraints on syntheses: The effect of water and alkali contents

Sample molar ratios are recorded in Table 3-1.

#### **3.3.1.1 Results**

After 1-3 days setting, samples A1 – A12 set into monoliths. Samples A13 and A14 set into powder cakes.

The <sup>27</sup>Al NMR spectra of samples A1 – A11 indicate substantial geopolymerisation. The spectra contain one main peak around 60 ppm, corresponding to geopolymeric (tetrahedral) aluminium. Little or no unreacted metakaolin remains, as indicated by the lack of characteristic metakaolin peaks at 3, 28 and 55 ppm. Samples A1 – A11 contain predominantly geopolymeric aluminium, although an increasing amount of unreacted metakaolin is present as alkali content decreases from sample A8 – A11. The amount of unreacted metakaolin increases markedly from sample A11 to sample A12, indicating that a minimum alkali content for geopolymerisation has been reached and corresponds to a K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> value of approximately 0.3. Samples A12 - A14 contain predominantly unreacted metakaolin.



Figure 3-1: <sup>27</sup>Al MAS NMR spectra of low K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> geopolymers K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios decrease up the page X axis scale is chemical shift relative to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>



Figure 3-2: <sup>27</sup>Al MAS NMR spectra of minimum K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> geopolymers K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios decrease up the page X axis scale is chemical shift relative to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>

#### 3.3.1.2 Discussion

The effect of decreasing the  $K_2O/Al_2O_3$  ratio significantly below 1 is to greatly lower the mechanical strength of the set sample, as established in the literature. However, it is notable that there appears to be a well-defined minimum  $K_2O/Al_2O_3$  value, below which geopolymerisation ceases altogether. Metakaolin dissolution under these conditions is irreversible so from the continuing presence of metahalloysite it is clear that its dissolution does not occur to a significant degree below a certain value of  $K_2O/Al_2O_3$ , in this case around 0.3. The existence of a sudden fall in the degree of reaction when  $M_2O/Al_2O_3 = 0.3$  is also observed in the analogous Li experiment. [Section 5.3.2] Presumably the pH of the alkali silicate solution is too low to dissolve metahalloysite in both systems.

The failure of the series with higher water content to set  $(K_2O/Al_2O_3)$  is probably an effect of concentration (e.g. of silicate species) rather than pH, as the difference in water content is only 30% which would be expected to have a small effect on pH.

The upper limit water content acts as an important constraint on what molar ratios are achievable. In conjunction with a lower limit on the amount of alkali necessary, the workability of the reaction slurry, and the use of reactants with a significant water content (e.g. K66 solution), the range of ratios that can be achieved within a conventional geopolymer system is limited. The sensitivity of the system to extra water appears to decline as  $K_2O/Al_2O_3$  increases to a value of 1 or higher.

# 3.3.2 Preparation of magnesium-containing geopolymers by addition of magnesium salts

#### **3.3.2.1 Results**

The XRD patterns of each of the set samples shows a broad amorphous peak due to geopolymer, unreacted quartz and cristobalite. Arcanite ( $K_2SO_4$ ) is present in all samples containing  $SO_4^{2^-}$ , [Figure 3-3]. Potassium perchlorate is present in all samples containing  $ClO_4^-$ . No magnesium sulfate phase (in any state of hydration) or magnesium perchlorate phase was detected in the patterns. The XRD pattern of heated sample B-ClO<sub>4</sub>-4 (examined using SEM) shows a geopolymeric broad peak and potassium chloride.



Figure 3-3: XRD patterns of geopolymers treated with water and MgSO<sub>4</sub> solution C=cristobalite, Q=quartz, A=arcanite, \* = Al sample holder, P= perspex sample holder

The XRD patterns of C1 and C2 show the successful removal of arcanite from the geopolymer in both powder and lump form. Both patterns show the characteristic XRD patterns of a geopolymer with no crystalline impurities other than unreacted quartz and cristobalite. [Figure 3-3] The patterns of C3 and C4 show no difference from a normal geopolymer, indicating little or no formation of arcanite.



Figure 3-4: <sup>27</sup>Al MAS NMR spectra of sample B-SO<sub>4</sub>-3 X axis scale is chemical shift relative to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>



Figure 3-5: <sup>29</sup>Si MAS NMR spectra of sample B-SO<sub>4</sub>-3 X axis scale is chemical shift relative to TMS

The <sup>27</sup>Al MAS NMR spectra of samples B-SO<sub>4</sub>-2, B-SO<sub>4</sub>-3, and B-SO<sub>4</sub>-4 showed overwhelmingly geopolymeric aluminium. The <sup>29</sup>Si MAS NMR spectra of samples B-SO<sub>4</sub>-2, B-SO<sub>4</sub>-3 and B-SO<sub>4</sub>-4 contained one main peak centred at 87 ppm which was asymmetric and narrow compared to a normal geopolymer peak.

SEM was used to examine B-SO<sub>4</sub>-5 and B-ClO<sub>4</sub>-4 (heated to remove potassium perchlorate).

Backscatter images of B-SO<sub>4</sub>-5 at 1000x magnification showed the presence of crystals  $1 - 10 \mu m$  long embedded in a matrix. EDS imaging confirmed that they were potassium sulfate crystals. [Figure 3-7] Magnesium is homogeneously dispersed throughout the matrix at magnifications below 10000x with occasional regions with very high magnesium content approximately  $1 - 20 \mu m$  in diameter [Figure 3-6]. In contrast to the magnesium-containing sample made using the hydroxide method [Section 4.3.3], the greatly magnesium-enriched areas in B-SO<sub>4</sub>-5 also contained significant quantities of silicon (but not aluminium). Overall, the spatial correlation of magnesium with silicon was slightly positive, and with aluminium was slightly negative.

SEI images of B-ClO<sub>4</sub>-4 at 200x shows a homogeneous smooth sample. However, under backscatter, there are fissures of size  $5 - 50 \mu m$  with rough material inside them. EDS mapping shows the presence of areas very high in potassium and chlorine, indicating potassium chloride in the fissures. Magnesium appears to be homogeneously distributed at magnifications of up to 10000x magnification except for occasional very magnesium-rich areas  $5 - 50 \mu m$  in diameter. The presence of magnesium has no noticeable effect on the concentration of aluminium, silicon and potassium except in the most magnesium-enriched areas, which are depleted of the other elements.



Figure 3-6: EDS maps of sample B-SO<sub>4</sub>-5 showing homogeneously distributed and particulate magnesium in the geopolymer matrix. Magnification = 3000x. In overlay, red = Si, blue = Mg, purple = Si + Mg



Figure 3-7: EDS maps of sample B-SO<sub>4</sub>-5 showing K<sub>2</sub>SO<sub>4</sub> grains in the geopolymer matrix. Magnification = 3000x. In overlay, yellow = K + S, blue = Si

#### 3.3.2.2 Discussion

The detection of arcanite and potassium perchlorate in XRD, combined with the observed white product formation at the geopolymer slurry surface suggests that the reaction of  $Mg^{2+}$  to displace K<sup>+</sup> begins immediately and is rapid upon magnesium salt addition to the geopolymer system. A double decomposition reaction to produce magnesium silicate, e.g.

 $Mg(ClO_4)_2(aq) + K_2SiO_3aq) \rightarrow MgSiO_3(s) + 2KClO_4(aq)$ 

is probable. The analogous formation of some magnesium aluminosilicate is also possible, however the concentration of aluminosilicate ions would be expected to be much lower than that of silicates. Another plausible reaction is the formation of magnesium hydroxide followed by subsequent reaction to enter the matrix, similar to the reaction discussed in sections 3.3.3 and 4.2.4. SEM studies show homogeneous magnesium distribution in these samples down to 1  $\mu$ m or below, indicating that any particulate silicate or aluminosilicate products are small.

<sup>29</sup>Si MAS NMR reveals a lower degree of silicate polymerisation than in typical geopolymers, reflected in the shift of the geopolymer peak to lower connectivity Q-environments. <sup>27</sup>Al MAS NMR shows that aluminium incorporation into the geopolymer network is still substantially complete.

Which samples with magnesium salts added formed geopolymers can be explained in terms of the double decomposition reaction. The column  $(K_2O-2MgO)/Al_2O_3$  in Table 3-2 shows an adjusted amount of free alkali, remaining assuming complete precipitation of magnesium silicate. Sample B-SO<sub>4</sub>-6 has a normal overall alkali to aluminium ratio but a very low adjusted value, so after the double decomposition reaction little alkali is available for metakaolin dissolution. The setting of sample B-ClO<sub>4</sub>-5 into a viable geopolymer is not unexpected as the adjusted alkali content being near to the minimum required for metakaolin dissolution. In addition, some dissolved silica is removed from the system by the double decomposition reaction, thus raising the expected pH at all alkali concentrations.

The solubilities of the different salts of magnesium and potassium are displayed in Table 3-8. Potassium perchlorate and potassium sulfate are quite insoluble and their precipitation unsurprising. The absence of crystalline magnesium and potassium acetate in the set samples probably indicates the continued existence of one or both species in a non-crystalline form (e.g. dissolved in pore water). The apparent absence of hydromagnesite in the XRD patterns of samples containing added heavy basic MgCO<sub>3</sub> is probably simply due to being obscured by noise. The transformation of hydromagnesite into magnesium hydroxide is highly thermodynamically unfavourable. <sup>131, 132</sup> No reaction to form magnesium hydroxide or magnesium silicate in the reaction mixture would be expected. It is also possible that a reaction occurs similar to that in magnesium (hydr)oxide-containing samples (Section 3.3.3.1) to form hydrotalcite.

The removal of potassium perchlorate in hot water from the powdered sample C1 is what would be expected, but in the case of the solid piece C2 reveals a fairly high degree of water diffusion through the sample. XRD on the samples heated in solutions of magnesium perchlorate shows no change, suggesting a low affinity of the geopolymer matrix for magnesium ions after setting.

Solubilities	g/100g H <sub>2</sub> O, 25 deg C				
Anion	Cation				
	K	Mg			
OAc	269	65.6			
$SO_4^{2-}$	12	35.7			
ClO <sub>4</sub>	2.08	100			
CO <sub>3</sub> <sup>2-</sup>	111	0.18			

Table 3-8: Solubilities of potassium and magnesium salts.From CRC Handbook of Chemistry and Physics, 88<sup>th</sup> ed.

# 3.3.3 Preparation of magnesium-containing geopolymers by addition of magnesium oxide and hydroxide

Molar ratios of magnesium (hydr)oxide-containing samples are recorded in Table 3-3.

#### **3.3.3.1 Results**

All samples set into monoliths.

The XRD patterns of all samples contained broad amorphous peaks due to geopolymer as well as peaks from periclase (MgO) and brucite ( $Mg(OH)_2$ ). The relative peak heights of brucite and periclase in samples with the same type of Mg additive were roughly in proportion to the amount of additive present.

Samples that contained light MgO (heated or unheated) or heavy MgO as additives also contained small amounts of hydrotalcite as well as unreacted cristobalite and quartz [Figure 3-8]. There was an additional pattern phase tentatively assigned as eitelite (Na<sub>2</sub>MgCO3) though no unequivocal assignment could be made.

The XRD patterns calculated using the Rietveld method were able to replicate the experimental patterns. [Figure 3-9] The amounts of periclase and brucite and total amount of magnesium in crystalline phases found by Rietveld XRD compared to the expected amounts in the samples is presented in Table 3-10. Samples showed apparent degrees of reaction between -15 and 70%. The apparent degree of reaction appeared to be bimodal, with many samples having degrees of reaction close to zero or between 60 and 75%.

Experimental uncertainty arises from carbonation of the raw magnesium hydr(oxides) and the unknown water content of the geopolymer in the XRD samples. A significant amount of MgO and synthesised  $Mg(OH)_2$  underwent carbonation to form hydromagnesite. Carbonation prevents accurate estimates of the true amount of brucite and periclase in the raw materials. Calculation shows that for all samples this uncertainty is equivalent to a degree of

reaction of approximately 10%. Uncertainty over the water content of the geopolymer phase in the XRD samples combines with this to give a final uncertainty in the degree of reaction of 35%.

The Rietveld method provides strong evidence for reaction in samples D3, D5, D6 and D8, which all have calculated degrees of reaction significantly higher than the experimental uncertainty. Samples D6 and D8 in particular have well fitted simulated patterns, one major phase (periclase) and. D8 shows signs of a significant amount of hydrotalcite formation, indicating that the magnesium (hydr)oxide species are reactive under these conditions. The control samples have reaction degrees that are zero within the experimental uncertainty.



Figure 3-8: XRD pattern of sample D4 Ht= hydrotalcite, B = brucite C = cristobalite, A = corundum, Q = quartz, E = eitelite, \* =sample holder

Sample	Additive type	Expected mass of crystalline magnesiu m phases (%)	Expected mass % brucite	Expected mass % periclase	Expected total moles crystallin e Mg <sup>2+</sup>	Observed mass % brucite	Observed mass % periclase	Observed total moles crystalline Mg <sup>2+</sup>	Observed mass % brucite / Expected mass % brucite	Observed mass % periclase / Expected mass % periclase	Calculated overall degree of reaction
D1	Mg(OH) <sub>2</sub> (synthesised)	15.7	15.7	0	0.3	15.2	0	0.3	1	N/A	3.8
D2	Mg(OH) <sub>2</sub> (synthesised)	26.9	26.9	0	0.5	26.3	0	0.5	1	N/A	2.2
D3	MgO (light)	10.7	8.2	1.8	0.2	3.8	0	0.1	0.5	0	66.2
D4	MgO (light)	13.9	10.7	2.4	0.2	6.6	1.5	0.2	0.6	0.7	25.6
D5	MgO (light)	18.9	14.5	3.2	0.3	6.9	0	0.1	0.5	0	57.6
D6	Heated Mg(OH) <sub>2</sub>	15	0.4	14.6	0.4	0	2.8	0.1	0	0.2	73.7
D7	Heated MgO (light)	12.7	0	12.5	0.3	0	8.7	0.2	N/A	0.7	30.4
D8	MgO (heavy)	16.1	3.8	12.3	0.4	1.5	4.5	0.1	0.4	0.4	60.4
Control1	MgO (heavy)	22.8	5.4	17.4	0.5	2.6	18.8	0.5	0.5	1.1	2.6
Control2	MgO (heavy)	10.8	2.5	8.3	0.2	3.5	9.1	0.3	1.4	1.1	-15

Table 3-9: Rietveld analysis results from geopolymers containing added magnesium (hydr)oxide.



Figure 3-9: Complete Rietveld pattern synthesis for sample D8

Red = calculated pattern, yellow = experimental pattern, bottom graph = difference plot. X axis is 2θ Co Kα. Blue regions are excluded from refinement because they contain bifurcated peaks from the aluminium sample holder. For both plots y axis = counts.

The <sup>27</sup>Al and <sup>29</sup>Si MAS NMR spectra [Figure 3-10 and Figure 3-11] of samples containing synthesised Mg(OH)<sub>2</sub> were typical geopolymeric spectra with a tetrahedral Al peak at 60 ppm and a broad <sup>29</sup>Si peak at -90 ppm. In contrast, the <sup>27</sup>Al MAS NMR spectrum of sample D5 also had an asymmetric peak at 9.1 ppm and the <sup>29</sup>Si MAS NMR spectrum had a shoulder on the main peak at -106 ppm. The peak in the Al spectrum corresponds to aluminium in a gibbsite-like coordination, in this case hydrotalcite [Section 1.2.8], as gibbsite was not detected by XRD in any metakaolin geopolymer, while hydrotalcite was.

The shoulder in the silicon spectrum is notable as no free silica was observed in any other potassium geopolymers synthesised using the conventional method. It could be attributed to free silica or silicate-substituted hydrotalcite.<sup>109</sup>

When examined using SEM, samples appeared homogeneous and smooth using secondary electron imaging (SEI) at magnifications below 1000x, after which roughness was visible in most (but not all areas) of the samples. [Figure 3-14] Backscatter (backscatter) imaging showed light coloured grains up to 100  $\mu$ m wide in a slightly darker matrix. At magnifications higher than 10000x spheres ~50 nm across due to gold coating obscured the surface of the samples.

EDS mapping showed that the grains observed using backscatter were regions of a potassium aluminosilicate phase embedded in a magnesium-containing potassium aluminosilicate phase, as well as regions smaller than 50  $\mu$ m that had very high magnesium content and were assumed to be embedded magnesium (hydr)oxide particles. [Figure 3-13]

The magnesium-containing and magnesium-free aluminosilicate regions were indistinguishable using SEI and did not appear particulate in samples at magnifications of up to 15000 - 20000x for samples D3 and D7. The magnesium-containing areas in sample D8 appeared mainly particulate at all magnifications above 1000x. In all three samples, the magnesium-rich areas were surrounded by diffuse, apparently non-particulate regions around 2 µm thick, mapped at 10000 - 20000x. [Figure 3-14, Figure 3-15].



Figure 3-10: <sup>27</sup>Al MAS NMR spectrum of sample D5 X axis is chemical shift relative to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> in ppm



Figure 3-11: <sup>29</sup>Si MAS NMR spectrum of sample D5 X axis is chemical shift relative to TMS in ppm



Figure 3-12: SEI Image of sample D8, 1000x magnification



Figure 3-13: EDS maps of sample D8, 1000x magnification In overlay, red =Mg, blue = Si, purple = Mg + Si



— 2.0 µm

Figure 3-14: SEI image of sample D7, 15000x magnification



Figure 3-15: EDS maps of sample D7, 15000x magnification Maps of the apparent transition from Mg rich area to aluminosilicate matrix. In overlay, red = Mg, green = Si, dark blue = Al

#### 3.3.3.2 Discussion

Rietveld analysis and MAS NMR suggests a substantial degree of reaction of magnesium (hydr)oxide in the geopolymer slurry to form hydrotalcite and/or some other amorphous material. SEM evidence is consistent with this conclusion.

Hydrotalcite formation [section 1.2.8] was observed by XRD and MAS NMR in samples containing hydromagnesite-containing light magnesium oxide or its derivative materials. In samples where there is little or no carbonate present (e.g. Q4) either carbonation from atmospheric  $CO_2$  occurs or a hydroxide or silicate anion-substituted hydrotalcite may have formed.

The formation of an amorphous magnesium (alumino)silicate or magnesiumcontaining geopolymer phase may also be present. A completely amorphous magnesium alumino(silicate) phase or a magnesium incorporation into the geopolymer structure (1.2.6) would explain the apparent high degree of reaction for sample D6 where there is no obvious XRD evidence for hydrotalcite formation. However, the best explanation remains the formation of poorly crystalline (and weakly x-ray diffracting) hydrotalcite with  $CO_3^{2-}$ , OH<sup>-</sup>, or silicate anions as the charge balancing anion.

The mechanism of reaction cannot be the simple dissolution of  $Mg(OH)_2$  in water followed by reaction, as its dissolution rate considering surface area would be expected to be in the order of  $10^{-10}$  molm<sup>-2</sup>s<sup>-1</sup> or lower under the highly alkaline conditions used here.<sup>133</sup> Magnesium silicate and magnesium aluminate are insoluble in water.<sup>83</sup> Any reaction that occurs probably does so at the surface of the magnesium (hydr)oxide particles.

The observed degrees of reaction due not correlate well with the particle size of the magnesium (hydr)oxide sources. The surface area of magnesium oxide particles calcined from brucite is frequently determined by particle porosity, which increases with water loss when calcined at temperatures up to 600°C. Many factors, including metallic<sup>134</sup> and anionic impurities and heating rate<sup>135</sup>, influence the surface area developed by magnesium oxide when calcined, and the surface areas of the different magnesium hydr(oxides) would have to be determined experimentally to correlate them with degree of reaction.

EDS mapping does not provide strong evidence for any individual reaction product. There is some evidence for magnesium diffusion into the matrix, but the presence of very fine particulate hydrotalcite or magnesium (hydr)oxide cannot be ruled out. In samples containing hydrotalcite, EDS is unable to distinguish hydrotalcite from the other phases (i.e. there are no areas with very high Mg and Al concentrations). The overall correlation between magnesium and silicon/aluminium in EDS maps is weakly negative, providing no evidence for MSH or a magnesiumsubstituted geopolymer.

The simplest conclusion is that magnesium (hydr)oxide (and/or magnesium carbonate) react in geopolymeric systems to form hydrotalcite with hydroxide or silicate (or carbonate) anions as the intralayer anions. The formation either of a distinct amorphous phase such as an amorphous magnesium alumino(silicate) or a magnesium-containing geopolymer phase is also possible.

#### 3.3.4 Thermal treatment

The molar ratios of the set geopolymers prior to firing are recorded in Table 3-6.

#### **3.3.4.1 Results**

Unexpectedly, all magnesium-containing samples fired above 1200°C bloated to form either misshapen solid forms or rounded lightweight ceramic foams [Figure 3-16]. Samples not containing magnesium sintered into hard dense partially vitrified cylinders. Samples fired at 975°C did not bloat. Fired samples E3 (firing 2), and E2 (firing 3) floated in ethanol, implying a bulk density of less than 0.8 gcm<sup>-3</sup>, that of ethanol.



Figure 3-16: Fired sample E3 (firing 3) cut open. Porosity consists of many closed pores.



Figure 3-17: Fired and unfired samples From left: Fired sample E3 (firing 3), unfired sample E2, fired sample E1 (firing 1)

The XRD patterns of the fired objects showed a range of crystalline product phases. A very broad amorphous peak centred around  $30^{\circ} 2\theta$  from a glassy phase was present in all patterns.

All magnesium-containing samples contained spinel, many as the major phase. Many of the samples E9 - E16 contain corundum or leucite, while few of the samples from E1 - E8 do. The crystalline phases formed in the fired samples are listed in Table 3-10.

Sample name	Major phase (s)	Minor phase(s)	Sample name	Major phase (s)	Minor phase(s)
E1	Mullite		E9	Mullite	
E2	Spinel	Mullite	E10	Spinel	Mullite, Corundum
E3	Spinel		E11	Spinel	Leucite, Forsterite
E4	Spinel	Forsterite	E12	Spinel, Leucite	Forsterite
E5	Mullite		E13	Mullite, Corundum	Leucite
E6	Spinel	Mullite, Corundum	E14	Spinel	Leucite, Corundum
E7	Spinel	Corundum	E15	Spinel	Leucite, Corundum, Forsterite
E8	Spinel	Forsterite	E16	Spinel	Leucite, Forsterite

 Table 3-10: Crystalline phases detected by XRD in geopolymers containing added magnesium (hydr)oxide after firing.

### 3.3.4.2 Discussion

The formation of spinel is favoured in compositions containing magnesium. The presence of corundum in many of the F samples, particularly in the presence of forsterite, indicates incomplete reaction of the corundum. This is not unexpected as corundum is highly stable and is frequently incompletely reacted in ceramics.

The foaming of geopolymer bodies has been observed before<sup>1</sup> in potassium geopolymers with  $SiO_2/Al_2O_3$  ratios higher than 4 at temperatures above 1200°C, and
is associated with a mass loss. The formation of foams in geopolymers containing magnesium occurs at lower  $SiO_2/Al_2O_3$  contents.

Bloating is observed in many clays as well as zeolites and other minerals. It occurs when there is a reaction that produces gas and a liquid present at the same temperature with a viscosity high enough to entrap bubbles.<sup>136, 137</sup> The potassium geopolymers used for thermal treatment are sufficiently far away enough in composition form the relevant eutectics that relatively little liquid would be formed at 1200°C. [Figure 3-18]. However the addition of magnesium oxide would be expected to greatly increase the amount of liquid present in the material. The viscosity of the liquid in the system evidently remains high despite the high MgO content. The identity of the foaming gas is unknown. 1200°C would be expected to be too high for water loss.  $CO_2$  loss from magnesium carbonate phases is a more likely alternative.

The formation of lightweight aggregates from zeolitic rock is an area of increasing interest.<sup>138</sup> The formation of bloated materials from sodium flyash geopolymers may be an economic way to produce lightweight aggregates for a range of applications including hydroponic plant growth media and cement aggregates. Magnesium may act as a useful bloating agent.



Figure 3-18: Phase diagram of system K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. The red circle denotes geopolymer compositions with no extra added Al<sub>2</sub>O<sub>3</sub> (e.g. E1 – E4, E9 – E12), the blue circle geopolymer composition with extra Al<sub>2</sub>O<sub>3</sub> added (e.g. E5 – E8, E13 – E16). From Kingery<sup>139</sup>, after Osborn and Muan.

# 3.4 Conclusions and future work on magnesium-containing geopolymers.

The successful synthesis of potassium metakaolin geopolymers is known to require an alkali content sufficiently high to dissolve most or all of the metahalloysite present [Section 1.1.2]. High water content is known to hinder the formation of the geopolymer phase.

It was shown here that there is a well defined minimum alkali level for geopolymerisation, below which metahalloysite dissolution does not occur.

Geopolymers with low alkali contents were shown to be particularly sensitive to excess water content.

The effects of adding magnesium as soluble salts and (hydr)oxide particles were found to have very different effects on the geopolymerisation reaction. Adding soluble magnesium salts causes an immediate reaction, probably forming magnesium silicate or magnesium aluminosilicate by direct reaction between dissolved magnesium and (alumino)silicate ions.

The amount of magnesium that can be incorporated into a geopolymer body through the addition of soluble salts is limited by the removal of alkali cations by precipitation of insoluble potassium salts. Even limited amounts of magnesium salt addition results in geopolymers with poor mechanical properties.

The addition of magnesium (hydr)oxide has a considerably less deleterious effect on the setting behaviour of geopolymers. The formation of hydrotalcite and/or hydroxide- and silicate-substituted hydrotalcite occurs. The formation of a magnesium-containing geopolymer matrix or amorphous magnesium (alumino)silicates are neither supported or contradicted by the experimental evidence. Very high magnesium contents can be achieved in well-setting bodies.

The addition of magnesium promotes bloating on heating of potassium geopolymers with moderate  $SiO_2/Al_2O_3$  ratios to form foamed bodies. The addition of magnesium containing minerals to sodium flyash geopolymers may provide a basis for the production of commercially viable lightweight aggregate materials.

The possibility of reaction between magnesium (hydr)oxide and geopolymer slurries should be investigated using techniques that directly characterise the product materials. <sup>25</sup>Mg MAS NMR, XPS or similar techniques would be the most obvious choice. Rietveld XRD experiments can provide a useful method of determining the degree of reaction but will only be quantitative if well-characterised raw magnesium sources are used, and sample preparation carried out to minimise ground samples exposure to atmospheric moisture and carbon dioxide after grinding. Reactive magnesium (hydr)oxide with high surface area should be used to ensure reaction.

# Chapter 4 Synthesis of geopolymers from hydroxides

# 4.1 Introduction

Solutions of sodium silicate and sodium aluminate may be used as raw materials for geopolymerisation.<sup>140</sup> Aluminium hydroxide reacts with alkali hydroxide to form an alkali aluminate solution, while silica forms alkali silicate under the same conditions. Therefore it was thought that aluminium hydroxide, silica and potassium hydroxide may react to generate all the species necessary for geopolymer formation *in situ*. This led to the development of the method, dubbed the 'hydroxide method'.

A range of different aluminium hydroxides and silica sources were used, and a range of compositions examined.

#### 4.2 Experimental

#### 4.2.1 Raw materials

The raw silica sources used were two types of silica fume (DORAL SF98 and Elkem SF-971U), and a naturally occurring microsilica (Microsilica New Zealand Microsil 600). Aerosil (98.3%) and extra light precipitated silica (99%, Merck) formed pastes that were too viscous to mix immediately upon KOH addition and could not be used. The raw aluminium sources used were two types of crystalline aluminium hydroxide (Riedel-de-Hahn (RDH) aluminium hydroxide 99% and Acros aluminium hydroxide), and a precipitated aluminium hydroxide gel (National Dairy Association of New Zealand (NDANZ)).

	Volume
	weighted
Raw material:	mean
	particle size
	D[4,3] (µm)
Acros Al(OH) <sub>3</sub>	62.031
RDH Al(OH) <sub>3</sub>	13.764
NDANZ Al(OH) <sub>3</sub>	54.751
SF98 silica fume	57.706
Elkem 971-U silica fume	48.094

Table 4-1: Mean particle sizes of Al(OH)<sub>3</sub> and SiO<sub>2</sub> raw materials

The multimodal particle size distributions of NDANZ Al(OH)<sub>3</sub>, SF98, Microsilica 600 and Elkem 971-U indicate particle agglomeration; after sonication their volume-weighted means decreased by an approximate factor of 10, to 7.452 $\mu$ m (SF98, 10 minutes sonication), 13.952  $\mu$ m (Elkem 971-U, 5 minutes sonication), 6.951 (Microsilica 600, 5 minutes sonication) and 6.696 $\mu$ m (NDANZ, 5 minutes sonication). Acros Al(OH)<sub>3</sub> showed no noticeable change in particle size distribution after 5 minutes sonication. Other aluminium sources were not sonicated.

The bimodal size distribution of NDANZ Al(OH)<sub>3</sub> indicated a significant number of particles of a size less than 20  $\mu$ m, in contrast with Acros Al(OH)<sub>3</sub> despite their similar volume-weighted means. SF98 retained a bimodal particle size distribution after 10 minutes sonication centred at ~1 and 10  $\mu$ m. Some agglomeration of SF98 was probably still present. The manufacturer's stated mean particle size is 1.5 $\mu$ m, which matches the smaller particle mode size well.

XRD analysis showed that Acros and RDH aluminium hydroxide were both highly crystalline gibbsite. Strong preferred orientation effects were observed for the RDH material. NDANZ Al(OH)<sub>3</sub> was found to be a mixture of gibbsite, bayerite, doyleite (all Al(OH)<sub>3</sub>) and boehmite (AlOOH). SF98, Microsil 600 and Elkem 971-U were observed to be completely x-ray amorphous.

# 4.2.2 Initial synthesis and the effect of varying the $H_2O/AI_2O_3$ ratio

Al(OH)<sub>3</sub> (Riedel de Hahn) was added to a solution of KOH and allowed to stand for approximately 1 minute, producing an opaque white suspension. Silica fume (SF98) was added and the resulting slurry was stirred by hand. All samples were thick pastes. Samples were pressed into greased molds, placed in a closed container and left overnight at 40°C. Compositions and molar ratios are recorded in Table 4-2.

All samples were analysed using XRD. Samples 1 and 2 were analysed using <sup>27</sup>Al- and <sup>29</sup>Si MAS NMR. Samples 2, 3 and 4 were examined using SEM.

The samples set into monoliths with some hairline cracks on their surfaces. All samples shattered during cutting with a bandsaw and could not be used for compressive strength testing, in contrast with geopolymers synthesised by the conventional method which can be cut with a bandsaw.

Sample name	SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/ Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O / Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/ K <sub>2</sub> O	H <sub>2</sub> O	КОН	SiO <sub>2</sub> source mass (g)	Aluminium source mass (g)	Type of silica used	Type Al used
F1	3.22	10.05	1.16	8.68	4	5	8	6	SF98	RDH
F2	3.22	11.50	1.16	9.92	5	5	8	6	SF98	RDH
F3	3.22	12.94	1.16	11.17	6	5	8	6	SF98	RDH
F4	3.22	15.83	1.16	13.66	8	5	8	6	SF98	RDH

Table 4-2: Initial samples compositions and molar ratios

#### 4.2.3 The effect of varying the K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios

Hydroxide-derived geopolymers were made using the method described in section 4.2.2. Microsilica 600 was used as the silicon source rather than SF98 because the latter was unavailable. NDANZ Al(OH)<sub>3</sub> was used as the aluminium source. The sample compositions are described in Table 4-3. All samples contained the same amount of alkali; G1 – G4 comprise a series with increasing alumina content but constant alkali content, while G5 – G8 comprise a series with increasing alumina and alkali content.

All resulting slurries were very thick pastes that were difficult to stir. G5 was particularly dry and resembled a wet powder cake more than a true paste.

Sample Code	SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/ Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O/ Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/ K <sub>2</sub> O	H <sub>2</sub> O	КОН	Silica source mass (g)	Aluminium source mass (g)	Silica source	Aluminium source
G1	4.04	12.46	1.38	9.01	4	4.5	8	4	Microsil	RDH
G2	2.80	9.56	0.96	9.97	4	4.5	8	6	Microsil	RDH
G3	2.14	8.02	0.73	10.93	4	4.5	8	8	Microsil	RDH
G4	1.74	7.53	0.59	12.67	4.56	4.5	8	10	Microsil	RDH
G5	4.04	9.45	0.92	10.26	2.67	3	8	4	Microsil	RDH
G6	2.80	9.56	0.96	9.97	4	4.5	8	6	Microsil	RDH
G7	2.14	9.59	0.98	9.80	5.3	6	8	8	Microsil	RDH
G8	1.74	9.69	0.99	9.78	6.7	7.5	8	10	Microsil	RDH

Table 4-3: Molar ratios of samples with varying  $K_2O/Al_2O_3$  and  $SiO_2/Al_2O_3$  ratios

# 4.2.4 Preparation of a hydroxide-derived magnesium-containing geopolymer

Magnesium hydroxide nitrate was prepared by adding a stoichiometric amount of KOH to a solution of  $Mg(OH)_2$  to produce magnesium hydroxide. Instead of magnesium hydroxide, the product was magnesium hydroxide nitrate  $[Mg_2(OH)_3(NO_3)]$ , as determined by XRD.

2.5 g H<sub>2</sub>O, 2.5 g KOH, 4 g SiO<sub>2</sub> [SF98] and 3 g Al(OH)<sub>3</sub> [RDH] were mixed to create a hydroxide-derived geopolymer slurry as described in section 4.2.2. 0.68 g Mg<sub>2</sub>(OH)<sub>3</sub>(NO<sub>3</sub>) was mixed into the slurry. The sample was pressed into a greased mold and left at 40°C overnight. The sample molar ratios were SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=3.47, H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 11.99, MgO/K<sub>2</sub>O = 0.52 and K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 1.16. The sample was examined using XRD and SEM.

#### 4.2.5 SEM preparation

Each hydroxide-derived sample examined using SEM was cut into a 4 mm slice, soaked in 1-butanol for 2 days, placed in a beaker of acetone for 1 hour, dried at 100°C overnight, coated in 7 nm of platinum and desiccated in the rotary desiccator and JEOL 5300 sample chamber for at least 2 days each.

# 4.3 Results and discussion

# 4.3.1 Initial synthesis and the effect of varying the $H_2O/Al_2O_3$ ratio 4.3.1.1 Results

All samples set into monoliths. Samples F2 ,F3 and F4 had hairline cracks on their surfaces, the amount of which increased with sample water content.

The XRD patterns of the set samples show an amorphous broad peak and a large narrow peak from crystalline gibbsite. The main gibbsite peak is far larger than all other peaks due to preferred orientation, as for the raw material [Figure 4-1]. No evidence of any other crystalline phases is evident.



Figure 4-1: XRD patterns of hydroxide-derived geopolymers with different H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios increase up the page (Acros Al(OH)<sub>3</sub> excepted) All visible peaks are from gibbsite. H<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> increases up the page.



Figure 4-2: Sample F2 backscatter image, 200x magnification. Aluminous regions are visible as dark grey specks. The two large very dark spots are regions with poor sample coating.

There is a striking difference between the SEI and backscatter micrographs of the set products. SEI at low magnifications (25 - 200x) [Figure 4-3] show a homogeneous light grey material with some darker spots. There is no obvious microstructural difference between samples 2, 3, and 4 at any magnification. Backscatter imaging likewise showed a light matrix with darker inclusions [Figure 4-2]; however, the location of the dark spots from the two imaging modes were almost mutually exclusive. EDS element mapping showed a homogeneous potassium aluminosilicate matrix phase with aluminous impurity particles almost completely devoid of silicon or potassium [Figure 4-4]. The aluminous phase corresponded to the darkened spots observed in backscatter imaging mode. A small amount of a silicaceous impurity phase with particle sizes from  $1 - 10 \mu m$ , probably silica, was also visible. As for lithium geopolymers [section 5.3.1], the darkened spots visible in backscatter mode tended to appear smoother in SEI mode than the rest of the samples and the difference is likely to be textural, resulting from sample processing rather than inherent in the sample.

The aluminous regions ranged in size from less than 1  $\mu$ m to nearly 50  $\mu$ m.



Figure 4-3: Sample F2 SEI image, 200x magnification. Embedded aluminous regions are indistinguishable from the geopolymer phase.



Figure 4-4: EDS maps of area in Figure 4-2 and Figure 4-3. Overlay: Purple = K + Al + Si, green = Al only.

The  $^{27}$ Al MAS NMR spectra of samples F1 – F4 [Figure 4-5] are similar and show two main peaks at approximately -59 and 8 ppm, corresponding to tetrahedral and octahedral aluminium respectively. The tetrahedral peak is considerably larger for both samples. A small shoulder on the octahedral peak near -3 ppm is present.

The <sup>29</sup>Si MAS NMR spectra of samples F1 - F4 [Figure 4-6] show a main peak at approximately -88 ppm corresponding to a geopolymeric phase, and a large shoulder due to silica near -105 ppm



Figure 4-5: <sup>27</sup>Al MAS NMR spectrum of sample F1 X axis scale is chemical shift relative to  $Al(H_2O)_6^{3+}$ 



Figure 4-6: <sup>29</sup>Si MAS NMR spectrum of sample F 1 X axis scale is chemical shift relative to TMS

#### 4.3.1.2 Discussion

XRD, SEM and MAS NMR show a partial reaction of both silica and aluminium hydroxide to form geopolymers.

XRD shows the presence of both crystalline gibbsite and an amorphous phase and no zeolitic phases are formed. The main peak at -59 ppm in the <sup>27</sup>Al MAS NMR spectra of the synthesised samples corresponds to a geopolymer, and the smaller peak at 8 ppm corresponds to Al(OH)<sub>3</sub>. Likewise, the broad peak at -88 ppm in the <sup>29</sup>Si MAS NMR spectra of the samples is consistent with a geopolymer, while the shoulder at -105.4 ppm indicates the presence of free silica. SEM and EDS mapping show a potassium aluminosilicate matrix with aluminous grains, corresponding to the unreacted Al(OH)<sub>3</sub> detected by XRD and MAS NMR.

The water content of the samples appears not to have affected the relative degree of dissolution of aluminium hydroxide or silica dissolution between samples G1 - G4 as inferred from the <sup>27</sup>Al- and <sup>29</sup>Si MAS NMR spectra of the samples.

The inability of the large batch of samples to be cut with a bandsaw indicates that geopolymers produced via the hydroxide method are weaker than geopolymers made using the conventional method, due to either the incomplete reaction or microcracking. The strength of the samples presumably decreases with increasing cracking caused by excess water in the reaction mixture. A loss in strength of conventional geopolymers with excess water is described in the literature<sup>2</sup> and in section 3.2.1, but is due to incomplete geopolymerisation rather than cracking.

# 4.3.2 The effect of varying the $K_2O/AI_2O_3$ and $SiO_2/AI_2O_3$ ratios

The samples discussed in this section have molar compositions shown in Table 4-3.

#### 4.3.2.1 Results

All samples set into monoliths, the colour of which varied.

Sample	Colour
G1	Dark brown
G2	Off-white
G3	Tan
G4	Tan
G5	Grey
G6	Grey
G7	Grey-brown
G8	Light grey

 Table 4-4: Mechanical properties of hydroxide-derived geopolymers with varying K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>

All samples except G1 and G5 appeared homogeneous to the eye. G1 and G5 were visibly inhomogeneous, with white regions of aluminium hydroxide contrasting with the bulk of the material.

Sample G1 had the properties of a silicate bonded object, having silicate bonded fracture behaviour, reagglomerating during grinding in a mortar and pestle and dissolving in water.



Figure 4-7: Backscatter image of sample G3, 190x magnification. The aluminous regions are large and irregularly shaped due to agglomeration in NDANZ Al(OH)<sub>3</sub>

SEM backscatter imaging showed a similar structure to the hydroxide-derived geopolymers in section 4.2.3, with a potassium aluminosilicate phase and aluminous impurities [Figure 4-7]. Notably, the aluminous impurities were larger and irregularly shaped, likely due to particle agglomeration in NDANZ Al(OH)<sub>3</sub> [Section 4.2.1]. Many samples displayed cracks running between and through aluminous regions.

The XRD patterns of raw NDANZ Al(OH)<sub>3</sub> [Figure 4-9] and set samples [Figure 4-8] indicate partial reaction to form geopolymers. In all cases a broad amorphous peak is present. Gibbsite is the only aluminium hydroxide phase remaining after reaction in sizeable quantities. No broad peaks from boehmite are present. Samples G1, G2, G5 and G6 appear to have had the highest degree of reaction, containing the smallest residual gibbsite peak compared to the height of the amorphous peak. Some potassium-substituted zeolite F was observed in G1, but was not detected in the other samples.



Figure 4-8: XRD patterns of hydroxide-derived geopolymers with varying  $K_2O/Al_2O_3$  and  $SiO_2/Al_2O_3$ 

Patterns normalised to same main peak height. Main peak height is proportional to the amount of unreacted  $Al(OH)_3$ . G = gibbsite, F = zeolite F, \* = sample holder





The <sup>27</sup>Al MAS NMR spectra of samples G1 – G8 all contain a geopolymeric peak around 60 ppm, and a peak at 8 ppm corresponding to unreacted Al(OH)<sub>3</sub>. [Figure 4-10] Sample G8 also has a small, narrow peak at 80 ppm corresponding to potassium aluminate. In series A the amount of geopolymeric tetrahedral aluminium compared to octahedral aluminium follows the trend G1 < G2 > G3 > G4. In series B the corresponding trend is G5 ~ G6 > G7 > G8.



Figure 4-10: <sup>27</sup>Al MAS NMR spectra of hydroxide-derived geopolymers. X axis scale is chemical shift relative to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>

#### 4.3.2.2 Discussion

Like the hydroxide-derived geopolymers discussed in section 4.3.1.2, samples G2 - G8 have undergone partial reaction to form a geopolymer matrix with embedded grains of aluminium hydroxide, as indicated by XRD, MAS NMR and SEM. Unlike in the earlier samples, the unreacted grains of Al(OH)<sub>3</sub> are irregular and vary widely in size, probably as a result of deagglomeration of the raw Al(OH)<sub>3</sub> during reaction.

The change in reactivity (as monitored using MAS NMR) with changing  $SiO_2/Al_2O_3$  ratio in hydroxide-derived geopolymers appears to be different to that in conventional geopolymers. Among samples G2 – G4 and G6 – G8, as the alumina content rises, there is an increasing amount of unreacted alumina. In metakaolin geopolymers, zeolitic products would be expected in samples with SiO2/Al2O3 below 2.4, particularly in samples G7 and G8 which have high alkali contents as well as high alumina contents. The presence of unreacted potassium aluminate in sample G8 is notable as it would be expected to be particularly reactive. Its presence indicates that there is no accessible reaction pathway (e.g. reaction with silicate species) to remove the potassium aluminate.

The best conclusion is that when there is insufficient silica present for complete geopolymerisation, there is no reaction pathway to remove the potassium aluminate formed from aluminium hydroxide. This prevents the dissolution of aluminium hydroxide from occurring to any large extent, except under the most alkaline conditions<sup>141</sup>, when small amounts of free potassium aluminate are formed.

This is in contrast to conventional metakaolin geopolymers, which form zeolitic products when the silica content is insufficient for geopolymerisation. The difference probably arises from the difference between metakaolin, where the raw material is an aluminosilicate, and the separate alumina and silica raw materials of the hydroxide method. Presumably in metakaolin the dissolution of silica from the metakaolin structure aids the dissolution of alumina (or vice versa), whereas in the hydroxide method system, this effect does not occur.

Sample G1 contains silicate bonded zeolites, as might be expected from a metakaolin geopolymer with such a high alkali content. Sample G5 is little different to G6. The pairs of samples G1 and G2, and G5 and G6 differ from each other only in terms of their alkali and water content. This indicates that when there is sufficient

silica for complete geopolymerisation, reactivity depends on the alkali and water content in a way similar to metakaolin systems.

The formation of zeolite F is notable, as zeolite F formation was formed in systems with low  $SiO_2/Al_2O_3$  ratios in other parts of this project. [Section 5.3.1, discussed in section 5.3.5].

# 4.3.3 Preparation of a hydroxide-derived magnesium-containing geopolymer

#### 4.3.3.1 Results

The sample set into a monolith.

XRD showed a broad amorphous peak with one large crystalline peak and a few small peaks from gibbsite similar to those in section 3.2.2.1. [Figure 4-11] No other peaks other than those of the aluminium sample holder were visible.



Figure 4-11: XRD pattern of the magnesium-containing hydroxide-derived geopolymer



Figure 4-12: Backscatter image of the magnesium-containing hydroxide-derived geopolymer, 5000x magnification



Figure 4-13: EDS maps of the magnesium-containing hydroxide-derived geopolymer, magnification 5000x. Overlay in bottom right is of Si and Mg maps only. Red = Si, blue = Mg, purple = Si + Mg SEI imaging showed a homogeneous surface at magnifications below 1000x. backscatter imaging showed aluminous particles similar to other hydroxide-derived samples in section 4.3.1. EDS mapping showed aluminous particles in a potassium magnesium aluminosilicate matrix. In contrast to the magnesium (hydr)oxide containing samples in section 3.2.3, little particulate magnesium was observed at any magnification below 60000x, and silicon and magnesium concentrations were positively correlated. [Figure 4-13] Magnesium and aluminium concentrations were weakly negatively correlated, while magnesium and silicon concentrations were weakly positively correlated. The likely product is hydrotalcite, however as in section 3.3.3, this is not apparent from EDS mapping.

#### 4.3.3.2 Discussion

SEM evidence for an amorphous magnesium silicate or aluminosilicate phase is good. The most likely product is a poorly crystalline hydrotalcite – however, amorphous magnesium silicate is also possible. The high degree of reaction compared to the samples in section 3.3.3 could be due to several factors, in particular:

- 1) The use of magnesium hydroxide nitrate rather than magnesium hydroxide as a raw material.
- 2) Particle size effects.
- 3) The high pH of the solution, particularly as the reaction begins.

The presence of nitrate in the raw material is probably highly important, as magnesium hydroxide nitrate hydrolyses in water to form  $Mg(OH)_2$ .<sup>142</sup> This could subsequently react or be dispersed in a colloidal state throughout the matrix. The raw material is likely to be more reactive towards silicate and aluminate ions as it is towards hydroxide ions.

The coordination environments of the elements in the sample have not yet been studied (e.g. using MAS NMR) and so a definite conclusion as to whether or not the reaction has occurred cannot yet be made.

#### 4.4 Conclusions and future work

The hydroxide method was shown to produce geopolymers with embedded grains of unreacted aluminium hydroxide. The size and morphology of the starting aluminium hydroxide affects that of the embedded aluminium hydroxide grains in the final product. The hydroxide-derived geopolymers respond to excessive water content by forming well-reacted geopolymers with hairline cracks, in contrast to metakaolin geopolymers, which have a low degree of reaction when excess water is present. The mechanical properties of the hydroxide-derived geopolymers are inferior to those produced using the conventional method.

The effects of changing component molar ratios in the hydroxide method system when  $SiO_2/Al_2O_3$  is sufficiently high for complete geopolymerisation are similar to those observed in metakaolin systems. In contrast to metakaolin systems, when  $SiO_2/Al_2O_3$  is low, however, aluminium hydroxide dissolution only occurs until no more free dissolved  $SiO_2$  is available, rather than forming zeolites or other aluminous products.

The addition of magnesium hydroxide nitrate to a hydroxide-derived geopolymer appears to produce a magnesium-containing geopolymer with very little residual magnesium hydroxide nitrate. This is likely to be a consequence of the choice of magnesium hydroxide nitrate as a starting material but may also be favoured by the highly alkaline conditions and varying aluminium and silicon concentrations during hydroxide method synthesis. Hydrotalcite formation is the most likely explanation but further tests will need to be performed.

Further studies employing suitable characterisation methods (e.g. MAS NMR or XPS) are planned. XRD studies using a methodology similar to that used to study magnesium-containing conventional geopolymer systems (Sections 3.2.3.3, 3.4) could also be used.

# Chapter 5 Lithium Geopolymers

#### 5.1 Introduction

A major aim of this project was to synthesise lithium geopolymers. As discussed in the literature review (Section 1.2.4), the silicate chemistry of lithium differs markedly from that of the other alkali metals. Specifically, compared to other alkali silicate (and hydroxide) solutions lithium silicate (and hydroxide) solutions have:

- slow or even zero rates of dissolution of silica.
- different composition ranges of solubility (lithium silicate solutions can have very high SiO<sub>2</sub>/Li<sub>2</sub>O ratios, but not a ratio of 1:1).
- slow rates of reequilibration within solution when Li<sub>2</sub>O or SiO<sub>2</sub> content is changed.
- unusual silicate speciation for most combinations of total dissolved solids content and SiO<sub>2</sub>/Li<sub>2</sub>O ratio.
- decreased solubility at high temperature, in contrast to other silicate solutions.
- adsorption of lithium ions onto solid particles e.g. of silica, passivating the particle surfaces.

To date, these differences and their underlying causes have precluded the synthesis of lithium geopolymers. Woolf found that lithium silicate solutions produced bodies with poor mechanical properties and only partially tetrahedrally coordinated aluminium<sup>143</sup>. Providing the insoluble 1:1 Li<sub>2</sub>O:SiO<sub>2</sub> composition region is avoided, there would be expected to be no precipitation of solid lithium silicates, whereas magnesium silicates are insoluble. However, as with magnesium-containing geopolymer systems, pH and metahalloysite dissolution issues create constraints on the compositions that result in well-setting geopolymers.

Our attempted syntheses focused around a method<sup>144</sup> reported in the literature involving a solid state reaction between a mixture of NaOH and KOH and a mixture of metakaolin and quartz, followed by hydration of the product to give solid (albeit weak) geopolymeric bodies. The use of this method to synthesise lithium geopolymers is the focus of this chapter.

The effect of altering the  $Li_2O/Al_2O_3$  ratio in reaction mixtures was examined in order to determine the constraints on composition in the lithium system, similar to the study of the potassium system in section 3.2.1. Changing the  $SiO_2/Al_2O_3$  ratio by the addition of silica (as solid silica, lithium silicate solutions and solid soluble lithium orthosilicate ( $Li_4SiO_4$ ) was examined and the effects of using these different silica sources was determined. An important processing factor was the sample size, and the effect of this was also examined.

#### 5.2 Experimental

#### 5.2.1 General method

Lithium geopolymers were synthesised by dry mixing halloysite or metahalloysite with ground LiOH.H<sub>2</sub>O (Pure Science) and heating the mixture to around 550°C for 4-28 hours in glazed porcelain crucibles. Silica fume was sometimes added to the reaction mixture. The resulting powders were called 'precursor powders'. The precursor powders were white and free flowing. Any desired dry additives such as Li<sub>4</sub>SiO<sub>4</sub> were combined with the precursor powder and then water added mixed in a glass beaker. Upon addition of water to a precursor powder a grey-white slurry formed. The viscosity of the slurry was sensitive to the amount of water added. The slurries were stirred and the mixture removed from the beaker within minutes to minimise alkali and silica leaching from the beaker. The resulting slurries were placed into greased molds, vibrated on the vibrating table, sealed in gladwrap and left to set at 40°C. The setting/curing time of the samples was usually two days, or up to four for slower samples. Samples generally experienced some shrinkage and were easy to remove from their molds. All samples were examined using XRD. Selected samples were characterised using other methods such as MAS NMR and SEM.

#### 5.2.2 The effect of varying the Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio

A series of samples with the compositions and molar ratios shown in Table 5-1 was prepared to examine the effect of changing the  $Li_2O/Al_2O_3$  ratio.

	Masses	in grams		Molar	ratios	
Precursor powder	Mass of metahalloysite (g)	Mass of LiOH.H <sub>2</sub> O (g)	Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Li <sub>2</sub> O	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>
H1	9.008	3.043	1.00	2.41	10.80	10.75
H2	9.0	2.732	0.89	2.41	11.38	10.18
H3	8.974	2.501	0.82	2.41	12.23	10.05
H4	8.976	2.256	0.74	2.41	13.54	10.03
H5	8.976	2.002	0.66	2.41	15.18	9.98
H6	9.016	0.974	0.32	2.41	30.15	9.60
H7	8.988	0.708	0.23	2.41	40.62	9.43

Table 5-1: Molar ratios of lithium geopolymers with varying Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios

All set samples were inert in cold flowing water except for sample H7 which partially disintegrated over time. All samples and precursor powders were examined using XRD and <sup>27</sup>Al MAS NMR. Samples H1, H4, H5 and H7 were also examined using <sup>29</sup>Si MAS NMR.

#### 5.2.3 The effect of varying the size of the samples

Inconsistency in the setting behaviour and strength of small samples (less than 4 g precursor powder) throughout the project led to a hypothesis that the size of the sample affected the setting reaction. To test this, a large batch of precursor powder  $(Li_2O/Al_2O_3 = 1)$  was made from 20.229 g LiOH.H<sub>2</sub>O and 60.830 g metahalloysite. The precursor powder was divided into four 8 gram samples, four 4 gram samples and four 2 gram samples, which were hydrated with varying amounts of water. Sample compositions and molar ratios are shown in Table 5-2.

The viscosity of the hydrated samples decreased greatly with increasing water content. Samples with low water contents (samples I2, I5 and I9) were dry slurries, while samples with high water contents (I4, I8, and I12) were medium or thin pastes. Samples with intermediate water contents had intermediate viscosities, gradually

progressing from high viscosity to low viscosity as water content increased. After setting, the samples' top and bottom surfaces were scratch tested and sample strength tested by hand. <sup>27</sup>Al MAS NMR, XRD and electron microscopy were performed on selected samples.

Set samples I1, I2, I5, I7,I 9, and I12 were ground and examined using XRD. Samples I1, I5 and I9 were examined using <sup>27</sup>Al and <sup>29</sup>Si MAS NMR. All samples were tested for hardness and strength.

	Masses i	n grams	Molar ratios			
Sample	Precursor	H <sub>2</sub> O	Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> /	H <sub>2</sub> O/Li <sub>2</sub> O	
F	powder	2 -	-2-2-5	$Al_2O_3$	22	
I1	8.0	5.0	0.98	2.41	9.81	
I2	8.0	4.8	0.98	2.41	9.42	
I3	8.0	5.2	0.98	2.41	10.20	
I4	8.0	5.6	0.98	2.41	10.99	
15	4.0	2.4	0.98	2.41	9.42	
I6	4.0	2.5	0.98	2.41	9.81	
I7	4.0	2.6	0.98	2.41	10.20	
I8	4.0	2.75	0.98	2.41	10.79	
I9	2.0	1.2	0.98	2.41	9.42	
I10	2.0	1.29	0.98	2.41	10.13	
I11	2.0	1.35	0.98	2.41	10.60	
I12	2.0	1.4	0.98	2.41	10.99	

 Table 5-2: Composition and molar ratios of lithium geopolymers with varying sizes

# 5.2.4 The effect of varying the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio

#### **5.2.4.1 Introduction**

The effect of changing the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio would be expected to depend on the method used to effect the change due to the slow dissolution of solid silica by lithium hydroxide, the composition region of instability of lithium silicate solutions and the slow reequilibration of silicate species in lithium silicate solutions. Initial experiments with the addition of solid silica suggested inhibition of zeolitisation by solid silica addition. It was desired to know what the effect of changes in Si/Al ratio were without the complication of solid silica dissolution. As lithium silicate solutions have slow reequilibration kinetics and a compositional region of instability, soluble lithium silicate was added as solutions similar to commercially available products, and as crystalline lithium orthosilicate,  $Li_4SiO_4$ . Commercial lithium silicate solutions have  $SiO_2/Li_2O$  ratios significantly greater than 1 and  $Li_4SiO_4$  has a  $SiO_2/Li_2O$  ratio of 0.5, between them representing lithium silicate solutions on either side of the unstable composition region. The reactivity of these compositions would therefore be expected to be different.

The products of reaction were analysed by XRD, <sup>27</sup>Al- and <sup>29</sup>Si MAS NMR and electron microscopy and their mechanical properties determined..

#### 5.2.4.2 Compositions containing added solid silica

Two series of lithium geopolymers were made, one with silica fume (Samples J1 - J5), and one with fused silica (J6 - 15).

To synthesise samples J1 - J5, a precursor powder with  $SiO_2/Al_2O_3 = 2.41$  and  $Al_2O_3/Li_2O = 0.99$  was prepared. Elkem 971-U silica fume was mixed with the precursor powder and water added.

To synthesise samples J6 - J10, a precursor powder with  $SiO_2/Al_2O_3 = 2.41$  and  $Al_2O_3/Li_2O = 0.96$  was prepared. Batches of precursor powder were mixed with Elkem 971-U silica fume or fused silica, and water added.

The resulting ratios of the two series are shown in Table 5-3. Samples with more added silica required more added water content to give workable mixtures. Samples were placed in greased molds, sealed with gladwrap and placed in the laboratory oven at 45°C.

Sample	Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Li <sub>2</sub> O	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>
J1	0.99	2.41	10.94	10.78
J2	0.99	3.01	10.94	10.78
J3	0.99	3.51	10.94	10.78
J4	0.99	4.01	11.72	11.55
J5	0.99	5.01	12.50	12.32
J6	0.96	2.41	9.59	9.21
J7	0.96	3.19	9.59	9.21
J8	0.96	3.69	9.59	9.21
J9	0.96	3.98	9.59	9.21
J10	0.96	4.67	9.59	9.21

Table 5-3: Molar ratios of lithium geopolymers containing added solid silica

# 5.2.4.3 Compositions containing added lithium silicate solution

Lithium silicate solutions were made by mixing silicic acid (JT Baker) and ground LiOH.H<sub>2</sub>O in water and leaving the mixture to stand at room temperature for a week as described by  $Iler^{67}$ . The resultant mixtures consisted of a colourless transparent viscous liquid and suspended solid precipitates. The details of the solutions are shown in Table 5-4.

Solutions were shaken to ensure homogeneity before use.

	Masses in grams			Silicate solution composition				
Silicate solution name	H <sub>2</sub> O	LiOH.H <sub>2</sub> O	Silicic acid	S/L molar ratio	wt% Li <sub>2</sub> O	wt% SiO <sub>2</sub>	wt% H <sub>2</sub> O	Precipitation
Silicate-1	57.13	4.00	7.00	2.18	2.18	9.49	88.33	Turbid
Silicate-2	58.59	4.00	15.00	4.67	1.90	17.78	80.32	Turbid
Silicate-3	11.20	0.80	1.57	2.45	2.19	10.72	87.10	Turbid
Silicate-4	11.48	0.80	2.25	3.50	2.04	14.28	83.68	Turbid
Silicate-5	11.20	0.80	3.38	5.25	1.92	20.19	77.88	None
Silicate-6	11.20	1.00	4.50	5.60	2.22	24.92	72.86	None

 Table 5-4: Lithium silicate solution compositions, molar ratios and precipitation behaviours.

 Turbid denotes a small amount of gelatinous precipitate that if shaken settled out from the solution over minutes or hours.

Lithium precursor powders were prepared by heating ground  $LiOH.H_2O$  and metahalloysite together in porcelain crucibles under the reaction conditions described in Table 5-5.

Precursor powder name	LiOH.H <sub>2</sub> O	Halloysite	Precursor powder Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	Reaction conditions
0.5	71.998	12.0	0.49	570 4.5 hrs
0.8	53.825	15.0	0.82	550 6.5 hrs
1.15	66.484	26.0	1.15	550 4hrs

Table 5-5: Compositions of precursor powders for lithium silicate addition

Sample name	Precursor powder Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	Mass precursor powder used (g)	Silicate solution used	Mass silicate solution (g)	Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>
K-0.5-C	0.49	8.005	H <sub>2</sub> O	5.28	0.49	2.41	9.62
K-0.8-C	0.82	8.000	H <sub>2</sub> O	5.66	0.82	2.41	10.70
K-1.15-C	1.15	14.000	H <sub>2</sub> O	8.99	1.15	2.41	10.06
K-0.5-1	0.490	7.974	Silicate-1	5.81	0.62	2.70	9.31
K-0.5-2	0.490	8.029	Silicate-2	5.80	0.61	2.95	8.30
K-0.8-1	0.820	8.000	Silicate-3	6.48	0.97	2.79	10.56
K-0.8-2	0.820	8.000	Silicate-4	7.53	0.98	3.24	10.84
K-0.8-3	0.820	8.000	Silicate-5	7.12	0.98	2.97	11.10
K-0.8-4	0.820	8.000	Silicate-6	9.52	1.05	3.70	12.75
K-1.15-1	1.150	8.000	Silicate-1	6.00	1.30	2.73	10.30
K-1.15-2	1.150	8.000	Silicate-2	7.63	1.32	3.18	11.78

 Table 5-6: Compositions and molar ratios of lithium geopolymers hydrated with water and lithium silicate solutions

The precursor powders were mixed with water (control samples) or lithium silicate solution in glass beakers, transferred to greased plastic molds, vibrated, sealed

with gladwrap and left for three days at 40°C. The  $H_2O/Al_2O_3$  ratios of the different samples were similar, whereas other ratios varied. Slurries containing mixes of lithium silicates were much less viscous than expected from samples, with most samples with  $H_2O/Li_2O$  ratio greater than 10 being thin pastes or fluids, and even the driest samples being workable pastes, whereas they would be unworkable with the same water content but no lithium silicate. Water contents were usually chosen to give viscosities similar to the control samples or in some cases, thinner.

The difference in viscosity at each given  $H_2O/Al_2O_3$  ratio is not unexpected as silicate solutions are widely used as flocculants for slip-casting of clays, etc.<sup>145</sup> XRD was performed on all samples. <sup>27</sup>Al MAS NMR was performed on K-0.5-C, K-0.8-C, K-0.5-2, K-0.8-1, and K-0.8-2.

#### 5.2.4.4 Compositions containing added solid Li<sub>4</sub>SiO<sub>4</sub>

The compositions of lithium geopolymers were altered by the addition of crystalline (soluble) lithium orthosilicate ( $Li_4SiO_4$ ). Ground LiOH.H<sub>2</sub>O and silica fume (Elkem 971U) were mixed with a spatula in stoichiometric quantities and heated to 550°C for several minutes. The initial products were tan coloured powder cakes with white inhomogeneities. The powder cakes were reground in a glass mortar and pestle and returned to the furnace at 550°C, left overnight, cooled in open air, ground, and stored in closed plastic containers. Several batches of  $Li_4SiO_4$  were made using this method, each batch used for a different precursor powder. Compositions are recorded in Table 5-7.

The lithium precursor powders used for lithium silicate solution addition [section 5.2.4.3] were used for these experiments. In addition, metahalloysite was used as a precursor powder with no further treatment. Lithium precursor powders and synthesised Li<sub>4</sub>SiO<sub>4</sub> powders were dry mixed in glass beakers. Water was added and the resulting pastes were placed into greased molds, sealed with gladwrap and left for 2 days at 40°C to produce lithium geopolymers with the compositions shown in Table 5-8. The prepared Li<sub>4</sub>SiO<sub>4</sub> powder used for the synthesis of samples L-00-1 and L-00-2 was analysed using <sup>29</sup>Si MAS NMR and XRD. Slices of the set samples after hydration were prepared and coated with platinum as described in section 2.2.4.

Matching		
Precursor	SiO <sub>2</sub>	LiOH.H <sub>2</sub> O
powder		
00	4.077	11.391
0.5	2.419	6.732
0.5b	4.912	13.509
0.8a	2.419	6.732

Table 5-7: Composition of Li<sub>4</sub>SiO<sub>4</sub> reaction mixtures

	Mas	sses in g	rams	Molar Ratios			
Sample	Precursor	H <sub>2</sub> O	Li4SiO4	Li2O/Al2O3	SiO <sub>2</sub> /	H2O/Li2O	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>
name	powder	1120	2140104	<u> 21</u> 20/111203	$\begin{vmatrix} I_2 O / A I_2 O_3 \\ A I_2 O_3 \end{vmatrix} = \begin{vmatrix} H_2 O / L I_2 O \\ H_2 O / L I_2 O \end{vmatrix}$		1120/111203
L-00-1	8.005	5.49	1.01	0.52	2.67	18.11	9.43
L-00-2	6.8	1.72	4.47	1.04	2.93	8.67	9.04
L-0.5-1	8.005	5.32	1.02	1.04	2.69	9.27	9.68
L-0.5-2	8.003	5.53	2.05	1.61	2.97	6.26	10.06
L-0.8-1	7.981	5.51	1.04	1.41	2.71	7.42	10.44
L-0.8-2	7.981	5.54	2.02	1.96	2.98	5.35	10.5

Table 5-8: Compositions and molar ratios of lithium geopolymers with Li<sub>4</sub>SiO<sub>4</sub> added.

#### 5.2.5 Thermal treatment

#### 5.2.5.1 Lithium geopolymer synthesis

One series of samples with varying  $SiO_2/Al_2O_3$  ratios and one series with varying  $Li_2O/Al_2O_3$  were prepared for thermal treatment.

Eight precursor powders with different  $Li_2O/Al_2O_3$  ratios were prepared by heating metahalloysite with ground LiOH.H<sub>2</sub>O at 550°C and mixed with water to give lithium geopolymers according to Table 5-9.

Five lithium geopolymers with different  $SiO_2/Al_2O_3$  ratios were prepared by reacting metahalloysite with LiOH.H<sub>2</sub>O at 550°C for 4 hours, then adding fused silica and hydrating the mixture with water according to Table 5-10.

	Masses in grams				Molar ratios			
	Precursor powder synthesis		Hydrated sample					
Composition	Metahalloysite	LiOH.H <sub>2</sub> O	Precursor powder used	H <sub>2</sub> O	Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Li <sub>2</sub> O	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>
M1	2.997	0.991	2.489	1.30	0.97	2.41	8.24	8.03
M2	3.01	0.8255	2.394	1.30	0.81	2.41	10.15	8.20
M3	3.001	0.805	2.141	1.20	0.79	2.41	10.68	8.45
M4	2.997	0.7576	2.240	1.20	0.75	2.41	10.78	8.03
M5	3.002	0.7267	2.111	1.20	0.71	2.41	11.91	8.49
M6	3.006	0.6999	2.131	1.20	0.69	2.41	12.22	8.39
M7	2.995	0.6654	1.854	1.00	0.65	2.41	12.23	8.01
M8	2.998	0.4991	1.397	0.75	0.49	2.41	15.94	7.82

 Table 5-9: Composition and molar ratios of lithium geopolymers with varying Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios for thermal treatment

	Mas	sses in grams		Molar ratios			
Composition	Precursor powder	H <sub>2</sub> O	SiO <sub>2</sub>	Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Li <sub>2</sub> O	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>
N1	4.0	2.6	0	0.98	2.41	10.18	10.00
N2	4.0	2.5	0.93	0.98	3.48	9.79	9.62
N3	4.0	2.5	1.23	0.98	3.83	9.79	9.62
N4	4.0	2.5	1.66	0.98	4.33	9.79	9.62

 Table 5-10: Composition and molar ratios of lithium geopolymers with varying SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios for thermal treatment

The water and precursor powders mixed to form medium or thin pastes. They were placed in greased molds, sealed and left to cure at 50°C for 4 days. At the end of the curing period, all samples had set but were weak.

Both sets of samples were ground for XRD analysis after 3 months.

### **5.2.5.2 Thermal treatment**

The samples were heated in the IRL amalgams furnace on vitreous silica plates. Samples M1 – M8 were fired at 1000°C for 48 hours and 1300°C for 8 hours (heating rate  $10^{\circ}$ C/min, free cooling overnight).

Samples N1 – N4 were fired at 1300, 1350 and 1400°C for 8 hours (heating rate  $10^{\circ}$ C/min, free cooling overnight).

# 5.2.5.3 Thermal analysis

10.394 mg of unheated sample M1 was ground and heated in an SDT Q600 DSC-TGA with a platinum pan under flowing nitrogen at 10°C min<sup>-1</sup> to 1200°C.

#### 5.3 Results and discussion

Sample H1 (section 5.2.2) is considered in isolation in order to examine the general features of the reaction before considering the effect of changing  $Li_2O/Al_2O_3$ .

#### 5.3.1 Lithium geopolymer synthesis

#### **5.3.1.1 Results**

The XRD pattern of the precursor powder H1 shows that the material was largely amorphous. [Figure 5-1] Small narrow crystalline peaks as a result of unreacted cristobalite and quartz are present. Lithium orthosilicate is present in small amounts. Some small broad peaks due to unreacted lithium hydroxide hydrate are present. The broad amorphous peak is skewed towards low angles and the overall appearance of the pattern is similar to that of metahalloysite, depicted in Figure 5-30.



Figure 5-1: XRD pattern of lithium geopolymer precursor powder H1 C = cristobalite, L = Li<sub>4</sub>SiO<sub>4</sub>, Q= quartz, H = LiOH.H<sub>2</sub>O, \* = sample holder



Figure 5-2: <sup>27</sup>Al MAS NMR spectrum of lithium geopolymer precursor powder H1 X axis scale is chemical shift relative to  $Al(H_2O)_6^{3+}$ 



Figure 5-3: <sup>29</sup>Si MAS NMR spectrum lithium geopolymer precursor powder H1 X axis scale is chemical shift relative to TMS

The <sup>27</sup>Al NMR spectrum of the fired precursor powder contains peaks at approximately 76, 64, 60, 31 and 3 ppm. [Figure 5-2] The signals at 76, 64 and 60 ppm were attributed to tetrahedral aluminium, while the signals at 31 and 3 ppm were attributed to 5-coordinate (5CN) and octahedral aluminium respectively. <sup>146</sup>

The peak heights decreased in the order 60 > 76 > 31 > 3, indicating significant conversion of 6CN to 4CN aluminium.

The <sup>29</sup>Si MAS NMR spectrum of the fired precursor powder showed one broad peak near -95 ppm due to unreacted metahalloysite. A small peak at -70 ppm was also observed [Figure 5-3], corresponding to silicon in  $Q^0$  coordination in lithium orthosilicate, Li<sub>4</sub>SiO<sub>4</sub>.

When hydrated, H1 set into a white monolith approximately 20 mm high and 20 mm wide. It could not be broken by applying pressure by hand, nor scratched with a fingernail on either flat surface. It had brittle fracture behaviour. It was stable under cold flowing water. Its mechanical resilience was well in excess of that of a wetted metahalloysite body.

The XRD pattern of the set sample contains narrow peaks assignable to quartz, cristobalite and a zeolitic phase similar to Li-exchanged zeolite F. [Figure 5-4] The zeolitic phase is the main phase, with peak heights several times that of the other crystalline species. The background of the pattern was slightly elevated between 25 and  $45^{\circ}$  20 where there were several major and several minor peaks. The peaks of quartz and cristobalite were unaffected by the setting reaction. The observed relative peak heights of the zeolite F phase were different to that of the PDF pattern (01-079-1893), indicating preferred orientation effects in the sample.


Figure 5-4: XRD Pattern of set lithium geopolymer H1 Z = Li-EDI, C = cristobalite, Q = quartz, H = LiOH.H<sub>2</sub>O

The <sup>27</sup>Al MAS NMR spectrum of the set sample contains a large narrow peak centred at 61.1 ppm, indicating overwhelmingly 4CN aluminium in the sample [Figure 5-5]. A small 6CN peak at 7.4 ppm due to unreacted metahalloysite is also present.

The <sup>29</sup>Si MAS NMR spectrum of the set sample contains one narrow peak at -85.3 ppm. [Figure 5-6] The peak is asymmetric, with its upfield base width exceeding that of the downfield base width. The position of the peak corresponds to  $Q^4(4Al)$  coordinated silicon, as found in zeolite F. The peaks in the spectrum of the precursor powder at -71 and -94.5 ppm are no longer present. A peak at -110 ppm due to the quartz and cristobalite impurities observed in XRD is not observed.



Figure 5-5: <sup>27</sup>Al MAS NMR spectrum of set lithium geopolymer H1 X axis scale is chemical shift relative to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>



Figure 5-6: <sup>29</sup>Si MAS NMR spectrum of set lithium geopolymer H1 X axis scale is chemical shift relative to TMS

#### 5.3.1.2 Discussion

The overall reaction examined here is best described as the synthesis of a largely amorphous precursor powder containing reactive silicate and aluminate species, followed by a hydration reaction which produces zeolites.

The XRD pattern and MAS NMR spectra of the precursor powder indicate a conversion of 5- and 6CN aluminium to x-ray amorphous 4CN species. A reaction forming some  $Li_4SiO_4$  has also occurred, although the bulk of the silicon remains in a metakaolinite-like environment. Overall, the reaction between LiOH and the metakaolin has resulted in lower Al coordination and Si connectivity.

The XRD pattern and MAS NMR spectra of the set sample indicate almost complete conversion of the precursor powder to lithium-zeolite F, or "Li-EDI". The zeolitic phase gives rise to the <sup>29</sup>Si MAS NMR peak at -85.3 ppm and the <sup>27</sup>Al peak at 61 ppm. Little or none of the aluminium- and silicon-containing precursor species observed using MAS NMR remain.

The <sup>27</sup>Al and <sup>29</sup>Si MAS NMR both show only one coordination environment, and the main peak in the <sup>27</sup>Al spectrum is narrower than the characteristic peak of a geopolymer. This indicates a high degree of short-range order in the product and suggests that the broad baseline elevation observed in the XRD is due to very fine or poorly crystalline zeolitic materials rather than a geopolymer. This is corroborated by the absence of the characteristic XRD amorphous broad peaks of both conventional geopolymer (symmetric, centred at  $20 - 25^{\circ} 2\theta$ ) and metahalloysite (centred  $30 - 35^{\circ} 2\theta$ , with maximum height at  $25^{\circ} 2\theta$ ).

The name Li-EDI is taken from the zeolite framework type (EDI = edingtonite-type) by Matsumoto<sup>147</sup> who synthesised it under similar conditions. Li-EDI has previously been synthesised by other research groups using microwave synthesis<sup>148</sup>. Another group reported a similar synthesis of Li-ABW using flyash as the raw aluminosilicate material.<sup>149</sup> The potassium analogue, K-F is formed by the reaction of KOH with metakaolin in more dilute systems, but the lithium and sodium analogues have not been synthesised in this manner.<sup>150</sup> The formation of the sodium analogue has been observed in sodium geopolymers seeded with alumina nanoparticles.<sup>151</sup>

The edingtonite framework type<sup>151</sup> is one of the group of fibrous zeolites (the 'natrolite group'), and is composed of edge-linked 4-rings of tetrahedral silicate and

aluminate groups, producing chains [Figure 5-7]. The unit cell (without charge balancing cations) is depicted in [Figure 5-8]. The fibrous morphology of Li-EDI results in preferred orientation of the crystallites, altering the relative heights of the Li-EDI peaks in the experimental XRD pattern relative to the PDF powder pattern. The experimental XRD pattern is very similar to that observed by Matsumoto, indicating that the preferred orientation is similar in both cases.

The hardening of the sample is due to Li-EDI formation and growth. This assertion is supported elsewhere in this report [Sections 5.3.2 and 5.3.4] Self-pelletising zeolite formation is well established in the patent<sup>152</sup> and general literature<sup>153</sup>.

The crystalline silica phases quartz and cristobalite have undergone little or no reaction. Crystalline silica is extremely slow to dissolve in alkali<sup>67</sup> at room temperature (section 1.2.2). Furthermore, lithium hydroxide is very slow to dissolve silica (section 1.2.4).

This is the first reported synthesis of Li-EDI from metakaolinite.



Figure 5-7: Single chain structure of EDI-type zeolites. After Szostak.<sup>154</sup>



Figure 5-8: Unit cell of EDI-type zeolite framework. From Atlas of Zeolite Structures, 5<sup>th</sup> Revised Edition.<sup>155</sup> Vertices may represent Si or Al depending on zeolite type.

# 5.3.2 The effect of varying the $Li_2O/AI_2O_3$ ratio

The molar ratios of samples H1 – H7 are described in Table 5-1.

## 5.3.2.1 Results

The XRD patterns of the precursor powders show largely amorphous materials with unreacted quartz and cristobalite impurities.[Figure 5-9] Samples H1, H2, H3, H4 and H5 also contain additional broad peaks which were assigned to LiOH.H<sub>2</sub>O.



Figure 5-9: XRD patterns of precursor powders with varying Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio decreases up the page C= cristobalite, L = Li<sub>4</sub>SiO<sub>4</sub>, Q = quartz, H = LiOH.H<sub>2</sub>O, \* = sample holder

The <sup>27</sup>Al MAS NMR spectra of the fired precursor powders show peaks at approximately 76, 64, 60, 31 and 3 ppm. [Figure 5-10] The signals at 76, 64 and 60 ppm are attributed to tetrahedral aluminium and the signals at 31 and 3 ppm are attributed to 5CN and octahedral aluminium respectively, as for sample H1.

The precursor powders may be divided into a high and a low  $Li_2O/Al_2O_3$  group. The high  $Li_2O/Al_2O_3$  group have similar <sup>27</sup>Al spectra to sample H1 [section 5.3.1]. In the high  $Li_2O/Al_2O_3$  group (H1, H2, H3, H4 H5), the main signal is at ~60 ppm, with a shoulder at ~64 ppm. Other peaks are smaller but separately resolved. Peak heights decreased in order 60 > 76 > 31 > 3, indicating significant conversion of 6CN to 4CN aluminium.

The low  $Li_2O/Al_2O_3$  samples have a peak height order of 31 ppm > 3 ppm > 60 ppm > 64 ppm > 78 ppm, indicating a lower conversion of 5- and 6CN Al to 4CN Al.



Figure 5-10: <sup>27</sup>Al MAS NMR spectra of precursor powders with varying Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio decreases up the page X axis scale is chemical shift relative to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>

The <sup>29</sup>Si MAS NMR spectra of precursor powders H1, 3, and 7 [Figure 5-11] contain a broad peak near -95 ppm due to unreacted metahalloysite. The spectrum of sample H1 contains a  $Q^0$  peak at -70 ppm due to Li<sub>4</sub>SiO<sub>4</sub>. The same signal appears as a shoulder in the spectrum of sample H3. This signal is not observed in precursor powder H7. [Figure 5-11]



Figure 5-11: <sup>29</sup>Si MAS NMR spectra of precursor powders with varying Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio decreases up the page X axis scale is chemical shift relative to TMS

Samples H1 - H5 set into monoliths. Sample H6 crumbled easily and did not have brittle fracture behaviour, but was somewhat bonded unlike a powder cake. Sample H7 set into a powder cake.

The XRD patterns of the set samples H1 - H6 are all similar to that of H1, containing narrow peaks due to quartz, cristobalite and Li-EDI, and a broad amorphous baseline elevation due to zeolitic species. [Figure 5-12]. Li-EDI is the main phase in all samples. In sample H7 Li-EDI is not present and the broad amorphous peak is that of metakaolin.

The zeolitic peak heights decrease with  $Li_2O/Al_2O_3$  ratio from sample H1 to H2, then change little until sample H6 and H6, at which point they decrease further.



Figure 5-12: XRD patterns of set lithium geopolymers with varying Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> decreases up the page Z = Li-EDI, C = cristobalite, Q =quartz, H = LiOH.H<sub>2</sub>O

The set samples display less variation in their <sup>27</sup>Al NMR spectra than the precursor powders. The spectra of all samples except for H7 exhibit one main signal at 61 ppm, indicating fairly complete reaction of the species present in the precursor

powders to form Li-EDI. [Figure 5-13]. Sample H7 shows rather different Al coordination similar to the high Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> precursor powders, but with a significant shoulder at 64ppm.

There is no apparent difference in the spectra of samples H1, H2, H3, and H4. Signals at 76 and 7 ppm are a small shoulder and small peak respectively. In samples H5 and H6 these signals are stronger and a previously unobserved peak at 31 ppm is now visible. The general trend is similar to that observed in section 3.2.1, with little change in reactivity as alkali content decreases until the minimum content required for metakaolin dissolution is reached, whereupon the amount of unreacted metakaolin increases rapidly.



Figure 5-13: <sup>27</sup>Al MAS NMR spectra of set lithium geopolymers with varying Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio decreases up the page X axis scale is chemical shift relative to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>

The <sup>29</sup>Si MAS NMR spectra set samples H1 and H3 feature a narrow peak around -85 ppm due to Li-EDI formation. A broad shoulder at -95 ppm increases in size from sample H1 to sample H3. Sample H7 displays only a broad peak centred between 95 and 100 ppm, similar to that metahalloysite [Figure 5-14]. The decrease in silicon solubility as  $Li_2O/Al_2O_3$  decreases appears to be less sudden that of aluminium, occurring as the lithium content decreases from that of sample H1 to H3.



Figure 5-14: <sup>29</sup>Si MAS NMR spectra of set lithium geopolymers with varying Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio decreases up the page X axis scale is chemical shift relative to TMS

When examined using SEM, set samples H1, H3, and H5 appear to be fairly homogeneous using SEI at low magnifications (below 200x) [Figure 5-16]. EDS mapping shows that the bulk of the samples is made up of an aluminosilicate phase, with aluminous impurities about  $5 - 200 \mu m$  across and smaller silicaceous impurities [Figure 5-17]. At a magnification of 20000x the aluminosilicate phase in sample H1 is

composed of rod-like crystallites approximately 0.05-0.2  $\mu$ m across and 0.3 to 0.5 $\mu$ m [Figure 5-15]. The aluminosilicate phase in samples H3 and H5 appears smooth, with visible crystallites only present as loose debris. [Figure 5-19]



Figure 5-15: SEI image of sample H1, 20000x magnification The rod-like crystalline structure of the sample is visible.



Figure 5-16: Backscatter image of sample H1, 200x magnification



Figure 5-17: Elemental maps of area in Figure 5-16 In overlay, yellow = aluminium + silicon, green = aluminium, red = silicon.



Figure 5-18: SEI image of H3, 200x magnification.



Figure 5-19: SEI image of H3, 20000x magnification. Rodlike crystals are only visible as debris.

#### 5.3.2.2 Discussion

The XRD patterns and MAS NMR spectra of samples H1 – H6 show a substantial but decreasing degree of conversion from precursor powder to Li-EDI. As for sample H1, the XRD pattern baseline and MAS NMR spectra of the set samples show no evidence of a true geopolymeric phase. SEM imaging shows that the size of the zeolite crystallites in the samples decreases as the lithium content falls below that of sample H1.

An increasing amount of an amorphous silicon containing phase is present as lithium content decreases, and is probably accompanied by an increasing amount of a highly disordered aluminous phase. The intensity of the zeolitic XRD peaks drops noticeably with Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio from sample H1 to sample H5. The size of the broad shoulder in the <sup>29</sup>Si MAS NMR spectra increases significantly from sample H1 to H3. An unreacted x-ray amorphous silicon-containing phase is indicated.

In contrast, the<sup>27</sup>Al MAS NMR spectra show that the aluminium is almost entirely tetrahedral in all samples in this group. However, EDS mapping suggests the presence of significant amounts of aluminous impurities. Presumably these are made up of a highly disordered aluminous phase that gives rise to little or no signal in the <sup>27</sup>Al MAS NMR spectra.

The addition of  $Li_4SiO_4$  to metahalloysite or lithium geopolymer precursor powders was found to encourage zeolite formation elsewhere in this report [section 5.3.4.1.3]. However, XRD, <sup>29</sup>Si MAS NMR and simple stoichiometry all indicate that in these samples' precursor powders  $Li_4SiO_4$  is not present in the amounts sufficient for the observed degree of zeolite formation. It is probable that much of the lithium in the precursor powders is present as the aluminous or aluminosilicate species responsible for the <sup>27</sup>Al MAS NMR signal at 76 ppm. Some LiOH.H<sub>2</sub>O is also present.

The amount of amorphous phase(s) present is inversely proportional to the amount of crystalline zeolite and the observed mechanical resilience of the samples, so is unlikely to be contributing to sample strength.

The formation of zeolites in these samples contrasts with sodium- and potassium geopolymer systems, where little or no zeolitic product is expected from samples with equivalent ratios. However, it is notable that the  $M_2O/Al_2O_3$  ratio required for dissolution of the metahalloysite and subsequent reaction is similar in the lithium and potassium systems. In the potassium system, a gradual but small increase in unreacted metahalloysite is observed as the  $K_2O/Al_2O_3$  ratio decreases until  $K_2O/Al_2O_3 < 0.3$ , whereupon unreacted metahalloysite predominates. The <sup>27</sup>Al MAS NMR spectra of the low alkali samples in both systems are similar to that of metahalloysite, showing that the metahalloysite (or precursor) species simply do not dissolve to the degree required for the formation of a strong product. Notably, however, some dissolution does occur in both systems.

#### 5.3.3 The effect of varying the size of the samples

## 5.3.3.1 Results

The results of the scratch and breaking tests are presented in Table 5-11. The tests, although qualitative, yield conclusive results. There is a trend towards better mechanical properties for large samples, with the exception of sample I5, which appears to be an anomaly probably due to low water content. The large samples are strong and do not scratch on either surface. The medium samples are likewise strong but scratch on the bottom surfaces, sometimes severely. The small samples are little more than powder cakes, breaking when handled and undergoing severe damage when scratched. Sample I5 is also little more than a powder cake.

Sample name	Top scratches	Bottom Scratches	Strong
I1	N!	Ν	Y
I2	N!	Ν	Y
I3	N!	Ν	Y
I4	Ν	Ν	Y
I5	Y	Y!	N!
I6	N!	Y	Y
I7	Ν	Y!	Y
I8	N!	Y	Y
I9	Y	Y	N!
I10	Y	Y!	N!
I11	Ν	Y	Ν
I12	Y	Y!	Ν

Table 5-11: Mechanical Properties of lithium geopolymers with varying sample size

The XRD patterns of the set are similar to those of the high  $Li_2O/Al_2O_3$  samples in section 5.2.2, with crystalline peaks resulting from quartz, cristobalite and Li-EDI [Figure 5-22].



Figure 5-20: <sup>27</sup>Al MAS NMR spectra of lithium geopolymers of different sizes



Figure 5-21: <sup>29</sup>Si MAS NMR spectra of lithium geopolymers of different sizes

The <sup>27</sup>Al MAS NMR spectra of the set samples I1, I5 and I9 are virtually indistinguishable from one another, all featuring a single main tetrahedral peak around 61 ppm, with a minor octahedral peak at 7ppm. [ Figure **5-20**]

The <sup>29</sup>Si spectra of the set samples I1, I5 and I9 all contain a narrow peak at -85 ppm. Samples I1 and I5 also have a narrow peak at -81 ppm, which is smaller than the peak at -85 ppm for sample I1 and larger than the peak at -85 ppm for sample I5. Sample I9 has only one narrow peak at -85 ppm.



Figure 5-22: XRD patterns of lithium geopolymers of different sizes Z = Li-EDI, C = cristobalite, Q = quartz,  $H = LiOH.H_2O$ 

#### 5.3.3.2 Discussion

The mechanical strength of the samples did not correlate strongly with the amount of zeolitic phase formed as detected by <sup>27</sup>Al MAS NMR and XRD. All examined samples have quite high levels of conversion of metahalloysite to Li-EDI, but the small samples and sample I5 have very poor mechanical properties.

The major difference between the large and small samples is presumably greater water loss from the small samples during setting. The <sup>27</sup>Al MAS NMR spectra of the small samples (including sample I5) are almost indistinguishable from those of the large samples, and their XRD patterns are similar. The conversion of metahalloysite to Li-EDI is not greatly hindered by water loss from the sample, although the samples do not gain strength. Possibly the zeolite crystals do not have time to grow and interlock. Alternatively, there may be more non-cementitious residual metahalloysite-like material similar to that observed in increasing amounts as  $Li_2O/Al_2O_3$  is decreased. [Section 5.3.2]

The difference in hardness of the upper and lower surfaces of the samples is probably due to a difference in water content or silicate ion concentration caused by water loss from the top surface but not at the bottom [Section 3.3.2.2].

The results indicate that within a narrow range, ( $\sim 9 < H_2O/Li_2O < \sim 11$ ) the water content strongly affects the hardening of the samples, but only weakly affects the overall degree of conversion of metakaolin to Li-EDI.

#### 5.3.4 The effect of varying the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio

### **5.3.4.1 Results**

#### 5.3.4.1.1 Compositions containing added solid silica

Samples J1 - J4 and J6 - J9 set into monoliths. Sample J5 was intermediate between a monolith and a powder cake, lacking brittle fracture behaviour but exhibiting some mechanical resilience. Sample J10 was a powder cake.

The XRD patterns of samples J1 – J5 show a gradual change in reactivity as silica fume is added. [Figure 5-23] Sample J1 shows the characteristic XRD pattern of a well-set lithium geopolymer, with substantially more Li-EDI than cristobalite or

quartz. Little unreacted LiOH.H<sub>2</sub>O is present. Samples containing silica fume (J2, J3 and J4) show altered reactivity. They contain no Li-EDI, but do zeolite A and zeolite X (presumably both being the lithium form). Some unreacted LiOH.H<sub>2</sub>O is present. Sample J5 has the characteristic XRD pattern of a poorly set lithium geopolymer, similar to that of metahalloysite. The peaks of LiOH.H<sub>2</sub>O are more clearly resolved for sample J5 than for other samples.

The XRD pattern of J6 is that of a well-reacted lithium geopolymer containing mainly Li-EDI. Samples with fused silica added (J7 - J10) contain zeolite A and X but no Li-EDI.



Figure 5-23: XRD patterns set lithium geopolymers containing added silica fume. Silica fume content increases up the page. Sample J1 contains no silica fume. E = Li-EDI, X = Zeolite X, A = Zeolite A, L = Li-ABW.



Figure 5-24: XRD patterns of set lithium geopolymers containing added fused silica Fused silica content increases up the page. Sample J1 contains no fused silica. Z = Li-EDI, C = cristobalite, Q =quartz, H = LiOH.H<sub>2</sub>O

Sample name	Crystalline	
Sample name	Phases	
K-0.5-C	Z	
K-0.8-C	Z	
K-1.15-C	Z	
K-0.5-1	-	
K-0.5-2	X, E	
K-0.8-1	-	
K-0.8-2	-	
K-0.8-3	-	
K-0.8-4	-	
K-1.15-1	-	
K-1.15-2	Z, L	

### 5.3.4.1.2 Compositions containing add lithium silicate solution

Table 5-12: Crystalline phases present in lithium geopolymers hydrated with water and lithium silicate solutions Z = Li-EDI, X = Zeolite X, A = Zeolite A, L = Li-ABW.

The samples hydrated with water set into monoliths, as did samples K-0.5-2 and K-1.15-2. Other samples were intermediate between monoliths and powder cakes, appearing to be weakly bonded bodies, but not displaying brittle fracture behaviour.

The XRD patterns of the samples hydrated with water (0.5-C, 0.8-C and 1.15-C) are shown in Figure 5-25. The samples hydrated with lithium silicate solutions are depicted in Figure 5-26, Figure 5-27, and Figure 5-28 (made from precursor powders with  $Li_2O/Al_2O_3 = 0.5$ , 0.8 and 1.15 respectively).

The XRD patterns of the samples hydrated with water all contain peaks due to Li-EDI, cristobalite and quartz. As for the samples with varying  $Li_2O/Al_2O_3$  ratios discussed in section 5.3.2, the sample with the most alkali has formed the most Li-EDI, but there is little difference between the two samples with lower alkali contents.

Of the samples with lithium silicate solution added, only K-1.15-2 has undergone a substantial amount of Li-EDI formation. K-0.5-2 shows a small amount. The formation of different zeolite types including Li-zeolite A and Li-zeolite X is observed for K-0.5-1, K-0.5-2. Li-ABW has been formed in K-1.15-1. Other samples have the characteristic XRD pattern of poorly set samples, similar to sample H7 in section 5.3.2.

 $^{27}$ Al MAS NMR shows almost complete conversion of aluminium to tetrahedral (zeolitic) coordination for the samples hydrated with water, partial conversion for sample K-0.5-2, and no conversion for samples K-0.8-1 and K-0.8-2. The location of the (narrow) zeolitic peak is at approximately 61 ppm for samples K-0.5-C and K-0.8-C, corresponding to Li-EDI and at 62 ppm K-0.5-2, corresponding to zeolite A.<sup>156</sup>



Figure 5-25: XRD patterns of lithium geopolymers hydrated with water Z = Li-EDI, C = cristobalite, Q = quartz



Figure 5-26: XRD patterns of lithium geopolymers hydrated with lithium silicate solutions, precursor powder Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 0.5 Z = Li-EDI, C = cristobalite, Q =quartz, H = LiOH.H<sub>2</sub>O, X = zeolite X, A = zeolite A



Figure 5-27: XRD patterns of lithium geopolymers hydrated with lithium silicate solutions, precursor powder Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 0.8 Z = Li-EDI, C = cristobalite, Q =quartz, H = LiOH.H<sub>2</sub>O, X = zeolite X, A = zeolite A



Figure 5-28: XRD patterns of lithium geopolymers hydrated with lithium silicate solutions, precursor powder Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> = 1.15 Z = Li-EDI, C = cristobalite, Q =quartz, H = LiOH.H<sub>2</sub>O, L = Li-ABW

## 5.3.4.1.3 Compositions containing added solid Li<sub>4</sub>SiO<sub>4</sub>

Li<sub>4</sub>SiO<sub>4</sub> analysis:

The <sup>29</sup>Si MAS NMR spectrum of  $Li_4SiO_4$  [Figure 5-29] showed only one silicon environment giving rise to a signal at 64 ppm, indicating a Q<sup>0</sup> environment. The XRD pattern (not shown) shows  $Li_4SiO_4$  as the main phase with small amounts of quartz, cristobalite, lithium carbonate, and a minor unidentified phase.



Figure 5-29: <sup>29</sup>Si MAS NMR spectrum of Li<sub>4</sub>SiO<sub>4</sub> X axis scale is chemical shift relative to TMS

The control powders used in these experiments were the same as in the samples containing added lithium silicate solution. The XRD patterns of the set samples containing  $Li_4SiO_4$  except for L-00-1 show a high degree of conversion of the precursor powder and  $Li_4SiO_4$  to Li-EDI. [Figure 5-30, Figure 5-31, Figure 5-32] L-00-1 has undergone only partial reaction. Li-ABW has formed as a minor phase in sample L-0.5-2. No  $Li_4SiO_4$  remains in any sample. Unreacted quartz and cristobalite are present in all samples.



Figure 5-30: XRD patterns of lithium geopolymers from  $Li_4SiO_4$  and metahalloysite Z = Li-EDI, C = cristobalite, Q = quartz,  $H = LiOH.H_2O$ 



Figure 5-31: XRD patterns of lithium geopolymers from  $Li_4SiO_4$  + precursor powder with  $Li_2O/Al_2O_3 = 0.5$ Z = Li-EDI, C = cristobalite, Q =quartz, H = LiOH.H<sub>2</sub>O, L = Li-ABW



Figure 5-32: XRD patterns of lithium geopolymers from  $Li_4SiO_4$  + precursor powder with  $Li_2O/Al_2O_3 = 0.8$ Z = Li-EDI, C = cristobalite, Q =quartz, H = LiOH.H<sub>2</sub>O

The <sup>27</sup>Al spectra of samples L-00-2, L-0.5-1, L-0.5-1, L-0.8-1 and L-0.8-2 all contain one tetrahedral peak near 61 ppm [not shown].

The <sup>29</sup>Si MAS NMR spectra of L-00-2 and L-0.5-1 show one narrow peak at approximately -85.5 ppm. The spectrum of L-0.5-1 also contains a narrow peak at -80.9 ppm. [Figure 5-33]



EDS elemental mapping shows an aluminosilicate phase with aluminous and silicaceous impurities for all samples.

Rod-like particles approximately 0.1  $\mu$ m wide and 0.5  $\mu$ m long, similar to those described in section 5.3.2 are visible in samples that had 2 g Li<sub>4</sub>SiO<sub>4</sub> added. [Figure 5-34].



Figure 5-34: SEI image of sample L-0.8-1, 20000x magnification Rod-like Li-EDI crystals are visible



Figure 5-35: SEI image of sample L-0.8-1, 200x magnification



Figure 5-36: Elemental maps of area in Figure 5-35

#### 5.3.5 Discussion

In general, the addition of silica as solid silica or lithium silicate solution hindered the formation of Li-EDI, while the addition of Li<sub>4</sub>SiO<sub>4</sub> promoted it.

The formation of Li-EDI is almost entirely replaced by zeolites A and X (both FAU-type [faujasite]) zeolites when a small amount of solid silica (either silica fume or fused silica) is added. At higher levels of solid silica addition, silica fume prevents zeolite formation altogether, while fused silica has little more effect than at low levels of addition.

The action of silica fume is not unexpected as the dissolution of silica fume would increase the concentration of dissolved silica and lower pH substantially. However, the action of fused silica is somewhat surprising as it would be expected to have low solubility in LiOH.H<sub>2</sub>O at 45°C [Section 1.2.2]. Its action may indicate surface adsorption of Li<sup>+</sup> and/or OH<sup>-</sup> ions by fused silica particles rather than limited silica dissolution. If so, the effect on pH of surface adsorption appears to be smaller than that of silica dissolution, particularly at high levels of silica addition.

Lithium silicate solutions had a similar effect to solid silica on the zeolite formation reaction. In most samples, zeolite formation was completely hindered, as indicated by XRD and <sup>27</sup>Al MAS NMR (e.g. sample K-0.8-1 and K-0.8-2). In the XRD pattern of one sample (K-0.5-2), very small peaks corresponding to zeolite A and X are the only zeolitic peaks. However, <sup>27</sup>Al NMR indicates a comparatively high degree of conversion of metakaolin to zeolitic species. Presumably the zeolites are very small or poorly crystalline. Notably, this sample was monolithic, and stronger than the equivalent sample hydrated with water (0.5-C). The sample with the highest overall lithium content (K-1.15-2) formed Li-ABW as a minor product phase.

In contrast, the samples resulting from  $Li_4SiO_4$  generally had XRD patterns indicating large amounts of crystalline zeolites present. The only sample with a low degree of conversion of metakaolin to zeolites (as indicated by XRD) was L-00-1, the sample with the lowest overall alkali level. Sample L-0.5-2 formed Li-ABW as a minor product phase.

When  $Li_4SiO_4$  dissolves, the  $Li_2O/SiO_2$  ratio of the resulting lithium silicate solution is high, and so pH would be expected to be high. The pH decreases as metahalloysite dissolves and the  $Li_2O/SiO_2$  ratio decreases. In contrast, the pre-made lithium silicate solutions that were mixed with precursor powders have a comparatively low pH. If lithium hydroxide is added the composition of the lithium silicate solution will pass through the 1:1  $Li_2O:SiO_2$  region of instability before reaching the high pH of the  $Li_4SiO_4$  solutions. Instead of reequilibrating to reach the high alkalinity of  $Li_4SiO_4$  solutions, some precipitation of solid lithium silicates probably occurs, lowering pH and removing the ability of the solution to dissolve metahalloysite. Presumably the precipitates are poorly crystalline, as no crystalline  $Li_2SiO_3$  was observed in these samples using XRD.

In analogous sodium and potassium geopolymer systems, high  $M_2O/Al_2O_3$  and  $SiO_2/Al_2O_3$  ratio encourage the formation of silicate bonded materials. In the highest  $Li_2O/Al_2O_3$  and  $SiO_2/Al_2O_3$  samples prepared using lithium silicate or  $Li_4SiO_4$ , there is no evidence of formation of silicate bonded objects. As the products are not silicate bonded, it may be useful to investigate higher ratios of  $Li_2O/Al_2O_3$  and  $SiO_2/Al_2O_3$  in order to yield new zeolitic or possibly even a true geopolymeric product.

#### 5.3.6 The thermal treatment of lithium geopolymers

### **5.3.6.1 Results**

The XRD patterns of unfired samples with no solid silica added showed Li-EDI, while the patterns of samples with fused silica added showed Li-zeolite A and Li-zeolite X, similar to the samples in sections 5.3.2 and 5.3.4.1.1 respectively.

Samples M1 – M8 fired at 1000°C were weak non-vitreous white objects speckled with pink spots ~0.5 mm across. Samples M1 – M8 fired at 1300°C were partially vitreous with irregular brown, grey and white areas. All of the fired objects had many hairline cracks and none were strong. Samples N1 – N4 fired at 1300 and 1350°C were partially vitreous with irregular brown, white and grey regions. Samples N1 – N4 fired at 1400°C melted.

All the heated samples formed  $\beta$ -eucryptite and  $\beta$ -spodumene. The amount of  $\beta$ -eucryptite compared to  $\beta$ -spodumene in the samples was compared by observing the location of the main peak, which was centred at 29.4°20 for  $\beta$ -eucryptite and at 29.8° 20 for  $\beta$ -spodumene, comparing the heights of the smaller  $\beta$ -eucryptite and  $\beta$ -spodumene peaks at 22.2 and 22.7° 20, and noting the presence or absence of the  $\beta$ -spodumene peak at 32.9° 20.

The XRD patterns of sample M1 fired at 1000°C shows well-crystalline and very pure  $\beta$ -eucryptite. As the Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio decreases from sample M1 to sample M8, there is a gradual decrease in the intensity of the  $\beta$ -eucryptite peaks. A small shoulder due to mullite appears and from sample M2 and increases in size as the Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio decreases. [Figure 5-37].

The XRD patterns of the samples M1 – M8 fired at 1300°C shows only  $\beta$ -eucryptite. As the Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratio of the samples decreased from M2 to M7 onwards, increasing  $\beta$ -spodumene and cristobalite were formed [Figure 5-38]. Sample M8 contained only  $\beta$ -spodumene and a small amount of mullite.

The XRD patterns of the samples with changing  $SiO_2/Al_2O_3$  ratios (N1 – N4) fired at 1000°C contained  $\beta$ -eucryptite or  $\beta$ -spodumene, with the amount of  $\beta$ -spodumene increasing at the expense of  $\beta$ -eucryptite as  $SiO_2/Al_2O_3$  increased. Sample N4 contains a small amount of cristobalite. [Figure 5-39].
The XRD patterns of samples N1 – N4 fired at 1350°C [Figure 5-40] were similar to the samples fired at 1300°C. Sample 1 only contained eucryptite. As  $SiO_2/Al_2O_3$  increased, increasing amounts of  $\beta$ -spodumene were present. This was accompanied by an increasing amount of cristobalite from sample N2 to N4.







Figure 5-38: XRD patterns of lithium geopolymers with varying  $Li_2O/Al_2O_3$  ratios fired at 1300°C  $Li_2O/Al_2O_3$  ratios decrease up the page  $E = \beta$ -eucryptite,  $S = \beta$ -spodumene, M = mullite



Figure 5-39: XRD patterns of lithium geopolymers with varying  $SiO_2/Al_2O_3$  ratios fired at  $1300^{\circ}C$  $SiO_2/Al_2O_3$  ratio increases up the page.  $E = \beta$ -eucryptite,  $S = \beta$ -spodumene



Figure 5-40: XRD patterns of lithium geopolymers with varying  $SiO_2/Al_2O_3$  ratios fired at 1350°C  $SiO_2/Al_2O_3$  ratio increases up the page. E =  $\beta$ -eucryptite, S =  $\beta$ -spodumene



Figure 5-41: TGA-DSC Trace of set lithium geopolymer M1



Figure 5-42: TGA-DSC Trace of set lithium geopolymer M1 (Limited scale)

## 5.3.6.2 Discussion

In samples M1 – M8 fired at 1000°C,  $\beta$ -eucryptite is the predominant phase in samples with close to the stoichiometric amount of lithium suitable for  $\beta$ -eucryptite formation (Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub>=1). When Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> is reduced below 1, the amount of  $\beta$ -eucryptite decreases. implying the existence of excess SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [see also Figure 5-14].

In the same samples fired at 1300°C, the gradual increase in the amount of  $\beta$ -spodumene formed indicates the inclusion of the excess SiO<sub>2</sub> into the  $\beta$ -eucryptite structure, forming an increasingly  $\beta$ -spodumene-rich solid solution with  $\beta$ -eucryptite. Further excess silica is crystallised as cristobalite. No crystalline aluminous phase found using XRD. Presumably an amorphous phase is formed. When there is sufficient amounts of the aluminous phase (sample M8), mullite is formed.

The phases formed in samples N1 – N4 at 1350°C are in accord with the phase diagram [Figure 5-43]. As SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> increases from the stoichiometric eucryptite composition to that of spodumene, the amount of  $\beta$ -spodumene increases and the amount of  $\beta$ -eucryptite decreases.

The behaviour of samples N1 – N4 fired at 1300° is more interesting. The general trend is for a decrease in the amount of  $\beta$ -eucryptite formed and an increase in spodumene. However, samples 4 and 5 have very similar XRD patterns, indicating that little extra spodumene is formed. Presumably the silica fume is not able to react with the eucryptite formed from Li-EDI to form spodumene at 1300°C, so remains amorphous.

Matsumoto<sup>147</sup> observed exothermic formation of  $\gamma$ -eucryptite at 780°C and endothermic  $\beta$ -eucryptite formation from Li-EDI above 900°C. The presence of sodium has been shown to induce simultaneous crystallisation of  $\gamma$ - and  $\beta$ -eucryptite at 720°C.<sup>147</sup> The results of the present TGA-DSC experiment suggest similar behaviour to that of the pure lithium system studied by Matsumoto. The crystallisation of  $\gamma$ - and  $\beta$ -eucryptite probably occurs at 760 and 850°C respectively in the present system, possibly reflecting the presence of trace amounts of iron impurities. This fits well with the observed formation of  $\beta$ -eucryptite during thermal treatment.



Figure 5-43: Phase diagram of the system  $LiAlSiO_4$  -  $SiO_2$ . After  $Roy^{157}$ 

## 5.4 Conclusions and future work

The favoured products when metahalloysite is dissolved in basic LiOH or lithium silicate solutions are zeolitic rather than truly geopolymeric. In particular, Li-EDI forms under the very alkaline conditions resulting from the hydration of lithium precursor powders in water or the dissolution of Li<sub>4</sub>SiO<sub>4</sub>.

At low levels of addition, solid silica causes the product of reaction from Li-EDI to Li-zeolite A and Li-zeolite X. At high levels of addition, the zeolitisation reaction is hindered altogether by silica fume but is insensitive to fused silica. In general, lithium silicate solutions with high SiO<sub>2</sub>/Li<sub>2</sub>O are not sufficiently alkaline to dissolve metahalloysite for zeolitisation. In contrast, lithium orthosilicate is sufficiently alkaline to assist reaction.

High lithium and silica contents encourage the formation of Li-ABW rather than silicate bonded objects, in contrast with conventional geopolymers.

Lithium geopolymers have similar a similar minimum alkali content to sodium and potassium geopolymers. They develop mechanical strength only within a narrower range of water contents, although the conversion of metakaolin to Li-EDI occurs with water contents outside this range.

Thermal treatment of lithium geopolymers results in  $\beta$ -eucryptite at a temperature of around 900°C. Added solid silica reacts to form  $\beta$ -spodumene around 1350°C. Simple firing of set objects results in inhomogeneous ceramic bodies but improved geopolymer processing or the use of conventional methods may avoid this problem.

The formation and thermal treatment of lithium geopolymers may be a viable route to lithium aluminosilicate ceramics. Future work should investigate improved processing methods to improve product homogeneity, whether adding silica to lithium geopolymers in soluble form (e.g.  $Li_4SiO_4$ ) lowers the reaction temperature of  $\beta$ -spodumene formation, and dilatometric studies on the product ceramic bodies.

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