

Modeling the Formation of Geopolymers

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Abstract

Geopolymers are a class of X-ray amorphous alkali aluminosilicate gel binder materials with potential applications in a wide range of areas. In particular, geopolymers can provide significant improvements over traditional Portland cement technology in applications requiring resistance to acid or salt attack, or thermal stability at temperatures up to 1000 °C. The quasi-zeolitic nature of some of the phases formed during geopolymerization is also of significant interest in immobilization of cationic waste streams. However, it is only recently that the structures and synthesis mechanisms of geopolymers have begun to be modeled. Micro- to nanostructural information has been obtained by MAS-NMR, microscopy and synchrotron pair distribution function analysis, which together have provided for the first time the ability to analyze both framework and non-framework cation sites and ordering within the geopolymer gel binder phase in detail. Comparison between the results of an empirical reaction kinetic model and data obtained by in situ energy dispersive synchrotron X-ray diffractometry is presented, and insight into the geopolymerization process and its influence on the microstructure of geopolymers is undertaken. The results presented will have significance in determining the performance of geopolymers in applications requiring controlled setting rates and rheology, or where long-term chemical stability is important.

Introduction

Geopolymeric materials show significant potential for utilization in a wide range of applications, including as a replacement for traditional Portland cements, as a possible encapsulant for toxic and/or radioactive wastes, and also as a relatively inexpensive yet heat-resistant ceramic material [1]. However, due to their primarily X-ray amorphous nature and the high levels of impurities introduced by the use of waste materials as a solid aluminosilicate source for geopolymerization, detailed analysis of the structure and reactivity of geopolymers has historically been somewhat elusive [2]. The development of such an understanding is central to the future widespread utilization of geopolymers, particularly in waste immobilization applications where extreme durability is required, but also (and no less importantly) in the construction industry, where the ability to predict whether or not a material will retain its structural integrity over a 50 year service life under loaded conditions is critical. The experience of 200 years' usage of Portland cements cannot be replicated in the short term in the laboratory, so the only way to persuade industry that geopolymer technology is sufficiently mature for use in construction applications is to develop a more complete, theoretically sound understanding of geopolymer properties and performance. An intensive recent research effort has provided some very significant advances in the development of such an understanding by the use of simplified model systems and the development of appropriate experimental techniques [3, 4]. Some of the results of these investigations, and their consequences for the understanding of geopolymer structure and synthesis, are discussed here.

Raw Material Sources for Geopolymerization

Geopolymers are formed by reaction of an alkaline solution (usually containing very high levels of dissolved hydroxide and/or silicate) with a solid aluminosilicate powder, forming an alkali-aluminosilicate gel phase with inclusions comprising unreacted solid precursor particles and/or any added fillers, for example aggregates [5, 6] or fibers [7-10]. Metakaolin, coal fly ash and blast furnace slag are the three aluminosilicate sources most commonly investigated – metakaolin primarily for higher-value ceramic-type applications due to its cost, and fly ash and slag for larger-scale concrete replacement applications. However, the calcium present in some fly ashes and in slags can greatly complicate the analysis of these systems. Synthetic aluminosilicate precursors are also used when a very high-purity raw material is necessary for analytical purposes or specific applications. Some of the analytical work presented here utilizes an aluminosilicate powder synthesized by the PVA-steric entrapment method [11], however the bulk of the results presented are for metakaolin-based systems. Extension of the results presented here to the analysis of fly ash systems is ongoing [1, 12], although modifications to some of the experimental techniques used are necessary to account for the different rheology and high impurity levels of fly ash geopolymers.

The Geopolymerization Reaction Process

Geopolymerization takes place via a complex multistep mechanism. The initial dissolution of the solid aluminosilicate source releases small silicate and aluminate species into the surrounding solution. These species are highly labile, and so undergo a series of rapid exchange and oligomerization reactions, also involving any silicate species that are initially present in the activating solution. As larger and larger oligomers form due to the very low water content and therefore the strong driving force for polymerization present in the system, the solution phase undergoes a gelation process. This greatly hinders the diffusive transport of dissolved species from the solid particle surfaces to the bulk of the geopolymer, meaning that in most cases unreacted aluminosilicate source particles will be present as inclusions in the binder. The structure of the gel continues to evolve and harden, eventually becoming a predominantly fully coordinated (Q^4) aluminosilicate network [13, 14], which is what is described as the ‘geopolymeric binder’ phase. This is clearly visible in Figure 1, which is a SEM micrograph of a polished metakaolin-based geopolymer specimen, showing the smooth binder phase, with voids where the very soft unreacted metakaolin particles have been removed during polishing.

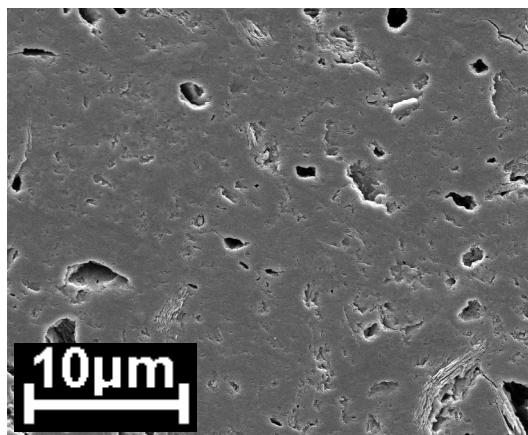


Figure 1. SEM micrograph of a geopolymer with overall (superficial) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.90$, synthesized by mixing metakaolin with sodium silicate solution. From [3].

Figure 2 presents a simplified conceptual model of some of the chemical processes occurring during the initial setting and later structural evolution of geopolymers.

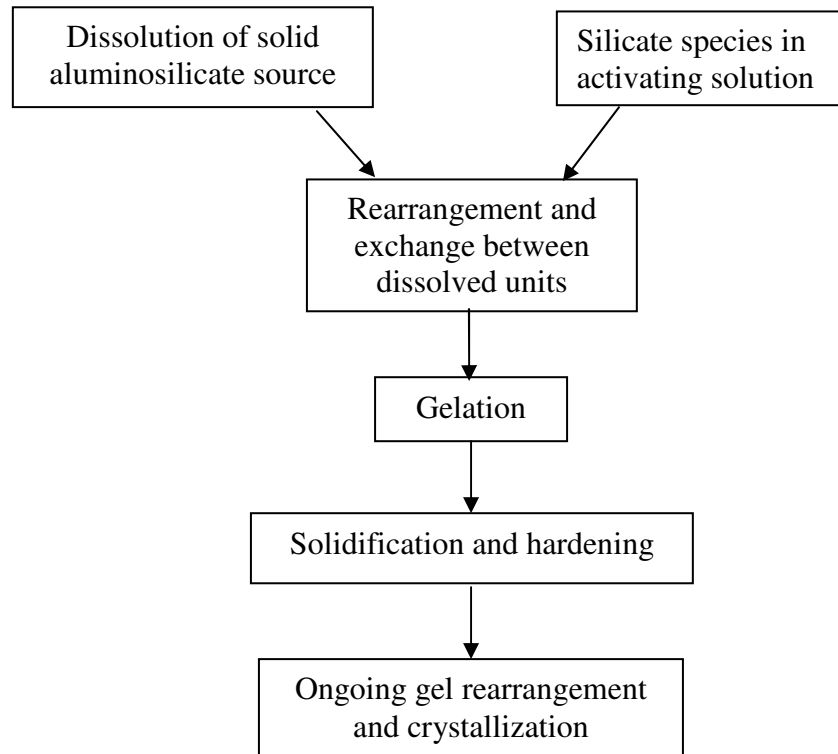


Figure 2. Processes occurring during geopolymerization.

To develop a detailed description of the process of geopolymerization, an understanding of each of these individual steps is highly desirable, however separating the effects of a single step from the others that are happening simultaneously, in a highly constrained and rapidly-solidifying system, is quite challenging. Initial work in this field has focused on the use of model systems, in particular aluminosilicate hydrogels [15] and zeolite synthesis systems [4], to describe certain aspects of the chemistry and rheology of reacting geopolymer slurries. However, to ensure that the full range of competitive and synergistic effects between the different processes is able to be analyzed, a means of examining the process of geopolymerization as a whole – from both experimental and computational viewpoints – is necessary.

Energy Dispersive X-ray Diffractometry

Energy dispersive X-ray diffractometry has been carried out in situ using white-beam synchrotron radiation on a laboratory-sized geopolymer sample, characterizing the rate of geopolymerization during the first 3 hours of the reaction process. By carrying out the reactions at a temperature ($\sim 40^\circ\text{C}$) where the geopolymer is just completing the solidification step shown in Figure 2, the rate of formation of this initial geopolymeric gel phase is able to be described. It must be noted that this phase will differ structurally from the final geopolymer gel observed after extended curing, as the presence of moisture and warmth allows the gel to continue rearranging itself into a more thermodynamically favorable form, involving very high degrees of crosslinking and also the formation of nanosized crystallites. These two stages of gel evolution,

denoted “Gel I” and Gel II” by Fernández-Jiménez *et al.* [16], are represented in a general sense by the “Solidification and hardening” and “Ongoing gel rearrangement and crystallization” boxes in Figure 2. The regime measurable by EDXRD roughly corresponds to the first of these. A sample set of EDXRD data is given in Figure 3. Full experimental details and detailed discussions of data processing and quantification issues are given in [4].

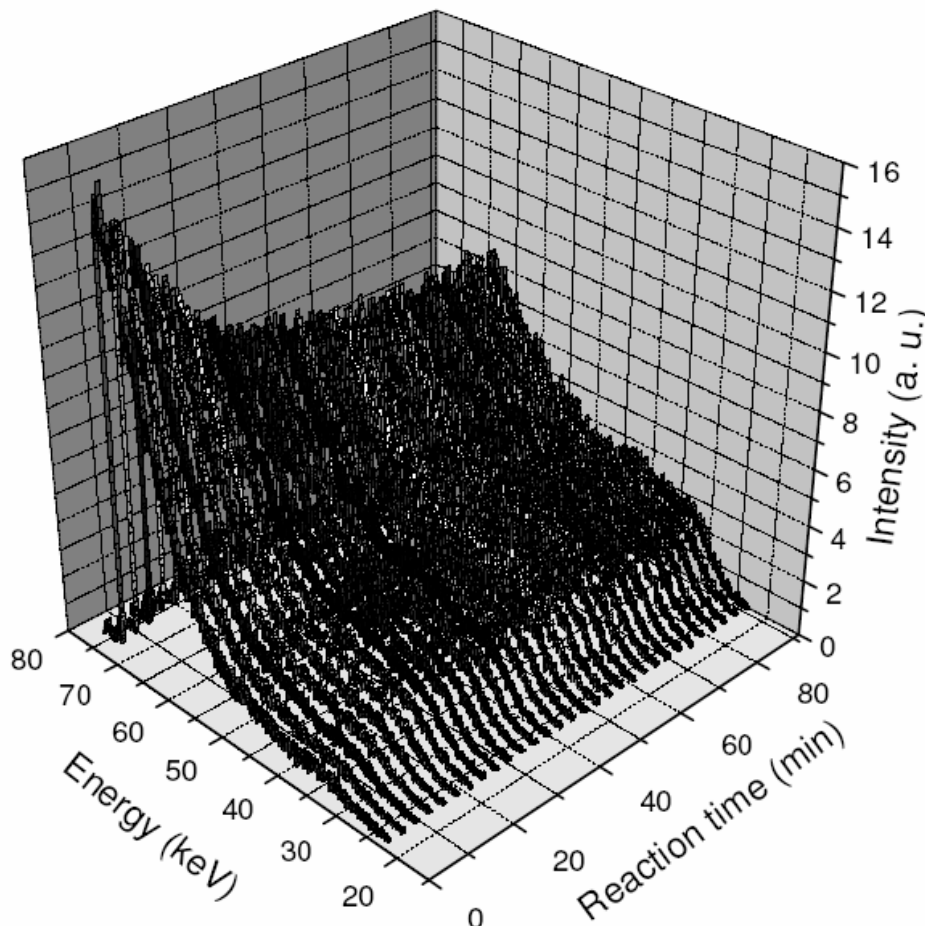


Figure 3. EDXRD data for the potassium silicate/metakaolin geopolymer system with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$, at 40°C . From [4].

Quantification of the data obtained by EDXRD provides a measure of the relative extent of formation of the initial gel phase. EDXRD experiments were run until no change in the spectra was observable over two consecutive periods of 5000 sec. At this point, it can be confidently asserted that “Gel I” formation is complete (as measurable by this technique), and that any future structural development can be classified as “Ongoing gel rearrangement and crystallization” according to the broad groupings in Figure 2.

Reaction Kinetic Modeling

The development of a reaction kinetic model for the early stages of geopolymerization is detailed in [4]. Briefly, description of the kinetics of aluminosilicate raw material dissolution, rearrangement of the monomeric $\text{Al}(\text{OH})_4^-$ and $\text{SiO}_x(\text{OH})_{4-x}^{x-}$ species released from the solid

source into various different aluminosilicate oligomers, and the combination of these oligomers to form amorphous and/or zeolite precursor gel networks, is described analytically. The variations in Si/Al ratio within each type of species present as the reaction progresses are monitored, the effect of silicate oligomerization in solution is described, and the influences of other factors including the alkali cation content and the generation and consumption of water during reaction are also modeled. A global measure of the extent of reaction is obtained by summing the fraction of Si and Al present that is included in these larger oligomeric and/or solidified gel species. Figures 4 and 5 show a comparison of selected model predictions with corresponding experimental 'extent of reaction' values obtained by EDXRD.

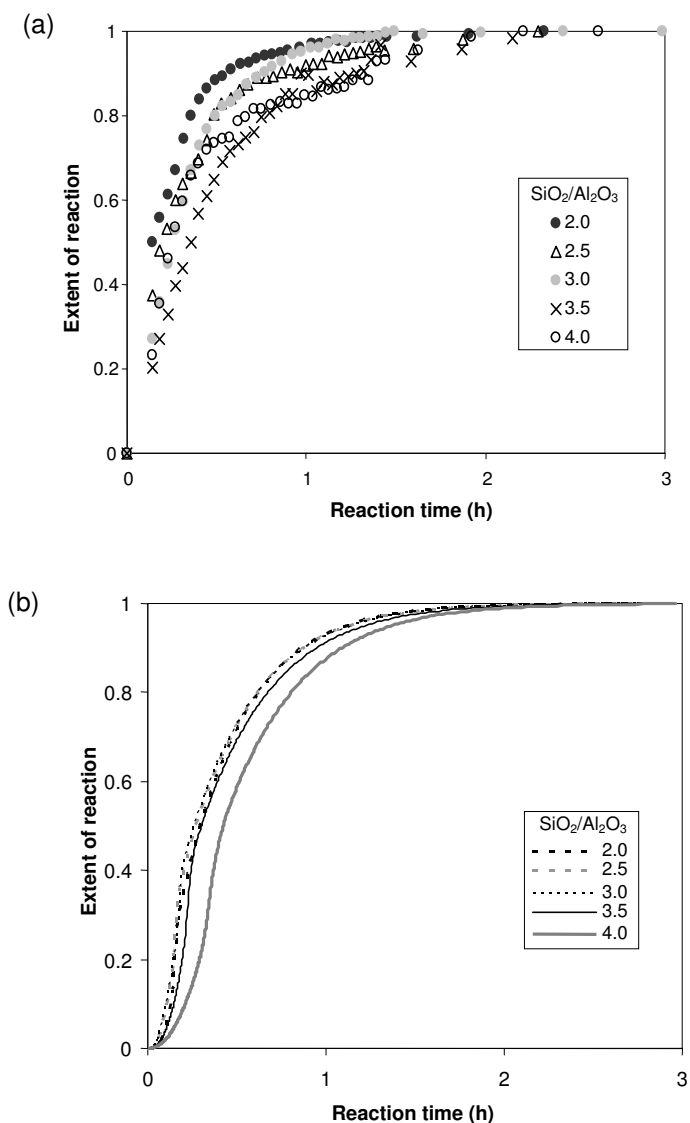


Figure 4. Comparison of (a) experimental EDXRD data and (b) model predictions for the rate of geopolymerisation of potassium silicate/metakaolin geopolymer systems with SiO₂/Al₂O₃ ratios as shown. From [4].

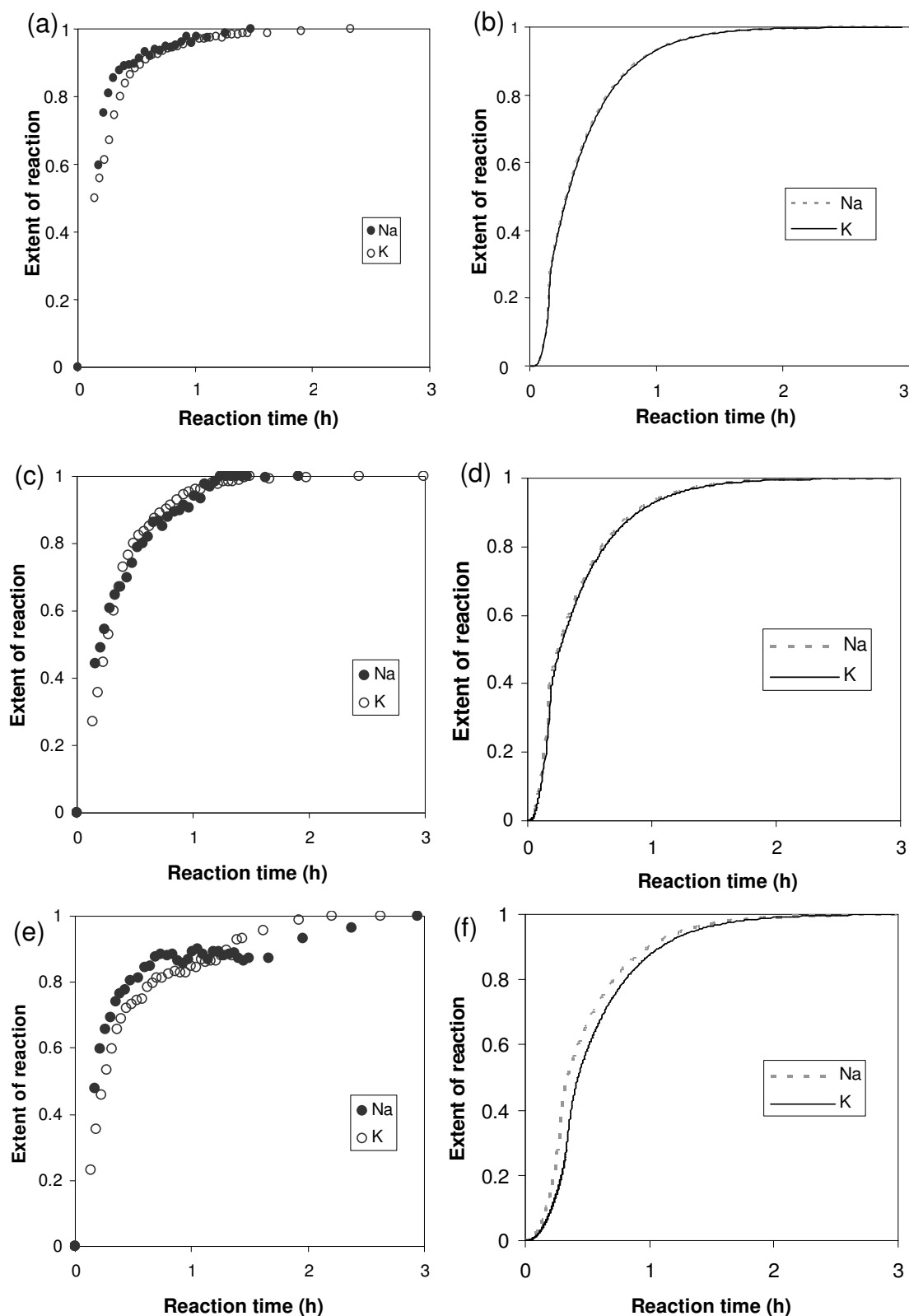


Figure 5. Comparison of reaction rates for Na- and K-silicate/metakaolin geopolymers with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.0$: (a) EDXRD and (b) corresponding model predictions; with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$: (c) EDXRD and (d) corresponding model predictions; and with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.0$: (e) EDXRD and (f) corresponding model predictions. From [4].

Figures 4 and 5 show that the model, even as a very simplified description of the full multistep, heterogeneous process that is geopolymerization, provides a relatively accurate description of a variety of phenomena associated with determining the rate of geopolymer formation. Figure 4a shows that the model predicts a general decrease in reaction rate with addition of silicate to the activating solution. This corresponds well to the majority of the experimental results shown in Figure 4a, with the exception of the highest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio depicted. This sample has significant limitations imposed on the achievable extent of reaction by the high degree of connectivity in the initial activating solution [17], and also due to mass transport hindrance by the very high viscosity of the solution phase present even in the initial stages of reaction. This latter effect in particular is not described in detail by the reaction kinetic model in its current form. However, it is notable that the model is able to predict close to the correct shape of the reaction extent-time curves, as well as describing most of the trend in reaction rate with $\text{SiO}_2/\text{Al}_2\text{O}_3$ variation.

Figure 5 shows comparisons between systems of identical $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, but with different alkali cations (Na or K) present. The model describes the differences between the roles of Na and K in geopolymerization purely via their effects on silicate polymerization equilibria, where K favors the formation of somewhat larger species [4, 18]. Even by the use of this relatively simplistic description of cation effects, the model is seen to match experimental observations remarkably well.

Molecular Structure of Geopolymers by PDF analysis

Because geopolymers are highly disordered on an atomic level, analysis of their nanostructure using 'traditional' crystallographic means is close to impossible. More sophisticated techniques are therefore required. Synchrotron X-ray pair distribution function (PDF) analysis (Figure 6) of a Cs-aluminosilicate ($\text{CsAlSi}_2\text{O}_6$) geopolymer heated to 1400°C has shown that the very short-range ordering in the geopolymer phase very closely resembles that of crystalline pollucite, but that the geopolymer is disordered on length scales $>10\text{\AA}$ [4].

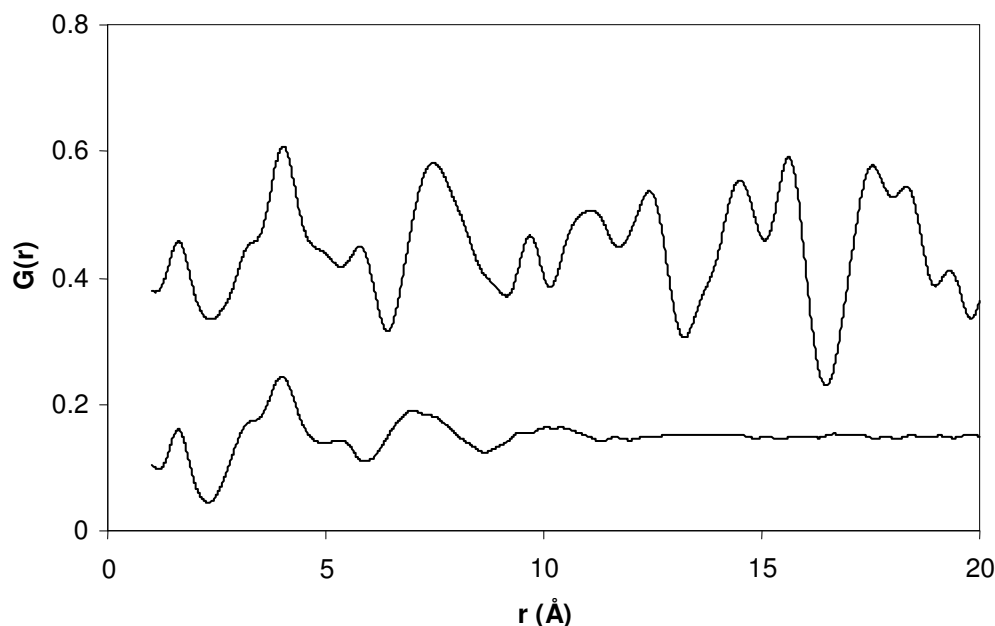


Figure 6. X-ray PDFs of a geopolymer and of crystalline pollucite (both $\text{CsAlSi}_2\text{O}_6$)

Modeling of PDF data by reverse Rietveld refinement and partial PDF decomposition shows that the primary change in short-range structure between the geopolymer and pollucite phases is a shift in the location of the charge-balancing Cs⁺ cations. These are able to find a more optimal site in the crystalline structure compared to their sometimes constrained positions in the geopolymer gel. However, the change in short-range ordering in the framework structure during the transformation from amorphous geopolymer to crystalline pollucite is very small.

Molecular Structure of Geopolymers by NMR

Magic angle spinning (MAS) NMR has also been widely applied to the study of geopolymers. ²H MAS-NMR has shown that there are very few bound hydroxyl groups in a well-reacted geopolymer system, that is, the aluminosilicate network is very close to fully-coordinated [19]. On this basis, ²⁹Si MAS-NMR spectra have been deconvoluted into component peaks, and the resulting Si/Al distributions used as comparison for the results of a statistical thermodynamic model for the geopolymer network structure [14, 20]. ²³Na and ³⁹K MAS-NMR have shown that, in a mixed-alkali geopolymer system, K is incorporated into charge-balancing sites in preference to Na [3, 19]. These results have not yet been incorporated in detail into the reaction kinetic model as presented here, however the difference in incorporation effectiveness between Na and K is likely to be significant in the detailed analysis of data such as those presented in Figure 5. While the relatively straightforward treatment used here provides an acceptable degree of accuracy – particularly when compared to the low level of model complexity required to generate such results – explicit description of the differences in geopolymer structure formation effectiveness between Na and K (and potentially other alkali cations as well) is an objective to be considered in future work.

Conclusions

Energy-dispersive X-ray diffractometry (EDXRD) provides a useful measure of the kinetics of geopolymerization, and a reaction kinetic model derived from a conceptual understanding of the geopolymerization process is able to describe well the trends in the EDXRD data. Both synchrotron pair distribution function analysis and MAS-NMR also provide valuable information and assist in the understanding of the structure of the final geopolymer phase.

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