The Use of Geopolymerization Process for Boron Fixation in Fly Ash

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Abstract: This research focuses on some efforts in laboratory scale to create artificial barriers by injecting alkalis to the heap of fly ash. The alkaline solution was combined from 2 to 12 Molar of sodium hydroxide and sodium silicate to have some variation of alkalis. Some barriers made from injecting alkalis with different concentration from 4M to 8M of sodium hydroxide show an optimum result. Internal shrinkage experiment which was conducted to examine the performance of geopolymer pastes indicated a rapid solidification less than one day. Boron concentration from specimens submerged in water determined by ICP Test was contributed by the barrier instead of the fly ash pile.

Key word: Boron; fly ash; leaching; geopolymer

1. Introduction

Fly Ash, a by-product of brown coal electric power plant, is produced in million tons in many countries and is partially discarded into landfills or disposal ponds near the power plant. It may result many problems besides its utilized improving the soil’s physical properties and raising the pH of acid soils. Leakage from ash ponds contains high sulphate, boric acid and other contaminants can actuate environmental impact problems. The potential toxicity posed by those contaminants in soil and ground water has been considered to cause phytotoxicity in plants especially by the accumulation of boron [1]~[7]. Boron leaching from fly ash by rainwater causes potential problems since soluble elements can enter the environment through contact of disposed fly ash with natural waters. Several research results have been contributed to trace elements leaching from fly ash, but only a few numbers considered boron leaching from fly ash [8]. Increasing of pH solution and some alkalis are reported playing an important role to control boron released from fly ash [9]~[12]. Alkali-activated fly ash to immobile high concentration of boron from specimens was reported by Palomo result a potential improvement [13]. Geopolymer technology was introduced in years to stabilize hazardous materials from fly ash. The idea of immobilizing heavy metals by application this technology was considered by many researchers as a barrier material [14]. Therefore, some constrained barriers need to be developed to separate fly ash dump from the natural environment.

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In this study, specimens were prepared by injecting sodium silicate and sodium hydroxide to fly ash which varies in sodium hydroxide concentration. Barrier created from paste then was devised as the alkali dissolved rapidly to retain boron leaching from fly ash beneath the barrier. The experiment to determine boron ion leaching from the specimens to the enclosed space was conducted by submerging the specimens in the deionised water. Boron ion concentration was then detected by ICPS (Inductively Coupled Plasma Spectrometry).

The objective of the present study, therefore, was to examine the performance of barriers to capture boron leaching from fly ash beneath the barrier. To observe the shrinkage of geopolymer pastes, pre-embedded gages were inserted and the result was compared to Portland cement paste. Furthermore, by looking into the performance of barriers generated by geopolymer paste with different concentration of alkali injection the authors proposed an initial impression of the potential application of geopolymer technology to the environment.

2. Experiments

(1) Materials and Mix Proportion
Fly ash having 2.33 g/cm³ of density adopted in this study is obtained from Sapporo, Japan. Its chemical composition and toxic substances are listed in Table 1 and Table 2 respectively.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>MnO₂</th>
<th>SO₃</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>(%)</td>
<td>59.5</td>
<td>22.84</td>
<td>6.33</td>
<td>2.44</td>
<td>0.96</td>
<td>0.02</td>
<td>1.63</td>
<td>1.14</td>
<td>0.08</td>
<td>0.21</td>
<td>1.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Chrom 6+</th>
<th>Arsenic</th>
<th>Fluorine</th>
<th>Boron</th>
<th>Selenium</th>
</tr>
</thead>
<tbody>
<tr>
<td>(μg/gr)</td>
<td>0.87</td>
<td>14</td>
<td>310</td>
<td>120</td>
<td>3.7</td>
</tr>
</tbody>
</table>

This study uses granular sodium hydroxide with 98% purity as alkali activator of fly ash with respective molarities of 2, 4, 6, 8, 10, and 12M. In addition, sodium silicate (SiO₂/Na₂O = 2.31 and solid content 57%) is mixed with sodium hydroxide with ratio 1:1 for polymerization activation. Both the liquids were mixed together, prepared one day before injecting to fly ash and kept in environmental control room.

(2) Specimens and Test Methods
All laboratory glassware which may contain borosilicate cannot be used in this study. Specimens were prepared by adopted 70 gr of fly ash in cylindrical plastic cases. The height of this container is 80 mm and 35 mm in diameter. The powder was compacted before it was then injected by the alkali activator. About 6 gr liquid aliquots of alkaline activators from different concentration was poured severally to the top of fly ash in each container to obtain about 1 cm of penetration. The method is fast and does not require any mixing since the paste begins to form and harden after all liquids dissolve into the powder. The plastic containers were then covered and kept for 7 days in the environmental control room having 60% and 20° C of RH and temperature respectively. A barrier from each geopolymer paste will be created just about 1 day after injection. Binders made from fly ash bound up with the alkaline injection can be separated from the ash to examine the penetrability of each activator and to measure their porosity. In other containers, to close a gap between the barrier and its container, a seal material is placed on periphery of the barrier as shown in Fig 1.

Specimens were submerged in 1 kg of de-ionized...
water as illustrated in Fig 2. The boron from specimens is leak out and measured in every 7 days during 100 days of the immersion. About 2 gram sample aliquots from the liquid are determined by ICPS for boron concentration by using boron standard solution. According to the research about measuring boron from fly ash, ICPS test is one of the most reliable methods [15]-[16].

Boron leaching from samples can be calculated from Eq.1 as:

\[
B(\%) = \frac{B(\text{ppm}) \times \text{Water(\text{gr})}}{\text{Sample(\text{gr})} \times B(\mu\text{g}/\text{gr})} \times 100% \quad (1)
\]

\(B(\text{ppm})\) is obtained from ICPS test, amount of de-ionized water as Water (gr), fly ash used in this study is 70gr or amount of fly ash bound by alkaline solution and initial boron contained in fly ash is 120 gr/gr.

The method proposed for the study of the shrinkage of geopolymer is based on an experimental work developed by Nawa for autogeneous shrinkage of high performance concrete [17].

In this study, free shrinkage strain of paste under sealed curing conditions was measured by pre-embedded strain gauge. As shown in Fig.3, a 30 mm long acrylic gauge from KM-30-120-H1-11Y3M2 designed by Kyowa was used. Specimen used in this measurement was cast in a cylindrical mold of 50mm in diameter and 100mm in length.

The measurement of shrinkage was carried out by measuring the change in linear length of the specimen. Subsequently, the strain gauge was placed vertically at the center of the mold which was finally filled with fresh paste. In order to prevent evaporation of moisture to the surrounding, the top surface of the specimen was sealed using a film sheet. All specimens were kept in the environmental control room. After mixing, the strain was continuously measured and recorded by a personal computer.

Fig.2 Method of measuring boron leaching from specimen

Fig.3 Experiment set up for shrinkage measurement

Geopolymer pastes are compared with Ordinary Portland Cement (OPC) paste and OPC paste with 40% replacement by blast furnace slag (BFS). In order to improve the workability, water-Reducing Agents Rheobuild SP8SBs and Glenium C316 were employed for OPC and geopolymer paste respectively. Paste specimens with liquid-powder ratio of 35% were prepared as given in Table 3.

![Table 3 Mix proportions of paste specimens (kg/m³).](image)

<table>
<thead>
<tr>
<th>Paste</th>
<th>NaOH (M)</th>
<th>liq/powder</th>
<th>powder</th>
<th>liquid</th>
<th>SP</th>
<th>BFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geop 4M</td>
<td>4</td>
<td>0.35</td>
<td>1410 (FA)</td>
<td>494 (alkali)</td>
<td>25.6</td>
<td>0</td>
</tr>
<tr>
<td>Geop 6M</td>
<td>6</td>
<td>0.35</td>
<td>1410 (FA)</td>
<td>494 (alkali)</td>
<td>25.6</td>
<td>0</td>
</tr>
<tr>
<td>Geop 8M</td>
<td>8</td>
<td>0.35</td>
<td>1410 (FA)</td>
<td>494 (alkali)</td>
<td>25.6</td>
<td>0</td>
</tr>
<tr>
<td>Geop 10M</td>
<td>10</td>
<td>0.35</td>
<td>1410 (FA)</td>
<td>494 (alkali)</td>
<td>25.6</td>
<td>0</td>
</tr>
<tr>
<td>OPC</td>
<td>-</td>
<td>0.35</td>
<td>1410 (OPC)</td>
<td>494 (water)</td>
<td>7.1</td>
<td>0</td>
</tr>
<tr>
<td>OPC+BFS</td>
<td>-</td>
<td>0.35</td>
<td>846 (OPC)</td>
<td>494 (water)</td>
<td>7.1</td>
<td>564</td>
</tr>
</tbody>
</table>
3. Results and Discussion

(1) Barriers from Dissolved Alkalis

Fig. 4 shows some barriers from fly ash bound up with alkalis. In average, 6 gram of alkaline solutions from 2M to 8M bind about 25% from total fly ash piled up in the container. Due to workability problems, 10M and 12M of alkali injection cannot bind more than 5% of the ash. The additional sodium silicate as a dense gel retains the solution to penetrate deeper. In this case, solution from 2M of sodium hydroxide binds more than others activator.

In contrast, less density of alkali as shown by 2M samples has higher porosity as shown in Fig.5. Moreover, due to workability problems, higher porosity also resulted by 12M samples.

(2) Boron Concentration

In the case of boron leaching from barriers, hardened pastes from the container were picked up and submerged in the de-ionized water.

For simplification, Fig. 6 shows the result only from 4 barriers. As a result, the barriers liberated almost all boron ions from the paste just after 10 days immersion. In other words, the barriers could not retain boron leaching from fly ash in the paste.

The result of boron leaching from specimens can be seen in Fig.7.
Specimens injected with 4M-10M alkali released boron ion less than that specimens made from 2M and 12M of sodium hydroxide. The boron ion detected from submerging water might be released by the barriers. It also can be seen obviously that 2M and 12 M specimens released more boron ion from the fly ash beneath their barrier. By the end of the experiment, for almost 10 months of immersion time, fly ash beneath some particular barriers was still dry while in some others was totally wet as illustrated in Fig.8. Consequently, solidification resulted by injecting alkalis is strong enough to prevent the water contact with the fly ash.

![Dry and wet specimens after 10 months immersion](image)

(3) Shrinkage of Some Pastes

Shrinkage of some binder pastes based on various concentration of sodium hydroxide is given in Fig.9.

![Comparison of shrinkage between some geopolymer and OPC pastes](image)

All geopolymer pastes show a very fast solidification. About one day after casting, there are almost no change in strain detected by embedded gauges.

It has generally been reported by many researchers that geopolymer products have low shrinkage. As a comparison, OPC paste or OPC and BFS paste show higher shrinkage in the early age due to chemical and autogeneous shrinkage [18]. The trend of this shrinkage promotes during the hydration time. By the end of the measurement (36 days), shrinkage of the paste of OPC and OPC mixed with BFS showed 680µ and 1060µ respectively while all geopolymer pastes showed less than 420µ.

4. Conclusion

As the result shown by shrinkage measurement, Geopolymer pastes harden rapidly and do not show large shrinkages. Consequently, the binders formed by injecting alkalis into fly ash solidified rapidly as the liquid diffused into the powder.

Due to porosity and workability problems, some barriers formed by injection of 4M-10M solution from sodium hydroxide combine with sodium silicate give the optimum result. Lower concentration of alkalis can diffuse deeper to the heap of fly ash and harden faster but have higher porosity due to weaker chemical bound in geopolymerization process. Higher concentrations of alkali have a possibility to form stronger chemical bound but too dense to penetrate the powder. As a consequence, this workability problem also causes higher porosity. Higher porosity was supposed to be the main cause of boron leaching from the barriers.

Alkali injection to piles of fly ash can form self barrier to fly as which can retain boron leaching from the powder beneath the hardened paste, but it cannot capture boron released from the barriers itself. Hardened barrier resist water penetrating to the powder but as was seen in the result from ICP Test, the barriers release almost all boron ions from their surface.
References