



## The effect of silica availability on the mechanism of geopolymerisation

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### ABSTRACT

The effect of silica availability on geopolymer binder formation is investigated in the geothermal silica–sodium aluminate–water system, using sodium silicate solution as an additional, highly available silica source. Time-resolved and spatially-resolved FTIR data are combined to provide a mechanistic understanding of the role of silica availability in controlling geopolymer nucleation and gel growth behaviour. A higher degree of alumina contribution to geopolymer gels and newly formed crystal phases is observed in systems with higher silica availability. Gel nucleation is observed to take place in the region immediately surrounding the solid silica source particles when no dissolved silica is initially supplied. Conversely, mixes which initially contain dissolved silica show nucleation in bulk regions, and involving more of the Al which is rapidly released from the sodium aluminate precursor. These differences in nucleation lead to a more chemically heterogeneous binder in the case where silica is released more gradually.

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### 1. Introduction

Geopolymer binders, formed by alkaline activation of aluminosilicate precursors, are attracting interest as a “green” cement [1–3], because through the use of industrial wastes such as geothermal silicas, fly ashes and mineralogical slags as source materials, there is the possibility to achieve a significantly lower CO<sub>2</sub> emission per tonne in comparison with OPC [1,2,4,5]. With increasing production volumes, geopolymer and other alkali-activated binders are also becoming cost-competitive with Portland cement, and have found utilisation in major infrastructure projects internationally; initially in the former Soviet Union and in China [6–8], and now increasingly in Australia and elsewhere internationally as the political and financial incentives for CO<sub>2</sub> emission reductions grow [3].

However, there are many aspects of geopolymer synthesis chemistry which are not yet fully understood. There has been detailed analysis of the roles played in the geopolymer synthesis process by the kinetics of availability of alumina [9–12] and calcium [13,14] within geopolymer-forming systems, and the effect of silica concentration is well known [15–19], but little has been published regarding the effect of the rate of silica release in determining geopolymer gel structure and reaction mechanisms. This is mainly due to the difficulty associated with separating the effects of silica availability (in terms of reaction kinetics) and silica concentration within the limitations of a standard ‘two-part’ (solid precursor plus alkaline activating solution) geopolymer mix.

Sodium aluminate solution and silica fume have previously been used to make simplified ‘two-part’ geopolymer mixtures [20], and the recent development of ‘one-part’ (solid precursor plus water) geopolymer mixes based on very finely divided silica (silica fume or geothermal silica) and solid sodium aluminate [21,22] provides opportunities for advances in this area. It is now possible to design geopolymer mixes with the same composition and alumina release rates, while tailoring the silica release rate by using either sodium silicate solution, geothermal silica, or a mixture of the two. This provides the opportunity to directly control silica release rates, and to study geopolymer chemistry and performance as a function of silica availability in the initial stages of the reaction.

From the information available to date, it is believed that high early silica availability should lead to faster conversion of solid aluminosilicate sources to geopolymer gel [23,24]. However, it is not known whether this more rapid conversion (which can also be achieved to some extent by nanoparticle seeding of the reaction mixture [25,26]) is specifically desirable in terms of microstructure and strength development. Thus, understanding geopolymer characteristics as a function of the rate of silica availability will be important in understanding and controlling the behaviour of geopolymeric binders.

Analysis of geopolymers using synchrotron radiation-based Fourier transform infrared (SR-FTIR) spectromicroscopy has shown the capabilities of this powerful technique in spatially-resolved investigation of chemical variations in geopolymeric binders [11]. This paper presents the results of an investigation using this technique, along with X-ray diffraction and time-resolved FTIR spectroscopy, to analyse the effects of timed release of silica on the nanostructure and microstructure of geopolymer binders. Sodium aluminate is the

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alumina source for all samples produced here; geothermal silica is used as a 'slow release' silica source, and waterglass (sodium silicate solution) where more rapid silica availability is desired.

## 2. Materials and methods

To synthesise a geopolymer mix with relatively slow silica availability (denoted G1), washed, dried and milled geothermal silica (Cerro Prieto geothermal power station, Mexico, 96 wt.% SiO<sub>2</sub>, loss on ignition 1.3 wt.%, remainder <0.5 wt.% of each of Na, Mg, Al, K, Ca, Mn and Fe [22]) was mixed with solid sodium aluminate (Aldrich; 55.2 wt.% Al<sub>2</sub>O<sub>3</sub> and 42.7 wt.% Na<sub>2</sub>O) to attain an SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of 3.0:1, and then water was added to this solid mixture to give an H<sub>2</sub>O/Na<sub>2</sub>O molar ratio of 7.0:1 (i.e. overall Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ≈ 1.3).

To provide more rapidly available silica, a commercial sodium silicate solution (Grade N, PQ Australia), with composition 8.9 wt.% Na<sub>2</sub>O, 28.7 wt.% SiO<sub>2</sub> and 62.4 wt.% H<sub>2</sub>O, was also used. Two mixes (denoted G2 and G3) were made with the addition of this silicate solution; a summary of the compositions of the three samples is presented in Table 1. In G2, the Si source blend was 85 wt.% from geothermal silica and 15 wt.% from sodium silicate solution (giving overall Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ≈ 1.4), while in G3, the Si source was 70 wt.% from geothermal silica and 30 wt.% from sodium silicate solution (giving overall Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ≈ 1.5). As the difference in Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> ratios across the sample set was less than 0.2, NaOH was not added to adjust the composition for these samples. Sodium aluminate was also used in samples G2 and G3 as the sole alumina source, as well as providing alkali, and the raw material composition was adjusted to maintain similar SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O/Na<sub>2</sub>O molar ratios of 3.0:1 and 7.0:1 respectively. Therefore, three mixes were made with different silica availabilities but similar compositions, with G3 having the highest silica availability in the early stages of the reaction and G1 having the lowest silica availability. All samples were sealed and cured at 40 °C until analysis.

Crystalline phases were identified using X-ray diffraction (XRD) (Phillips PW-1800) with CuKα X-rays, operating at 30 mA and 40 kV with 0.02° 2θ steps, 2 s step<sup>-1</sup>. Structural characteristics of geopolymeric binders were also studied using attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy. ATR-FTIR spectra were collected using a Varian FTS 7000 spectrometer, with a Specac MKII Golden Gate single reflectance diamond ATR attachment with KRS-5 lenses. Absorbance spectra were collected from 4000 to 400 cm<sup>-1</sup> at a resolution of 2 cm<sup>-1</sup> and a scanning speed of 5 kHz, with 32 scans/spectrum.

Synchrotron FTIR spectromicroscopy (SR-FTIR) was used to investigate the structural heterogeneity of geopolymer samples, using the microscopy endstation on BL8 (Infrared Spectroscopy) at the Australian Synchrotron, Melbourne. Sample preparation included cutting with a diamond saw, then polishing with increasing fineness up to 6 μm diamond paste, using the same polishing technique as applied previously for the study of geopolymers by electron microscopy [27]. By using the optical microscope attached to the FTIR microscopy endstation, regions of interest were defined on each sample as rectangles 30 × 20 points in size, on a 10 μm grid spacing. A 20 × 20 μm aperture size was used. After defining the positions, FTIR data were collected at each point using an ATR crystal, 64 scans/spot, from 3000 to 700 cm<sup>-1</sup>.

**Table 1**  
Molar ratios of the components of the three samples used in this paper.

Sample	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O/SiO <sub>2</sub>	H <sub>2</sub> O/Na <sub>2</sub> O
G1	3.0	0.43	7.0
G2	3.0	0.46	7.0
G3	3.0	0.50	7.0

The hierarchical clustering analysis (HCA) method was applied to the analysis of SR-FTIR data using the CytoSpec software package. Baselines were corrected across the full spectra, then the region from 800 to 1200 cm<sup>-1</sup> in each spectrum was normalised using the Vector normalisation method. Finally, smoothing was applied using the average smoothing algorithm as implemented in the Cytospec software.

## 3. Results and discussion

### 3.1. Characterising crystalline phases

Fig. 1 shows the XRD data obtained for three geopolymer samples with different silicon availabilities after different curing times. Crystalline phases identified include quartz (SiO<sub>2</sub>; Powder Diffraction File (PDF) card: 00-046-1045), sodium metasilicate (Na<sub>2</sub>SiO<sub>3</sub>·9H<sub>2</sub>O; PDF: 00-019-1239), sodium silicate (Na<sub>4</sub>SiO<sub>4</sub>; PDF: 00-032-1154), zeolite A (approximately Na<sub>2</sub>Al<sub>2</sub>Si<sub>1.85</sub>O<sub>7.7</sub>·5.1H<sub>2</sub>O; PDF: 00-038-0241), faujasite (approximately Na<sub>2</sub>Al<sub>2</sub>Si<sub>4</sub>O<sub>12</sub>·8H<sub>2</sub>O; PDF: 00-039-1380), analcime (approximately Na<sub>3.6</sub>Al<sub>3.6</sub>Si<sub>12.4</sub>O<sub>32</sub>·14H<sub>2</sub>O; PDF: 00-044-0052) and natrite (Na<sub>2</sub>CO<sub>3</sub>; PDF: 00-037-0451). The formation of carbonates is attributed to improper sealing of the samples, which allows atmospheric CO<sub>2</sub> to react with the sodium-rich pore solutions. As the intensity and sharpness of the carbonate peaks in the XRD results did not change over time, and no obvious difference was observed at 1400 cm<sup>-1</sup> (which is a sensitive and well-defined band related to C–O vibrations in carbonates [28]) in the FTIR spectra of the three samples, the differences in the extent of carbonation between samples do not appear significant.

Quartz, which is recognisable in all samples after two days (Fig. 1a), is the main crystalline phase present in geothermal silica, and the sodium silicate phases which are formed in the early stages of the reaction in samples G2 and G3 are absent in G1. After four days (Fig. 1b), zeolite A is the main crystal phase recognisable in G1, while in G2 and G3 there are also some peaks related to faujasite. In 21 days, G1 has also developed the faujasite phase, and the XRD data for all samples after three weeks look reasonably similar to each other, although differing in the relative concentrations of the zeolitic phases (faujasite and zeolite A). This indicates that similar chemical changes are taking place in all samples, but with different rates. Sample G1, with the lowest Si availability, was the sample which took the longest to develop the zeolitic phases. Sample G2 shows the highest extent of crystallite formation, and the sharpest zeolite diffraction peaks, while G3 shows less faujasite than G2.

There are two main differences between G1 and the other two samples, after 21 days (Fig. 1c). One is the formation of a considerable amount of analcime in G1, which is a very minor phase in G2 and G3, and the other is the absence of the sodium silicate phase which is formed in the other two samples. Analcime is a relatively high-silica crystalline phase, and the formation of higher amounts of this phase indicates that there has most likely been a high-silica environment in the regions of the gel in which it formed, as has been discussed previously for geopolymer-forming systems [11] and for zeolite synthesis by hydrothermal transformation of gels and clays [29].

The formation of analcime in G1 is somewhat unexpected, as samples G2 and G3 have higher silica availability than G1, meaning that the formation of silica-rich crystals could be expected in these samples rather than G1. The fact that this was not observed may be due to the heterogeneity of the samples, leading to the growth of different phases in local areas, or also it could be a sign of a higher degree of Si contribution to the final geopolymer binder due to the favourable activating energy of the transformation of such regions (compared to less Si-rich regions) to higher-Si crystallites, as has been explained in detail elsewhere [11].

The formation of identifiable sodium silicate phases in G2 and G3 is also relatively unusual in geopolymer-forming systems, and indicates

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