In-situ Immobilization of Cesium-Contaminated Montmorillonite using Phosphoric Acid Geopolymer

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1. Introduction

Radioactive cesium (Cs-137) became a major environmental concern after the Fukushima Daiichi accident due to its strong adsorption onto clay structures, resulting in large volumes of contaminated soil requiring effective immobilization[1][2]. Among various matrices, geopolymers have emerged as attractive material for the efficient immobilization of radionuclides owing to their dense and chemically durable aluminosilicate network. However, most geopolymer systems rely on calcined precursors such as metakaolin to increase reactivity and applying this calcination approach to contaminated soil would incur substantial cost and raise volatilization concerns of radionuclides during treatment[3]. To overcome this limitation, we introduced an *in-situ* approach with acid pre-treatment prior to geopolymerization, allowing partial dissolution of the montmorillonite structure without physical treatment. This pre-reaction enabled in-situ geopolymerization of cesium (Cs)-contaminated soil without a physical treatment step, providing a practical route for immobilization process.

2. Materials and Methods

2.1 Materials

The raw materials for geopolymer synthesis were Ca-montmorillonite (STx-1b, CMS), commercial metakaolin (MetaMax®, BASF), 85% H_3PO_4 (Samchun Chemical), and $NaNO_3$, CsCl (Sigma-Aldrich). The reactions were performed using deionized water (DIW).

2.2 Preparation of simulated Cs-contaminated soil

The Cs-contaminated soil (Cs-MMT) was prepared by adsorbing Cs onto Ca-montmorillonite to simulate Fukushima Cs-contaminated soil. In a typical reaction, 40g of MMT were dispersed in 500mL of 0.5M $NaNO_3$ aqueous solution and spiked with 1000 ppm Cs. The resulting suspension was stirred for 2days at 300 rounds per minute (rpm) to allow ion exchange equilibration[1][2] and washed by DIW for 2 times. The MMT suspension was centrifuged at 5000 rpm for 10 minutes (m) and the solid residue was dried at 75°C for 48 hours (h) and crushed prior to the next reaction. The elemental (Cs, Al, Si) contents were determined by ICP-MS following hydrofluoric acid (HF) digestion, yielding a Cs uptake of 5.44 mg Cs per gram of MMT.

2.3 Geopolymer synthesis

Phosphoric acid geopolymers were synthesized according to the molar ratios shown in Table 1. Before geopolymerization, Cs-MMT was pre-reacted with 1M, 5M or 10M H_3PO_4 solutions and mixed using mixer (ARE-310, Thinky corporation, Japan) for 2 m at 1800 rpm prior to 1 h reaction. During reaction, the mixtures were shaken at 160 rpm. For the 1M pre-reaction condition, 2.4g of 1M H_3PO_4 was used and for the 5M condition, 4.15g of 5M H_3PO_4 was used for the pre reaction respectively, followed by supplementation with 85% H_3PO_4 to achieve the optimized ratio[4]. After pre-reaction, 85% H_3PO_4 solution and metakaolin was added to achieve the targeted geopolymer ratio and mixed using a mixer for 4 m at 1800 rpm. For the instant condition, Cs-MMT was directly mixed with 10M H_3PO_4 and metakaolin without a pre-reaction step. After mixing, geopolymer mixtures were poured into cubic PTFE plastic molds (20mm×20mm×20mm) and sealed to prevent evaporation. The specimens were cured under 60°C for 24 h[5].

Table 1 : Molar ratio (composition) of the geopolymer

Si / Al	Si / P	Al / P	Liquid / Solid ratio	Cs-MMT content (wt%)

1.4	1.02	0.73	1.4	30

2.4 Characterization

The compressive strength of prepared geopolymer were measured by a universal testing machine (ST-1001, Salt Inc., South Korea). X-ray diffraction (XRD) analysis was performed by an X-ray diffractometer (MiniFlex, Rigaku, Japan). Attenuated total reflection Fourier transform infrared spectroscopy (FT-IR, Nicolet iS10, Thermofisher scientific, USA) was used to test the vibration of chemical bonds in the synthesized samples. The morphology was observed by scanning electron microscope (SEM), and energy dispersive spectrometer (EDS) was used to analyze elemental composition of samples (JSM-7800F Prime, JEOL, Japan).

3. Results and discussion

The compressive strength results of the prepared geopolymer are displayed in Fig. 1. The synthesized geopolymer exceeded the waste form acceptance criteria in Korea repository (3.45 MPa). The acid pre-reaction increased the strength, reaching a maximum of approximately 25 MPa.

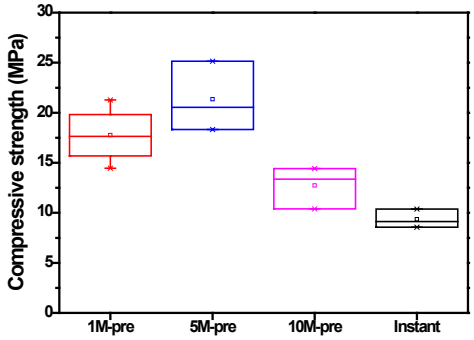


Fig. 1. Compressive strength of geopolymer cured at 60°C for 24 h.

Fig. 2 represents the XRD patterns of geopolymer and it has a broad diffraction pattern which indicates amorphous geopolymerization was occurred. Patterns at 20° and 22.5° 2-theta regions also showed that the MMT structure was slightly preserved, suggesting that Al released from the MMT framework participated in geopolymerization, while the Cs-incorporated domains of the MMT structure were retained without complete dissolution.

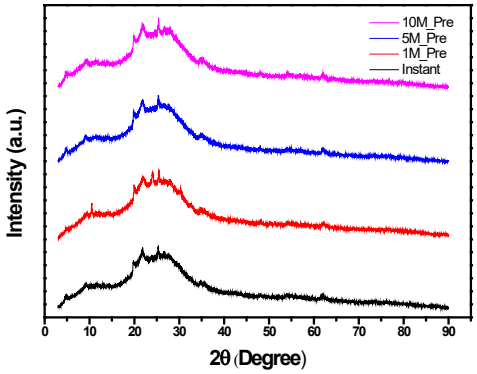


Fig. 2. XRD patterns of geopolymer cured at 60°C for 1 day.

Fig. 3 represents the FT-IR spectra of geopolymer. The broad IR bands at 3400 cm^{-1} and 1635 cm^{-1} can be attributed to surface –OH and H–O–H vibrations, respectively. The significant peak observed at 1050 cm^{-1} represents to Si–O–T and P–O–T (T = Si or Al), and the peak at 915 cm^{-1} represents P–O, and Al–O–P vibrations, indicating that the geopolymer framework was formed through a phosphate network. The peak at 790 cm^{-1} corresponds to Si-O-Si vibration, which indicate the montmorillonite siloxane group is preserved, but Al layer participates in geopolymer network generation.

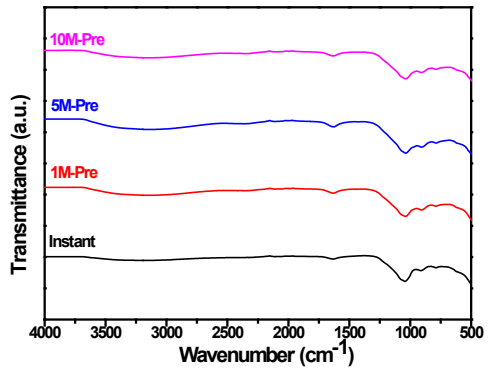


Fig. 3. FTIR spectra of the geopolymer cured at 60°C for 24h.

The SEM was performed to examine the morphology of pre-reacted geopolymers. The SEM images and EDS results confirmed that geopolymer network was formed with a fraction of the MMT structure remaining preserved.

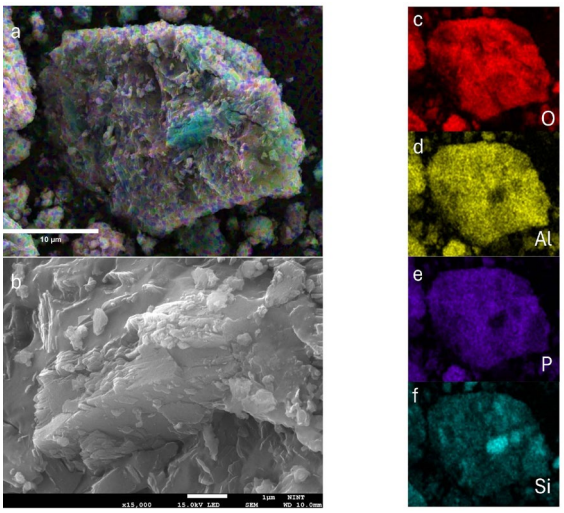


Fig. 4. SEM images (a, b), and EDS analysis (c, d, e, f) of geopolymer for 10M pre-reaction.

4. Conclusion

The phosphoric acid geopolymer was synthesized by utilizing the *in-situ* acid pre-treated Cs contaminated soil as a precursor. The geopolymerization and partial dissolution of MMT framework were validated by the XRD, FTIR, and SEM-EDS analyses. The compressive strength test revealed that pre-treatment could increase the formation of denser geopolymer network. Furthermore, the acid pre-treatment of the contaminated soil enables its use as a geopolymer precursor without the need for additional substrate (e.g., metakaoline). Consequently, partially replacing the metakaolin with the contaminated soil, this approach enables direct *in-situ* geopolymerization without additional modification process, and can save the cost and process times.

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