Fly ash-based inorganic polymers: understanding the precursor-to-product composition relationships

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Abstract

Much of the existing research regarding inorganic polymer binders (IPBs) has focused on the characterization and evaluation of a variety of aluminosilicate sources with significant levels of variation from one source to the next and inhomogeneity within a given source; the basic mechanisms that govern product formation, microstructure development and ultimately, engineering properties of IPBs, are still poorly understood. This work seeks to quantify the effects of pore solution composition and speciation as well as equilibration temperature on composition, structure, and solubility of sodium aluminosilicate hydrate (N-A-S-H), the primary binding phase in low-calcium IPBs. N-A-S-H is synthesized from reagent grade precursors, allowing complete stoichiometric control of the solution-to-product reaction stage and eliminating variables that complicate the precursor-to-solution compositional relationships.

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I. INTRODUCTION

Inorganic polymer binders are becoming an attractive alternative concrete binder because they eliminate the need for ordinary portland cement (OPC), which is extremely energy and carbon intensive to produce. These binders are synthesized by the activation of an aluminosilicate powder by a highly alkaline aqueous solution, most commonly sodium or potassium hydroxide [1]. Bulk Si/Al, Na/Al, and H_2O/Na ratios are considered the most important compositional parameters, and activating solutions with pre-dissolved silica are often employed to achieve target molar ratios [2]. Fly ash is perhaps the most economically viable aluminosilicate source for IPBs since it is available on a large scale at a relatively low cost. In 2013, coal-burning power plants produced roughly 53 million tons of fly ash, of which just under half was reused beneficially [3]. Fly ash-based IPBs have the added benefit of conserving greenfield space by diverting fly ash from landfills.

Previous research has demonstrated comparable mechanical properties (compressive strength, stiffness) [4]–[6], as well as superior dimensional stability [7] and durability (resistance to corrosion, alkali-silica reaction, acid attack) [8]–[10] of IPBs compared to OPC concrete. Much of the previous work on these materials, however, has taken a trial-and-error approach to dealing with the significant variation in composition and morphology between fly ash sources; widespread use of fly ash-based IPBs requires a better understanding of the basic chemistry that governs their product formation, microstructure development and ultimately, engineering properties.

The general process of alkali-activation of aluminosilicate solids involves dissolution of the initial solid particles by alkali hydrolysis followed by condensation, reorganization, and polymerization of the hydrolyzed silicate and aluminate species. The end product is a highly crosslinked tetrahedral sodium aluminosilicate hydrate (N-A-S-H) gel composed of either poly(sialate) (-Si-O-Al-O-), poly(silate-siloxo) (Si-O-Al-O-Si-O), or poly(sialate-disiloxo) (Si-O-Al-O-Si-O-Si-O) groups [11]. While synthetic calcium silicate hydrate [12] and calcium aluminosilicate hydrate [13] have been studied previously in the context of portland cement based binders, limited research has been published with regards to synthesizing and characterizing N-A-S-H gels [14].

The current research seeks to link the composition, structure, and solubility of N-A-S-H equilibrium phases with to their aqueous chemistry. Synthetic N-A-S-H gels are prepared from reagent grade materials across a range of compositions at various temperatures to allow complete stoichiometric control of the constituents and eliminate variability in the composition and solubility of solid precursors. The composition, structure, and solubility of the precipitated gels are then determined. The results are key to the development of thermodynamic modeling for these materials, ultimately transforming our ability to use portland cement-free IPBs.

II. MATERIALS AND METHODS

N-A-S-H gels are synthesized following methods similar to those described by Myers et al. [13] to produce calcium aluminosilicate hydrate gels. Stock solutions of (1) 2M sodium hydroxide, 0.4M silicic acid, and (2) 0.1M sodium aluminate are combined to obtain bulk molar Si/Al ratios of 1-2 and NaOH concentration of 1M (nominal pH = 14). Stock solution (1) is prepared by dissolving silicic acid powder in 400 mL 5M NaOH and diluting to 1L with CO_2-free Milli-Q water. Stock solution (2) is prepared by dissolving sodium aluminate powder in CO_2-free Milli-Q water. Samples are allowed to equilibrate at 4°C, 25°, or 50°C in 50 mL polypropylene tubes, rotated continuously at 8 rpm. Equilibration times are determined based on the time it takes for Si^{4+} and Al^{3+} concentrations to stabilize.

Aliquots of supernatant are taken from each sample after solids are allowed to settle for 20 minutes, filtered through a 0.2 μm polyvinylidene difluoride syringe filter, diluted, and acidified with 3% HNO_3. Concentrations of Na^+, Si^{4+}, and Al^{3+} concentrations are then measured by inductively coupled plasma optical emission spectrometry (ICP-OES). Aqueous hydroxide activities in the original (non-filtered) sample are measured using a standard pH electrode. The solids are then triple-rinsed by filling each tube with ~30 mL Milli-Q water, shaking manually to disperse the solids, centrifuging at 2000g for 10 minutes, and decanting the supernatant. The solids are then freeze dried at 5 Pa, -50°C for 24 hours before analysis. Extra care is taken to prevent sample carbonation by working in an N_2-filled glove box.

The composition of the solids is measured by hydrofluoric acid digestion followed by solution analysis using ICP-OES, and its structure is investigated using solid-state nuclear magnetic resonance (NMR) and X-ray diffraction (XRD). Structurally bound water is measured using thermogravimetric analysis (TGA). Temperature-dependent solubility products (K_{sp}) of the N-A-S-H gel are determined by monitoring the pH and ionic concentration of the solution over time until equilibrium is reached using ICP-OES.

III. RESULTS & DISCUSSION

To date, preliminary data have been collected regarding the change in Si^{4+} and Al^{3+} concentrations over time for samples with bulk Si/Al of 1 and 2. Si^{4+} and Al^{3+} concentrations for synthetic IPBs equilibrated at 25°C with bulk Si/Al = 1 are shown in [Fig. 1]. $[Si^{4+}]$ and $[Al^{3+}]$ both drop significantly between measurements taken at one month and four months. Between four and six months,
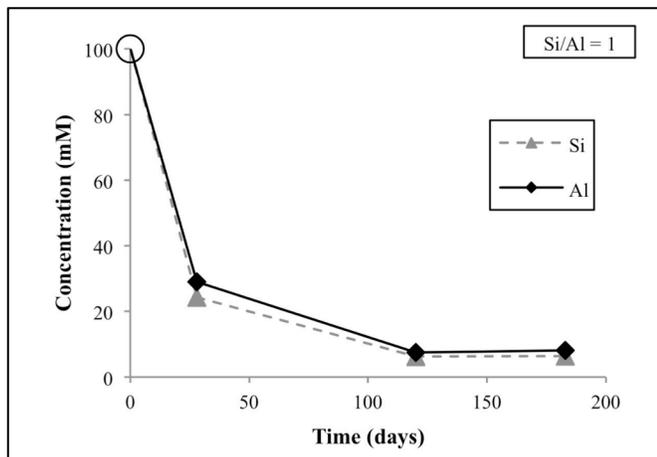
Fig. 1. Change in supernatant composition over time of synthetic IPBs with Si/Al = 1 equilibrated at 25°C. Open circles represent estimated initial concentrations. Lines are for eye guides only.

Fig. 2. Change in supernatant composition over time of synthetic IPBs with Si/Al = 2 equilibrated at 25°C. Open circles represent estimated initial concentrations. Lines are for eye guides only.

$[Si^{4+}]$ increased slightly from 6.27 mM to 6.36 mM (1.4 %) and $[Al^{3+}]$ increased from 7.47 mM to 8.17 mM (9.5 %). These relatively small changes between four months and six months suggest that this sample has approached equilibrium after four months, and since concentrations are expected to decrease over time as more Si and Al are incorporated into the solid phase, the small increase in measurement concentrations is probably due to experimental error.

Si^{4+} and Al^{3+} concentrations for synthetic IPBs equilibrated at 25°C with bulk Si/Al = 2 are shown in [Fig. 2]. For these samples, $[Si^{4+}]$ remains relatively constant between one month and four months while $[Al^{3+}]$ drops significantly during this time period, indicating that more aluminum is incorporated into the solid phase over time. Between four months and six months, $[Si^{4+}]$ increases from 78.9 mM to 82.7 mM (4.78 %), while $[Al^{3+}]$ decreases from 1.48 mM to 1.12 mM (24.1 %). Due to the relatively large change in $[Al^{3+}]$ between four months and six months, it appears that this sample has not equilibrated after four months. As more data become available, a more defined cutoff for establishing equilibrium conditions will be established and equilibrium times will be determined for all samples. Future replicates will allow an error analysis, which will also be helpful in determining which measurements fall within expected error ranges.
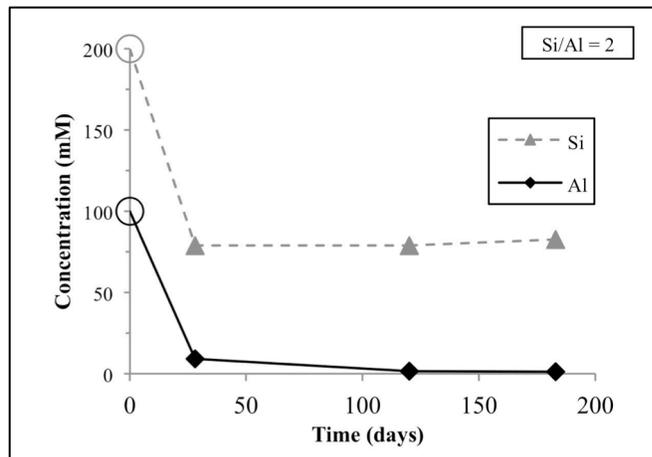
IV. FUTURE WORK

In future work, the N-A-S-H gels produced with Si/Al varying from 1 to 2 will be analyzed following the methods described previously to determine the effects of varying synthesis composition and temperature on product composition, structure, and solubility. Subsequently, the ratio Si/Na in the silicon stock solution will be varied to determine its impact on the N-A-S-H gels. Finally, a thermodynamic model will be created and validated that will predict product phase assemblages based on synthesis composition and temperature.

V. ACKNOWLEDGEMENTS

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