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Properties of alkali-activated slag-fly ash-metakaolin hydroceramics for immobilizing of simulated sodium-bearing waste

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ABSTRACT

This work is a continuation of previous study of the alkali-activated slag-fly ash-metakaolin hydroceramics (ASFMH) waste form which was designed for solidifying simulated sodium-bearing waste (S-SBW). The thermal stability, resistances to gamma irradiation, freeze–thaw, and water immersion of ASFMH waste form were investigated systematically. The thermal stability results showed that the physical appearance of ASFMH waste forms was intact and without external cracking after calcination at 300, 500, 800 and 1000 °C. Importantly, the main crystalline phase of ASFMH waste form is still analcime after being calcined at 500 °C. The irradiation results indicated that the strong gamma irradiation could not induce the lattice damage of crystalline phases. The durability tests suggested that the compressive strength loss of ASFMH waste forms was 5.07, 19.04 and 10.51% after 500 kGy doses of gamma irradiation, 5 freeze–thaw cycles and 90 days of water immersion, respectively. It is suggested that ASFMH waste form designed for immobilizing S-SBW shows superior basic properties.

1. Introduction

The radioactive sodium-bearing waste (SBW) with high-radioactivity generated from nuclear fuel reprocessing operations contains radioactive constituents, heavy metals (Goles et al., 2001), as well as high contents of sodium and cladding materials (aluminum, zirconium, and stainless steel) (Chipman et al., 1989; Bader, 2005). The researchers of the Idaho National Engineering and Environmental Laboratory (INEEL) propose four treatment processes for the handling of SBW. The four alternatives are: (a) steam reforming, (b) calcination, (c) cesium ion exchange with immobilization, and (d) direct evaporation (Lauerhass et al., 2003). In consideration of the uncertainties result from technical and operational risk for each of the four treatment technologies, the preferred treatment method is inclined to choose the third way. Therefore, various matrices were proposed for the immobilization of SBW, such as glass (Bevilacqua et al., 1996; Ojovan and Lee, 2007; 2011), ceramic (or synrock) (Buykx et al., 1988; Luo et al., 1998; Burakov et al., 2010) and magnesium potassium phosphate (Vinokurov et al., 2009). Although glass and ceramic can be effectively and readily used to immobilize high-sodium content wastes. However, vitrification and ceramic technologies are much more difficult and expensive compared to cementation (Ojovan and Lee, 2014).

In recent years, the zeolite-like materials “hydroceramics” (Siemer et al., 2000, 2001; Siemer, 2002a, 2002b; Grutzeck and Siemer, 1997; Bao et al., 2004, 2005; Bao and Grutzeck, 2005; Krishnamurthy et al., 2001; IAEA, 2013; Drace et al., 2012; Abdel Rahman et al., 2015), which were prepared from aluminosilicate source materials (metakaolin, vermiculite etc.) by alkaline activation and hydrothermal process at a mild temperature (90–200 °C), were designed to solidify and stabilize the radioactive SBW. A wide range of salt molecules (e.g., sodium nitrate and nitrite) contained in SBW can be accommodated within zeolitic structures of hydroceramics (Grutzeck and Siemer, 1997; Siemer et al., 2001). However, the hydroceramics prepared from metakaolin have the shortcoming of low mechanical strength (lower than 5 MPa) (Bao et al., 2004, 2005). The recent studies showed that the mechanical strength of hydroceramics could be improved greatly by

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introducing slag and fly ash (Chen et al., 2010; Wang et al., 2011, 2012, 2015). Importantly, the normalized release rates of the main elements including fission products (Sr and Cs) indicated that the modified hydroceramics possessed high chemical durability when carrying about 40 wt% of S-SBW (Chen et al., 2010; Wang et al., 2015).

According to the definition by the International Atomic Energy Agency (IAEA), the nuclear waste form must be non-fragile, insoluble with favorable thermal and radiation stability except for good mechanical and chemical stability (IAEA, 1993). Besides, freezing and thawing are the significant aggression that negatively affects the durability of cement-based waste form (Eskander et al., 2011; Glasser, 2011). Furthermore, a cementitious monolith may be contacted or immersed by various surrounding media such as rain, ground and underground waters (Ojovan and Lee, 2014). Thus, the resistance to water immersion is also a substantial problem to the strength and mass degradation of cementitious nuclear solidified body under underground environment. Therefore, as a kind of cementitious material, the hydroceramic waste form should be safely evaluated by comprehensive considerations of the thermal stability, irradiation resistance and durabilities in terms of freezing–thawing and water immersion. However, there are almost no related reports on these properties of hydroceramics for immobilizing SBW.

In this work, it is intensively investigated the thermal stability, resistances to gamma irradiation, freezing–thawing and water immersion of ASFMH waste forms designed for immobilizing S-SBW. The purpose is through testing the compressive strength loss, analyzing the crystalline phase transformation, lattice damage and observing the physical appearance stability to assess the basic properties and security of ASFMH nuclear waste form. In addition, the reaction degree was checked to understand the reactive phase content of ASFMH waste form.

2. Experimental method

2.1. Raw materials, S-SBW slurry and ASFMH waste forms

The same raw materials (blast-furnace slag, type F fly-ash and metakaolin) and water glass (the SiO_2/Na_2O molar ratio was 3.18) used in the previous study have also been employed in this work. The source and chemical compositions of raw materials and water glass were described in previous paper (Wang et al., 2015).

The S-SBW slurry was designed based on the main components of the typical high level radioactive waste existed in China (Song, 1995). The reagents and their compositions are given in Table 1. The specific details for preparing the S-SBW slurry were described eleswere (Wang et al., 2015). All elements of S-SBW slurry were introduced as nitrates and dissolved in a 3 M nitric acid solution. Then, the S-SBW solution was denitrated by adding formic acid (Nakamura et al., 1978; Kubota et al., 1979; Shirahashi and Kubota, 1992). Subsequently, the S-SBW solution was concentrated to approximate 65 wt% of salt contents, whose pH value was adjusted with NaOH. After the above steps, the S-SBW solution became a brownish red slurry. In order to avoid the escape of fission product Cs during processing, the calcination process was omitted compared with the disposal of Hanford's SBW by Bao et al. (2005). The S-SBW slurry in this study could be directly mixed with raw materials to prepare ASFMH waste form.

Table 1
Chemical compositions of S-SBW

Element	Concentration (g/L)	Compound	Concentration (g/L)
Al	15.9	$Al(NO_3)_3{\cdot}9H_2O$	220.98
^{133}Cs[a]	1.76	$CsNO_3$	2.58
Fe	17.4	$Fe(NO_3)_3{\cdot}9H_2O$	125.83
K	0.45	KNO_3	1.16
Na	51.2	$NaNO_3$	189.28
Mn	2.69	$Mn(NO_3)_2$	8.84
^{88}Sr[a]	0.61	$Sr(NO_3)_2$	1.47
^{95}Zr[b]	0.014	$Zr(NO_3)_4{\cdot}5H_2O$	2.82
HNO_3	165.7	HNO_3	165.7
RE[c]	–		
Tc[c]	–		
U + TRU[c]	–		

[a] Nonradioactive ^{133}Cs, ^{88}Sr were substituted for radioactive ^{137}Cs and ^{90}Sr, respectively.
[b] ^{95}Zr was used to displace ^{93}Zr because of the potential impact of ^{93}Zr on environment.
[c] Rare earth elements, radioactive ^{99}Tc, Uranium and transuranic nuclides (TRU) were not considered.

The formulas of ASFMH waste forms were designed as follows. The molar ratio of Si/Al/Ca/Na of ASFMH waste forms was fixed to 2: 1: 0.25: 1 by adjusting the contents of raw materials, S-SBW (dry-mass basis) and NaOH. Solid dosage of sodium silicate in water glass occupied one-seventh of raw materials. The contents of S-SBW (dry-mass basis) was changed from 12.5 to 50 wt%. The specific formulas, preparation and hydrothermal process details were described in the published paper (Wang et al., 2015). In this study, all the samples were processed at 180 °C for 24 h.

2.2. Reaction degree

According to the literatures (Fernández-Jiménez et al., 2006, 2008), the "reaction degree" was checked to determine the reactive phase content of starting materials. To be specific, 1 g powders of ASFMH waste form were subjected to an acid attack with 250 ml of 1:20 (v/v) HCl to ascertain the amount of raw materials and S-SBW that had been converted to "zeolitic materials and cementitious materials" after alkaline activation and hydrothermal process.

2.3. Thermal stability and gamma irradiation resistance tests

Thermal stability and gamma irradiation resistance of ASFMH waste form were examined by exposing samples to elevated temperatures and strong gamma irradiation, respectively. In the thermal stability test, the monolithic samples were calcined in a muffle furnace at a heating rate of 5 °C/min from room temperature to 300, 500, 800 and 1000 °C, respectively. After holding for 2 h, the specimens were cooled inside the furnace to room temperature naturally. In the irradiation test, the samples were irradiated by an industrial irradiator using ^{60}Co gamma radiation source at a dose rate of 8.28 kGy h^{-1} until the accumulative irradiation doses reached 500 kGy.

After calcination and gamma irradiation, the compressive strengths of all samples were tested by WDW 1000 universal testing machine (Sansi Instruments Inc., Shenzhen, China). The phase transformation and the lattice damage induced by thermal shock and gamma irradiation were analyzed by X-ray diffraction (XRD) and fourier transform infrared (FT-IR) spectroscopy. The XRD patterns were obtained with a D/max-RB X-ray diffractometer (Rigaku Inc., Tokyo, Japan) using CuKα radiation. FT-IR spectra were scanned in the range of 400-4000 cm^{-1} with a 380 IR spectrophotometer (Nicolet Inc., Dane, Madison, WI, USA). Moreover, the whole physical appearance of ASFMH waste form was also observed to evaluate the shape stability against the thermal treatment and gamma irradiation.

2.4. Resistances to freeze–thaw and water immersion tests

In the freeze–thaw test, the samples were kept at −20 °C for 3 h,