



Dissolution behaviour of source materials for synthesis of geopolymer binders: A kinetic approach



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ABSTRACT

Controlling the initial release rate of alumina and silica from source materials is known to have a significant effect on the nanostructure of geopolymer gel and its final mechanical properties. However, most of the studies regarding the solubility of source materials take an equilibrium approach, and there is a gap in understanding of the release rates at far-from-equilibrium conditions. In the present study, the initial dissolution rate of some geopolymer precursors is characterised. The liquid to solid ratios are designed to be sufficiently high to minimise precipitation of hydration products, and the effects of solution alkalinity and milling on dissolution rates are investigated. While fly ash and blast furnace slag particles seem to release Si and Al at approximately similar rates, metakaolin shows a distinctively higher release of Si from the very early time of dissolution. Increasing solution alkalinity increases the dissolution of source materials up to some point, and the greatest effect is observed on fly ash particles. The most interesting result of milling is observed on fly ash particles where the release rate of silica has become higher than alumina, while contrasting behaviour is observed in the non-milled fly ash system. The opposite behaviour is observed in the slag system where milling rapidly increases the release rate of Al while the release rate of Si is increased slowly.

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1. Introduction

Geopolymers are low calcium binding materials that can convert aluminosilicate wastes such as fly ash, slag and metakaolin into strong cementitious binders. These alkali-activated binders are acid-, heat- and fire- resistant (Van Jaarsveld et al., 1997; Duxson et al., 2007a, 2007b, Provis and van Deventer, 2009), and they can be utilised as a green alternative to Portland cement due to the carbon dioxide savings achievable in their production process (Phair, 2006; Duxson et al., 2007a, 2007b). In the geopolymerisation reaction, an aluminosilicate source is usually activated by alkali silicate solutions to produce the tetrahedral geopolymeric network (Provis and van Deventer, 2007, 2009). The release rate of silicate and aluminate species from source materials is critical in controlling the synthesis process of geopolymers and the development of binding gel. A high initial dissolution rate of silicate is known to accelerate the conversion of aluminosilicate materials to geopolymers (Fernández-Jiménez et al., 2006; De Silva et al., 2007), while the availability of aluminium in the source materials, and its release rate, are known to control geopolymer gel properties (Fernández-Jiménez et al., 2006; De Silva et al., 2007).

During geopolymer formation, dissolution, hydrolysis and condensation reactions take place. Depending on the concentration of Si in the system, condensation reactions can occur between aluminate and silicate species, or between silicate species themselves. While the dissolution of various compounds from aluminosilicates causes a gradual increase in Al and Si concentration in solution, this will stabilise when the Al and Si concentrations reach equilibrium with respect to the solid/gel phases present (Antonic et al., 1993). Dissolution behaviour of aluminosilicate compounds is controlled by the relationship between the forward and backward reactions leading to equilibrium. Forward reactions are related to the action of solvent in breaking the surface bonds (Si—O—Al), and formation of soluble species, and, therefore, are dependent on pH. Backward reactions are related to the reaction between soluble species in solution, on or with the surface of dissolving solid, and hence the concentration and speciation of aluminium and silicon in solution are critical in determining the rate of the backward reaction (Antonic et al., 1993).

Many researchers have published investigations on the dissolution of aluminosilicate compounds, and possible leaching of elements from various sources (Wang et al., 1999; Praharaj et al., 2002; Popovic et al., 2005; Jankowski et al., 2006; Gitari et al., 2009; Izquierdo and Querol, 2012; Crundwell, 2014; Granizon et al., 2014; Müllauer et al., 2015; Simonova et al., 2015). However, most of the studies are conducted in equilibrium conditions where

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both forward and backward reactions are controlling the release of elements. Authors have previously examined the role of aluminate and silicate release rates in controlling geopolymer nano-structure and gel growth behaviour (Hajimohammadi et al., 2010, 2011). In the early stages of the reaction, rapid release of alumina is shown to hinder the dissolution of silica particles, and more crystalline zeolite products and a more continuous gel microstructure is observed with slower alumina release rate (Hajimohammadi et al., 2010). In slowly released silicate systems, gel nucleation is observed to take place very close to the solid silica source particles, while nucleation happens in bulk regions in systems that initially contain dissolved silica. These differences in nucleation lead to a more chemically heterogeneous binder in slow silicate released systems (Hajimohammadi et al., 2011). Thus, understanding the initial dissolution rates of source material in far-from-equilibrium conditions is essential to understanding and controlling the behaviour of final geopolymeric binders.

In this paper, the dissolution rate of some geopolymer precursor materials is examined using a kinetic approach. The liquid to solid ratios were designed to be sufficiently high to minimise precipitation of hydration products. The dissolution behaviour of some geopolymer source materials is characterised, and the effects of pH and particle size distribution on dissolution behaviour are presented. These results have implications for the selection of geopolymer precursor materials and the mix design of geopolymer binders, and explain some of the behaviour of geopolymers in the literature.

2. Materials and methods

Fly ash (FA) can be used as a secondary raw material in many products such as concrete, and the main reason for the wide use of this material is its commercial availability throughout most of the world. Its utilisation in solid products provides an effective means of disposal of what is otherwise often a hazardous waste (Tsiridis et al., 2006). Fly ash is a popular material for synthesis of geopolymers due to its easy availability and the high workability of the binders formed (Palomo et al., 1999; Fernández-Jiménez et al., 2006; Provis and van Deventer, 2009). Metakaolin (MK) has been widely used as a supplementary cementitious material (SCM) to enhance the durability and strength of Portland binders, as well as being an important intermediate in ceramic processing. MK is also known to have a much faster dissolution rate than FA in alkali hydroxide and alkali silicate solutions and is a suitable source of aluminosilicate for geopolymer production (Davidovits, 1991; Duxson et al., 2007a, 2007b). Granulated blast furnace slag (GBFS) is an amorphous material containing depolymerized calcium silicate glasses and some poorly crystalline phases (Lea, 1970). The calcium aluminosilicate framework of GBFS is valuable to the cement and concrete industry, and it has been used mainly as a supplementary cementitious material in Portland cement concrete for enhancing its properties and long term durability. Also, having the key network forming cations in geopolymers (Al^{3+} and Si^{4+}) together with the potential for making hydrated calcium silicate gel (C-S-H) which is known to improve the setting and strength characteristics of geopolymers, GBFS can be used in geopolymer production blended with fly ash or metakaolin (Glukhovskiy et al., 1980; Van Deventer et al., 2007).

The most important selection criterion for a solid silica source in the synthesis of geopolymers is the dissolution rate, which must be fast so that the solution will rapidly become rich in Si. Therefore, both the structure and surface area of the solids are important. Two silica sources that have been used to some extent as additives in the concrete industry to enhance the properties of mortars and concretes, and have good potential in making high-quality geopolymeric materials, are rice hull ash (RHA) and geothermal silica (GTS) (Gomez, 2003; Chindaprasirt et al., 2008). GTS is a solid waste from geothermal power plants. Dissolved silica, in a hot stream of supersaturated water from lower levels of rock formations, precipitates as the water cools down after its discharge from the geothermal field and through heat exchangers

(Gómez-Zamorano et al., 2004; Hajimohammadi et al., 2008). The silica particles should have a high enough surface area for reaction, but not too high to compromise workability of the geopolymer paste. Geothermal silica has a very small particle size; however, the particles are aggregated. This gives a sufficiently high surface area for reaction and gives good workability without excessive water demand (Hajimohammadi et al., 2008). Unburnt rice husk has a very low density (90–150 kg/m³) and, therefore, has a large dry volume, and its rough and abrasive surface is very resistant to natural degradation. The cement and concrete industry can help in the disposal of this solid waste by consuming large quantities of it (Chandra, 1997).

The fly ash used in this research was sourced from Gladstone Power Station Queensland, Australia. Metakaolin, with the brand name of Metastar 402, was sourced from Imerys Minerals, UK. Granulated blast furnace slag was obtained from Independent Cement, Australia. Geothermal silica was obtained from the Cerro Prieto geothermal power station, Mexico. Rice hull ash was provided by Sunrice, Griffith, NSW, Australia. The results of X-Ray Fluorescence (XRF) analysis of all of the precursor materials are presented in Table 1.

The GTS is milled to reduce the particle size (BET surface area approximately 30 m²/g), and then washed with distilled water at 80 °C (liquid to solids ratio = 10) for 30 min to remove the salts that are associated with raw GTS. The resulting slurry is filtered and washed with more distilled water, and then dried at 40 °C and milled again before use. This method has been used previously to purify geothermal silica (Rincon, 1999). The purified geothermal silica is 96% SiO₂ and contains a small amount of various salts (Rincon, 1999).

A laboratory ring mill was used for milling material for different time intervals. A Malvern Mastersizer 2000 laser-diffraction particle-size analyser was used for measuring the particle size distribution of materials before and after milling. A Perkin-Elmer 3000 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used for elemental analysis of dissolved materials. Sodium hydroxide solutions were made at concentrations of 0.05, 0.1, 0.2 and 0.3 M using sodium hydroxide pellets (Sigma-Aldrich) and deionised water. The raw materials were mixed in polyethylene bottles (to avoid Si contamination) with the NaOH solutions, at liquid to solid weight ratios of 100:1 for FA, MK and GBFS and 200:1 for GTS and RHA. The higher liquid to solid ratio for the silica materials was designed to simplify the dissolution analysis since these materials show much higher extents of dissolution than the aluminosilicates. The liquid/solid ratios were designed to be sufficiently high in all cases to minimise problems due to reprecipitation during the leaching experiments. Suspensions were mixed for various time intervals before centrifuging, filtration and dilution with 5% HCl. At the beginning of each set of tests, some experiments were repeated to test reproducibility, which was within a standard error of 5%.

3. Results and discussion

3.1. Particle size distribution

Fig. 1 presents the particle size distributions of the raw materials studied after different milling times. The RHA, which initially has very fine particles ($d_{50} = 8 \mu\text{m}$), shows fewer changes in its size distribution after 5 min of milling among all samples. However, results show that milling gives a narrower size distribution and more submicron particle formation in this sample. The average particle size is reduced to 4 μm after 5 min milling. Milling of RHA is known to be beneficial for its application as an additive to cement (Bui et al., 2005). Although partial replacement of cement with RHA is very cost effective, and RHA can improve the properties of cement, the porous structure of this material increases the water demand, which is usually compensated by using superplasticizers. However, milling RHA to finer particles is believed to destroy the porous structure of this material (by breaking up porous aggregates of nanosized particles) and, therefore, reduce its water demand (Bui et al., 2005).

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