Vacuum distillation of a mixture of LiCl–KCl eutectic salts and RE oxidative precipitates and a dechlorination and oxidation of RE oxychlorides

Hee Chul Eun*, Hee Chul Yang, Yung Zun Cho, Han Soo Lee, In Tae Kim

Nuclear Fuel Cycle Process R&D Group, Korea Atomic Energy Research Institute, P.O. Box 150-1 Yuseong, Daejeon 305-353, Republic of Korea

ABSTRACT

In this study, a vacuum distillation of a mixture of LiCl–KCl eutectic salt and rare-earth oxidative precipitates was performed to separate a pure LiCl–KCl eutectic salt from the mixture. Also, a dechlorination and oxidation of the rare-earth oxychlorides was carried out to stabilize a final waste form. The mixture was distilled under a range of 710–759.5 Torr of a reduced pressure at a fixed heating rate of 4 °C/min and the LiCl–KCl eutectic salt was completely separated from the mixture. The required time for the salt distillation and the starting temperature for the salt vaporization were lowered with a reduction in the pressure. Dechlorination and oxidation of the rare-earth oxychlorides was completed at a temperature below 1300 °C and this was dependent on the partial pressure of O_2. The rare-earth oxychlorides (NdOCl/PrOCl) were transformed to oxides (Nd_2O_3/PrO_2) during the dechlorination and oxidation process. These results will be utilized to design a concept for a process for recycling the waste salt from an electrorefining process.

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1. Introduction

One possible alternative to the existing reprocessing processes of a spent nuclear fuel is a pyrochemical process using a high-temperature molten salt [1]. This pyrochemical process shows promise for an advanced nuclear engineering design because of its compactness, economy, radiation resistance and nonproliferation [2]. Of all the unit operations of a pyrochemical process, an electrorefining is a key step [2,3]. During this electrorefining process, certain amounts of waste salts containing some metal chloride species such as rare-earth chlorides are generated. In the electrorefining process, a reuse of the waste salts is very important from an economical as well as an environmental point of view. In order to reuse the waste salts from an electrorefining process, it is necessary to separate the rare-earth chlorides from the waste salts. An oxidation method can be used to achieve that because it converts the rare-earth chlorides to rare-earth oxychlorides or oxides precipitated as insoluble compounds. Among the various oxidation methods, a promising and potential alternative method is by sparging O_2 gas [4,5]. The rare-earth chlorides in the waste salts are precipitated by sparging O_2 gas and during this process, pure LiCl–KCl eutectic salts can be recovered from the waste salts. However, a considerable amount of LiCl–KCl eutectic salts is discharged as a mixture of LiCl–KCl eutectic salts and rare-earth oxidative pre-

cipitates. Also, rare-earth oxidative precipitates such as rare-earth oxychlorides can be an obstructive factor when trying to achieve a stable solidification for a final waste form because of the presence of Cl [6–8]. Therefore, a separation of the LiCl–KCl eutectic salts from this mixture and a stabilization of the rare-earth oxychlorides are essential to reuse these salts, to reduce the high level waste volume and to stabilize a final waste form. A distillation process can be used for a salt recovery from the mixture [9–11], and a dechlorination and oxidation of the rare-earth oxychlorides can convert them to stable oxide forms at a high temperature of more than 1200 °C [5].

In this study, a vacuum distillation of LiCl–KCl eutectic salts in a mixture of LiCl–KCl eutectic salts and rare-earth oxidative precipitates was performed to evaluate the characteristics of a salt distillation at a fixed heating rate with a reduction in the pressure. Also, a dechlorination and oxidation of the rare-earth oxychlorides was carried out to investigate the conversion characteristics of the oxychlorides to oxides at a fixed heating rate with various partial pressures of O_2.

2. Experimental and methods

2.1. A vacuum distillation of a mixture of LiCl–KCl eutectic salts and rare-earth oxidative precipitates

The experimental apparatus for a vacuum distillation of a mixture of LiCl–KCl eutectic salts and rare-earth oxidative precipitates is composed of an alumina tube, a load cell, an electric heater, a
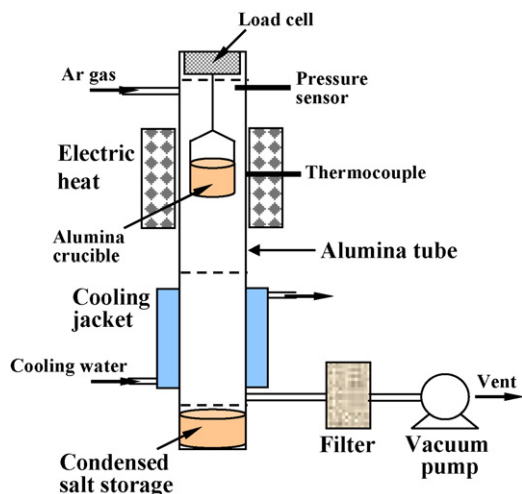
Fig. 1. A schematic of experimental apparatus for a vacuum distillation of a salt.

Fig. 2. Oxidative precipitation of rare-earth chlorides in the LiCl–KCl eutectic melts by sparging O_2 gas with a temperature.

alumina crucible, a cooling jacket, a condensed salt storage, a filter and a vacuum pump as shown in Fig. 1. This mixture was obtained from an oxidative precipitation of rare-earth chlorides (Ce/Eu//Nd/PrCl$_3$) in LiCl–KCl eutectic melts by sparging O_2 gas. Table 1 shows the experimental conditions for the vacuum distillation of the mixture. The temperature of the furnace was programmed to rise from room temperature to 1200 °C with a heating rate of 4 °C/min. The reduced pressure was adjusted from 710 Torr to 759.5 Torr by using a vacuum pump. During a vacuum distillation of the mixture, Ar gas was injected into the furnace to maintain an inert atmosphere. The patterns of the salt distillation could be confirmed by the mass reductions detected in the load cell with changes of the temperature and time.

2.2. Dechlorination and oxidation of the rare-earth oxychlorides

Dechlorination and oxidation of the rare-earth oxychlorides was performed to stabilize the final waste form by a thermo-gravimetric analyzer (SDT 2960; TA Instrument Co.). The experimental conditions are shown in Table 1. The temperature of the furnace was programmed to rise from room temperature to 800 °C with a heating rate of 50 °C/min. After an initial rapid heating, the furnace was slowly heated to 1300 °C with a heating rate of 5 °C/min. Four partial pressures of oxygen were tested: 21, 50, 75 and 100% of oxygen and the remainder consisted of pure nitrogen (>99.9%).

3. Results and discussion

3.1. Properties of the mixture of LiCl–KCl eutectic salts and rare-earth oxidative precipitates

The oxidative precipitation of rare-earth chlorides in LiCl–KCl eutectic melts by sparging O_2 gas reached more than 99.9% at 650 °C as shown Fig. 2. Also, it was found that about 65 wt.% of the LiCl–KCl
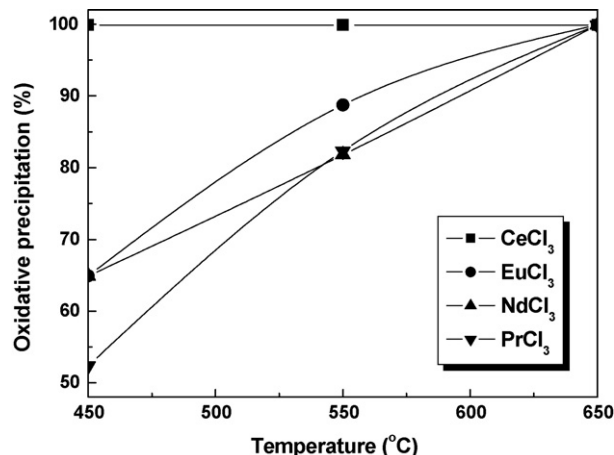
Table 1
Detailed experimental conditions

	Vacuum distillation	Dechlorination and oxidation
Sample mass	12 g	15–16 mg
Heating rate	4 °C/min	50 °C/min (~800 °C)
		5 °C/min (~1300 °C)
Temperature	~1200 °C	~1300 °C
Reduced pressure	710/755/759.5 Torr	–
Injection gas	Ar	O_2 (21/50/75/100%)

eutectic salts was recovered from the LiCl–KCl eutectic melts containing rare-earth chlorides by sparging O_2 gas and about 35 wt.% of them was discharged as a mixture of LiCl–KCl salts and rare-earth oxidative precipitates (oxychlorides or oxides). This mixture had about 90 wt.% of LiCl–KCl eutectic salt and about 10 wt.% of insoluble rare-earth oxidative precipitates. Fig. 3 shows the XRD-patterns of the rare-earth oxidative precipitates. As shown in Fig. 3, the rare-earth oxidative precipitates were composed of rare-earth oxychlorides (NdOCl/PrOCl) and oxides (CeO$_2$/Eu$_2$O$_3$/PrO$_2$). Thus, it is considered that a separation of the LiCl–KCl salts from the mixture used in this study can be accomplished effectively by a salt distillation process based on the large differences in the vapor pressures [9–11].

3.2. Vacuum distillation of a mixture of LiCl–KCl eutectic salts and rare-earth oxidative precipitates

The vapor pressure as a function of the temperature considerably affects a salt distillation [12–14]. If the vapor pressure of a salt can be increased, the required temperature and time for a salt distillation will be reduced. A reduced pressure by a vacuum pump increases the vapor pressure and elevates the vaporization rate [15]. Therefore, a vacuum distillation can produce efficient results for the separation of LiCl–KCl eutectic salts from a mixture of LiCl–KCl eutectic salts and rare-earth oxidative precipitates. Fig. 4 shows the thermal mass reductions of the mixture by a vacuum distillation. It was found that the required time for the salt distillation
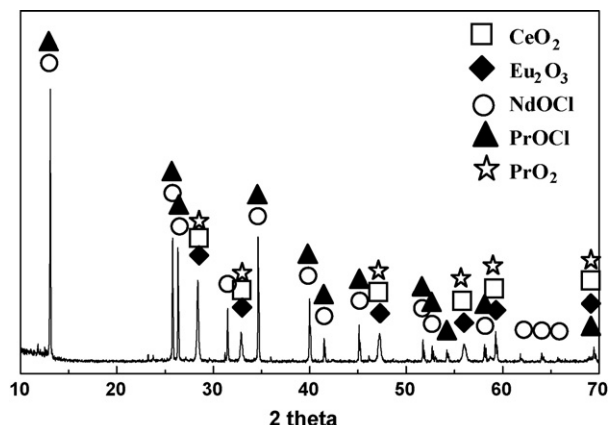

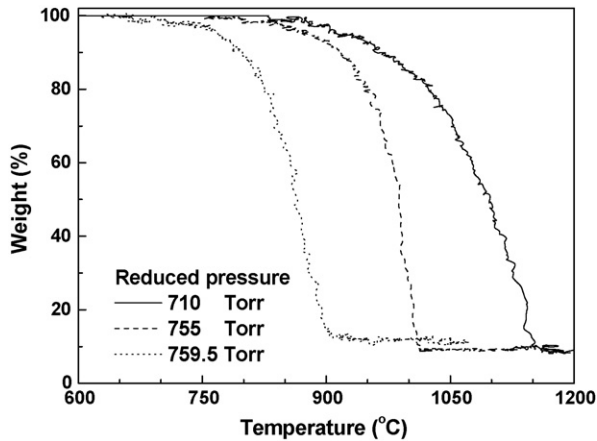Fig. 3. XRD patterns of the rare-earth oxidative precipitates.

Fig. 4. Thermal mass reductions of a mixture of the LiCl–KCl eutectic salt and the rare-earth oxidative precipitates with a pressure reduction.

Fig. 6. Thermal mass reductions of the rare-earth oxychlorides at a fixed heating rate (5 °C/min) under various partial pressures of O_2.

and the starting temperature of the salt vaporization were lowered with a reduction in the pressure. At 710 Torr and 759.5 Torr of the reduced pressure, the starting temperatures of the salt vaporization were about 825 °C and 700 °C, respectively. The salt distillation was almost completed at a temperature below 1000 °C. According to previous reports, LiCl–KCl eutectic salts are distilled under a vacuum at approximately 1100 °C [16,17]. It was confirmed that the distillation temperature of the salt can be reduced further by a reduction in the pressure. In the above conditions, it appeared that the required time for the salt distillation had a difference of 1 h. After the salt distillation, the remaining samples were characterized to identify the transformations of the rare-earth oxidative precipitates by XRD (D8 Advance; KBSI). Fig. 5 shows the XRD patterns of the remaining samples. The remainder consisted of rare-earth oxychlorides and oxides like the rare-earth oxidative precipitates shown in Fig. 3. This means that the transformations of the rare-earth oxidative precipitates in the mixture did not occur during the vacuum distillation process of the mixture. It is thought that this resulted from maintaining an inert atmosphere by injecting Ar gas during the vacuum distillation.

3.3. Dechlorination and oxidation of the rare-earth oxychlorides

As shown in Fig. 5, the remainder obtained from the salt distillation had rare-earth oxychlorides such as NdOCl and PrOCl. These oxychlorides can be an obstructive factor when trying to achieve a stable solidification for a final waste form [6–8]. Dechlorination
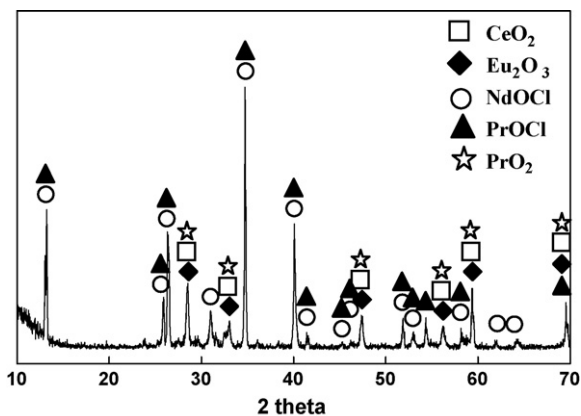
and oxidation of the rare-earth oxychlorides is essential to stabilize a final waste form. Fig. 6 shows the thermal mass reductions of the rare-earth oxidative precipitates containing NdOCl and PrOCl at a fixed heating rate of 5 °C/min under various partial pressures of O_2. According to Fig. 6, a dechlorination and oxidation of them seemed to be dependent on the partial pressure of O_2. The termination temperature of the dechlorination and oxidation was reduced to about 60 °C under 100% of a partial O_2 pressure in comparison to 21% of a partial O_2 pressure. Also, it was confirmed that the dechlorination and oxidation was completely finished at a temperature below 1300 °C and the mass reduction was about 6.4%.

After the dechlorination and oxidation, remaining materials were identified to investigate the transformations of them by XRD (D8 Advance; KBSI) and the results are shown in Fig. 7. As shown in Fig. 7, the oxides ($CeO_2/Eu_2O_3/PrO_2$) were maintained during the dechlroination and oxidation, however, the oxychlorides (NdOCl/PrOCl) were converted to stable oxides (Nd_2O_3/PrO_2). Based on the above results, it is postulated that the dechlorination and oxidation of the rare-earth oxychlorides happens simultaneously at a high temperature of more than 1200 °C under an oxidative atmosphere [5]. The reaction of the dechlorination and oxidation of them can be expressed by the following equations;

$$NdOCl + \tfrac{1}{4}O_2(g) \rightarrow \tfrac{1}{2}Nd_2O_3 + \tfrac{1}{2}Cl_2(g) \tag{1}$$

$$PrOCl + \tfrac{1}{2}O_2(g) \rightarrow PrO_2 + \tfrac{1}{2}Cl_2(g) \tag{2}$$

Fig. 5. XRD-patterns of remaining samples after the vacuum distillation of a mixture of the LiCl–KCl eutectic salts and the rare-earth oxidative precipitates.
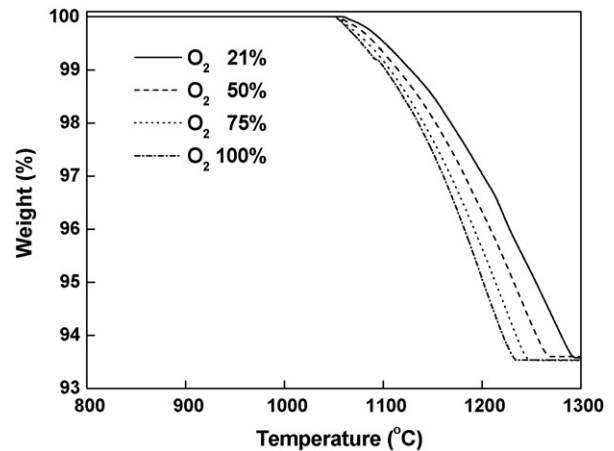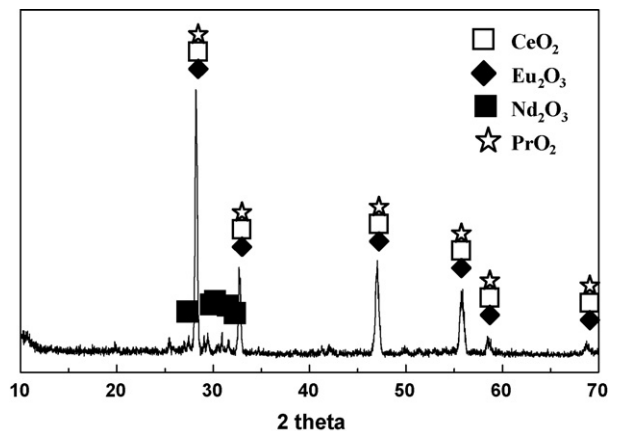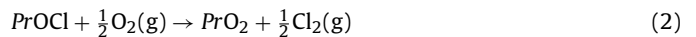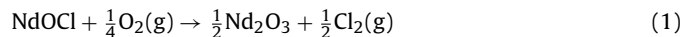

Fig. 7. XRD-patterns of remaining materials after the dechlorination and oxidation of the rare-earth oxidative precipitates containing the rare-earth oxychlorides.

The mass reductions of them shown in Fig. 6 agree well with the stoichiometric values associated with the above equations.

4. Conclusion

A vacuum distillation of a mixture of LiCl–KCl eutectic salts and rare-earth oxidative precipitates was performed to recover a pure LiCl–KCl eutectic salt from the mixture. Also, a dechlorination and oxidation of the rare-earth oxychlorides was carried out to stabilize the final waste form. The pure LiCl–KCl eutectic salt was almost completely separated from the mixture by a vacuum distillation. The required time for the salt distillation and the starting temperature of the salt vaporization were diminished with a reduction in the pressure. The salt distillation was completed at a temperature below 1000 °C. Also, it was confirmed that the rare-earth oxychlorides (NdOCl/PrOCl) were transformed to oxides (Nd_2O_3/PrO_2) at a temperature below 1300 °C during a dechlorination and oxidation, and the dechlorination and oxidation of them was an oxygen-dependent reaction. In addition, the mass reduction of the rare-earth oxidative precipitates containing the rare-earth oxychlorides by TGA was about 6.4%, which agrees well with the stoichiometric values. These results will be utilized to design a concept for a process for recycling the waste salt from an electrorefining process and to reduce a high level waste volume.

Acknowledgements

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