Progress in Nuclear Energy 53 (2011) 969–973

Contents lists available at ScienceDirect

Progress in Nuclear Energy

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

Recovery of minor actinides from spent molten salt waste and decontamination of molten salt waste

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ARTICLE INFO

Article history:
Received 30 October 2010
Received in revised form
28 April 2011
Accepted 1 May 2011

Keywords:
Pyrochemical process
Hydrometallurgy
Radioactive salt waste
Lanthanide
Actinide
Pyridine resin

ABSTRACT

Recovery of minor actinides from spent molten salt is one of the important issues. Decontamination of spent molten salt waste is also the problem to be solved for establishment of pyrochemical reprocessing. The decontamination method of spent molten salt waste with recovery of minor actinides has been proposed. Our proposed process is based on the hydrometallurgical process. This process consists of the following processes. First, the spent molten salt waste is dissolved in aqueous solution. Next, the minor actinides are recovered by chromatographic techniques using the pyridine resin in the methanolic hydrochloric acid solution. In the last process, the spent molten salt waste is decontaminated by the cation-exchange chromatography. In the present paper, the adsorption behavior of minor actinides, rare earth elements, alkaline earth elements, and alkali metal elements on pyridine resin is reported. The demonstration experiment of the recovery of the minor actinides from simulant spent molten salt waste is also reported.

1. Introduction

Nuclear energy is one of the most important energy systems. The innovative nuclear system such as FBR is desired for the sustainable energy demand. Various types of reprocessing systems have been proposed in order to fulfill the requirement for the novel nuclear cycle with innovative nuclear system. The pyrochemical reprocessing is one of the promising methods (Inoue, 2002; Inoue and Koch, 2008). The spent molten salt waste generated from the pyrochemical reprocessing includes alkali metal, alkaline earth, and rare earth fission products, along with residual actinides. The decontamination of spent molten salt waste and the reuse of salt are required for volume reduction or minimization of radioactive waste. Main candidate decontamination process in the world is the ion exchange process using zeolite (Harrison et al., 2008; Lexa and Johnson, 2001; Lexa, 2003; Simpson and Sachdev, xxxx). In this method, the fission products are removed by the direct ion exchange of molten salt waste at the high temperature. Recently, the oxidative precipitation (Cho et al., 2009) and Czochralski method (Lee et al., 2009) were proposed in Korea as new decontamination process. By the way, the recovery of residual minor actinides in salt waste is an important issue for the volume reduction of radioactive waste. For the recovery of the minor actinides, above decontamination process is not sufficient. We have been investigating the separation of various nuclides in hydrochloric acid solution (Suzuki et al., 2008). The separation of minor actinides and rare earth elements is already achieved (Suzuki et al., 2003; Ikeda et al., 2004). Since the molten salt waste mainly consists of alkali metal chlorides, our separation method can be applied to the decontamination of spent molten salt waste and the removal of minor actinides by dissolution of salt waste in aqueous solution. We propose the decontamination process of spent molten waste with minor actinide recovery by using hydrometallurgical method. In the present paper, feasibility of the proposed process is discussed.

2. Experimental

2.1. Pyridine resin

The resin used in the present experiment was highly porous tertiary pyridine type resin embedded in silica beads. The average diameter of silica beads is 60 mm. The pyridine resin was made by synthesizing 4-viniylpyridine of 80 wt% and m/p-divinylbenzene of 20 wt% dissolved in mixed solvent of 60 vol% acetophenone and 40 vol% diethylphthalate in high porous silica beads.

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doi:10.1016/j.pnucene.2011.05.001

2,2′-Azobisisobutyronitrile (AIBN) and 1,1′-azobiscyclohexane-1-carbonitrile were used as synthesis initiator. The chemical structure of this resin is presented in Fig. 1.

2.2. Adsorption experiments of elements in salt waste on pyridine resin

The adsorption behavior of alkali metal ions, alkaline earth ions, and rare earth ions on pyridine resin and their separation behaviors in the methanolic hydrochloric acid solution were investigated in order to obtain the basic data for radioactive salt waste treatment by carrying out the chromatography. A 1 cm^3 portion of the solution dissolving of alkali metal, alkaline earth, and rare earth stable isotope ions was fed into a 50 cm column with a water jacket, packed with pyridine resin. The feed solutions were adjusted to the desired eluent composition. The elements in effluent from column were detected by ICP–MS (Thermo Fisher Scientific Inc. X7). The adsorption behavior of alkali metal, alkaline earth, and rare earth ions in lithium chloride aqueous solution was also investigated by similar method of the case of methanolic hydrochloric acid solution.

The adsorption behavior and separation phenomenon of minor actinides in methanolic hydrochloric acid solution were also investigated by using the minor actinide sample solution with fission products. This sample was prepared by removal uranium and plutonium from the irradiated MOX fuel by using the ion exchange. ^{137}Cs, ^{144}Ce, ^{155}Eu, ^{241}Am, and ^{243}Cm were detected in the minor actinide solution by γ-ray spectrometer. The experiment was carried out using a column of 10 cm height and 8 cm^3 column volume. A 1 cm^3 of the minor actinide solution was fed into this column, and eluted by the methanolic hydrochloric acid solution of 25 vol% methanol.

3. Results and discussion

3.1. Adsorption behavior of elements in salt waste

The typical chromatogram of alkali metal, alkaline earth, and rare earth ions using methanolic hydrochloric acid solution is shown in Fig. 2. This chromatogram was obtained with eluent of methanolic hydrochloric acid solution with 60 vol% methanol addition. The solid symbols are alkali metal ions. The double circle is strontium ions. The blank symbols are rare earth ions. The distribution coefficients can be calculated by using the obtained chromatogram. The distribution coefficient (K_d) is calculated by using following equation; $K_d = (V - V_0)/V_s$, where V, V_0, and V_s are the effluent volume at the elution peak, the dead volume of the column packed with resin, and the volume of resin, respectively. The simple diagram for definition of above terms is shown in Fig. 3. The distribution coefficients of alkali metal ions, alkaline earth ions, and rare earth ions in methanolic hydrochloric acid solution are shown in Fig. 4. All ions have the maximum adsorption using solution of 60 vol% methanol. The increase of adsorption with methanol adding can be explained by the dielectric effect (Marcus and Maydan, 1963), the decrease of adsorption caused by methanol adding over 60 vol% is deduced due to the dilution of chlorine ions. The order of adsorption amount on pyridine resin is following; rare earth > alkaline earth > alkali metal. The order of adsorption amount among the rare earth elements was not varied with increase in the methanol ratio; i.e., the lighter elements are more strongly adsorbed comparing the heavier elements among the rare earth except yttrium. The adsorption behavior of yttrium is similar to that of strontium, especially lower methanol concentration. The adsorption order of alkali metal is varied with increase in the methanol ratio; lithium is most adsorbed less than 50% of methanol, however if over 50%, potassium becomes most adsorbed ion among the alkali metal. The resolutions were also evaluated for the estimation of degree of separation. We adopted the overlap at 10% valley as the resolution (R), which was given by $R = (V_2 - V_1)/(\Gamma_2 + \Gamma_1)$, where V_i is the effluent volume at the elution peak, Γ_1 and Γ_2 are the right side width of subject ion and the left side width of base ion at 10% height of each peak maxima, respectively. These terms are shown in Fig. 3. Lithium was selected as the base of separation degree in the case of less than 50% methanol addition and potassium was selected in the case of more than 50%. The resolutions are shown in Fig. 5. The resolutions of strontium, yttrium and gadolinium are indicated. The resolutions of their ions from alkali metal ions have maximum under the condition of 30–50 vol% methanol addition. The resolutions of strontium and yttrium are not sufficient for decontamination of salt waste. The resolution between gadolinium and potassium exceeds 1, thus the

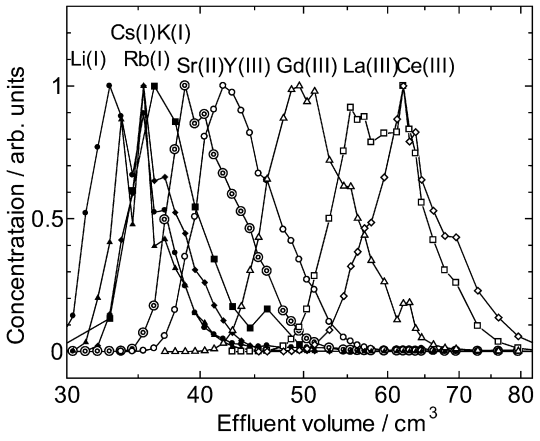

Fig. 2. Typical chromatogram. Eluent was the methanolic hydrochloric acid solution. The volume ratio of conc. HCl:MeOH = 6:4.

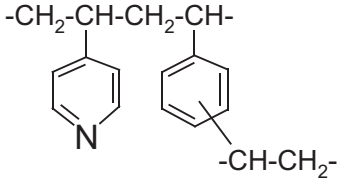

Fig. 1. Chemical structure of tertiary pyridine type resin.

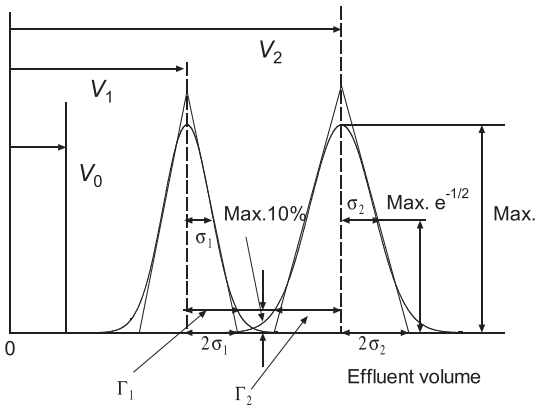

Fig. 3. Diagram for definition of technical terms obtained from chromatogram.