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Editorial

1000 at 1000: Geopolymer technology: the current state of the art

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The term geopolymer was first used by Davidovits [1] to describe synthetic alkali aluminosilicate materials that could more broadly be termed "inorganic polymers" [2]. Although geopolymer formation is complex, a simplified reaction mechanism shown in Figure 1 outlines the various steps of the process.

The process shares many similar steps to sol-gel processing, in which gel precursors are produced and then converted into crystalline ceramics. The geopolymerization process does not generally involve the crystallization step; the final desired product is a crystallographically disordered ("X-ray amorphous") alkali-aluminosilicate. At various steps in the process, beginning with the source of the aluminosilicate, there are many experimental variables that can lead to different microstructures and hence a range of physical, mechanical, chemical, and thermal properties. This difference was indicated in the review of Duxson et al. when comparing the microstructures of a geopolymer derived from metakaolin to one derived from fly ash, when both were activated with NaOH [3]. The former showed a more uniform grain size compared to the fly ash material that exhibited a wide distribution of particle sizes. These different microstructures were reflected in the mechanical properties of the two materials; Duxson et al. reported that the fly-ash materials are generally more durable and stronger [3]. Some later SEM images in the review article suggest that possibly flaw sizes in some of the fly ash samples may be significantly larger than those in metakaolin-based materials, which would lead to weaker samples when tested in tension and a lower Weibull modulus.

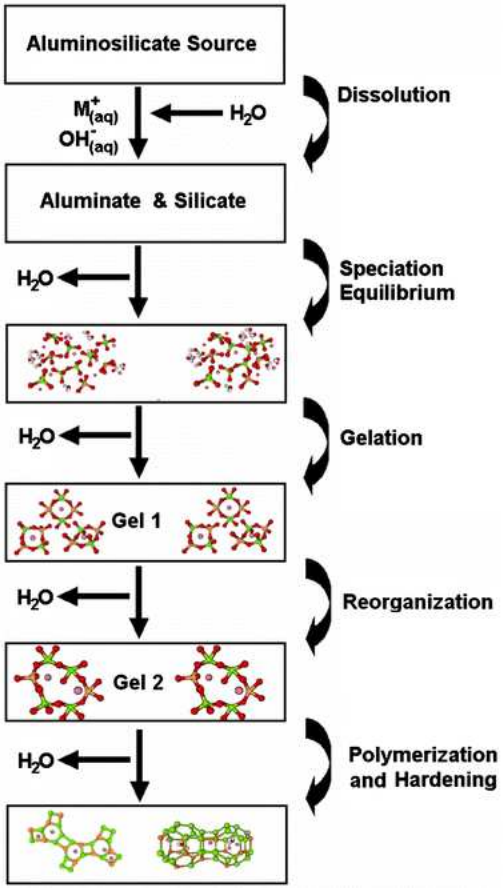

Figure 1. Conceptual model for geopolymerization. [3] with permission Springer Nature.

At the time the review was published, the structure of geopolymers had been the topic of considerable research. Local structural arrangements of the Si^{4+} and Al^{3+} cations in geopolymeric gels have been probed using ^{27}Al and ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. Both cations were found to primarily occupy tetrahedrally coordinated sites linked by bridging oxygens [4].

Although geopolymer gels are essentially X-ray amorphous, showing just a broad single diffraction peak, X-ray diffraction (XRD) has been used to study the development of crystallites within the gels as a function of time and temperature. Under certain conditions of temperature, alkali cation, and Si/Al ratio, a transition from the amorphous geopolymer to a zeolite structure can be produced using a range of different aluminosilicate sources. These structures can be seen using scanning electron microscopy (SEM) and inferred from ^{29}Si MAS-NMR that show chemical shifts characteristic of zeolite spectra. From an application point-of-view the nature of the crystalline transformation is particularly important in determining the mechanical properties of the final material.

A major interest in geopolymers was that they could significantly reduce greenhouse gas emissions associated with the production of cement [5]. Utilizing industrial waste, such as fly ash - a product of coal combustion – as an aluminosilicate source for geopolymers is therefore attractive. A challenge is that fly ash does not have a well-defined chemical composition, there is a broad particle size distribution, and a mix of glassy and crystalline phases [6]. All of these factors affect gelation and the eventual microstructure of the hardened geopolymer.

A major motivation to continue to investigate this material is for the development of geopolymer concrete derived from fly ash. At the time of the influential review by Duxson et al, which described the current state of the art in geopolymer science up through 2006 (it was accepted in

July 2006) and has been cited 1529 times (WoS Core), geopolymers from fly ash were identified to offer potential economic advantages over ordinary Portland cement and “showed promising improvements” over traditional Portland cement concrete.

The major conclusion drawn from the review is that geopolymer technology has “the potential for wide-scale utilization in the construction industry.” So, what is the current state of geopolymer technology over the past fifteen years since the review of Duxson et al.?

Firstly, geopolymer concrete has moved from an emerging technology to a structural material that has been used in a number of architectural applications. One example, the world’s first structural use of geopolymer concrete, is the Global Change Institute at the University of Queensland that was built in 2013. The 33 precast floor panels are made from geopolymer concrete made using a combination of blast furnace slag and fly ash – both waste materials - as the source of aluminosilicates. A more ambitious building project using geopolymer concrete was the Brisbane West Wellcamp Airport in Toowoomba, Australia, which was built using 100,000 tonnes of geopolymer concrete and completed in 2014 [7]. Uptake of geopolymer (or, more broadly, “alkali-activated cementitious material”) technology worldwide has become much more widespread during this timeframe, with standards and commercial supply chains being put into place in several regions worldwide. The sourcing and/or pre-processing of appropriate aluminosilicate precursors remains a logistical challenge in some areas [6], but the commercialization of geopolymer binders has succeeded in an increasingly broad range of applications, from construction to nuclear waste immobilization. The properties of the final geopolymers can be rather sensitive to processing variables such as alkalinity and curing temperature, but the factors controlling material performance are now much better understood to support larger-scale deployment as a quality-controlled material.

Many of the recent studies of geopolymers have also looked at applications beyond those which solely require mechanical strength and durability but are rather based on characteristics including their ion exchange capacity and porosity. Rogers et al. have investigated geopolymers as hosts for rare earth activator ions such as Sm^{3+} and Eu^{3+} for use as phosphors. [8] Through ion-exchange with potassium the rare-earth ion is located directly in the cavities in the geopolymer structure during gelation. Metakaolin-based geopolymers have been used as adsorbents to separate ammonium (NH_4^+) from wastewaters. [9] Similarly, geopolymers have been used to trap metals in water treatment residue [10] and considered for immobilizing low and intermediate level nuclear wastes [11]. Other applications that utilize the porous structure of geopolymers include use as biomaterials for bone restoration, and also as a drug release substrate [12].

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