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Vacuum distillation of a mixture of salt and rare-earth oxidative precipitates and dechlorination and oxidation of rare-earth oxychlorides

Hee-Chul Eun,a Hee-Chul Yang,b Yong-Jun Cho,b Eung-Ho Kim,b In-Tae Kim,b
a University of Science and Technology, P.O. Box 52 Yuseong, Daejeon 305-333, Korea, ehc2004@kaeri.re.kr
b Korea Atomic Energy Research Institute, 150 Deokjin-Dong, Yuseong-Gu, Daejeon, 305-353 Korea

1. Introduction

Pyrochemical process shows promise for an advanced nuclear engineering because of its compactness, economy, radiation resistance and non-proliferation[1]. Of all the unit operations of a pyrochemical process, an electrorefining is a key step[1-2]. 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 aspect. In order to reuse the waste salts from an electrorefining process, it is necessary to separate the rare-earth chlorides from the waste salts, and an oxidation of these rare-earth chlorides in the waste salts can be utilized. Among the various oxidation methods, a promising and potential alternative method is by sparging O_2 gas[3-4]. However, only about 65 wt% of the salt can be recovered by this method, and the rest is discharged as a mixture of LiCl-KCl eutectic salt and rare-earth oxidative precipitates.

In this study, a vacuum distillation of a mixture of LiCl-KCl eutectic salt and rare-earth oxidative precipitates was performed to completely recover a pure LiCl-KCl salt. Also, a dechlorination and oxidation of rare-earth oxychlorides was carried out to stabilize the final waste form.

2. Methods and Results

2.1 Vacuum distillation of a mixture of LiCl-KCl eutectic salt and rare-earth oxidative precipitates

To completely recover salt from a mixture of LiCl-KCl eutectic salt and rare-earth oxidative precipitates, a vacuum distillation of the salt was carried out by using thermo-gravimetric analyzer specially made for vacuum distillation of a salt. The temperature for salt distillation was heated to 1200 ℃ with a heating rate of 4 ℃/min. The pressure is reduced from 710 torr to 759.5 torr. Figure 1 shows a thermal mass reduction of the mixture of LiCl-KCl eutectic salt and rare-earth oxidative precipitates by the vacuum distillation. It was shown that required time for the salt distillation and starting temperature of the salt vaporization were diminished with 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 ℃ and 700 ℃, respectively. In these two conditions, required time for the salt distillation had a difference of 1 hr. After the salt distillation, it was confirmed that a transformation of the rare-earth oxidative precipitates didn't occur.

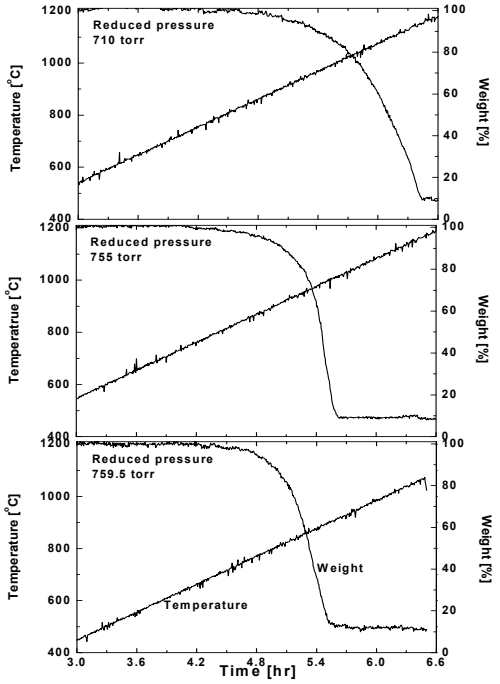

Figure 1 Thermal mass reduction of a mixture of LiCl-KCl eutectic salt and rare-earth oxidative precipitates by the vacuum distillation

2.2 Dechlorination and oxidation of rare-earth oxychlirides

After the salt distillation, the residues (rare-earth oxidative precipitates) had rare-earth oxychloride such as NdOCl and PrOCl. These oxychlorides can be an obstructive factor when trying to achieve a stable solidification for the final waste form. A dechlorination and oxidation of the rare-earth oxychlorides was performed to stabilize the final waste form by thermo-gravimetric analyzer (SDT 2960; TA Instrument Co.). The temperature of the furnace was programmed to rise from room temperature to 800 ℃ with a heating rate of 50 ℃/min. After an initial rapid heating, the furnace was slowly heated to 1300 ℃ with a heating rate of 5 ℃/min. Four oxygen partial pressures were tested: 21, 50, 75 and 100 % of oxygen and the remainder consisted of pure nitrogen (>99.9%). Figure 2 shows the

thermal mass reduction as a function of the temperature of the rare-earth oxychlorides at a fixed heating rate under various O_2 partial pressures. The dechlorination and oxidation of rare-earth oxychlorides at high temperatures appeared to be an oxygen-dependent reaction.

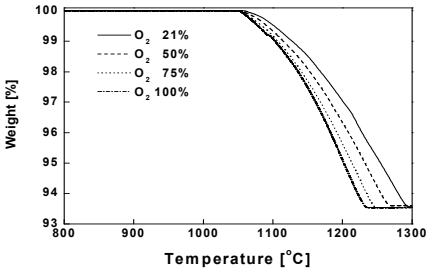

Figure 2 Thermal mass reductions of the rare-earth oxychlorides at a fixed heating rate (5 ℃/min) under various O_2 partial pressures.

3. Conclusion

A vacuum distillation of a mixture of LiCl-KCl eutectic salt 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 totally 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 reducing the pressure. Also, it was confirmed that the rare-earth oxychlorides were transformed to oxides by an O_2 injection at a temperature below 1300 ℃ and a dechlorination and oxidation of them was an oxygen-dependent reaction. The above results will be utilized for a reuse of the waste salt from an electrorefining process and a volume reduction of a high level waste.

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