Annals of Nuclear Energy 101 (2017) 31–35

Contents lists available at ScienceDirect

Annals of Nuclear Energy

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

Leaching performance of uranium from the cement solidified matrices containing spent radioactive organic solvent

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ARTICLE INFO

Article history:
Received 3 August 2016
Received in revised form 26 September 2016
Accepted 30 September 2016

Keywords:
Radioactive waste
Cementation
Solidification
Uranium
Spent organic solvent
Leachability

ABSTRACT

The spent radioactive organic solvent (TBP/OK) was solidified by sulfoaluminate cement (SAC) with addition of zeolite, $Ca(OH)_2$ and T-80 type emulsifier (Tween 80). Leaching characteristics of uranium immobilized in the solidified matrices was investigated through the semi-dynamic leaching test. The leaching behavior was evaluated by several leaching parameters and predicted by one-dimensional radionuclide decay model based on the Fick's second law. The results showed that the leaching rate and the cumulative leaching fractions (CLF) of uranium in 42 d were 5.70×10^{-7} cm/d and 4.80×10^{-5} cm, respectively. The solidification material used in present work was acceptable for solidification of uranium. The predictive values of CLF of uranium from the solidified matrices by the mathematical model were consistent with the experimental data in leaching period.

1. Introduction

Radioactive spent organic solvent (tri-butyl phosphate/kerosene, TBP/OK) is one of the important low and intermediate level liquid radioactive wastes, which are very difficult to dispose of. They are usually produced in the PUREX-process for the nuclear fuel recycle of the nuclear power plants (Helen et al., 2005; Barinova et al., 2013). TBP/OK are mainly used as extractant to separate uranium and plutonium from the mixed solution (IAEA, 1992). The performance of TBP/OK will decrease with the increase of the frequency of use (Barinova et al., 2013). It is important to treat and dispose of these spent organic solvents.

Different technologies have been employed to dispose of the spent organic solvent, including incineration (Helen et al., 2005), distillation (IAEA, 1992), plasma treatment (IAEA, 2004), cement solidification method (Pente et al., 2008; Zhang et al., 2015), wet oxidation (IAEA, 1992), alkaline hydrolysis and solidification (Valsala et al., 2008), electrochemical oxidation (Galla et al., 2003) etc. Among these methods, incineration is relatively expensive, the cement solidification technology is considered to be a probable alternative to incineration because of the simple process, low cost, ordinary raw materials and long-term stability. Cement has been widely used to solidify the different kinds of radioactive wastes (Shen et al., 1994; Canpolat et al., 2004; Li and Wang, 2006; Osmanlioglu, 2006; Abdel Rahman et al., 2007; Abdel Rahman and Zaki, 2009, 2011; Sinha et al., 2009; Sun and Wang, 2010; Ojovan et al., 2011; Sun et al., 2011a,b, 2014), including the spent radioactive organic solvent (Greenhalgh, 1986; Li and Wang, 2013; Zhang et al., 2015). However it is difficult to solidify the spent radioactive organic solvent due to the poor compatibility of TBP/OK with cement.

The cements were used for the solidification of TBP/OK and the leaching performance of radionuclides (Sr^{2+}, Co^{2+}, Cs^{+}) was investigated In our previous study (Zhang et al., 2015). The radionuclides (Sr^{2+}, Co^{2+}, Cs^{+}) can be effectively solidified in the waste forms through chemical fixation and physical encapsulation (Shi and Spence, 2004; Li and Wang, 2013; Deng et al., 2015), the leaching performance during long-term storage requires study because the radionuclides might leach out through the porous structure (Ligia et al., 2004; Haque, 2016). A certain concentration of uranium was present in TBP/OK. Therefore, the leaching behavior of uranium in the solidified form should been studied further in order to deal with the waste safely.

The objective of this study was to investigate the leaching performance of uranium from the cement solidified matrices containing spent radioactive organic solvent. The TBP/OK containing certain concentration of uranium was solidified using sulfoaluminate cement (SAC) together with other auxiliary materials (zeolite,

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http://dx.doi.org/10.1016/j.anucene.2016.09.055
0306-4549/

Ca(OH)2) by emulsification-solidification method with the help of T-80 type emulsifier. The leaching model was established by Fick's second law and used to predict the leaching behavior.

2. Material and methods

2.1. Matrix materials

Sulfoaluminate cement was provided by Tangshan Polar bear Building Materials Company. The XRD patterns and chemical composition of SAC were presented in previous study (Zhang et al., 2015). The XRD pattern of zeolite was illustrated in Fig. 1. Zeolite named natural Clinoptilolite was supplied by Beijing Heding Power Technology Company. Hydrated lime ($Ca(OH)_2$) was provided by Tianjin Union Lab Chemical Reagent Company. T-80 type emulsifier, as a non-ionic emulsifier, supplied by Haian Jiangsu Petrochemical Plant, is polyoxyethylene sorbitan monooleate. The mass density of T-80 is 1.08 g/ml. TBP was supplied by Guangdong Shantou Xi long Chemical Company. Uranyl nitrate was supplied by SPI Chem., USA.

2.2. Simulated TBP/OK

The simulated radioactive spent organic solvent (TBP/OK) used in this work was made by the following method. The mixture solution which total volume is 1 L consisted of 0.3 L of TBP and OK. However, there are radiation degradation products of radioactive organic solvent in the actual radioactive spent organic solvent (Osmanlioglu, 2006), such as monobutyl phosphate, dibutyl phosphate, etc. For the sake of convenience, the effect of the radiation degradation products of TBP on the solidification was not considered in this paper.

In the leaching experiment, the certain uranyl nitrate ($UO_2(NO_3)_2$) was added to the emulsion which consisted of the simulated radioactive spent organic solvent, tap water and T-80 type emulsifier. The mass content of U(VI) in each solidified waste form was 0.141 g.

2.3. Solidification

The solidified waste forms were made in accordance with the components listed in Table 1, which was used in our previous study (Zhang et al., 2015).

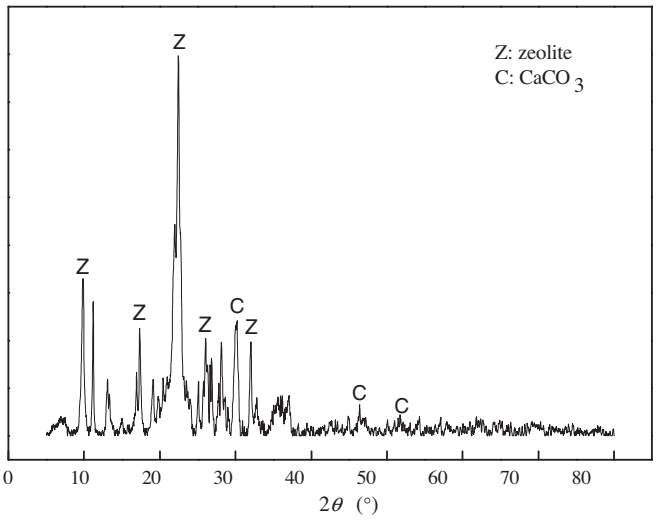

Fig. 1. The XRD patterns of zeolite.

Three steps were necessary to solidify the radioactive spent organic solvent by SAC: (1) The mixed solution consisting of TBP/OK and water was emulsified by T-80 type emulsifier; (2) The emulsion blending with uranyl nitrate was added to the solid mixture which was composed of zeolite, $Ca(OH)_2$ and SAC under continuous stirring of 3 min; (3) The uniform cement pastes was casted into the molds with a dimension of $\varphi 50 \times 50\ mm^3$ cylinders. After 28 d standard curing (T&H: 25 ± 5 °C, ⩾90%), the samples were prepared and used for compressive strength test according to the standard in GB 14569.1-2011 (CSBTS, 2011).

2.4. Leaching experiment

The leaching characteristic of U(VI) in the waste matrices cured for 28 d was analyzed in the leaching test. The experiment was carried out at 25 ± 2 °C according to the Chinese National Standard GB 7023-2011 (SEPA, 2011). Deionized water with 1.4 μS/cm electric conductivity was selected as the leachant and changed at 1, 3, 7, 10, 14, 21, 28, 35, 42 and 52 d after the leaching test began. Thereby this experiment was also considered semi-dynamic leaching test. The waste matrices were fixed in the plastic container with 1.5 L leachant, as shown in Fig. 2. The leaching rate and the cumulative leaching fraction of U(VI) were measured by MUA model trace uranium analyzer through the leachates from the plastic container.

3. Results and discussion

3.1. Leachability

The compressive strengths of the solidified matrices cured for 28 d was 8.83 MPa, which met the requirement of GB14569.1-2011. Therefore, the leaching test should be undertaken in the next step. Excellent radionuclide retention capacity is very important to the solidified waste forms for the long-term storage in the disposal sites. The aim of leaching test is to evaluate the leachability of U (VI) in the solidified wastes. The cumulative fraction leached and leaching rate are important parameters, which can be calculated as follows (SEPA, 2011).

$$R_n = \frac{a_n/A_0}{(S/V)(\Delta t)_n} \tag{1}$$

$$P_t = \frac{\sum a_n/A_0}{S/V} \tag{2}$$

where R_n is the leaching rate of certain cation at the nth leaching period, cm/d; a_n is the mass of leached certain cation at the nth leaching period, g; A_0 is the total original mass of certain cation in a solidified sample, g; S is the total exposed surface area of a solidified sample, cm^2; V is the total volume of a sample, cm^3; $(\Delta t)_n$ is the duration of the nth leaching period, d; P_t is the cumulative fraction leached of certain cation i on the t th day, cm; t is the total durative days of a solidified sample immerged, d, $t = \Sigma(\Delta t)_n$.

The leaching rates and the cumulative fractions leached of U(VI) were illustrated in Figs. 3 and 4, respectively. The leaching rates of U(VI) at the 42 d and 52 d were 5.70×10^{-7} cm/d and 5.17×10^{-7} cm/d, while the cumulative fractions leached in 42 d and 52 d were 4.80×10^{-5} cm and 6.35×10^{-5} cm, respectively. It was fairly obvious that the leaching performance of U(VI) from the solidified matrices met the requirements of GB14569.1-2011. The results showed that the leaching rate of nuclide in the early stage of leaching (1–10 d) was higher than that in the late period (10–52 d). The leaching rule of the solidified matrices was consistent with the previous research (Sun and Wang, 2010; Sun et al., 2011b). The comparison of the leaching rate and the cumulative