Transactions of the Korean Nuclear Society Autumn Meeting
Goyang, Korea, October 24-25, 2019

Durability and leaching behavior of geopolymer waste form for HyBRID sludge waste

Jinmo Ahn [a], Wooyong Um [a,b,c*]
[a] *Division of Advanced Nuclear Engineering, POSTECH, 77, Cheongam-ro, Nam-gu, Pohang, South Korea*
[b] *Division of Environmental Science and Engineering, POSTECH, 77, Cheongam-ro, Nam-gu, Pohang, South Korea*
c Nuclear Environmental Technology Institute, POSTECH, 77, Chongam-ro, Nam-gu, Pohang, South Korea
[*]Corresponding author: wooyongum@postech.ac.kr

1. Introduction

The hydrazine based reductive metal ion decontamination (HyBRID) process with sulfuric acid is recently developed for decontamination of the primary coolant system of the nuclear reactor and considered as an attractive process consisting of hydrazine, copper ion, and sulfuric acid without any organic chelates. After the HyBRID process, the condensed radioactive wastewater is generated and contains residual hydrazine and sulfuric acid with radionuclides such as cobalt-60 and nickel-63 [1]. This wastewater is converted to HyBRID sludge waste by a solid-liquid separation process that involves the addition of cristobalite (SiO_2) and barium hydroxide ($Ba(OH)_2$). The HyBRID sludge waste is the final product of the HyBRID process formed through $BaSO_4$ precipitation, containing high content of sulfate.

The presence of sulfate in HyBRID sludge waste may cause defective cement waste forms due to the potential formation of sulfate bearing mineral such as ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$]. Therefore, instead of cement waste form, a geopolymer waste form was proposed in this study for solidification of HyBRID sludge waste.

2. Methods and Results

2.1 Preparation of waste forms

Kaolinite ($Al_2Si_2O_5(OH)_4$, CAS number 1332-58-7; Sigma Aldrich Inc. USA) was calcined at 750 °C for 4 h to transform to the metakaolin (MK). Ordinary Portland cement (OPC) was obtained from Sampyo Industry co. (South Korea) and used to make cement waste form for comparison. The chemical compositions of MK, OPC, and HyBRID sludge determined by X-ray fluorescence (XRF) are shown in Table 1. KOH (45%, CAS number 1310-58-3) was obtained from Sigma Aldrich, and mixed with powder type of fumed silica (FS, 0.2-0.3 µm of particle size, Sigma-Aldrich, CAS number 112945-52-5) and deionized (DI) water to make alkaline activator.

2.2 Geopolymer synthesis

All geopolymers were formulated with the desired molar ratios of Si/Al, K/Al, and H_2O/Al by matrix calculation. The raw materials, OPC for cement waste form and MK for geopolymer waste form, were initially blended with HyBRID sludge waste. Each mixture was then mixed with DI water for cement waste form or alkaline activator solution for geopolymer waste form using a Fisher Vortex-Genie 2 (Fisher Scientific) for 5 min at room temperature. The wet pastes were homogenized using a planetary centrifugal mixer (ARE 310, Thinky, Japan) for 90 s at 1000 RPM. The geopolymer paste was then cast into a polyethylene cylinder mold (diameter 23 mm, height 46 mm). The air bubbles were expelled by vibration for 15 min. Each paste was sealed by a cap and cured at room temperature (25 ± 1 °C) for 28 d.

Table 1. Chemical compositions of metakaolin and HYBRID sludge waste (wt%)

	SiO_2	Al_2O_3	BaO	SO_3	CaO	LOI*
MK	54.8	39.5	-	-	-	4.89
OPC	20.2	5.01	-	2.39	63.6	3.59
HYBRID sludge	45.8	2.04	28.9	13.8	1.23	4.42

*LOI: loss of ignition

2.3 Characteristics of both waste forms

X-ray diffraction (XRD) patterns of dried HyBRID sludge waste, cement, and geopolymer samples obtained by the Rigaku diffractometer are shown in Fig. 1. The major constituents of HyBRID sludge waste before solidification were barite ($BaSO_4$, 01-083-3078) and cristobalite (SiO_2, 01-082-0512), and these phases still remained dominant after solidification for both geopolymer and cement waste forms. Ettringite mineral was not detected in geopolymer waste form.

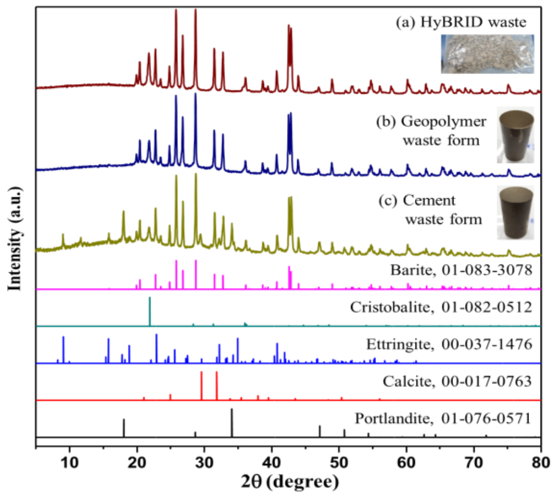

Fig. 1. XRD patterns of (A) HyBRID sludge waste after drying (105 °C, 2 h), (B) geopolymer sample with 40 wt% HyBRID sludge waste; the chemical composition of geopolymer is $K_2O{\cdot}3.2SiO_2{\cdot}Al_2O_3{\cdot}12H_2O$, and (C) cement waste form with 40 wt% HyBRID sludge waste.

The compressive strength of the cured specimens was determined according to ASTM C39 [2] by using a universal testing machine (ST-1002, Salt Inc., South Korea).

The compressive strength of geopolymer specimens containing 40-wt% of HyBRID sludge varied with the Si/Al molar ratios (Fig. 2). The HyBRID sludge waste (40-wt%) influenced the compressive strength of geopolymers at Si/Al ratios of 1.4 - 1.8, but no observable difference was found at Si/Al = 2.0 ratio between potassium-based geopolymers with and without waste.

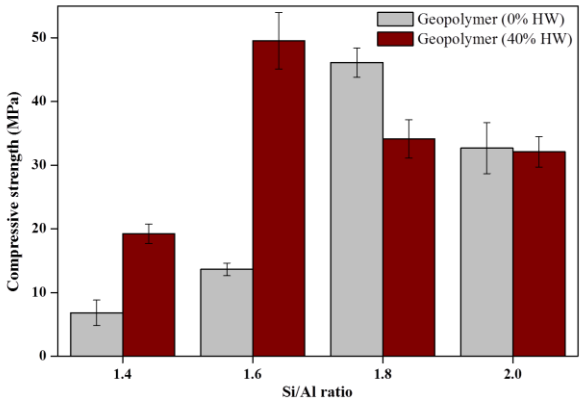

Fig. 2. Variation of compressive strength of potassium-based geopolymers with and without 40 wt% of HyBRID sludge waste with different Si/Al molar ratios (1.4-2.0).

2.4 Leaching experiment

A semi-dynamic leaching test (ANSI/ANS 16.1) was performed following the American Nuclear Society standard method [3].

The variations of the D_{eff} values of cobalt and barium are plotted in Fig. 3. The average D_{eff} values of both cations are sufficiently low ($<10^{-16}$), indicating that leaching barely occurred in the geopolymer waste forms. This result is consistent with previous data indicating that a geopolymer binder is good applicants for the immobilization of cations [4].

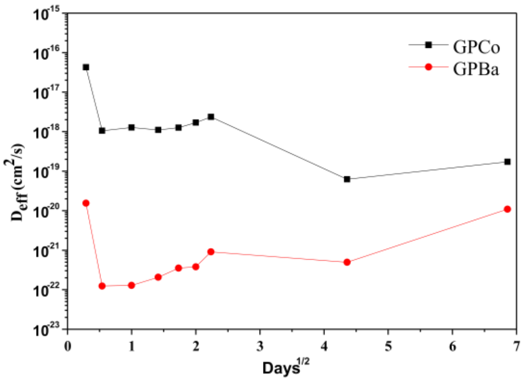

Fig. 3. Effective diffusivity of Co and Ba solidified from the geopolymer waste form in the DI leaching solution.

3. Conclusions

Sulfate-rich radioactive waste is an abiding challenge for cementitious solidification due to the formation of sulfate mineral such as ettringite. Such secondary mineral can cause the disintegration of cement waste form, resulting in the increase of leachability. Therefore, we developed a calcium-free geopolymer waste form to solidify the high sulfate HyBRID sludge waste. Potassium-based geopolymer showed high compressive strength and low leachability of cobalt. Based on these results, sulfate-rich HyBRID waste was successively solidified into a calcium-free geopolymer waste form.

REFERENCES

[1] J.S. Song, H.J. Cho, M.Y. Jung, S.H. Lee, A Study on the Application of CRUDTRAN Code in Primary Systems of Domestic Pressurized Heavy-Water Reactors for Prediction of Radiation Source Term, Nuclear Engineering and Technology, 49 (2017) 638-644.

[2] ASTM C39, Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, C39M-18, ASTM International, West Conshohocken, PA, 2018.

[3] A.N.S.I. (ANSI), Measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure, ANS/ANSI-16.1 Standard, 2003.

[4] C. Shi, A. Fernandez-Jimenez, Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements, Journal of Hazardous Materials, 137 (2006) 1656-1663.