

BAYER PROCESS WASTE STREAM AS POTENTIAL FEEDSTOCK MATERIAL FOR GEOPOLYMER BINDER SYSTEMS

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Abstract

Recent developments in Mineral Polymer i.e. Geopolymer, binder technology points to a wide range of potential engineering applications within the mineral processing and mining sectors. Most notably, the principal raw feedstock materials required for this class of binders may be derived from both extractive and processing mineral waste materials such as clays, fly ash or red mud. It is the reaction of such solid mineral alumino-silicates with alkali silicate solutions that produces the chemical network structures characteristic of Geopolymer binders. The resulting high performance binder product can be mixed, placed and formed in the same manner as Portland cement mixtures with diverse applications in mineral waste processing, civil and geotechnical applications such as road pavement and embankments and in waste stabilization technologies and backfill mining cementing operations. Similar opportunities also exist in re-use options for Bayer process waste streams and in bauxite residue management.

This Paper presents fundamental synthesis parameters of Geopolymer binders with specific reference to oxide compositional limits of feedstock materials. In particular, experimental results disclosing the role of silica and alkali species present in feedstock materials and their impact on engineering properties such as strength development are presented. Geopolymer systems with high alkali contents ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.2$) are shown to be characterised by high strength, low porosity and a dense, fine grained microstructure. Such properties may be equivalently achieved with high silica and low alumina contents ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.5\text{--}3.8$). The observed synthesis parameters suggest potential beneficial and novel applications for red-mud as raw feedstock material in a variety of building product and civil construction applications.

1 Introduction

Commercial exploitation of Red mud solid residues from the Bayer process for obtaining alumina from bauxite in large scale construction and civil applications continues to attract considerable research interest [Mymrinm, 2003; Sglavo, 2000]. This interest arises partly because of the peculiar chemical and mineralogical composition of this material. The highly alkaline residue (pH = 10–12.5) is composed primarily of fine particles, ranging typically between 50°A and 1 µm, comprising silica, aluminium, iron, calcium and titanium oxides with iron impurities providing the brick red colour. These basic chemical characteristics strongly mirror a range of feedstock materials currently being explored for geopolymerisation reactions. Geopolymers represent a family of emerging synthetic compounds produced by reactions between aluminosilicate solids and an alkali silicate solution [Davidovits, 1994; van Jaarsveld, 1998] somewhat akin to zeolitic processes linked to the Bayer process.

The mineralogy of red mud suggest it can either partially or fully supplement the aluminosilicate fraction requirements for Geopolymer formulation with added advantage of providing essential alkali ions required for synthesis. Class F fly ash, which is high in aluminosilicate and low in calcium, is however the traditionally preferred raw material for large volume geopolymerisation reactions partly because of availability and relatively better understood technical performance [Palomo, 1999].

While several attempts have been made to develop a range of red mud-based products such as ceramic products (bricks, tiles, mortar and concrete [Sglavo, 2000] through conventional routes, minimal information exists on geopolymerisation reactions involving this material. Successful use or incorporation of red mud into Geopolymers will enable applications in both concrete construction and geotechnical applications i.e. road pavement, embankments as well as mineral waste stabilization technologies.

Thus, this study attempts to examine the relationships between chemical formulation, micro structure and mechanical properties of selected fly-ash based geopolymer systems to explore compositional limits relevant to red-mud mineralogy. The microstructure, studied by SEM, and the compressive strength of several fly ash-derived geopolymer formulations have therefore been investigated to determine the interrelationships of key oxide components and their implications on alternative feedstock sources such as Bayer process waste stream materials.

2 Experimental

All geopolymer samples were prepared from fly ash, alkali silicate solution, alkali hydroxide and distilled water. A Class F fly ash supplied by Pozzolanic Enterprises, Australia, was used throughout this work. The fly ash was mostly amorphous with the majority of particles passing minus 45 µm sieve.

The alkali silicate solution was supplied by PQ Australia and had the following concentrations: sodium silicate (8.9 wt% Na_2O , 28.7 wt% SiO_2 , and 62.5 wt% H_2O). Several geopolymer formulations were prepared with the different proportions of ingredients selected to allow the effect of alkali and silica content to be assessed.

The samples were prepared by initially mixing alkali hydroxide, alkali silicate solution and cooled, followed by the fly ash. All samples were mixed then immediately poured into preheated moulds which were sealed. All formulations were cured at 85°C for 2 hours, after which they were demoulded and cooled in a refrigerator to slow the reaction. Compressive strengths were measured on 25.4 mm cubes and SEM was performed on fracture faces.

The effect of molar concentrations of Na_2O and SiO_2 were thus analysed by a combination of electron microscopy and strength testing. The series of samples with compositional ratios ie $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.7$ to 3.9 differed in the proportion of the silica added in solution compared to that added as solid (fly ash).

Table 1. Nominal chemical composition of formulated geopolymer systems.

Nominal mix composition Alkali series	Na ₂ O/Al ₂ O ₃ Ratio
0.6Na ₂ O.3SiO ₂ .Al ₂ O ₃ .10H ₂ O	0.6
0.8Na ₂ O.3SiO ₂ .Al ₂ O ₃ .10H ₂ O	0.8
1.0Na ₂ O.3SiO ₂ .Al ₂ O ₃ .10H ₂ O	1.0
1.2Na ₂ O.3SiO ₂ .Al ₂ O ₃ .10H ₂ O	1.2
Nominal mix composition Silicate series	SiO ₂ /Al ₂ O ₃ Ratio
Na ₂ O.2.7SiO ₂ .Al ₂ O ₃ .10H ₂ O	2.7
Na ₂ O.3.0SiO ₂ .Al ₂ O ₃ .10H ₂ O	3.0
Na ₂ O.3.5SiO ₂ .Al ₂ O ₃ .10H ₂ O	3.5
Na ₂ O.3.9SiO ₂ .Al ₂ O ₃ .10H ₂ O	3.9

3 Results

3.1 The effect of alkali content

The fractured sample surfaces typically contain voids left by extracted whole unreacted particles. Some of the samples have unreacted particles making up a significant proportion of their volume.

In general, the microstructures of geopolymer samples looked similar to images previously published for these materials [Palomo, 1999; Silverstrim, 1997]. The condensed gel phase in the samples consisted of rounded growths with bridging between them (Figure 1). As also observed in Figure 1 for Na₂O/Al₂O₃ = 0.6 and 1.2, the respective gel phase matrices varied in densification and the amount of bridging material between spherical particles. Essentially therefore, the samples may be viewed as composites comprising of gel phase and partially reacted spherical particles. As such, the strength of the unreacted particles, the interfaces between them and the geopolymer matrix can be expected to have a significant bearing on the overall strength of the material.

Despite the range of compressive strengths in these four samples, there was not a great difference in their microstructures. There was however a slight decrease in the number of unreacted particles and an increase in the size of spherical-shaped particles with increasing alkali content Na₂O/Al₂O₃ = 0.6 through to 1.2 as seen from Figure 1.

The compressive strengths of the series samples show a progressive increase for samples with Na₂O/Al₂O₃ = 0.6, 0.8 and 1.0 then a decrease at ratios of 1.2, as shown in Figure 2. As the role of the alkali in geopolymers is partially to balance the charge of the aluminate groups in the tectosilicate, it is not unexpected to find that the compressive strength goes through a maximum when the alkali and alumina concentrations are equal. The other role of alkali in the system is to increase the solubility of the aluminosilicate, as indicated by Equation 1.

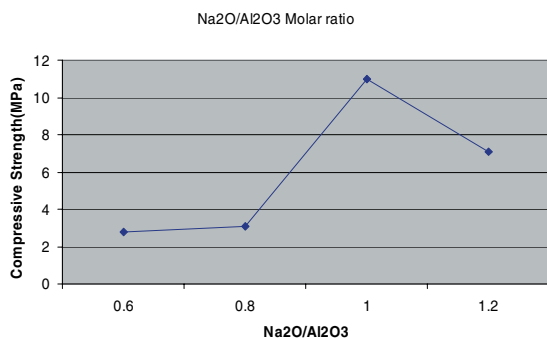
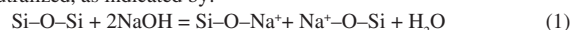


Figure 2: Effect of varying alkali concentrations i.e. Na₂O/Al₂O₃ = 0.6, 0.8, 1.0, 1.2 on compressive strength

In an alkaline medium (e.g. containing sodium ions) a conventional silica depolymerisation reaction is likely to occur, with any excess NaOH tending to disrupt internal Si-O-Si links of the silica tetrahedron after the acidic hydroxyl groups at the surface of the silica have been neutralized, as indicated by:



It is therefore possible that in the case of fly ash, the charge-balancing role is dominant, whereas, dissolution may be dominant for other types of feedstock material.

In agreement with previous results, the higher samples were found to be much stronger than at lower pH (50 times the strength at pH 12). Indeed, approximately twofold increase in Na₂O molar concentration from Na₂O/Al₂O₃ = 0.6 to 1.0 quadruples the strength.

3.2 The effect of silica content

The change in strength with silica content was quite dramatic, in particular the small change (11%) from SiO₂/Al₂O₃ = 3.5 to 3.9 gave a 62% strength increase as shown in Figure 3. The four samples with SiO₂/Al₂O₃ = 2.7 3.0 3.5 and 3.9 indicated trends of silica concentration on the structure and strength of geopolymers. As expected, this variable had the most dramatic effect on the microstructure and the strength.

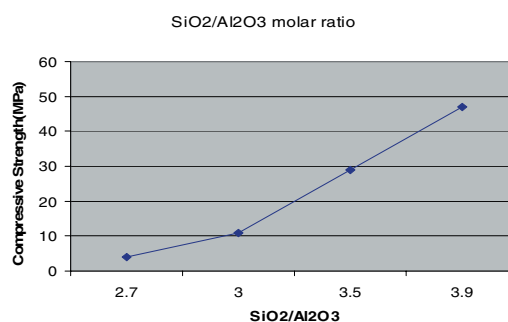


Figure 3. Effect of varying silica content on compressive strength of geopolymers systems

From Figure 3, the difference in compressive strengths between SiO₂/Al₂O₃ = 3.0 and 3.5 was greater than that between ratios of 2.7 and 3.0 or 3.5 and 3.9, as would be expected given the silica concentrations. Also, the compressive strengths of the Si series of samples followed the changes in the microstructure in the expected way, i.e. the densest, finest grained samples being also the strongest as shown in Figure 4.

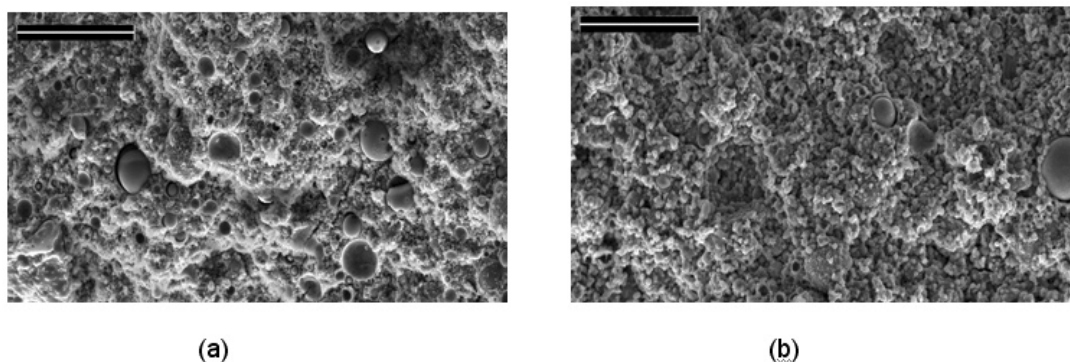


Figure 1: Microstructures of samples containing different alkali levels.
(a) $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 0.6$ (b) $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1$. Scale bar represents 50 μm .

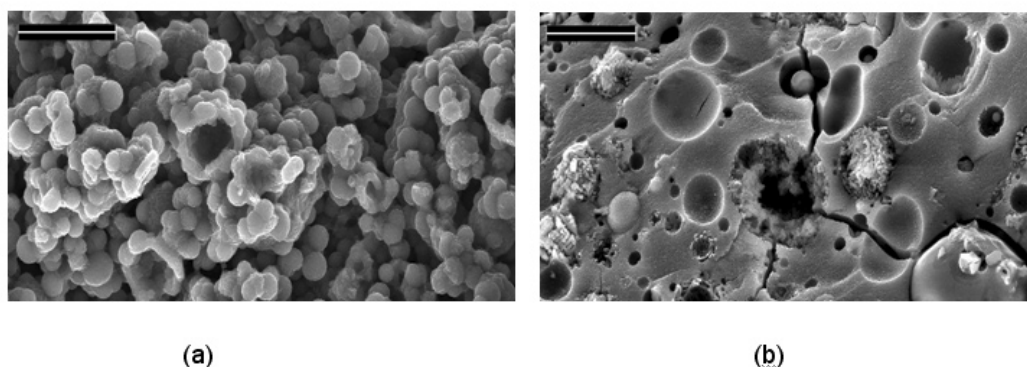


Figure 4: High magnification images of geopolymers containing different amounts of silica (a) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.7$ (b) and $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.9$. Scale bar represents 1 μm .

4 Discussion

It was observed that the investigated fly ash-based formulations had characteristic complex microstructures and structural variety. In particular, some of the samples contained some crystalline material, particularly those samples with the highest strength and the densest microstructure.

The compressive strengths of the samples in general could be related to both the composition and the microstructure in a logical way. The compressive strengths were however generally quite low. These findings and their implications on feedstock material selection may be best understood by examining the fundamental dissolution and condensation reactions occurring during synthesis. Compared with zeolite reactions, condensation in geopolymers appears to be more complex due to the existence of a variety of oligomeric silicate species. The process may be further complicated by the overlap of dissolution processes, hydrolysis and condensation reactions, which regulates the speciation conditions for condensation. In this context, the continuously changing environment of concentration of various species and the pH value of the liquid phase also remains critical.

With reference to red mud residues from the Bayer process, aluminium loss due to the formation of an insoluble by-product named 'Bayer sodalite', $(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}) \cdot \text{Na}_2\text{X}$, where X may be CO_3^- , SO_4^- , 2OH^- , 2Cl^- or a mixture of them, depending on the digesting liquor composition. It is conceivable that available free Al ions derived from red mud at high pH may result in initial formation of a variety of aluminate species.

Given that aluminate anions for the reaction are solely derived from the dissolution of mineral oxides under alkaline conditions, monomeric $[\text{Al}(\text{OH})_4]^-$ ions are probably the only aluminate species existing under high alkaline conditions [Swaddle, 2001]. On the other

hand, silicate species come from both soluble alkaline silicates and the dissolution of mineral oxides. In the specific case of fly ash or for red mud-based systems, the silicate species from the dissolution of particles are difficult to predict because the hydrolysis process of amorphous silica is kinetically dependent on various factors, such as the activity of the particles, temperature, time, and the concentration and pH value of alkaline silicate solutions.

Silicon solubility, on the other hand, is generally much less than aluminium under alkaline conditions. Thus, aluminate anions are likely to react with silicate species from alkaline silicate solutions. Alkaline (mainly Na and K) silicate solutions used in the production of geopolymers, typically have high SiO_2 concentrations above 5 M, and $\text{M}_2\text{O}/\text{SiO}_2$ ratios of 0.66–0.83 by the addition of NaOH. These alkaline silicate solutions have a high content of polymeric silicate species, as demonstrated by Barbara et al. [Barbosa, 2000]. Therefore, the condensation in geopolymers will likely occur between monomeric $[\text{Al}(\text{OH})_4]^-$ and a variety of silicate species, including monomers and oligomers.

The Al/Si ratio in geopolymer compositions are however known to have an important influence on the structure and mechanical properties of the geopolymer materials, since the Al component mostly determines the condensation process. Solid-state NMR Al^{29} results [Barbosa, 2000] showed that the peak of the $[\text{AlO}_4]$ unit linked to four tetrahedral $[\text{SiO}_4]$ units is relatively sharp in geopolymers. Furthermore, a higher Al composition as may be found in red mud derived systems points to condensation occurring more readily, leading to a dense network structure due to the removal of more hydroxyl groups. Therefore, as expected, geopolymers composed of a higher Al component may be brittle, and have high hardness.

5 Conclusions

The results followed expected theoretical trends and there were clear correlations between composition, microstructure and strength. It was found that high strength was related to low porosity and a dense, fine grained microstructure. Such a structure was found in geopolymers with high alkali contents ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.2$). High silica and low

alumina contents ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.5\text{--}3.8$) also produced this structure however there was a limit beyond which the strength deteriorated. The observed synthesis parameters suggest potential beneficial and novel applications of red-mud as raw feedstock material in a variety of building product and civil construction applications.

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