

# Characterization of geopolymer cements and concretes: Structure/property relations and commercial utilization

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## ABSTRACT

Geopolymers (alkali aluminosilicate inorganic polymers) have been developed over the past 30 years as a high-performance environmentally-sustainable, low-CO<sub>2</sub> cementing binder system. This paper presents the results of the characterization of reacting and reacted geopolymer systems by a variety of methods including MAS NMR, SEM and in situ ATR-FTIR, as well as insight obtained by modeling techniques. The role of different system components, in particular the specific role of added silicate in the activating solution, are discussed in detail, and their implications for the design of geopolymer concretes with optimal properties while minimizing environmental impact and production costs are analyzed. Various issues affecting the commercial acceptance of geopolymer technology are also discussed, and the opportunities for geopolymers to play a role in the development of a sustainable cement industry presented.

## 1. INTRODUCTION

Geopolymers are a class of alkali aluminosilicate binder materials that are increasingly finding utilization in niche applications for which the chemistry underlying ordinary Portland cement (OPC) is less than ideally suited [1]. For example, their low permeability and high internal pH means that geopolymer concretes display good resistance to chloride-induced corrosion of steel reinforcing [2, 3]. Good acid and freeze-thaw resistance properties [4, 5] also make geopolymer concretes ideal for use in aggressive conditions – for example in sewer pipes where sulfate attack is a major problem, or for road surfacing in cold areas where resistance to chloride penetration and freeze-thaw cycling is critical.

The environmental benefits of geopolymer concrete are also significant, most notably the readily achievable >50% reduction in CO<sub>2</sub> emission compared to OPC, with further gains beyond this being targeted by mix optimization [6]. Applications of geopolymers and geopolymer-like materials in toxic [7, 8] and nuclear [9, 10] waste immobilization have also shown significant promise. The strong binding of Cs<sup>+</sup> and Sr<sup>2+</sup> within the “proto-zeolitic” [11, 12] aluminosilicate geopolymer framework is

particularly advantageous for encapsulation of these problematic radioactive elements, and treatment under the highly alkaline, silica-rich conditions of geopolymerization can lead to very effective immobilization of some toxic metals [13]. The high-temperature properties of geopolymers are also of some importance in construction applications, as appropriately-formulated geopolymers can display very good dimensional stability up to 1000°C [14]. Geopolymer concrete binds very strongly to steel reinforcing [15], and shows remarkable resistance to ASR, which is particularly notable considering its very high alkali content [16, 17].

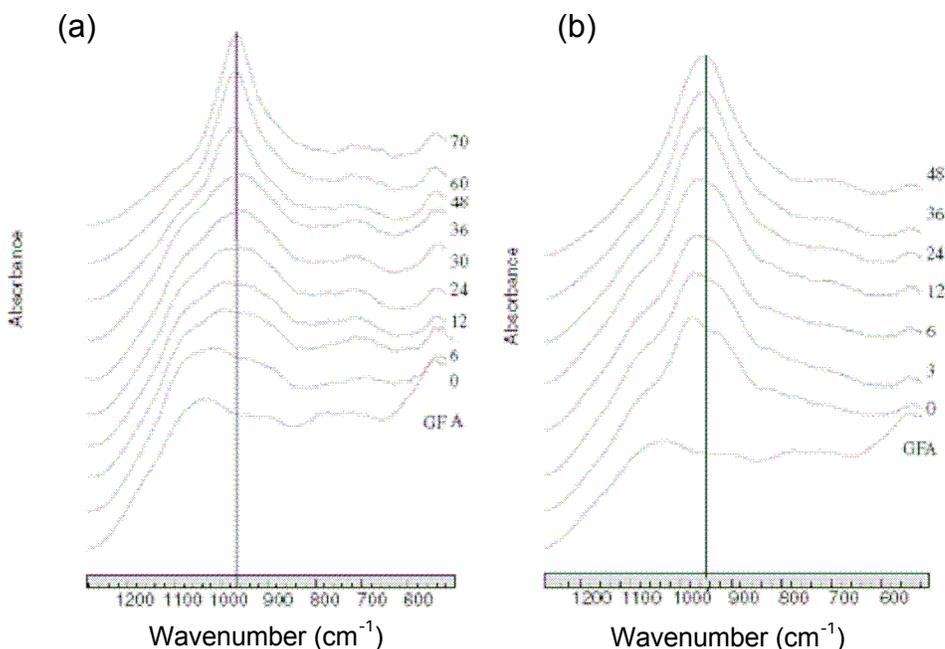
For all these technological and environmental reasons, geopolymer cements and concretes must be considered a viable material choice for a wide range of applications. The commercial drivers for the uptake of geopolymer technology are discussed in detail elsewhere [6], but it is believed that a favorable business case can in fact be put forward for the use of geopolymeric materials in a variety of circumstances. However, one of the major constraints on the widespread acceptance of geopolymers is the fact that these materials are still a relatively immature field of research, both in academia and in the commercial world. There is therefore a feeling in some areas that simply not enough is known about the mechanisms controlling the process of geopolymerization and the properties of the geopolymer products. This is manifested through the absence of accepted standards describing geopolymer performance and formulations (unlike for OPC, which has well-established standards for almost every aspect of its behavior). Work on developing such standards is ongoing, and intensive research into various aspects of geopolymer technology is currently being undertaken. This paper details the results of some recent experimental and theoretical work, including the development of new techniques for analysis of reaction kinetics during geopolymerization and the generation of a broader understanding of structure/property relations in geopolymers.

## **2. GEOPOLYMERIZATION KINETICS**

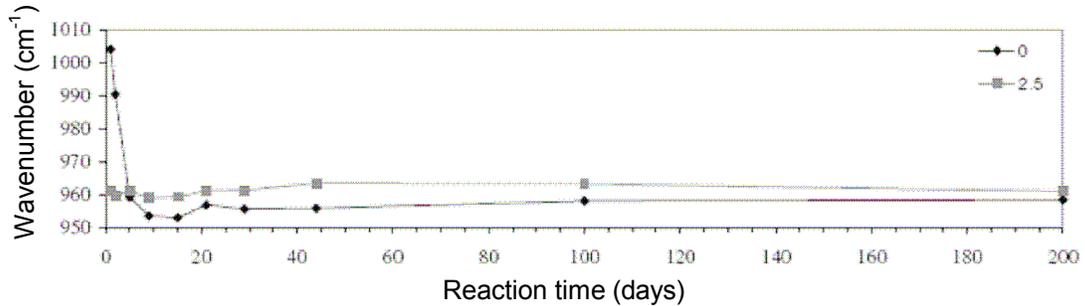
Various methods are available which provide valuable information for the in situ study of geopolymerization kinetics. Differential scanning calorimetry was the first instrumental technique successfully applied to the study of geopolymerization [18], and has since provided valuable information regarding the energetics of geopolymerization. Isothermal conduction calorimetry is very difficult to conduct successfully on Ca-free geopolymer systems due to the small heat flows involved, but has been applied to the study of geopolymerization in metakaolin/Ca(OH)<sub>2</sub> mixtures [19]. Energy-dispersive X-ray diffractometry (EDXRD), utilizing synchrotron radiation, has also recently been applied to the study of geopolymerization and has provided a number of advances in the understanding of reaction mechanisms [20]. A detailed empirical reaction

kinetic model for geopolymerization has also been developed, and provides a good match to experimental observations from EDXRD as well as additional insight into the specific roles of particular chemical species present in the reacting geopolymer slurry [21]. Without recapitulating the model formulation in detail here, various insights extracted from it will be used to provide explanations for some of the trends presented from new experimental data in this paper.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) is a surface-sensitive technique, but also one that allows rapid collection of FTIR spectra from reacting slurry systems such as geopolymers [22]. Figure 1 shows ATR-FTIR spectra for the reaction of fly ash with sodium hydroxide (Figure 1a), and with sodium silicate (Figure 1b). The extent of geopolymerization is able to be measured by quantification of the position and intensity of the main T-O-T (T: Si or Al) asymmetric stretch peak, located at  $\sim 950\text{-}1000\text{ cm}^{-1}$ , as detailed in reference [22]. Figure 2 shows a comparison between the positions of this peak in the same two systems over an extended period of time. The shift in this peak shows the effects of both Al substitution into the geopolymer gel network, and also variations in the network connectivity. The combination of these two factors provides a valuable measure of the extent of geopolymer gel development.



**Figure 1.** In situ ATR-FTIR spectra showing the reaction of (a) 6M sodium hydroxide and (b) sodium silicate solution (6M NaOH, 2.5M SiO<sub>2</sub>) with fly ash to form geopolymers. Numbers refer to time after initial mixing, spectrum GFA is unreacted fly ash. Data from [22].



**Figure 2.** Main T-O-T asymmetric stretch peak position extracted from ATR-FTIR spectra for the same reactions as represented in Figure 1 ([SiO<sub>2</sub>] = 0 and 2.5M), for up to 200 days. Data from [22].

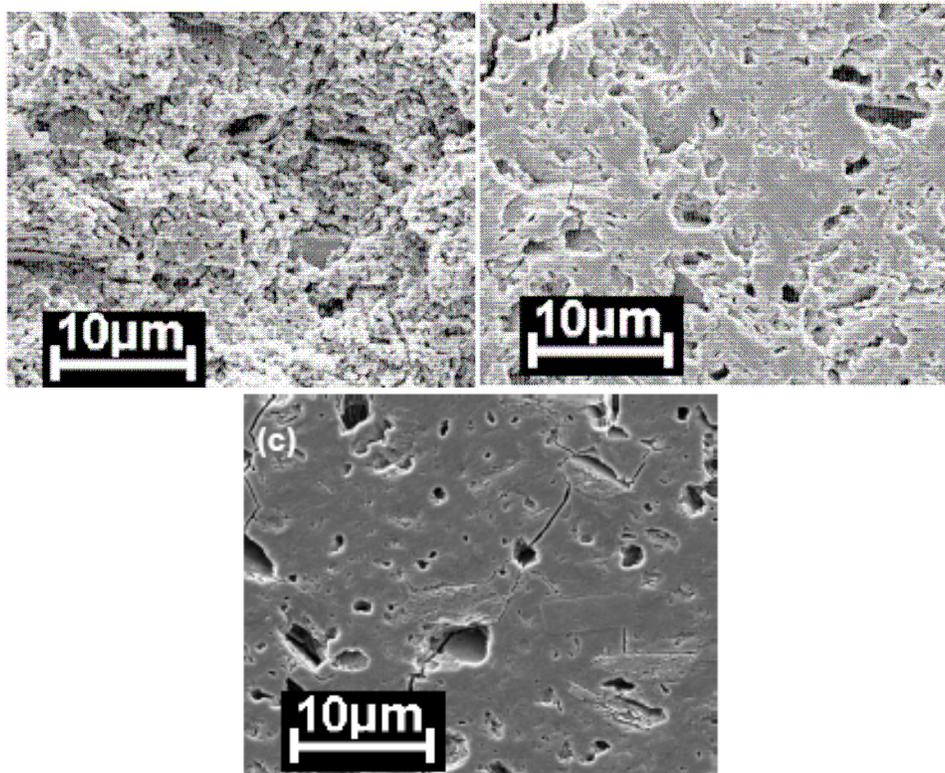
Figures 1 and 2 show clearly that there are reaction processes during geopolymerization that take place on a wide range of time scales. The initial setting of a geopolymer is relatively rapid, as shown by Figure 1, in the presence of either a silicate or a hydroxide activating solution. However, structure development continues for an extended period of time after this, with the hydroxide-activated system in particular showing significant structural changes up to approximately 20 days at 40°C. The interplay between the early-stage structure formation and later-stage structure development will play a highly significant role in determining the properties of the final geopolymeric material.

### 3. GEOPOLYMER MICROSTRUCTURE AND PERFORMANCE

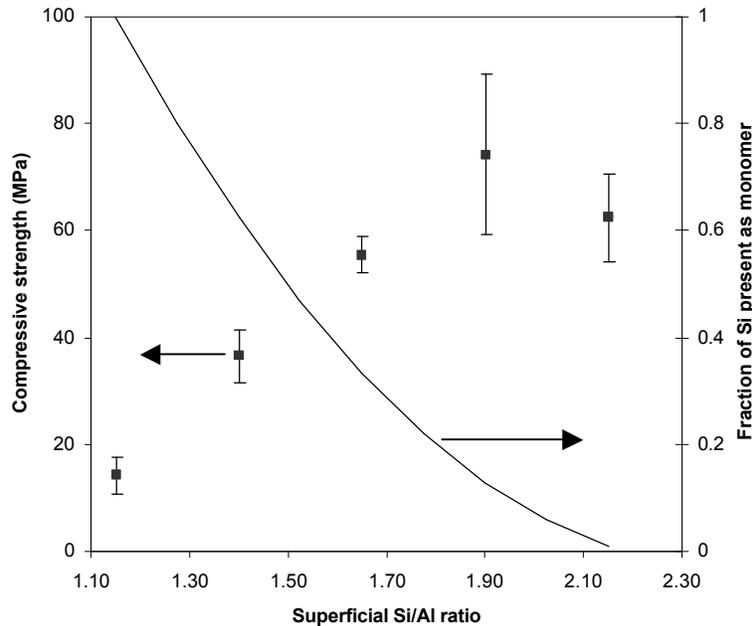
Probably the most important aspect of the development of a new material for construction applications is developing the link from formulation and processing, via microstructure, to performance and properties. Recent work in the field of geopolymers has been heavily focused in this area, and has elucidated the key role played by dissolved silicate monomers in the development of high-performance geopolymer products. It is well known that the dissolution of silica forms a wide array of small species (oligomers) in alkaline solution, and this is equally true in aluminosilicate systems. Of these species, the monomer is the most reactive by a significant margin – and in fact the kinetics of some of the nanoparticle formation processes that occur in silicate solutions can be explained almost entirely by reaction kinetic schemes in which all reactions occur by addition or elimination of monomers [23]. Given that geopolymers are synthesized by reacting a solid aluminosilicate source with an alkaline silicate solution, the proportion of this initial dissolved silicate that is supplied as monomers must obviously play a large role in determining the kinetics of the very early stages of geopolymerization. However, the importance of silicate speciation is by no means limited to a kinetic role in the early stages of geopolymerization – rather, it has recently been shown

that the microstructure of geopolymers is determined in large part by this parameter [24].

Figures 3 and 4 show clearly the effect of silicate speciation on geopolymer microstructure and performance. Figure 3 shows SEM micrographs of geopolymers formed by reaction of metakaolin with sodium silicate solutions of varying silica content, and Figure 4 shows a comparison between the 28-day compressive strength of metakaolin-based geopolymers and the proportion of the silica in the activating solutions that is initially present as monomers. It can be seen from Figure 3 that geopolymers with little or no added silicate have a very rough microstructure, whereas the addition of more silicate (i.e. a reduction in the fraction of silica present as monomers, from Figure 4) gives a smooth microstructure and corresponds to a higher-strength product.



**Figure 3.** SEM micrographs of metakaolin-based geopolymers with Si/Al = (a) 1.15, (b) 1.50 and (c) 1.65, showing the transition from rough to smooth microstructure with increased silicate addition



**Figure 4.** Compressive strength (plotted as points) of metakaolin-based geopolymers (metakaolin Si/Al ratio 1.15), with a curve showing the fraction of silicate in the initial activating solutions that was present as monomers. Strength data from [24], speciation curve from [21].

A significant factor underlying the differences in microstructure between high- and low-silica geopolymers is the differing extent of syneresis possible in the two different classes of systems. Low-silica geopolymers, formed from primarily monomeric silicate solutions, consist initially of a highly labile (high-Al and with many non-bridging oxygen sites) aluminosilicate gel. This gel is then highly prone to micro-scale syneresis [25] whereby, as the gel shrinks strongly in very localized areas, the particulate microstructure observable in Figure 3 is generated. This type of microstructure corresponds with a low-strength product with a relatively large mean pore radius. On the other hand, high-silica geopolymers contain a much less labile gel phase due to the lower levels of Al and non-bridging oxygen sites, so the rate of microscale syneresis is very much lower. This means that the gel will not collapse to form a particulate structure, but rather will maintain a smooth appearance, with pores too small to observe by SEM. This is shown most strongly by the overall and skeletal densities of geopolymers as calculated from  $N_2$  absorption data [24], where the low-silica samples (e.g. Figure 3a) have a lower overall density but a higher skeletal density than high-silica samples.

#### 4. GEOPOLYMER NANOSTRUCTURE AND PERFORMANCE

Magic angle spinning (MAS) NMR has provided a wealth of information relating nanostructural and compositional aspects of geopolymers. This is of particular value in developing an understanding of the role of the alkali cations in the development of geopolymer mechanical performance. For instance, recent work [26] has shown a statistically significant mixed alkali effect in strength data for Na/K-aluminosilicate geopolymers, with the mixed Na/K geopolymers showing strengths up to 25% higher than either of the pure alkali endmember compositions. This has been ascribed at least in part to phase segregation in the mixed alkali-systems, observable under TEM [26], but the reasons for this phase segregation are only clearly understood by comparison with multinuclear MAS-NMR results.

$^{23}\text{Na}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$  and  $^{39}\text{K}$  MAS NMR data have been collected for a range of pure- and mixed-alkali geopolymers, showing the effect of the different cations on the extent and rate of aluminum and alkali cation incorporation into the geopolymeric binder structures [27-31]. These data are briefly summarized in Table 1 below.

**Table 1.** Summary of MAS-NMR results for relative incorporation rates of different elements in geopolymers.

Element	Preferred incorporation conditions/locations
Na	Hydrates strongly in solution, so relatively less strongly driven into gel structure than K, charge-balances tetrahedral Al sites.
K	Incorporated into gel in preference to Na in mixed alkali systems, charge-balances tetrahedral Al sites.
Al	Rapid initial incorporation, Al-O-Al bond formation energetically disfavored but possible under certain circumstances.
Si	Incorporated more gradually into the final gel structure, but still labile enough that local (nearest-neighbor) Si/Al coordination is close to equilibrium.

The preferential incorporation of K over Na into the geopolymer gel structures in mixed-alkali systems provides a possible explanation for some of the observed phase segregation in these geopolymers, as the initial regions formed will be relatively rich in K whereas the regions formed later in the reaction process will be relatively rich in Na. It has been observed [32] that very different zeolite structures are formed by crystallization of mixed alkali-aluminosilicate systems depending on the

Na/(Na+K) ratio, and so it is not surprising that similar phenomena would be observed in geopolymerization.

Rapid incorporation of Al into the geopolymer gel leads to an initially Al-rich gel, dubbed 'Gel I' by Fernández-Jiménez *et al.* [31]. This gel has relatively low strength, and if it is not transformed to the more silica-rich 'Gel II' through the presence of sufficient silica in the activating solution, it will undergo syneresis as outlined previously, and provide a geopolymer with poor mechanical performance. However, the transformation of this initial gel to a more silica-rich form by incorporation of dissolved silicate species (primarily as monomers) provides the microstructural stabilization and resistance to syneresis observed in the micrographs of Figure 3. This also corresponds to improvements in mechanical properties as observed in Figure 4. However, when the amount of added silica passes a critical point, seen from Figure 4 to correspond to an overall Si/Al ratio of ~1.90 for metakaolin-based systems, mechanical performance begins to degrade. At very high levels of silica addition, the strength is reduced by the large quantity of unreacted metakaolin present due to the alkalinity of the activating solution being too low to give anywhere near full dissolution, which introduces large defects into the structure [24].

## **5. ENVIRONMENTAL BENEFITS OF GEOPOLYMER CEMENTS**

It has been calculated [6] that the use of geopolymers provides the potential for at least 80% savings in raw materials CO<sub>2</sub> emission when compared with ordinary Portland cements. Even greater savings are possible by the use of an activator with the lowest possible dissolved solids (NaOH + SiO<sub>2</sub>) content to achieve the desired mechanical and rheological performance. Utilization of fly ash or slag as the solid aluminosilicate source for geopolymerization removes entirely the highly significant CO<sub>2</sub> emissions due to the OPC clinkering process. Using an alkaline solution in place of water to activate the solid source, as is required for geopolymer synthesis, does reintroduce some CO<sub>2</sub> emission, as does the use of metakaolin as a source material. However, the economic drivers for the minimization of both activator dissolved solids and metakaolin content are very strong, as these are also the most expensive of the ingredients used in geopolymer synthesis. Therefore, the activation of fly ash or slag with the least possible amount of activator, containing the lowest practicable quantities of dissolved NaOH and SiO<sub>2</sub>, provides not only the most environmentally-friendly but also the most economically competitive formulation for geopolymers. It is in this area that further research is intensively being conducted, working towards accurately quantifying and optimizing the relationship between geopolymer performance and cost (either financial or environmental).

## 6. CONCLUSIONS

The effects of geopolymerization kinetics, binder microstructure and nanostructure on the properties of geopolymeric materials have been the subject of intense scrutiny over the past several years, and the level of understanding that has resulted from this analysis now places the research field on a strong footing for discussion of commercial utilization. The relationships between silicate speciation, nanostructure and microstructure are critical to the understanding of the mechanical strength performance of geopolymers, with the silicate monomer concentration seen to have a very significant effect. The environmental benefits of geopolymerization are highly significant, with regard both to waste utilization and to CO<sub>2</sub> emission reduction.

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