



This is a repository copy of *Phase evolution of Na₂O–Al₂O₃–SiO₂–H₂O gels in synthetic aluminosilicate binders.*

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/164373/>

Version: Accepted Version

Article:

Walkley, B. orcid.org/0000-0003-1069-1362, San Nicolas, R., Sani, M.-A. et al. (3 more authors) (2016) Phase evolution of Na₂O–Al₂O₃–SiO₂–H₂O gels in synthetic aluminosilicate binders. *Dalton Transactions*, 45 (13). pp. 5521-5535. ISSN 1477-9226

<https://doi.org/10.1039/C5DT04878H>

© 2016 The Royal Society of Chemistry. This is an author-produced version of a paper subsequently published in *Dalton Transactions*. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Phase evolution of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ gels in synthetic aluminosilicate binders

Brant Walkley¹, Rackel San Nicolas^{1,2,*}, Marc-Antoine Sani³, John D. Gehman^{3,4}, Jannie S.J. van Deventer^{1,5}, John L. Provis⁶

¹ Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

² Department of Infrastructure Engineering, The University of Melbourne, Victoria 3010, Australia

³ School of Chemistry and Bio21 Institute, The University of Melbourne, Victoria 3010, Australia

⁴ GehmanLab, Woodend, Victoria 3442, Australia

⁵ Zeobond Pty Ltd, P.O. Box 23450, Docklands, Victoria 8012, Australia

⁶ Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, United Kingdom

Abstract

This study demonstrates production of stoichiometrically controlled alkali-aluminosilicate gels ('geopolymers') via alkali-activation of high-purity synthetic amorphous aluminosilicate powders. This method provides for the first time a process by which the chemistry of aluminosilicate-based cementitious materials may be accurately simulated by pure synthetic systems, allowing elucidation of physicochemical phenomena controlling alkali-aluminosilicate gel formation which has until now been impeded by the inability to isolate and control key variables. Phase evolution and nanostructural development of these materials are examined using advanced characterisation techniques, including solid state MAS NMR spectroscopy probing ²⁹Si, ²⁷Al and ²³Na nuclei. Gel stoichiometry and the reaction kinetics which control phase evolution are shown to be strongly dependent on the chemical composition of the reaction mix, while the main reaction product is a $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ type gel comprised of aluminium and silicon tetrahedra linked via oxygen bridges, with sodium taking on a charge balancing function. The alkali-aluminosilicate gels produced in this study constitute a chemically simplified model system which provides a novel research tool for the study of phase evolution and microstructural development in these systems. Novel insight of physicochemical phenomena governing geopolymer gel formation suggests intricate control over time-dependent geopolymer physical properties can be attained through careful precursor mix design. Chemical composition of the main N-A-S-H type gel reaction product as well as the reaction kinetics governing its formation are closely related to the Si/Al ratio of the precursor, with increased Al content leading to an increased rate of reaction and decreased Si/Al ratio in the N-A-S-H type gel. This has significant implications for geopolymer mix design for industrial applications.

Introduction

Alkali-activated aluminosilicate cements, known as 'geopolymers', offer opportunities for use as an alternative to Portland cement (PC) in many applications including concrete production, with a reduction in associated CO₂ emissions by over 80% achievable when compared to PC-based binders¹⁻³, as well as in refractory, construction, radioactive waste immobilisation, biomaterial, fibre composite and other niche applications. Despite this, the use of geopolymers in the construction industry is not yet widespread due in part to the difficulty associated with achieving reproducible performance and stoichiometry of the key binding phases formed in these systems when waste or by-product materials are used as their main precursors². This is linked to the current incomplete understanding of the fundamental fluid-particle reactions occurring during the reaction of a concentrated alkaline solution with a reactive aluminosilicate powder, which leads to the precipitation of the alkali aluminosilicate 'geopolymer' gel product and thus defines the formation and performance of the resulting cementitious binder.

Even under small variations in the chemical and physical characteristics of the raw materials used, the physical properties of geopolymers can show significant differences^{2, 4-6}.

The compositions of commonly used aluminosilicate precursors, such as fly ash (a by-product of coal combustion) and ground granulated blast furnace slag (a by-product of iron-making) vary significantly between sources, and sometimes as a function of time from a single source, which complicates the design and analysis of geopolymer formulations^{2, 7}. Variations in precursor chemistry have also caused difficulty in determining the role of each chemical species in phase evolution and microstructural development during the setting and hardening of geopolymer cement.

Despite the rapidly increasing number of studies investigating the chemistry of geopolymers, the literature is often conflicting and experimental analysis can involve a large number of unconstrained parameters^{8, 9}. It is necessary to develop a method to study these materials that permits strict control of the stoichiometry, to investigate relationships between precursor chemical composition and the thermodynamics and reaction kinetics which govern phase evolution, mechanical performance, dimensional stability and long-term durability in geopolymer systems¹⁰. Only through such a method can key variables dictating the final physicochemical properties of geopolymer binders be isolated and controlled to allow resolution of phenomena

which are fundamental for geopolymer mix design in practical settings.

One approach to mitigate this problem has been through synthesis of geopolymer precursor powders and binder phases in the laboratory under controlled conditions. A limited number of studies detailing the synthesis and characterisation of phases simulating those found in geopolymer binders can be found in the literature¹¹⁻²⁰. Most of these studies described the reaction of nitrate solutions containing silicon and aluminium, via a sol-gel procedure, to form alkali aluminosilicate or calcium-alkali-aluminosilicate gels. These studies generally investigate the effect of alkali cations, alkaline earth cations or aluminium on CaO-SiO₂-H₂O (C-S-H) type or Na₂O-Al₂O₃-SiO₂-H₂O (N-A-S-H) type gels by addition of these ions after formation of the gel (either by direct addition of an ion source or by mixing two different gels together). However, in geopolymer systems involving the alkali-activation of an aluminosilicate precursor, all reactive species are initially present and participate simultaneously in the reaction; it is well known that the rates at which Si and Al are supplied as nutrients for a geopolymer gel-forming reaction are fundamental in controlling the properties of the hardened binder^{21, 22}. The addition of ions after formation of the main reaction products restricts the ability to control gel stoichiometry and homogeneity in these systems, as well as possibly modifying the structural role of the cations if the degree of approach to thermodynamic equilibrium is restricted by transport or kinetic limitations. Furthermore, the use of high amounts of water and the presence of nitrates lead to differences in alkalinity and ionic strength, and can significantly affect the dissolution, reaction mechanisms and phase formation.

Thus, in order to accurately replicate the reaction conditions present during alkali-activation of reactive cementitious precursors, this study utilises high-purity synthetic aluminosilicate amorphous precursor powders synthesised via an organic steric entrapment solution-polymerisation route as described in detail previously^{23, 24}, to develop a novel class of stoichiometrically controlled geopolymers. These geopolymers are synthesised from pure precursors under the same physical and chemical conditions which prevail during alkali-activation of commonly used aluminosilicate geopolymer precursors such as metakaolin and fly ash, and provide insight into the role of precursor chemistry in the phase evolution of geopolymer systems. Through rigorous analysis of this model system, we resolve important relationships between precursor chemistry and the final structure of the alkali aluminosilicate geopolymer gel which have significant implications for geopolymer mix design.

Materials and Methods

Geopolymer binder synthesis

The aluminosilicate precursor powders used in this study were synthesised via an organic steric entrapment solution-polymerisation route²⁴, with the empirical compositions 2SiO₂·Al₂O₃ and 4SiO₂·Al₂O₃ chosen to span the range of bulk silicon and aluminium contents typically found in aluminosilicate pozzolans such as siliceous fly ash and me-

takaolin, with the first specifically representing the composition of metakaolin. The activating solution was prepared by dissolution of sodium hydroxide powder (AnalaR 99 wt.%) in sodium silicate solution (N grade, modulus (molar ratio SiO₂/Na₂O) = 3.3, 37.5 wt.% total solids, PQ Australia) and distilled water. The stoichiometry was designed to obtain an activating solution modulus of SiO₂/Na₂O = 1, a water/solids ratio of 0.75 and a cation ratio of Na/Al = 1.18 in the reaction mixture (see Table 1). The activating solution was mixed with the aluminosilicate precursor powder to form a homogeneous paste, which was cast in sealed containers and cured at ambient temperature for 7, 28 and 224 days.

Table 1. Molar ratios in the precursor powder and the reaction mixture for each sample

Sample	Empirical Formula	Precursor powder		Reaction mixture	
		Si/Al	Na/Al	Si/Al	Na/Al
A	2SiO ₂ ·Al ₂ O ₃	1.00	0.00	1.50	1.18
B	4SiO ₂ ·Al ₂ O ₃	2.00	0.00	2.50	1.18

Characterisation

For all characterisation techniques except environmental scanning electron microscopy/energy dispersive X-ray spectroscopy (ESEM/EDX), the hardened pastes were ground by hand using a mortar and pestle and immersed in acetone to remove loosely bound water and halt the geopolymerisation reaction. This method is thought not to induce any significant changes in the geopolymer gel structure²⁵.

Thermogravimetric analysis was performed on powdered samples of approximately 30 mg in an alumina crucible using a Perkin Elmer Diamond instrument, at a heating rate of 10°C/min between 30°C and 1000°C, with a nitrogen purge at 200 mL/min. To ensure consistent initial conditions, the samples were held in the instrument at 30°C for 20 minutes prior to the commencement of heating.

X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance instrument with Cu K α radiation, a nickel filter, a step size of 0.020°, a dwell time of 3 seconds and a 2 θ range of 3 - 70°.

Environmental scanning electron microscopy (ESEM) was conducted using an FEI Quanta instrument with a 15 kV accelerating voltage and a working distance of 10 mm. Geopolymer samples were cut and polished using non aqueous lubricants and immediately analysed in low vacuum mode (0.5 mbar water pressure) using a backscatter detector. A Link-Isis (Oxford Instruments) X-ray energy dispersive (EDX) detector was used to determine chemical compositions.

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy experiments were performed using a Varian FTS 7000 spectrometer with a Specac MKII Golden Gate single reflectance ATR attachment with KRS-5 optics and diamond ATR crystal, scanning 32 times at a resolution of 4 cm⁻¹.

Solid state ²⁹Si MAS NMR spectra were collected at 119.141 MHz on an Agilent (Varian) VNMRS-600 (14.1 T) spectrometer using a 4 mm triple resonance bioMAS probe. The ²⁹Si MAS NMR experiments for precursor powders and geopol-

ymers cured for 7 days employed a pulse width of 4 μ s, a pulse angle of 47°, a relaxation delay of 45 s and 1024 scans, while ^{29}Si MAS NMR experiments for geopolymers cured for 28 and 224 days employed a pulse width of 7 μ s, a pulse angle of 90°, a relaxation delay of 120 s and 1024 scans. Solid state ^{27}Al MAS NMR spectra were acquired at 156.261 MHz with a pulse width of 4 μ s, a pulse angle of 90°, a relaxation delay of 2 s and 1024 scans. Solid state ^{23}Na MAS NMR spectra were acquired at 158.632 MHz with a pulse width of 5 μ s, a pulse angle of 90°, a relaxation delay of 3 s and 512 scans. When probing quadrupolar nuclei in samples with a distribution of quadrupolar interactions, a single 90° pulse cannot equally excite different nutation rates experienced by each chemical environment and consequently may introduce biased signal intensities. Small tip angles (<20°) are commonly used to remove the nutation issues, however large quadrupolar interactions may cause additional intensities from satellite transitions to be present in the signal, and some of the central-transition intensity may be lost to the first-order spinning sidebands. Consequently the ^{27}Al and ^{23}Na MAS NMR spectra presented here cannot be used confidently for quantification, and are only interpreted qualitatively. All experiments were performed at 10.0 kHz spinning speed and 25°C. ^{29}Si , ^{27}Al and ^{23}Na chemical shifts were referenced to external samples of tetramethylsilane (TMS), aluminium chloride hexahydrate as a 1.0 M aqueous solution or as a powder, each at 0 ppm, and NaCl powder at 7.2 ppm²⁶. All data were processed using NMRPipe²⁷. Deconvolution of the ^{29}Si MAS NMR spectra was performed by Gaussian peak deconvolution: a single Gaussian peak is used to represent each expected $\text{Q}^n(\text{mAl})$ species within the sample, and these peaks are used to develop a simulation of the ^{29}Si MAS NMR spectra that is fitted using a least squares fitting method. The relative concentration of each silicon environment can be determined from the intensity of the corresponding peaks in the ^{29}Si MAS NMR spectra. Peak assignments were made with reference to the literature. The minimum possible number of peaks was used to enable an accurate and meaningful interpretation of the spectra, with the requirement that the intensities of adjacent peaks vary smoothly, consistent with the thermodynamics of a statistical distribution of Si and Al sites within a Q4 aluminosilicate network^{28, 29}.

Figure 1. Differential thermogravimetric curves for the precursor powder and geopolymer binder for samples A and B as marked. Successive curves are offset by 0.04 units for clarity.

Results and Discussion

Practical considerations and effect of physical/chemical characteristics of precursors

The D_{50} value for each of the two aluminosilicate precursors has been reported previously as 10.60 μm and 12.75 μm , for A and B respectively²⁴, which is comparable to that of many common fly ashes. The Brunauer-Emmet-Teller (BET) surface areas of the aluminosilicate precursor powders are $142 \pm 2 \text{ m}^2/\text{g}$ and $147 \pm 2 \text{ m}^2/\text{g}$, respectively²⁴. This surface area

is an order of magnitude higher than those typically found for fly ashes of low unburnt carbon content, which are on the order of 0.1 - 10 m^2/g ^{30, 31}.

Figure 2. X-ray diffraction data for the precursor powder and geopolymer binder for a) sample A and b) sample B, cured for 7, 28 and 224 days.

During geopolymer synthesis the reaction mix hardened and formed a solid binder within approximately 2 minutes of initial mixing, indicating that the precursor powders are highly reactive. A relatively high water/solids mass ratio ($w/s = 0.75$) was also required to create a homogeneous paste during alkali activation. Both the high reactivity and high water requirement are consistent with the observation of a high surface area (resulting from intraparticle porosity) for each of the precursor powders.

Differential thermogravimetry

Differential thermogravimetric (DTG) data for the precursor powders and geopolymer binders are presented in Figure 1, and are broadly consistent with observations for geopolymers synthesised from metakaolin or fly ash. The mass losses from both the precursor powders and the geopolymers take place predominantly below 300°C. The mass loss peaks at 100 – 200°C in the DTG curves of the precursor powders and geopolymers are consistent with the removal of adsorbed water (present also in the precursor powders due to their hygroscopic nature), and the water supplied by the activating solution during geopolymer synthesis^{32, 33}.

A small mass loss peak is observed at 320°C in the DTG curve of geopolymer A cured for 224 days, and is associated with the loss of more tightly physically bound and zeolitic water³², however this peak is absent at 7 or 28 days. This suggests that rearrangement and structural ordering of the water-containing phases (e.g. zeolites) in this sample will continue as the reaction progresses. The DTG curve of the geopolymer B cured for 224 days also exhibits a mass loss peak at approximately 320°C. A small mass loss peak at approximately 270°C is also observed in the DTG curves for sample B cured for 7 and 28 days which is also likely to be due to the release of water from a transient phase which is formed at early age in this sample; this peak is also consistent with the temperature range in which more tightly physically bound and/or zeolitic water would be released from aluminosilicate materials³².

The DTG curves of both geopolymer formulations at all curing ages are relatively featureless at higher temperatures, with the gradual weight loss observed up to approximately 700°C attributed to dehydroxylation of the small number of bound silanol groups present^{32, 34, 35}.

X-ray Diffraction

X-ray diffraction data collected for the precursor powders and geopolymer binders are presented in Figure 2. The X-ray diffractograms for both precursor powders display a broad featureless hump at about 20 – 25° 2 θ typical of amorphous aluminosilicate glasses, while the X-ray diffractograms for the geopolymer binders in both samples exhibit a hump at approximately 29° 2 θ consistent with the formation of an N-

A-S-H type geopolymer gel^{36, 37}. The broad geopolymer hump in the X-ray diffractogram of sample A is approximately twice the intensity of that in sample B, indicating that the alkali-activation reaction has occurred to a greater extent in sample A. After 224 days of curing small amounts of the crystalline phases paragonite ($\text{NaAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$) (PDF # 12-0165), albite ($\text{NaAlSi}_3\text{O}_8$) (PDF # 10-0393) and sodium carbonate (Na_2CO_3) (PDF# 25-0815) are observed to have formed in sample A, while small amounts of paragonite are also observed in sample B. The moderately broad reflection which appears at approximately $23^\circ 2\theta$ in the XRD data for sample B cured for 224 days shows similarity with that of numerous zeolites, particularly within the Nickel-Strunz 09.GA group (natrolite, edingtonite, thomsonite, and related phases). This is likely to be due to a slight increase in ordering in the zeolite-like geopolymer gel phase during extended curing³⁸, consistent with the mass loss peak attributed to zeolitic water in the DTG curve for sample B as discussed above.

Figure 3. Infrared spectra (reported as transmittance) of the precursor powder and geopolymer binder for a) sample A and b) sample B, cured for 7, 28 and 224 days. Re-scaled plots highlighting the $1000\text{-}800\text{ cm}^{-1}$ region for the c) $2\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ and d) $4\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ formulations are provided for clarity.

Fourier transform infrared spectroscopy

FTIR spectra collected for each precursor powder and each geopolymer are presented in Figure 3. The spectra of both precursor powders exhibit bands at 1760 cm^{-1} which are attributed to H-O-H bending modes and indicate the presence of adsorbed water (a consequence of the hygroscopic nature of the precursor powders). The broad band centred at $\sim 1080\text{ cm}^{-1}$ is assigned to the asymmetric stretching vibrations of Si-O-T bonds (T = tetrahedral Si or Al) in highly polymerised silicates and aluminosilicates. This band in the spectrum of the $4\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ precursor is approximately twice the intensity of the corresponding feature in the $2\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ precursor, consistent with the designed chemistry of the powders. The Al(VI) present in the mullite-like structures which have previously been identified in the precursors using ^{27}Al MAS NMR²⁴ exhibit a shoulder at 1200 cm^{-1} ³⁹ and a band at 560 cm^{-1} ⁴⁰ as seen in Figure 3. The weak band observed at 800 cm^{-1} in Figure 3 is assigned to symmetric stretching of Si-O-Si bonds³⁹, and the band at 720 cm^{-1} is assigned to pseudo-lattice vibrations of small aluminosilicate rings^{41, 42} and vibrations of internal Si-O-Al oxygen bridges⁴². The small band observed at 1470 cm^{-1} is commonly assigned to asymmetric stretching of O-C-O bonds in carbonates⁴³, which may result from the presence of very small amounts of residual organics remaining from the powder synthesis²⁴.

The spectra of the geopolymer products exhibit stronger water bands at 1650 cm^{-1} , indicative of the presence of free and chemically bound water, while the small band at 1380 cm^{-1} indicates the presence of a small amount of sodium carbonate⁴⁴ as identified by XRD in some of the samples. A very intense sharp band is observed at approximately 960

cm^{-1} and is assigned to asymmetric stretching of T-O-T bonds⁴⁵. The shift of this band from 1080 cm^{-1} in the precursor powder to approximately 960 cm^{-1} in the geopolymer binder indicates that alkali-activation has generated a framework consisting of SiO_4 and AlO_4^- tetrahedra, consistent with the formation of an N-A-S-H gel. When extra sodium ions are associated with the polymerised tetrahedral aluminosilicate framework beyond the quantity required to balance the negative charges of AlO_4^- tetrahedra, the number of non-bridging oxygens in the structure increases and the band due to asymmetric stretching of Si-O-T bonds appears at a lower wavenumber than in a fully polymerised aluminosilicate framework⁴⁵. At each stage of curing for both samples this band is observed at wavenumbers similar to those previously observed for Si-O-T bonds in alkali-activated fly ash^{21, 46, 47}, although the position of this band in Figure 3 at the lower end of that wavenumber range indicates a high fraction of Al-O-Si linkages compared to Si-O-Si in the N-A-S-H gel reaction products of both samples^{47, 48}. This band shifts position to higher wavenumbers at later stages of curing (Figure 3c and d), suggesting that increased curing time facilitates structural rearrangement of the reaction products and greater formation of Si-O-Si linkages in the N-A-S-H gel, indicating preferential dissolution of Al from the precursor during early stages of reaction, with delayed dissolution of Si occurring as curing time is increased. The shoulder at approximately 870 cm^{-1} is assigned to the asymmetric stretching of Al-O-Si bonds linking AlO_4 and SiO_4 groups^{49, 50}, while the presence of a shoulder at approximately 1080 cm^{-1} on the main sharp peak in these spectra indicates that the geopolymer binders contain some unreacted precursor material.

The difference FTIR spectra of each geopolymer binder, obtained by subtraction of the spectra of the respective precursor powders from those of the hardened products at each age, are presented in Figure 4. By subtracting the spectra of the unreacted powders from those of the binders, the remaining spectral features can be attributed solely to the binder product. The two geopolymer formulations show bands at very similar wavenumbers and exhibiting very similar intensities, indicating the formation of a reaction product that exhibits little change in its bonding environments as a function of curing age.

Figure 3. Infrared spectra (transmittance) of the geopolymer binders cured for a) 7 days, b) 28 days and c) 224 days with infrared spectra of corresponding precursor powders subtracted.

A number of bands not readily observable in the spectra of the precursor powders or geopolymer binders are resolved in the subtracted spectra, Figure 4. The band at 1150 cm^{-1} is assigned to Si-O-Si bridge vibrations⁵¹, while 5-membered single rings and 6-membered double rings comprised of TO_4 tetrahedral units will contribute to the bands at 580 cm^{-1} and 500 cm^{-1} ⁴². The shift of these bands to higher wavenumbers at later age suggests that the Si/Al ratio of these aluminosilicate rings has increased^{21, 47, 51}. These FTIR results suggest that the N-A-S-H gel formed by alkali-activation of

each precursor powder displays a comparable local chemical structure, despite the differing initial compositions. The molecular structure of the gel shows only minor changes after the first 7-28 days, even as longer-range crystalline ordering is continuing gradually to develop as identified by XRD and DTG.

Environmental scanning electron microscopy/energy dispersive X-ray spectroscopy

BSE images of the hardened specimens (Figure 5) show a dense and homogeneous geopolymer binder (dark grey), with partially reacted aluminosilicate precursor powder particles (light grey) embedded within the matrix, in a distribution that is characteristic of geopolymer systems⁵². The geopolymer binder of sample B appears to have more embedded residual particles than sample A, consistent with the XRD data presented in Figure 2, and suggesting a greater extent of reaction for the system with a lower Si/Al ratio. Elemental maps of both geopolymer binders show two distinct phase regions in each, one higher in Si content and one higher in Al content, at both 7 and 28 days of age.

Incongruent dissolution of the precursor particles is indicated by the presence of a thin shell of higher Si content ($\text{Si/Al} \approx 3.5$) surrounding the residual precursor grains (Figure 6), which is most likely due to preferential dissolution of aluminium over silicon during the early stages of reaction before stoichiometric release of aluminium and silicon commences⁵³. Preferential dissolution of Al from aluminosilicate glasses and minerals via Al-proton exchange reactions has been previously observed and results in the formation of an aluminium deficient layer on the surface of the aluminosilicate material⁵³⁻⁵⁶. Si atoms previously bonded to Al via Si(IV)-O-Al(IV) linkages are subsequently exposed and dissolution of liberated Si occurs. The thermodynamic basis of this mechanism lies in the fact that Al-O bonds are not as strong as Si-O bonds, and are therefore more easily broken⁵⁴.

Figure 4. ESEM backscattered electron images and EDX elemental maps of the geopolymer binder cured for 28 days for samples A and B as marked.

Consequently formation of Al-O-Si linkages is preferential over Si-O-Si linkages^{38, 57}. It follows that increased Al content will lead to an increased rate of dissolution of aluminosilicate materials. This has been observed experimentally^{54, 58}, and provides a likely explanation for the larger extent of reaction observed at early age (cured 7 days) for the binder for sample A compared with sample B. Consistent with this observation, cation ratios for the geopolymer binder A cured for 7 days, as observed by ESEM-EDX (Figure 7a), exhibit a range of values clustered around two distinct regions. These regions are attributed to a reaction product phase with $2 \leq \text{Si/Al} \leq 4.5$ and $1.5 \leq \text{Na/Al} \leq 2$, and another which exhibits cation ratios much more similar to the bulk composition of the reaction mix ($\text{Si/Al} \approx 1.5$ and $\text{Na/Al} \approx 1.2$). No regions of the binder are observed to exhibit compositions equal to that of the precursor powder ($\text{Si/Al} = 1$ and free from Na), indicating that all precursor powder particles have

been chemically altered during alkali-activation, although their morphology remains intact. During the early stages of reaction, the Al-O linkages present in the interior of precursor particles are likely to be at least partially shielded from interactions with the activating solution due to the tortuous route the activating solution must take to reach the particle interior, even where the particles are highly porous. The extent to which this occurs will increase with increasing precursor particle diameter, and consequently the Si/Al ratios of the partially leached precursor particles vary, as seen Figure 7a. Soluble aluminium reduces the solubility of silica in water as aqueous Al species adsorb onto the surface of solid silica particles and hinder the dissolution process^{54, 59-61}.

Figure 5. ESEM backscattered electron (BSE) images and EDX spectra of each region identified in the micrograph of the geopolymer binder cured for 7 days for sample A.

Figure 7. Summary of atomic ratios Na/Al versus Si/Al (between 66 and 85 measurements per sample) for reacted and unreacted regions of the a) sample A and b) sample B geopolymer binders cured for 7, 28 and 224 days, as marked, determined by ESEM – EDX analysis. Approximate regions defined for N-A-S-H determined from⁶² (outlined in green) and⁶³ (outlined in blue). Approximate region of N-A-S-H chemistry outlined in red determined in the study presented here.

Cation ratios for the 28-day cured geopolymer A exhibit a tighter cluster of values similar to that of the reaction mix ($\text{Si/Al} \approx 1.5$ and $\text{Na/Al} \approx 1.2$), as well as another region of values where $2 \leq \text{Si/Al} \leq 4$ and $1.2 \leq \text{Na/Al} \leq 1.5$ and a more even distribution than at earlier age. Cation ratios for the 224-day cured geopolymer A are tightly clustered around the bulk composition at $\text{Si/Al} \approx 1.5$ and $\text{Na/Al} \approx 1.2$, with only two of the measured points exhibiting slightly higher Si content, and three higher Na content. Regions with anomalously high Na content appear to exhibit a high degree of porosity, suggesting that the high Na content in these regions is deposited by desiccation of a pore solution rich in NaOH⁶⁴. BSE images for geopolymer A cured for 28 and 224 days show that as the reaction proceeds, the Si-rich (partially dealuminated) precursor powder particles continue to react and that after 224 days, with the exception of the aforementioned Na-rich deposits, a predominantly homogeneous binder has formed, meaning that the chemical composition of the binder moves toward that of the reaction mix.

Cation ratios for 7-day cured geopolymer B (Figure 7b) display a broad range of values within the region $0.25 \leq \text{Si/Al} \leq 4$, $0.25 \leq \text{Na/Al} \leq 1.75$ and $2 \leq \text{Si/Na} \leq 5$. However, after 28 days these values cluster around two distinct regions; one with $0.25 \leq \text{Si/Al} \leq 0.75$ and $0.25 \leq \text{Na/Al} \leq 0.50$, and the other with $2.5 \leq \text{Si/Al} \leq 5$ and $0.75 \leq \text{Na/Al} \leq 1.75$. These regions are attributed to a mixture of the partially dealuminated residual precursor powder particles with an N-A-S-H gel of variable Si/Al ratio, similar to that formed in sample A, and an Al-rich region, respectively. This Al-rich region is like-

ly to be an intimate intermixture of the residual undissolved mullite-type glass from the precursor particles²⁴, along with some contribution from N-A-S-H gel, as the formation of any new discrete high-alumina phases is unlikely in these systems which do not contain calcium or magnesium. The N-A-S-H gel formed in sample B exhibits a higher Si content than that of sample A, and as such less Na cations will be required to charge balance the AlO_4 tetrahedra. This is consistent with the lower Na content of the N-A-S-H gel in geopolymer B.

The thin shell of higher Si content surrounding the precursor powder particles in geopolymer A is absent from the BSE images of geopolymer B. It is possible that the higher Si content of the $4\text{SiO}_2\text{-Al}_2\text{O}_3$ precursor powder in this mix has resulted in closer-to-congruent dissolution of Al and Si, and this will be discussed in detail below during analysis of the ^{29}Si MAS NMR results.

Solid state MAS NMR spectroscopy

^{27}Al MAS NMR spectroscopy

The ^{27}Al MAS NMR spectra of the precursor powders and geopolymer binders for both sample formulations are presented in Figure 8. The precursor powders consist of poorly ordered Al(IV) environments as well as Al(V) and Al(VI) mullite-like environments²⁴.

In both samples the Al(V) and Al(VI) environments are largely consumed upon alkali-activation, producing Al(IV) (indicated by the peak at centred at $\delta \sim 59$ ppm), consistent with previous observations for alkali-activation of reactive aluminosilicates³. Some Al(VI) remains in sample B, in agreement with the assignment of the very Al-rich regions identified in the EDX data to residual mullite-like glass. The resonance attributed to Al(IV) is approximately 2 ppm downfield of that of the precursor powder, within the region of q^4 environments which have been observed in metakaolin-based^{65, 66} and fly ash-based geopolymer binders^{28, 67}. The presence of exclusively Al(IV) in the gel is expected due to the presence of excess charge balancing Na cations⁶⁸. The breadth of the resonance assigned to Al(IV) (along with the amorphous nature of these binders as identified by XRD) suggests that the Al(IV) within the geopolymers A and B exists within a disordered aluminosilicate structure.

The peak assigned to Al(IV) remains essentially unchanged in the spectra of the geopolymer binders at different curing ages, indicating that the nanostructural changes involving Al sites occur predominantly within the first 7 days of curing. However, this does not preclude structural rearrangement in which Al remains in a similar coordination state and bonding environment. A small peak at approximately 8 ppm is evident in the spectra of geopolymer A cured for 224 days and geopolymer B cured for 7, 28 and 224 days. This peak is assigned to the Al(VI) within the paragonite identified in the XRD data for these more mature binders⁶⁹.

^{29}Si MAS NMR spectroscopy

The ^{29}Si MAS NMR spectra of the precursor powders and geopolymer binders, with associated deconvolutions, are presented in Figure 9. Both precursor powders consist pre-

dominantly of a highly polymerised Si-rich phase in which Si exists as $Q^4(\text{OAl})$ environments, as well as a phase containing mullite-like structures where Si exists in lower coordination states²⁴. The dependence of chemical shift on Al substitution within $Q^4(m\text{Al})$ environments has been widely reported⁷⁰⁻⁷², and is commonly used for identification of Si environments within ^{29}Si MAS NMR spectra. This, however, implicitly assumes solely of Si(IV) – O – Al(IV) linkages exist within these phases. Lower coordination Si species (Q^1 , $Q^2(m\text{Al})$ or $Q^3(m\text{Al})$) are not commonly observed in aluminosilicate glasses with no alkalis or alkali earths, and consequently these environments are not expected in the precursor for samples A and B. The apparently lower coordination Si species contributing to the ^{29}Si MAS NMR spectra of these samples are instead likely those which participate in Si(IV) – O – Al(V,VI) bonding. This significantly alters the observed chemical shift of the $Q^4(m\text{Al})$ environments compared to the situation when all Al is tetrahedral⁷¹ and consequently each peak within the -85 ppm to -105 ppm cannot be straightforwardly assigned to a single Si environment.

Alkali activation of both samples A and B results in the formation of four new Si environments indicated by the peaks at -84.5 ppm, -88 ppm, -95 ppm and -101.5 ppm and attributed to $Q^4(4\text{Al})$, $Q^4(3\text{Al})$, $Q^4(2\text{Al})$ and $Q^4(1\text{Al})$, respectively. This is indicative of the formation of a highly polymerised, highly Al substituted Si environment characteristic of formation of an N-A-S-H gel^{12, 28, 70, 73}. Peaks attributed to the residual precursor powder are marked in grey in Figure 9²⁴. The higher intensity of these peaks in the ^{29}Si MAS NMR spectra of geopolymer B compared to geopolymer A at equivalent ages indicates a lower extent of reaction during alkali-activation of the $4\text{SiO}_2\text{-Al}_2\text{O}_3$ precursor powder, consistent with the ESEM BSE images, XRD and ^{27}Al MAS NMR analysis for these samples.

The quantification of the component peaks for the two geopolymer mixes at each age is summarised in Figure 10. A significant relative increase in the peaks attributed to $Q^4(1\text{Al})$ and $Q^4(2\text{Al})$ (-101.5 and -95 ppm, respectively), with a corresponding decrease in the peak attributed to $Q^4(4\text{Al})$ (-84.5 ppm), is observed in the spectra of geopolymer A at 28 days compared to 7 days. This suggests that some degree of structural rearrangement and greater crosslinking within the N-A-S-H gel via formation of Si-O-Si linkages occurs with increased curing time, but this is predominantly complete by 28 days, consistent with the TGA and XRD data for this sample. For the main N-A-S-H gel reaction product in sample A, preferential dissolution of Al from the precursor powder, and more rapid cross-linking of Al-containing species, occurs during the first 7 days of alkali-activation. This results in the formation of an N-A-S-H gel with high amount of Al-O-Si linkages, after which dissolution of Si becomes dominant and structural rearrangement of the N-A-S-H gel occurs through crosslinking via condensation reactions between Si-OH groups to create Si-O-Si linkages, resulting in an apparent increase in the Si/Al ratio of the gel. This is consistent with the observations for this sample by FTIR and SEM-EDX as discussed above.

Figure 6. ^{27}Al MAS NMR spectra of the precursor powder and geopolymer binder a) sample A and b) sample B. Data for precursor powders reproduced from²⁴. Spinning side bands are indicated by *.

Figure 9. ^{29}Si MAS NMR spectra of: a) sample A geopolymer cured 224 days, b) sample B geopolymer cured 224 days, c) sample A geopolymer cured 28 days, d) sample B geopolymer cured 28 days, e) sample A geopolymer cured 7 days, f) sample B geopolymer cured 7 days, g) sample A precursor, and h) sample B precursor. In each case the fit is the sum of the deconvoluted peaks. In a) – d) deconvoluted peaks attributed to the unreacted precursor are shown in grey. Peak label subscripts indicate environments existing within the precursor powder (p) and reaction product (r). Data for precursor powders reproduced from²⁴.

Figure 10. Normalised intensity of peaks attributed to new $\text{Q}^4(\text{mAl})$ silicon environments formed upon alkali-activation of the a) $2\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ geopolymer binder and b) $4\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ geopolymer binder.

As the reaction for geopolymer B progresses the Si/Al ratio of the N-A-S-H gel reaction product decreases slightly between 7 and 28 days (visible in Fig 10 as a relative decrease in $\text{Q}^4(3\text{Al})$, $\text{Q}^4(2\text{Al})$ and $\text{Q}^4(1\text{Al})$ and a relative increase in $\text{Q}^4(4\text{Al})$) and then increases significantly after 224 days. The greater Si content of the precursor powder for this sample has provided excess Si (in the form of both $\text{Q}^n(\text{mAl})$ and $\text{Q}^4(0\text{Al})$) during the initial stages of reaction and consequently a slower rate of dissolution is observed. By the same mechanism discussed above, preferential dissolution of Al from the precursor powder occurs past 7 days of curing, resulting in the formation of greater amounts of $\text{Q}^4(4\text{Al})$ (and hence a decrease in the Si/Al ratio). Exhaustion of the available Al content in the precursor powder then allows dissolution of Si to become dominant at later ages.

^{23}Na MAS NMR spectroscopy

The ^{23}Na MAS NMR spectra of the geopolymer binders are presented in Figure 11. The ^{23}Na MAS NMR spectra for both samples exhibit a single broad resonance at approximately -4 ppm which is attributed to sodium associated with aluminium-centred tetrahedra in a charge balancing capacity within the alkali aluminosilicate gel framework⁶⁵. This resonance is observed in the spectra of both samples at all curing ages, indicating that there is no observable variation in the environment in which Na in these geopolymer binder exists. Previous studies have reported a narrow resonance at approximately 0 ppm within the ^{23}Na MAS NMR spectra of low-Si alkali-activated metakaolin geopolymers at early age, which was attributed to aqueous sodium cations which provide a charge balancing function for $\text{Al}(\text{OH})_4^-$ in the pore solution of these binders⁶⁵. The absence of any significant amount of free pore solution alkalis remaining in the samples studied here after 7 days of curing is likely to be due to the high reactivity of the precursor powders and drying of the samples prior to analysis.

Figure 7. ^{23}Na MAS NMR spectra of the geopolymer binder for sample A (black line) and sample B (grey line) cured for 7, 28 and 224 days as marked

Perspectives

The N-A-S-H type gel reaction products in each geopolymer are chemically similar to those produced through alkali-activation of metakaolin⁷⁴ or fly ash^{62, 63} at SiO_2 and Al_2O_3 contents similar to those of the high-purity synthetic amorphous aluminosilicate powders used here, however local cation coordination environments within these gels show significant differences, providing insight into the role of precursor chemistry in the phase evolution of alkali-aluminosilicate gels in geopolymer systems. The absence of K^+ , Mg^{2+} and Fe^{3+} from the systems studied here suggests that these network modifying cations are likely to control local coordination environments of network forming cations Al^{3+} and Si^{4+} and subsequent development of the microstructure and physical properties of aluminosilicate geopolymers.

The dependence of dissolution rates of Al and Si species on the precursor Al/Si ratio suggests careful design of geopolymer precursor chemistry can enable control of precursor dissolution and the degree of polymerisation of Si-O-T linkages within the N-A-S-H gel as a function of time. As the N-A-S-H gel degree of polymerisation and Al/Si ratio has been shown to dictate material properties and performance (such as strength and durability)^{21, 74-76}, this can be extended to enable control of geopolymer physical properties as a function of curing time (for example increasing early strength development and durability) by selection of precursors or mixtures of precursors which will enable formation of the desired N-A-S-H gel chemistry. These findings have significant implications for geopolymer mix design. The synthetic gels produced here consequently provide a promising new direction of inquiry into the durability of these materials.

Conclusions

Stoichiometrically controlled alkali-aluminosilicate gels are produced via alkali-activation of high-purity amorphous aluminosilicate powders. The chemistry of the precursor strongly affects gel microstructure during alkali-activation. Chemical composition of the main N-A-S-H type gel reaction product as well as the reaction kinetics governing its formation are closely related to the Si/Al ratio of the precursor, with increased Al content leading to an increased rate of reaction and decreased Si/Al ratio in the N-A-S-H type gel. Paragonite is formed in each geopolymer cured for 224 days, while small amounts of albite and sodium carbonate are formed in alkali-activated $2\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ cured for 224 days.

Despite their differing chemical compositions, each N-A-S-H type gel comprises of aluminium and silicon tetrahedra linked via oxygen bridges, with sodium taking on a charge balancing function. The predominant gel microstructure in each sample is formed after curing for 7 days however relative proportions of local coordination environments evolve

with increased curing time due to structural rearrangement as the alkali-activation reaction progresses. Preferential dissolution of Al from the precursor controls phase evolution during the early stages of reaction and suggests that the reaction kinetics governing alkali-activation of aluminosilicate precursors, including potential incongruity of dissolution, are strongly dependent on precursor chemical composition.

The stoichiometrically controlled alkali-aluminosilicate gels produced in this study constitute a chemically simplified model system which provides a novel research tool for the study of phase evolution and microstructural development within geopolymer systems. This has significant relevance to the study of physicochemical phenomenon controlling key durability issues associated with alkali-aluminosilicate gels designed for refractory, construction, radioactive waste immobilisation, biomaterial, fibre composite and other niche applications. Furthermore, the findings presented here indicate intricate control over time-dependent geopolymer physical properties can be attained through careful precursor mix design, which in turn is enabled by a comprehensive understanding of the physicochemical phenomena governing geopolymer gel formation.

AUTHOR INFORMATION

Corresponding author

*Author to whom correspondence should be addressed. Phone: +61 424 320 182. Email: rackel.san@unimelb.edu.au

Author Contributions

All authors have given approval to the final version of the manuscript.

Funding Sources

This work has been funded in part by the Australian Research Council (ARC), including support through the Particulate Fluids Processing Centre, a Special Research Centre of the ARC. The University of Melbourne also provided support through an Overseas Research Experience Scholarship to support an extended visit by the first author to the University of Sheffield.

Notes

The authors declare no competing financial interest.

Acknowledgements

We wish to thank and acknowledge Dr Susan Bernal, University of Sheffield, for very helpful discussions on this topic over several years, and Mr Roger Curtain, Advanced Microscopy Facility, The University of Melbourne for assistance with scanning electron microscopy experiments.

References

1. M. C. G. Juenger, F. Winnefeld, J. L. Provis and J. H. Ideker, *Cement and Concrete Research*, 2011, **41**, 1232-1243.
2. P. Duxson, J. L. Provis, G. C. Lukey and J. S. J. van Deventer, *Cement and Concrete Research*, 2007, **37**, 1590-1597.
3. J. Davidovits, *Journal of Thermal Analysis*, 1991, **37**, 1633-1656.
4. J. L. Provis and J. S. J. van Deventer, *Geopolymers: Structure, Processing, Properties and Industrial Applications*, Woodhead, Cambridge, 2009.
5. C. J. Shi, P. V. Krivenko and D. M. Roy, *Alkali activated cements and concretes*, Taylor and Francis, London, 2006.
6. P. Duxson and J. L. Provis, *Journal of the American Ceramic Society*, 2008, **91**, 3864-3869.
7. P. Duxson, A. Fernandez-Jimenez, J. L. Provis, G. C. Lukey, A. Palomo and J. S. J. van Deventer, *Journal of Materials Science*, 2007, **42**, 2917-2933.
8. S.-D. Wang, X.-C. Pu, K. L. Scrivener and P. L. Pratt, *Advances in Cement Research*, 1995, **7**, 93-102.
9. J. S. J. Van Deventer, J. L. Provis and P. Duxson, *Minerals Engineering*, 2012, **29**, 89-104.
10. J. L. Provis, A. Palomo and C. Shi, *Cement and Concrete Research*, 2015, DOI: 10.1016/j.cemconres.2015.04.013.
11. X.-m. Cui, L.-p. Liu, G.-j. Zheng, R.-p. Wang and J.-p. Lu, *Journal of Non-Crystalline Solids*, 2010, **356**, 72-76.
12. I. Garcia-Lodeiro, A. Fernández-Jimenez, A. Palomo and D. E. Macphee, *Cement and Concrete Research*, 2010, **40**, 27-32.
13. I. Garcia-Lodeiro, A. Palomo, A. Fernández-Jiménez and D. E. Macphee, *Cement and Concrete Research*, 2011, **41**, 923-931.
14. G. Zheng, X. Cui, W. Zhang and Z. Tong, *Journal of Materials Science*, 2009, **44**, 3991-3996.
15. S. Mallicoat, P. Sarin and W. M. Kriven, in *Developments in Advanced Ceramics and Composites: Ceramic Engineering and Science Proceedings*, John Wiley & Sons, New York, 2008, pp. 37-44.
16. M. Gordon, J. L. Bell and W. M. Kriven, in *Advances in Ceramic Matrix Composites X*, John Wiley & Sons, New York, 2004, pp. 95-106.
17. R. J. Myers, E. L'Hopital, J. L. Provis and B. Lothenbach, *Dalton Transactions*, 2015, **44**, 13530-13544.
18. R. J. Myers, E. L'Hôpital, J. L. Provis and B. Lothenbach, *Cement and Concrete Research*, 2015, **68**, 83-93.
19. B. Subotić, A. M. Tonejc, D. Bagović, A. Čizmek and T. Antonić, in *Studies in Surface Science and Catalysis*, eds. J. Weitkamp, H. G. Karge, H. Pfeifer and W. Hölderich, Elsevier, Amsterdam, 1994, vol. 84, pp. 259-266.
20. S. Yang, A. Navrotsky and B. L. Phillips, *Journal of Physical Chemistry B*, 2000, **104**, 6071-6080.
21. A. Hajimohammadi, J. L. Provis and J. S. J. van Deventer, *Chemistry of Materials*, 2010, **22**, 5199-5208.
22. A. Hajimohammadi, J. L. Provis and J. S. J. van Deventer, *Cement and Concrete Research*, 2011, **41**, 210-216.
23. B. Walkley, J. L. Provis, R. San Nicolas, M. A. Sani and J. S. J. van Deventer, *Advances in Applied Ceramics*, 2015, **114**, 372-377.
24. B. Walkley, R. San Nicolas, M. A. Sani, J. D. Gehman, J. S. J. van Deventer and J. L. Provis, *Powder Technology*, (submitted) 2016.
25. I. Ismail, S. A. Bernal, J. L. Provis, S. Hamdan and J. S. J. Deventer, *Journal of Materials Science*, 2013, **48**, 3566-3577.
26. M. Fechtelkord, F. Stief and J.-C. Buhl, *American Mineralogist*, 2001, **86**, 165-175.
27. F. Delaglio, S. Grzesiek, G. Vuister, G. Zhu, J. Pfeifer and A. Bax, *J Biomol NMR*, 1995, **6**, 277-293.
28. S. A. Bernal, J. L. Provis, B. Walkley, R. San Nicolas, J. D. Gehman, D. G. Brice, A. R. Kilcullen, P. Duxson and J. S. J. van Deventer, *Cement and Concrete Research*, 2013, **53**, 127-144.
29. J. L. Provis, P. Duxson, G. C. Lukey and J. S. J. van Deventer, *Chemistry of Materials*, 2005, **17**, 2976-2986.
30. E. C. Arvaniti, M. C. G. Juenger, S. A. Bernal, J. Duchesne, L. Courard, S. Leroy, J. L. Provis, A. Klemm and N. De Belie, *Materials and Structures*, 2015, **48**, 3687-3701.

31. E. C. Arvaniti, M. C. G. Juenger, S. A. Bernal, J. Duchesne, L. Courard, S. Leroy, J. L. Provis, A. Klemm and N. De Belie, *Materials and Structures*, 2015, **48**, 3675-3686.
32. S. A. Bernal, E. D. Rodriguez, R. Mejía de Gutiérrez, M. Gordillo and J. L. Provis, *Journal of Materials Science*, 2011, **46**, 5477-5486.
33. H. Rahier, B. Van Mele and J. Wastiels, *Journal of Materials Science*, 1996, **31**, 80-85.
34. E. D. Rodríguez, S. A. Bernal, J. L. Provis, J. Paya, J. M. Monzo and M. V. Borrachero, *Cement and Concrete Composites*, 2013, **35**, 1-11.
35. P. Duxson, G. C. Lukey and J. S. J. van Deventer, *Journal of Non-Crystalline Solids*, 2006, **352**, 5541-5555.
36. J. L. Provis, G. C. Lukey and J. S. J. van Deventer, *Chemistry of Materials*, 2005, **17**, 3075-3085.
37. G. K. Sun, J. F. Young and R. J. Kirkpatrick, *Cement and Concrete Research*, 2006, **36**, 18-29.
38. J. L. Provis and S. A. Bernal, *Annual Review of Materials Research*, 2014, **44**, 299-327.
39. J. Temuujin, K. Okada and K. J. D. MacKenzie, *Ceramics International*, 1999, **25**, 85-90.
40. X.-H. Jin, L. Gao and J.-K. Guo, *Journal of the European Ceramic Society*, 2002, **22**, 1307-1311.
41. M. Handke, M. Sitarz and W. Mozgawa, *Journal of Molecular Structure*, 1998, **450**, 229-238.
42. W. Mozgawa, *Journal of Molecular Structure*, 2001, **596**, 129-137.
43. S. A. Bernal, J. L. Provis, V. Rose and R. Mejía de Gutiérrez, *Cement and Concrete Composites*, 2011, **33**, 46-54.
44. C. K. Huang and P. F. Kerr, *American Mineralogist*, 1960, **45**, 311.
45. W. K. W. Lee and J. S. J. van Deventer, *Langmuir*, 2003, **19**, 8726-8734.
46. C. A. Rees, J. L. Provis, G. C. Lukey and J. S. J. van Deventer, *Langmuir*, 2007, **23**, 8170-8179.
47. A. Fernández-Jiménez and A. Palomo, *Microporous and Mesoporous Materials*, 2005, **86**, 207-214.
48. C. A. Rees, Ph.D., The University of Melbourne, 2007.
49. V. C. Farmer, *The Infrared Spectra of Minerals*, Mineralogical Society, London, 1974.
50. J. A. Gadsden, *Infrared spectra of minerals and related inorganic compounds*, Butterworths, London, 1975.
51. M. Criado, A. Fernández-Jiménez and A. Palomo, *Microporous and Mesoporous Materials*, 2007, **106**, 180-191.
52. S. A. Bernal, R. San Nicolas, R. J. Myers, R. Mejía de Gutiérrez, F. Puertas, J. S. J. van Deventer and J. L. Provis, *Cement and Concrete Research*, 2014, **57**, 33-43.
53. E. H. Oelkers, J. Schott and J.-L. Devidal, *Geochimica et Cosmochimica Acta*, 1994, **58**, 2011-2024.
54. E. H. Oelkers and S. R. Gislason, *Geochimica et Cosmochimica Acta*, 2001, **65**, 3671-3681.
55. J.-M. Gautier, E. H. Oelkers and J. Schott, *Geochimica et Cosmochimica Acta*, 1994, **58**, 4549-4560.
56. E. H. Oelkers and J. Schott, *Geochimica et Cosmochimica Acta*, 1995, **59**, 5039-5053.
57. C. E. White, J. L. Provis, G. J. Kearley, D. P. Riley and J. S. J. van Deventer, *Dalton Transactions*, 2011, **40**, 1348-1355.
58. W. H. Casey, H. R. Westrich and G. R. Holdren, *American Mineralogist*, 1991, **76**, 211-217.
59. R. K. Iler, *Journal of Colloid and Interface Science*, 1973, **43**, 399-408.
60. H. A. Gasteiger, W. J. Frederick and R. C. Streisel, *Ind Eng Chem Res*, 1992, **31**, 1183-1190.
61. B. R. Bickmore, K. L. Nagy, A. K. Gray and A. R. Brinkerhoff, *Geochimica et Cosmochimica Acta*, 2006, **70**, 290-305.
62. A. Fernández-Jiménez and A. Palomo, *Cement and Concrete Research*, 2005, **35**, 1984-1992.
63. F. Winnefeld, A. Leemann, M. Lucuk, P. Svoboda and M. Neuroth, *Construction and Building Materials*, 2010, **24**, 1086-1093.
64. S. A. Bernal, R. San Nicolas, J. S. J. van Deventer and J. L. Provis, *ALCONPAT Journal*, 2015, **5**, 30-41.
65. P. Duxson, G. C. Lukey, F. Separovic and J. S. J. van Deventer, *Industrial and Engineering Chemistry Research*, 2005, **44**, 832-839.
66. T. T. Tran, S. A. Bernal, D. Herfort and J. Skibsted, *Proceedings of the 10th International Congress for Applied Mineralogy*, Trondheim, 2011, 707-715.
67. F. Puertas and A. Fernandez-Jimenez, *Cement and Concrete Composites*, 2003, **25**, 287-292.
68. J. F. Stebbins, S. Kroeker, S. Keun Lee and T. J. Kiczanski, *Journal of Non-Crystalline Solids*, 2000, **275**, 1-6.
69. H. J. Jakobsen, N. C. Nielsen and H. Lindgreen, *American Mineralogist*, 1995, **80**, 247-252.
70. P. Duxson, J. L. Provis, G. C. Lukey, F. Separovic and J. S. J. v. Deventer, *Langmuir*, 2005, **21**, 3028-3036.
71. G. Engelhardt and D. Michel, *High-resolution solid state NMR of silicates and zeolites*, Wiley, Chichester, 1987.
72. J. Klinowski, *Progress in Nuclear Magnetic Resonance Spectroscopy*, 1984, **16**, 237-309.
73. I. García-Lodeiro, A. Fernández-Jiménez, A. Palomo and D. E. Macphee, *Journal of the American Ceramic Society*, 2010, **93**, 1934-1940.
74. P. Duxson, J. L. Provis, G. C. Lukey, S. W. Mallicoat, W. M. Kriven and J. S. J. van Deventer, *Colloids and Surfaces A*, 2005, **269**, 47-58.
75. A. Fernández-Jiménez, A. Palomo, I. Sobrados and J. Sanz, *Microporous and Mesoporous Materials*, 2006, **91**, 111-119.
76. L. Weng, K. Sagoe-Crentsil, T. Brown and S. Song, *Materials Science and Engineering B*, 2005, **117**, 163-168.