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<th>Nazari, Ali; Maghsoudpour, Ali; Sanjayan, Jay G.</th>
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Boroaluminosilicate geopolymers: role of NaOH concentration and curing temperature

Ali Nazari,* a Ali Maghsoudpour b and Jay G. Sanjayan a

a) Centre for Sustainable Infrastructure, Faculty of Science, Engineering and Technology, Swinburne University of Technology, Victoria, 3122, Australia
b) Department of Geopolymer and Concrete, WorldTech Scientific Research Center (WT-SRC), Tehran, Iran
* Corresponding author, Tel: +61 3 92148370, Email: alinazari@swin.edu.au

In the present paper, effects of concentration of sodium hydroxide solution (NaOH) and curing temperature on properties of boroaluminosilicate fly ash-based geopolymers are studied. Geopolymers, cement-free eco-friendly construction materials, are formed by alkali activation of an aluminosilicate source. By changing alkali activator from silica-rich to boron-rich one, it may be possible to have boroaluminosilicate binders. Results obtained indicated formation of B–O bonds in these types of geopolymers. Increasing of NaOH concentration was observed to reduce compressive strength due to changes occurs in the nature of reactions between alkali activator and fly ash particles. Establishment of unwanted complex compounds as well as formation of non-stoichiometric aluminosilicate binders instead of boroaluminosilicate ones were supposed to be the main reason of this strength reduction. Additionally, curing temperature had a strong effect on formation of new phases in specimens. Various microstructures were observed in boroaluminosilicate binders, where presence of needle-like crystals was the main difference between these types of geopolymers and aluminosilicate one.

I. Introduction

Emission of greenhouse gases through industrial activities is of major impact on global warming and it is believed that at least 5-7 % of CO₂ release to the atmosphere is due to the production of ordinary Portland cement (OPC).¹ Enormous efforts have been made by research community around the world in developing alternative concretes to reduce global carbon emissions. Geopolymers, eco-friendly materials produced from industrial by-products such as fly ash, slag or metakaolin, are considered as the main possible low carbon alternative to Portland cement concrete. This has led to significant research activities around the world in geopolymers in recent years. Australia is a leader in this field and is also leading the world in the number of field applications, where geopolymer concrete has been applied in real world constructions.² Therefore, it is worthwhile to investigate utilization of these by-products and to characterize them for further usage in construction.
Fly ash is the most common aluminosilicate source for geopolymer production. Several fly ash types are produced all around the world with various chemical compositions. Experimental surveys show that aluminosilicate geopolymers made from different types of fly ashes have unpredictable strengths. This has been shown in some previously published works. By the anticipated increasing demands on production of eco-friendly materials, it is of importance to provide stable high quality fly ash sources for production geopolymers. Unfortunately, attaining high compressive strength by means of the most of fly ash types is impossible. Therefore, alternative methods should be investigated to adopt suitable alkali activation process and materials for low quality fly ash types.

Modification methods to obtain high strength geopolymer concrete vary from optimizing mixture proportions to changing curing conditions. Several additive materials such as ordinary Portland cement (OPC), slags and nanoparticles are being used to improve mechanical properties of geopolymers. Curing at higher temperatures for faster strength gain is also of interest. Another way for increasing the strength is to change type of alkali activator. In aluminosilicate geopolymers, a mixture of sodium silicate (Na$_2$SiO$_3$) or potassium silicate (K$_2$SiO$_3$) together with sodium hydroxide (NaOH) or potassium hydroxide (KOH) is used. Some works mention the use of other types of alkali activators; this cause non-traditional mixtures such as aluminogermanate geopolymer, phosphoric acid-based geopolymers with Si–O–Al–O–P–O structures and borosilicate geopolymers.

Williams and van Riessen developed borosilicate geopolymers by alkali activation of silica fume. Their alkali activator was a mixture of NaOH and anhydrous borax (Na$_2$B$_4$O$_7$). It is supposed that Al–O bonds are substituted in some extent by B–O bonds. They could achieve compressive strength of up to 57 MPa for a paste, which is high enough for engineering usages. However, silica fume is not widely available to guarantee consistent production of high strength geopolymers. By using fly ash as the raw material, it is anticipated that some parts of aluminosilicate bonds are remained. Therefore, a complex structure which is called boroaluminosilicate is formed. In the authors’ previous work, boroaluminosilicate geopolymers were introduced. The variables of that work were liquid to solid and borax to NaOH weight ratios. Additionally, the type of fly ash used in that work was different; aluminosilicate geopolymer produced by that fly ash had better compressive strength than those produced by the fly ash of this work. Therefore, fly ash of that study is called high quality while the fly ash used in this work is designated as low quality. The effects of NaOH concentration on compressive strength and microstructure variation of specimens is of special interest in this paper.

II. Experimental procedure

A low quality fly ash for production aluminosilicate geopolymers was selected for this study. The fly ash was purchased from Flyash Australia Pty Ltd. Experimental investigations on various aluminosilicate geopolymer pastes by using this fly ash resulted in a maximum compressive strength of 16.9 MP at 90 days of curing. This value is not suitable for application of geopolymers as a construction material. Chemical composition of this fly ash is as following: 45.8 % SiO$_2$, 22.1 % Al$_2$O$_3$, 1...
11.8 % Fe₂O₃, 10.1 % CaO, 4.2 % SO₃, 0.5 % Na₂O and L.O.I was 3.4 %. Average fly ash particle size was 16 µm and the BET specific surface was 75.9 m²/g. Fig. 1 illustrates particle size distribution of the utilized fly ash.

Alkali activator was a mixture of anhydrous borax and NaOH. Anhydrous borax was produced by heating borax decahydride (Na₂B₄O₇·10H₂O) at 150 °C for 30 min to dry the water and subsequent heating at 300 °C for 15 h to remove intermolecular water. Produced anhydrous borax was then mixed with NaOH solution with different concentrations. Sigma Aldrich NaOH flakes with 97 % purity were dissolved in tap water to make NaOH solution with concentrations of 5, 8, 12 and 14 M. NaOH solution then was added to anhydrous borax and mixed for one minute to make alkali activator. After that, it was left in room conditions to cool down. Anhydrous borax to NaOH weight ratio was 0.7.

To make geopolymers, alkali activator (anhydrous borax + NaOH) to fly ash weight ratio of 0.8 was used. Specimens were mixed for 5 minutes by a laboratory available mixture. One percentage of the water was replaced by polycarboxylate superplasticizer to keep the workability of all mixtures in an acceptable range (between 60 -65 mm). Mixture proportions of geopolymeric pastes have been illustrated in Table 1.

Specimens were poured into 50 mm polypropylene cubic moulds in two layers. The half-filled moulds in each step were vibrated for 45 sec. After that, moulds were covered by wet polythene sheets for 24 h for pre-curing purposes. Then, the specimens were demoulded and cured at different temperature for 24 h in accordance to Table 1. Compressive strength of the specimens was achieved at 3, 7, 28 and 90 days of curing (24 hours oven curing is included) according to the ASTM C109 standard.

Microstructure of the produced specimens was evaluated by SEM and FT-IR analyses. VEGA TESCAN microscope in secondary electron mode was used for SEM analysis to consider both fracture surface and microstructure. To do FT-IR analysis, a tiny part of those specimens cured for 90 days were powdered and mixed with KBr at a concentration of 0.2–1.0 wt.% to make KBr disks. FT-IR analysis was performed by a BRUKER TENSOR27 apparatus.

### III. Results and discussion

#### a. Compressive strength

Fig. 2 shows compressive strength of all geopolymer mixtures. It is evident that by increasing curing time from three to 90 days, compressive strength rises as well. However, compressive strength of a specific mixture at 90 days of curing is not much different by that at early ages. Additionally, comparison between compressive strength of aluminosilicate geopolymer (maximum of 16.9 MPa) produced from the fly ash used in this study and boroaluminosilicate geopolymers shows the successful alkali activation of low quality fly ash by anhydrous borax and NaOH mixtures.

Although some scatterings are observed in compressive strength results, G1-G4 specimens with NaOH concentration of 5 M seem to have higher strengths. This is an interesting finding opposing results obtained from aluminosilicate geopolymers, where higher concentration of NaOH causes dissolution of more Si⁴⁺ and Al³⁺ into alkali activator and higher strength. Here, by increasing of NaOH concentration, as Table 1 illustrates, the amount of borax in alkali activator
decreases and less B–O bonds are supposed to form. This can show the positive and strong effect of B–O bonds on compressive strength of boroaluminosilicate geopolymers. However, this relationship has not been approved for heterogeneous materials such as OPC or geopolymer concrete. Among G5-G8 specimens with NaOH concentration of 8 M, two mixtures namely G7 and G8 have high strengths. This is while among G9-G12 specimens with NaOH concentration of 12 M, only one mixture namely G11 has high strength. Finally, among G13-G16 specimens with NaOH concentration of 14 M, no mixture has high strength. Therefore, it is suggested that low and medium NaOH concentrations are being used for production of boroaluminosilicate geopolymers.

Curing temperature has an irregular effect on compressive strength evolution of the considered boroaluminosilicate geopolymer mixtures. Regardless of NaOH concentration of 12 M, the highest and lowest strengths are attainable by curing at 90 and 40 °C respectively and any NaOH concentration. For specimens with NaOH concentration of 12 M this condition is exactly in the opposite form and highest and lowest strengths are acquired by curing at 40 and 90 °C respectively.

On the whole, successful synthesis of boroaluminosilicate geopolymers seems to depend on the mixture proportions (e.g. NaOH concentration) than age and temperature of curing.

b. Fracture surface and microstructure

Microstructure of some selected specimens has been illustrated in Fig. 3. This figure shows that various types of microstructures are formed during alkali activation of high-boron content mixtures. Especially, some needle-like crystals are seen in some microstructures which are not observed in a traditional aluminosilicate geopolymer. Unfortunately, there is no evidence for addition of borax or boron into alkali activators to consider their effects on geopolymerization. Therefore, no mechanism can be adopted for formation of these particles. However, our suggested mechanism is as following:

Borax reacts with NaOH and forms sodium perborate:

\[
2\text{Na}_2\text{B}_4\text{O}_7 + 2\text{NaOH} \rightarrow 4\text{NaBO}_2 + \text{H}_2\text{O}
\]  

This reaction takes place between 60 to 90 °C. Needle-like crystals are seen more clearly in Figs 3b and 3d, which have been cured at 70 °C. However, during the initial mixing of borax and NaOH, some heat is released and hence, possibility of formation of sodium perborate in alkali activator is anticipated. Therefore, it is possible to have sodium perborate even in specimens cured at 25 and 40 °C. After this stage, it is probable that some of the available oxides in the utilized fly ash react with sodium perborate and change its crystalline shape. Some evidence on the effect of silica on crystalline growth of sodium perborate is available. Although these needle-like crystals are not proved to be based on sodium perborate, one may discuss that reaction between fly ash particles and sodium perborate helps their formation. In fact, functional groups of sodium perborate can react with oxides such as SiO₂, Al₂O₃ and Fe₂O₃ in fly ash particles and form different microstructures than traditional aluminosilicate geopolymers. Such a type of functionalizing has been reported for OPC concrete where carbon-based functional additives can change the microstructure of hydrated cement to flower-shape crystals (by adding graphene oxide) or other strange types (by adding graphite oxide).

Regardless of needle-like crystals, from Fig. 3, one can observe eight different fracture surfaces which can show
differently, mechanisms of fracture with respect to aluminosilicate geopolymers. In traditional aluminosilicate geopolymers made from different sources of aluminosilicates, the resultant fracture surfaces are approximately same. Although some differences are observed among various sources of aluminosilicates, for a specific aluminosilicate source, even by changing parameters such as NaOH concentration, alkali activator content and curing temperature, microstructures are very similar containing a paste with some unreacted fly ash particles. In boroaluminosilicate geopolymers, there are little unreacted particles, and a condensed paste with different fracture surfaces and crystals is observed.

Another interesting feature of these boroaluminosilicate geopolymers is their fracture surface, where little cracks are seen. In traditional aluminosilicate geopolymers, unreacted fly ash particles are a barrier to propagating crack and therefore, affect on crack’s path. A typical microstructure of aluminosilicate geopolymers containing several cracks has been given in the authors’ previous work [19]. Here, in boroaluminosilicate geopolymers, because of formation of a condensed paste, changing the path of crack is less likely to happen. However, branching of cracks or continuing in one direction only indicates the mechanism of crack propagation and does not reveal the strength of geopolymers. Although branching of crack may dissipate the applied stress, the final strength of a brittle cement matrix structure depends on another aspect, namely the strength of the paste. Therefore, in the studied boroaluminosilicate geopolymers, probable formation of functional crystals with the aim of sodium perborate functional groups is anticipated to form pastes with higher strengths.

The mechanism of formation of different pastes’ microstructures may depend on NaOH concentration. In high NaOH concentrations (12 and 14 M), the amount of borax available in alkali activator significantly reduces and hence, mechanism of reaction of alkali activator and fly ash particles changes as well. In these specimens, some aluminosilicate compounds may form. This may be the reason of appearing few cracks in microstructure of specimens with NaOH concentrations of 12 and 14 M, Figs. 3f and 3g respectively.

c. FT-IR result

Aluminosilicate geopolymers have Si–O tetrahedrons, connected via corner sharing bridging oxygen, and that tetrahedrons with n bridging oxygen’s are denoted as Qn (n = 0, 1, 2, 3, or 4). All of these bonds have been addressed in the literature and the previous work. FT-IR spectra of all of 16 considered specimens have been illustrated in Figs. 4-7. Main B-O stretching bonds are appeared between 1380-1310 cm⁻¹.

Fig. 4 illustrates FT-IR spectra of specimens with NaOH concentration of 5 M. For all four mixtures, main aluminosilicate bonds and B-O bonds are formed. For all figures indicating FT-IR spectra of specimens (including Fig. 4) many peaks were achieved; their data points were removed to show the figures better. Only the position of B-O bonds has been illustrated for comparison purposes. Although it has not been approved for heterogeneous materials, this may be why the specimens in this group have higher strengths than other groups. Formation of stretching B-O bond may help strengthening of geopolymers. Formation of N-H stretching bond in G3 specimen with the highest strength (Fig. 4c) is totally different. This indicates formation of other types of bonds as a result of curing at 70 °C. G3 and G4 specimens (cured at 90 °C with FT-IR spectra illustrated in Fig. 4d) have the strongest B–O bond in this group. Therefore, it is suggested that
for specimens with NaOH concentration of 5 M cured at above 70 °C, functional groups of sodium perborate can effectively react with cement particles. However, they may be formed in G1 and G2 specimens cured at below 70 °C with fewer amounts. The other interesting point is the unclear effect of CO\textsubscript{2} on strength evolution of geopolymers. While in OPC concrete\textsuperscript{31} and aluminosilicate geopolymer concrete\textsuperscript{32, 33}, carbonation due to CO\textsubscript{2} absorption causes reduction of strength, in boroaluminosilicate geopolymer it does not have a clear effect.

For geopolymer mixtures with NaOH concentration of 8 M, and in specimens cured at below 70 °C (G5 and G6 with FT-IR spectra illustrated in Figs. 5a and 5b respectively), no B–O bond is observed. On the other hand, formation of this bond is seen in G7 and G8 specimens cured at above 70 °C. Additionally, main aluminosilicate bonds are different here, and it seems that for G5 and G6 specimens, weaker Si–O bonds are formed. This may indicate that for specimens with medium level of NaOH concentration, some complex compounds are formed, which negatively affect on compressive strength evolution. However, this negative effect improves by formation of boroaluminosilicate compounds from functional groups of sodium perborate at higher temperatures. Again, absorption of CO\textsubscript{2} has an unclear effect on strength gain. N-H bonds are also totally different in these specimens, which may indicate formation of other unwanted compounds.

Fig. 6 shows FT-IR spectra for mixtures with NaOH concentration of 12 M. Specimen G11 with much higher strength than other specimens in this group has the strongest B–O bond. Same as specimens with NaOH concentration of 8 M, here, no B–O bond is observed for the specimens cured at below 70 °C (G9 and G10 specimens). For all specimens, weak Si–O bonds are formed. Formation of N-H bonds is also different and many weak and strong bonds are seen in this region. Therefore, for this concentration of NaOH, formation of complex compounds due to unbalanced ratio between aluminosilicate and boroaluminosilicate precursors may result in the lowest strength. Only G11 specimen cured at 70 °C may be considered to have functional groups of boroaluminosilicate compounds.

Fig. 7 illustrates FT-IR spectra for mixtures with NaOH concentration of 14 M. G13 specimen in Fig. 7a has a very weak B–O bond while G14 reveals no B–O bond. Additionally, G15 and G16 specimens in Figs. 7c and 7d respectively have stronger B–O bond than G13; however, in comparison with specimens with NaOH concentrations of 5 and 8 M, in this group, strength is not high. While in aluminosilicate geopolymers increasing of NaOH concentration results in easier dissolution of Si\textsuperscript{4+} and Al\textsuperscript{3+} into alkali activator\textsuperscript{20} and formation of more geopolymeric compounds, in boroaluminosilicate ones it decreases the amount of borax and subsequent compounds containing B–O bonds. Higher strength of this group with respect to specimens with NaOH concentration of 12 M may be due to formation of some aluminosilicate compounds (not complex unwanted ones). This can be seen by comparing Figs. 6 and 7, where increasing of NaOH concentration results in formation of stronger stretching Si–O bonds. Additionally, G13 and G14 specimens with lower strengths have more complicated N-H bond formation region than G15 and G16 specimens. Once again, it is probable to have complex unwanted compounds in G13 and G14 specimens.

**IV. Conclusions**
It is possible to make geopolymers by a different alkali activator, namely borax + NaOH, where formation of functional groups causes changes in aluminosilicate compounds in geopolymers and creates boroaluminosilicate binders. One possible reason of strength gain of these classes of geopolymers may be formation of stronger compounds containing B-O bonds. By increasing of NaOH concentration and hence, decreasing borax content, more complex compounds and non-stoichiometric aluminosilicate bonds are formed and compressive strength decreases. Microstructure of some specimens, especially those cured at 70 °C, shows needle-like crystals, which may be due to formation of boroaluminosilicate bonds between functional groups of sodium perborate and fly ash particles.

References


Table 1. Mixture proportions of the specimens

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<tr>
<th>Sample designation</th>
<th>NaOH concentration (M)</th>
<th>Content of NaOH flakes (Kg/m³)</th>
<th>Content of water (Kg/m³)</th>
<th>Content of superplasticizer (Kg/m³)</th>
<th>Curing temperature (°C)</th>
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Borax to NaOH solution weight ratio: 0.7; alkali activator (anhydrous borax + NaOH) to fly ash weight ratio: 0.8; Content of fly ash: 1197 Kg/m³; Content of borax: 394 Kg/m³
Fig. 1. Particle size distribution of fly ash
Fig. 2. Compressive strength of specimens; NaOH concentrations are as following: G1-G4: 5M, G5-G8: 8 M, G9-G12: 12 M and G13-G16: 14 M.
Fig. 3. SEM micrographs of a) G2, b) G3, c) G5, d) G7, e) G9, f) G10, g) G13 and h) G16 specimens
Fig. 4. FT-IR analysis results for specimens with NaOH concentration of 5 M; Curing temperature for a, b, c and d are 25 °C (G1), 40 °C (G2), 70 °C (G3) and 90 °C (G4) respectively.
Fig. 5. FT-IR analysis results for specimens with NaOH concentration of 8 M; Curing temperature for a, b, c and d are 25 °C (G5), 40 °C (G6), 70 °C (G7) and 90 °C (G8) respectively.
Fig. 6. FT-IR analysis results for specimens with NaOH concentration of 12 M; Curing temperature for a, b, c and d are 25 °C (G9), 40 °C (G10), 70 °C (G11) and 90 °C (G12) respectively.
Fig. 7. FT-IR analysis results for specimens with NaOH concentration of 14 M; Curing temperature for a, b, c and d are 25 °C (G13), 40 °C (G14), 70 °C (G15) and 90 °C (G16) respectively.
Boroaluminosilicate geopolymers from a fly-ash source have a variety of microstructures. This may be due to different mechanisms of geopolymerization.