

A study of separation and solidification of group II nuclides in waste salt delivered from the pyrochemical process of used nuclear fuel



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ABSTRACT

If group II nuclides, which contain high heat-generative elements, in waste salt are fabricated into a waste form rich in group II nuclides, the waste form can be used in radionuclide thermoelectric generator applications. For this reason, the separation of group II nuclides in salt (LiCl, LiCl-KCl) was conducted, after which a waste form rich in them was fabricated. In this study, group II nuclide chlorides in salt were effectively separated into a carbonate or oxychloride form, and the separated nuclides were successfully fabricated into a homogenous and stable glass waste form with high contents (45–50 wt%) of these nuclides.

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1. Introduction

A nuclear energy cycle regarded as a prospective energy source for the future generation is to pursue further safer operations, high proliferation resistance and a reduced environmental impact of long lived radioactive waste [1]. The pyrochemical process of used nuclear fuel with molten salt as a reaction medium is one of the key processes to realize the nuclear energy cycle [2,3]. This process is used electrochemically to partition fission products and recover U and TRU metals as valuable resources from used nuclear fuels in a molten salt bath [3,4]. In the pyrochemical process, LiCl or LiCl-KCl eutectic waste salts containing small amounts of group II nuclide chlorides (BaCl_2 , SrCl_2) are generated as radioactive waste. These waste salts are heat-generating and water-soluble substance and therefore, must be fabricated into a stable waste form for permanent disposal [4,5]. However, they are also not compatible with conventional solidification processes given that waste salts can easily become vaporized during the solidification process [6–8]. For this reason, it can be effective to convert group II nuclide chlorides into a thermally stable form and separate them from the

waste salt before solidification. This method can facilitate a reduction of radioactive waste generation and simplify the fabrication of a stable waste form. The reactive distillation process is very effective when used to convert rare earth chlorides into an oxychloride or an oxide form and then easily separate them from LiCl-KCl eutectic salt [4]. This is one of key processes to realize the method.

This paper presents results pertaining to the separation of group II nuclides in salt (LiCl, LiCl-KCl) using a reactive distillation process and describes the fabrication of the separated group II nuclides into a glass waste form. Based on the results, a method capable of the separation and solidification of group II nuclides in waste salt delivered from the pyrochemical process of used nuclear fuel is evaluated.

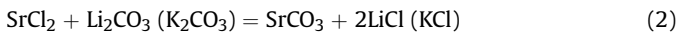
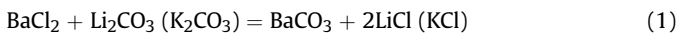
2. Experimental and methods

The equipment for the reactive distillation test of LiCl-KCl eutectic salt containing rare earth chlorides was also used in this study [4]. This equipment is composed of a chamber for reaction and distillation, electric heaters, a cooling water circulator, and a vacuum pump. To recover almost all of the vaporized electrolytes only in the receiver, the equipment was designed as a body with a vaporization chamber and condensation chamber, three heaters

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installed to generate temperature gradients in the chamber, and a cooled wall positioned only under the bottom of the receiver. The chamber, sample boat, and receiver were made using Inconel 625 because the salt is highly corrosive under the distillation conditions. The salt distillation in the equipment is subjected to the forces of temperature gradients at a reduced pressure. As the waste salt surrogate, LiCl and LiCl-KCl mixture (molar ratio of LiCl: 0.58) containing BaCl₂ (Alfa Aesar, 99%) and SrCl₂ (Alfa Aesar, 99%) were prepared. The group II nuclide chlorides were included at a level of 5.0 wt% in LiCl and LiCl-KCl mixture. As the chemical agent for reactive distillation, Li₂CO₃ (Aldrich, 99%) and K₂CO₃ (Aldrich, 99%) were used.

Reactive distillation tests of the LiCl and LiCl-KCl mixture containing the group II nuclide chlorides were conducted in a glove box charged with argon gas (>99.999%). The concentrations of O₂ and H₂O in the glove box were maintained below 10 ppm. The LiCl and LiCl-KCl mixture containing group II nuclides chlorides and Li₂CO₃ (for the LiCl) and K₂CO₃ (for the LiCl-KCl mixture) were mixed in a polypropylene bottle before being added to the sample boat. At this time, the mass of salt (LiCl, LiCl-KCl mixture) was 45.0 g, and the masses of SrCl₂ and BaCl₂ were 2.5 g, respectively. The reactions between Li₂CO₃ (K₂CO₃) and the group II nuclide chlorides were predicted as following equations. The chemical agent was injected at 1.0 molar ratio of the group II nuclide chlorides.



The sample boat was charged into the reaction chamber, and the chamber was then heated to the proper temperatures for the reactions between the rare earth chloride and the alkali carbonate mixture. The temperatures for the reactions were determined to be 450 °C (for the LiCl-KCl mixture) and 650 °C (for the LiCl). These reactions were conducted for 1.0 h. In the reactions between Li₂CO₃ (K₂CO₃) and the group II nuclide chlorides, CO₂ gas can be generated if the group II nuclide chlorides are converted into an oxide form. Therefore, the pressure in the chamber was reduced by 100 Torr from ambient pressure to vent the gaseous material generated during the reactions. After the reaction process, the pressure in the chamber was reduced for the salt distillation process by 1.0 Torr from 100 Torr, and the vaporization chamber and condensation chamber were heated to the given temperatures (Heater-1, 2: 920 °C, Heater-3: 700 °C). These conditions were maintained to distill the salt for 2.0 h.

After the reactive distillation step, the fabrication of the separated group II nuclides into a glass waste form was conducted in an electric furnace. The electric furnace can be heated to 1500 °C under an air condition. The fabrication of the separated group II nuclides was performed using the CaO-SrO-BaO-SiO₂ system [9]. The compositions for the fabrication of the separated group II nuclides were determined to produce group II nuclide-rich waste form, as detailed in Table 1. The melting temperature for the compositions was 1350 °C in all cases, and this temperature was fixed through the melting tests of the compositions, ash shown in Table 1. After melting for 1 h, a waste form of the separated group II was obtained by quenching the melts in a graphite crucible.

The amount of group II nuclides in the salt recovered from the reactive distillation tests was measured to calculate their separation ratios by dissolving the salt in 0.1 M HNO₃ and analyzing them through ICP-OES (Optima 8300, PerkinElmer). The salt recovery efficiency was determined using the ratio of the mass fraction of the recovered salt from the reactive distillation test over the initial mass of salt. The residual compounds in the sample boat and the waste forms were identified by an XRD (D8 Advance A25, Bruker,

Table 1

Compositions for the fabrication of the separated group II nuclides after the reactive distillation test of salt containing group II nuclides [wt%].

	CaO	SrO	BaO (Ba ₄ OCl ₆)	SiO ₂
GW1	17.10	13.10	31.40 (39.90)	38.40
GW2	12.90	14.90	35.7 (45.30)	36.50

Conditions: Cu target, 40 kV, 40 mA, 0.2°/sec) analysis. High resolution images of the waste forms were obtained by means of FE-SEM (Magellan 400, FEI Company). The glass-transition temperature (T_g) was measured under the N₂ condition at a heating rate of 10 °C/min using TGA-DTA (TG/DTA 6300, Seiko Instrument) and TMA (TMA/SS 6000, Seiko Instrument) instruments. Density levels were determined using the Archimedes method. A chemical durability test for the waste forms was conducted using PCT (Product Consistency Test) as a static leaching test (ASTM Standard C 1285-02) [10]. In the PCT, the waste forms were crushed to a 100–200 mesh size, and then immersed in purified water (sample mass 1 g vs water volume 10 ml) for 7 days at 90 °C. After completing the PCT, the samples were filtered, and then analyzed by means of ICP-OES (Optima 8300, PerkinElmer).

3. Results and discussion

3.1. Thermodynamic equilibrium calculations of reactions between group II nuclides and chemical agents

Before conducting the separation of group II nuclides in salt, the Gibbs free energies of the reactions between the group II nuclide chlorides and the chemical agents (Li₂CO₃, K₂CO₃) were calculated by means of software (HSC-Chemistry 5.1) [11], and the results are shown in Table 2. In this calculation, the initial amounts were determined using the reactive distillation test conditions. According to Table 2, the reactions using Li₂CO₃ are not effective when compared with the reactions using K₂CO₃, and the reactions between SrCl₂ and the chemical agents are superior to the reactions between BaCl₂ and these agents. The activities of the reactions increase with an increase in the temperature. Table 2 also shows that the conversions of group II nuclide chlorides into a carbonate form are more active than their conversions into an oxide form.

Considering the Gibbs free energies of the reactions between the group II nuclide chlorides and the chemical agents, thermodynamic equilibrium calculations of the conversions of group II nuclide chlorides into a carbonate form were carried out at 450–900 °C to predict the results of the reactions under the reactive distillation conditions using software (HSC-Chemistry 5.1) [11], and the results are presented in Fig. 1. Fig. 1(a) shows the thermodynamic equilibrium results of the reactions between the group II nuclide chlorides and Li₂CO₃. According to Fig. 1(a), SrCl₂ can be effectively converted into SrCO₃, independent of the temperature. On the other hand, it is not effective to convert BaCl₂ into BaCO₃. This conversion increases with an increase in the temperature; however, the conversion ratio reaches approximately 0.1. Hence, Li₂CO₃ can remain as an unreacted agent, as shown in Fig. 1(a). Fig. 1(b) shows the thermodynamic equilibrium results of the reactions between the group II nuclide chlorides and K₂CO₃. Fig. 1(b) indicates that the conversions of the group II nuclide chlorides into a carbonate form can be effective, and the effects of the temperature on these conversions are very minor. Accordingly, very little residual K₂CO₃ remains as an unreacted agent, as shown in Fig. 1(b). Based on these thermodynamic equilibrium results, the injections of the chemical agents were determined to be 1.0 for the separation of the group II nuclides in salt.

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