Nuclear Engineering and Design 300 (2016) 67–73

Contents lists available at ScienceDirect

Nuclear Engineering and Design

journal homepage: www.elsevier.com/locate/nucengdes

Immobilization of simulated low and intermediate level waste in alkali-activated slag-fly ash-metakaolin hydroceramics

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HIGHLIGHTS

- Evaluation of the suitability of ASFMH for solidifying simulated S-LILW.
- The introduction of S-LILW avails forming zeolitic phases of ASFMH waste forms.
- The ASFMH waste forms have low leachability and high compressive strength.

ARTICLE INFO

Article history:
Received 29 June 2015
Received in revised form 5 January 2016
Accepted 6 January 2016

ABSTRACT

In the current study, the alkali-activated slag-fly ash-metakaolin hydroceramic (ASFMH) waste forms for immobilizing simulated low and intermediate level waste (S-LILW) were prepared by hydrothermal process. The crystalline phase compositions, morphology, compressive strength and aqueous stability of S-LILW ASFMH waste forms were investigated. The results showed that the main crystalline phases of S-LILW ASFMH waste forms were analcime and zeolite NaP1. The changes of Si/Al molar ratio (from 1.7 to 2.2) and Ca/Al molar ratio (from 0.15 to 0.35) had little effect on the phase compositions of S-LILW ASFMH waste forms. However, the hydrothermal temperature, time as well as the content of S-LILW (from 12.5 to 37.5 wt%) had a major impact on the phase compositions. The compressive strength of S-LILW ASFMH waste forms was not less than 20 MPa when the content of S-LILW reached 37.5 wt%. In addition, the aqueous stability testing was carried out using the standard MCC-1 static leach test method; the normalized elemental leach rates of Sr and Cs were fairly constant in a low value below 5×10^{-4} g m^{-2} d^{-1} and 3×10^{-4} g m^{-2} d^{-1} after 28 days, respectively. It is indicated that ASFMH waste form could be a potential host for safely immobilizing LILW.

1. Introduction

Low and intermediate level waste (LILW) in China generates from high-level liquid waste (HLLW) processed by the extraction separation process after removing transuranic nuclides (TRU) and ^{90}Sr, ^{137}Cs (Song, 1995). It contains large amounts of nitrates, especially sodium nitrate and aluminum nitrate. And, LILW still remains the two radionuclides of strontium and cesium, which is of concern to the safety of ecological environment and biosphere. Therefore, LILW is required to be stabilized into a solid form suitable for storage either on site or off site at a repository.

For LILW, the main immobilization technology that is available commercially and has been demonstrated to be viable is cementation. Ordinary Portland cement (OPC) is the most common type of cement used for immobilizing LILW (Ojovan et al., 2011; Ojovan and Lee, 2014; Glasser, 2011; Eskander et al., 2011). In addition, other composite cements such as cement mixed with zeolite, kaolinite and other active alumina–silica materials (Sakr et al., 1997; Shaaban and Assi, 2011; El-Kamash et al., 2002, 2006) are used to dispose LILW. The above cements are hydraulic cementitious materials that have the ability to react with water under ambient conditions to form a hardened and water-resistant product (Ojovan and Lee, 2014). These hydration products are mainly calcium silicate hydrate (C–S–H), portlandite (CH), monosulphate, ettringite and even tobermorite. However, cement-based matrices have a

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http://dx.doi.org/10.1016/j.nucengdes.2016.01.011
0029-5493/

disadvantage of relatively high leachability of radionuclides. Besides cement and composite cements, the alternative cementing system based on aluminosilicate is known as geopolymer. Geopolymer is a kind of 3D amorphous inroganic polymer which is composed of AlO_4 and SiO_4 tetrahedral structural units (Davidovits, 1991). The ingredients of geopolymer are a soluble alkali silicate and a reactive aluminosilicate precursor such as metakaolin. Comparing with cement-based matrices, geopolymer has the characteristics of lower heat output, moderate strength, low permeability and high thermal stability (Ojovan and Lee, 2014). Therefore, geopolymers get increasing attention as an alternative for solidifying LILW (Fernandez-Jimenez et al., 2005; Aly et al., 2008, 2012; Perera et al., 2006, 2007).

Zeolites are known host phases for many kinds of ions including radioactive nuclides. It was reported that strontium and cesium can be accommodated in zeolites either through in-situ incorporation during synthesis process or through subsequent cation exchange (Grutzeck and Siemer, 1997). In recent years, the zeolite-like materials "hydroceramic" (Grutzeck and Siemer, 1997; Siemer, 2002; Bao et al., 2004, 2005; Chen et al., 2010) have been designed for solidifying and stabilizing the highly alkaline sodium-bearing waste (SBW) generated from HLLW. The ingredients of hydroceramics are different from that of cement and geopolymer. Hydroceramics are predominantly crystalline zeolite phases, such as zeolite A, sodalite, cancrinite and analcime (Bao et al., 2005; Chen et al., 2010; Wang et al., 2011, 2012). The NaOH solution dissolves the metakaolin or other active alumina–silica materials in much the same way as in geopolymers but abundant water or hydroxides provide the water to create crystalline silicates instead of an amorphous matrix (Ojovan and Lee, 2014). Because of the multiphase zeolites, hydroceramic is able to sequester cations in both the lattice positions and the channels and voids in its tectosilicate framework structure. It can also accommodate a wide range of salt molecules (e.g., sodium nitrate and nitrite) within these same openings, thus rendering them insoluble (Grutzeck, 2005). Recently, we prepared the alkali-activated slag-fly ash-metakaolin hydroceramic (ASFMH) matrix (Wang et al., 2011, 2012). It was found that ASFMH mainly consisted of crystalline analcime phase and had superior strength and chemical stability.

In this work, ASFMH waste forms containing simulated LILW (S-LILW) were prepared by hydrothermal process. The effects of Si/Al, Ca/Al molar ratio of the starting materials, hydrothermal temperature, time and contents of S-LILW on the phase compositions of ASFMH waste form were systematically investigated. Also, the morphology and compressive strength were discussed. Furthermore, the aqueous stability of S-LILW ASFMH waste form was evaluated.

2. Experimental method

2.1. Raw materials

Metakaolin, type-F fly ash and blast-furnace slag were used to prepare S-LILW ASFMH waste forms. Water glass (the modulus (SiO_2/Na_2O molar ratio) was 3.11) was used as alkali activator. The details of three raw materials and alkali activator were described elsewhere (Wang et al., 2012). The chemical compositions of raw materials and water glass are shown in Table 1.

2.2. Preparation of S-LILW and S-LILW ASFMH waste forms

Table 2 lists the initial main chemical compositions of LILW. The preparation of S-LILW was similar to the literature (Liang et al., 2000). The nonradioactive ^{133}Cs, ^{88}Sr (tagging with * in Table 2) were used as trace elements of ^{137}Cs, ^{90}Sr. TRU and ^{99}Tc were not considered. All elements of S-LILW were introduced as nitrates and dissolved in a 0.5 M-nitric acid solution to ensure the initial S-LILW was acidic. The S-LILW solution was denitrated at 90 °C by adding formic acid as a reductant (Kubota et al., 1979; Shirahashi and Kubota, 1992; Nakamura et al., 1978). After denitration, the S-LILW solution was concentrated by evaporation. Finally, the pH value of the solution was adjusted to 12–13 with NaOH. The S-LILW solution then became a brownish red sludge, which could be directly mixed with raw materials to prepare the S-LILW ASFMH waste form.

Table 1
Chemical compositions of raw materials and water glass (wt%).

Components	Raw materials			
	Metakaolin	Fly ash	Slag	Water glass
SiO_2	54.7	54.27	29.8	25.82
Al_2O_3	41.33	22.94	12.47	
Fe_2O_3	1.17	6.44	2.7	
TiO_2	0.7	1.26	1.97	
CaO	0.08	2.46	35.06	
MgO	0.18	3.79	8.16	
MnO			0.73	
K_2O	0.25	3.55	0.66	
Na_2O	0.13	0.3	0.33	8.55
SO_3	0.14	0.21	2.14	
H_2O				59.34
Loss	1.23	4.69	1.28	
Total	99.89	99.91	95.3	93.71

The molar ratio of Si/Al/Ca/Na for S-LILW ASFMH waste forms was controlled by adjusting the contents of raw materials (metakaolin, fly ash and slag), water glass, S-LILW and NaOH. NaOH was utilized to regulate the sodium content of the system. The specific formulas of S-LILW ASFMH waste forms are shown in Table 3. The contents of S-LILW, water glass, and NaOH in the formula of S-LILW ASFMH waste form are designed on the basis of 100 g raw materials (metakaolin + fly ash + slag). The ratio of water to solid was regulated to about 0.35–0.40 and the specific water content changed slightly with the content of S-LILW. The detailed preparation and hydrothermal process were similar to the ASFMH matrix (Wang et al., 2012). Accordingly, the sample pastes were prepared by thorough mixing raw materials, water glass, NaOH and S-LILW in a cement paste mixer. After that, the pastes were molded in a stainless steel mold and procured at room temperature for 24–36 h until the sample pieces set. After demolding, all samples were transferred into sealed steam saturated pressure vessels (teflon-lined hydrothermal reactor) and processed at different temperatures (150–210 °C) for 12–60 h. Afterward, all samples were taken out and dried at 105 °C for 3 h.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained with a D/max–RB X-ray diffractometer (Rigaku Inc., Tokyo, Japan) using Cu Kα radiation. Scanning electron microscopy (SEM) images were observed using a MT-1000 scanning electron microscope (Hitachi Inc., Tokyo, Japan). The compressive strengths were tested by WDW 1000 universal testing machine (Sansi Instruments Inc., Shenzen, China).

Aqueous stability tests were carried out using the MCC-1 static leach test method at 90 °C in deionized water within cylindrical teflon container for a series of eight test durations: 0–1, 1–3, 3–7, 7–14, 14–21, 21–28, 28–35 and 35–42 days (Materials Characterization Center, 1981; State Environmental Protection Administration of China, 1986). The trace elements for radionuclides (Sr^{2+} and Cs^{+}) in the leachate were determined by using an AA-700 atomic absorption spectrophotometer (Perkin-Elmer Inc., Hopkinton, MA, USA). Electrical conductivity and pH value were