

## Structural Evolution of Phosphate-Based Geopolymer Waste Forms to Immobilize Radioactive Borate Waste

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### 1. Introduction

Radioactive borate is problematic to be solidified using cement material, because the soluble borate such as  $B(OH)_3$  hinders the hydration reaction of cement waste form [1]. Especially, tetrahydroxyborate formed as a result of reaction between borate and hydroxide ions can react with the calcium oxide or calcium hydroxide in the cement. The insoluble calcium borate phase formed by this reaction deposits on the surface of cement particles, resulting in the setting retardation and poor mechanical strength of cement waste form [1].

Geopolymers are inorganic materials and can be formed at room or low temperatures (under 100 °C). They are synthesized by combining amorphous aluminosilicate materials such as coal ash (fly ash, bottom ash, and pond ash) and metakaolin with alkaline activators such as sodium silicate or potassium silicate solution [2]. The structure of a geopolymer is composed of a polymeric Si-O-Al framework and the negative charge is balanced by an alkaline cation such as  $Na^+$  or  $K^+$ . Because geopolymer can be formed at low calcium condition, it can immobilize the radioactive waste which is difficult to be solidified using cement.

Recently, the phosphate-based geopolymer fabricated using phosphoric acid was developed and incorporated into the geopolymer category because of similar polycondensation process in geopolymer formation. The phosphate-based geopolymers show some attractive properties such as high early-age strength and chemical stability depending on the mix formulations. However, the application research on the immobilization of radioactive waste is still very limited.

In this study, we investigated immobilization of radioactive borate waste using phosphate-based geopolymer waste form. In addition, the structural evolution of it according to the increase of the waste loading was studied.

### 2. Methods and Results

#### 2.1 Fabrication of phosphate-based geopolymer waste form and characterizations

A simulated borate waste was prepared as reported previously (Table 1) [3].  $Na_2B_4O_7 \cdot 10H_2O$ ,  $NaNO_3$ ,  $KNO_3$ ,  $Ca(NO_3)_2 \cdot 4H_2O$ ,  $Zn(NO_3)_2 \cdot 6H_2O$ , and  $Mg(NO_3)_2 \cdot 6H_2O$  were mixed with 1 L of deionized water (DIW) homogeneously. The mixture was dried in an electric oven and milled in a micro grinder to obtain fine powders [3].

Table 1: The target chemical composition of borate waste

Element	Concentration (ppm)
B	221,490
Na	76,000
K	2,333
Ca	1,600
Zn	583
Mg	495

Metakaolin, phosphoric acid (85%), and DIW were used as raw materials of phosphate-based geopolymer waste forms. The liquid/solid ratio of geopolymer was kept constant as 2.2 and the waste loading was 10 wt% to 40 wt%. The cement waste form consisted of 20 wt% ordinary Portland cement, 40 wt% blast furnace slag, and 40 wt% class F fly ash. The mass ratio of water to cement materials was kept constant at 0.4 and waste loading was 10 wt%. Raw materials and borate waste were mixed using a thinky mixer. After homogeneous mixing, the fresh geopolymer and cement mixtures were poured into plastic cylindrical molds with a diameter of 30 mm and a height of 60 mm. The geopolymers and cement waste forms were cured following the curing conditions (Table 2).

The 7-days compressive strength, X-ray diffraction (XRD), and solid-state  $^{11}B$ ,  $^{27}Al$ , and  $^{31}P$  magic-angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) analysis were performed to investigate the structural evolution of geopolymer waste form by addition of different borate wastes.

Table 2: The mix proportions of phosphate-based geopolymer and cement waste forms

Sample	L/S ratio	Waste loading (wt%)	Curing conditions
P0	2.2	-	RT <sup>a</sup> for 4d + 60 °C for 2d + RT for 1d
P10		10	
P20		20	
P30		30	
P40		40	60 °C for 4d + 90 °C for 1d +
PH10		10	
PH20		20	

PH30		30	RT for 2d
PH40		40	
Cement	0.4	10	RT for 28d

<sup>a</sup> RT: room temperature (25 ± 1 °C)

## 2.2. Effect of curing condition on the compressive strength of phosphate-based geopolymer waste forms

All geopolymer waste forms exceeded the waste form acceptance criteria (3.445 MPa) and showed the higher waste loading and compressive strength than cement waste form (2 MPa) prepared with 10 wt%, despite shorter curing days (~7d) compared to ~28 d for cement [3]. The compressive strength of geopolymer waste form that cured at room temperature and 60 °C (P0-30 geopolymers) decreased with an increase in waste loading and P40 geopolymer waste form was not hardened (Table 3). On the contrary, the compressive strength of geopolymer waste form (PH10-40 geopolymers) that cured at 60 °C and 90 °C was proportional to the waste loading (Table 3). It is believed that the additional high temperature curing contributed to the acceleration of geopolymerization and strength development [4]. Interestingly, the maximum compressive strength of 26 MPa was achieved at 40 wt% borate waste (PH40 in Table 3).

Table 3: The compressive strength of phosphate-based geopolymer and cement waste forms

Sample	L/S ratio	Compressive strength (MPa)
P0	2.2	23 ± 3
P10		10 ± 2
P20		10 ± 1
P30		9 ± 2
P40		Not hardening
PH10		9 ± 2
PH20		12 ± 3
PH30		15 ± 4
PH40		26 ± 2
Cement		0.4

## 2.3 Effect of borate waste on the structural evolution of phosphate-based geopolymer waste form

As a result of XRD analysis, amorphous phase and two crystalline phases were observed in the geopolymer waste forms. The sodium tetraborate crystalline phases (borax, tricalconite, and frolovite) present in the borate waste [3] were not observed. Sassolite (B(OH)<sub>3</sub>, #00-030-0620) was observed in all geopolymer waste forms. It indicates that 4-coordinated boron units of borate waste transformed to the 3-coordinated boron unit due to the strong acidic environment of phosphoric activator. Anatase (TiO<sub>2</sub>, #00-004-0477) is an impurity present in the raw material [3].

The solid-state <sup>11</sup>B MAS NMR analysis showed the two resonance signals at -4 ppm and -20 ppm. These are attributed to the 4-coordinated boron unit and 3-coordinated boron unit respectively. The 3-coordinated boron resonance signal was dominant at all geopolymer waste forms. The 4-coordinated boron resonance signal was attributed to the unreactive borate waste.

The Si-O-P-O-Al unit which is main network in phosphate-based geopolymer was confirmed in all geopolymer waste forms via <sup>27</sup>Al and <sup>31</sup>P MAS NMR analysis. Especially, the isolated phosphate tetrahedral unit associated with two boron atoms (Q<sup>0</sup>2B) resonance signal was observed in PH30 and PH40 geopolymer, which showed high compressive strength. It is believed that this secondary network formation attributed to the strength development in phosphate-based geopolymer

## 3. Conclusions

In this study, the borate waste was immobilized using phosphate-based geopolymer waste form for the first time. All geopolymer waste forms exceeded the waste form acceptance criteria, and showed the better waste loading as well as mechanical strength compared to cement waste form. The highest 7-day compressive strength (26 MPa) was found in the geopolymers containing 40 wt% of borate waste. The boron phosphate bonding unit was confirmed in geopolymers containing 30 wt% and 40 wt% of borate waste. It is believed that the secondary network formation is attributed to the strength enhancement in phosphate-based geopolymer.

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