Journal of Nuclear Materials 384 (2009) 256–261

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

Treatment of a waste salt delivered from an electrorefining process by an oxidative precipitation of the rare earth elements

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ARTICLE INFO

Article history:
Received 24 April 2008
Accepted 25 November 2008

ABSTRACT

For the reuse of a waste salt from an electrorefining process of a spent oxide fuel, a separation of rare earth elements by an oxidative precipitation in a LiCl-KCl molten salt was tested without using precipitate agents. From the results obtained from the thermochemical calculations by HSC Chemistry software, the most stable rare earth compounds in the oxygen-used rare earth chlorides system were oxychlorides (EuOCl, NdOCl, PrOCl) and oxides (CeO_2, PrO_2), which coincide well with results of the Gibbs free energy of the reaction. In this study, similar to the thermochemical results, regardless of the sparging time and molten salt temperature, oxychlorides and oxides were formed as a precipitant by a reaction with oxygen. The structure of the rare earth precipitates was divided into two shapes: small cubic (oxide) and large plate-like (tetragonal) structures. The conversion efficiencies of the rare earth elements to their molten salt-insoluble precipitates were increased with the sparging time and temperature, and Ce showed the best reactivity. In the conditions of 650 °C of the molten salt temperature and 420 min of the sparging time, the final conversion efficiencies were over 99.9% for all the investigated rare earth chlorides.

1. Introduction

Pyroprocessing of a spent light–water reactor oxide fuel can separate the uranium and transuranic elements from a spent fuel by using an electrochemical technique in a molten salt medium at a high temperature, and has been considered as a proliferation-resistant and environment-friendly technology because a separation of plutonium alone is impossible and the final volume and radiological toxicity of the radioactive waste can be greatly reduced. It can enhance the effective utilization of uranium resources as well, when combined with a sodium-cooled fast reactor (SFR) system [1–3]. Generally, a pyroprocessing of a spent oxide fuel includes several steps: disassembly and decladding of a oxide spent fuel, a electrolytic reduction process to convert the spent oxide fuel to a metal, actinide separation by an electrorefining process and a manufacturing of the resulting actinides mixture to a suitable fuel for use in an advanced reactor [4]. During the pyroprocessing of spent oxide fuels, two different types of waste salts are generated: one is LiCl waste salt containing alkali and alkaline-earth fission products from an electrolytic reduction process, and the other is LiCl-KCl eutectic waste salt containing rare earth fission products from an electrorefining process. Since these waste salts are radioactive and heat generative, they must be fabricated into durable waste forms that are compatible with the environment inside a geological repository for a long time. It is generally believed that the decontamination of waste salts from fission products and a recycling of these salts in a main process, i.e. electrolytic reduction and electrorefining process, is crucial from the standpoint of their economical as well as their environmental aspects because such a recycling of a waste salt can minimize the quantity and toxicity of a waste requiring a final geological disposal. In order to reuse these waste salts, the fission products in a waste salt must be removed. At present, various studies are ongoing to remove fission products from a waste salt; a salt-zeolite ion exchange [5], an oxide precipitation with an oxidant addition such as Li_2O [6] or V_2O_5 [7], phosphate precipitation [8,9] and a carbonate precipitation [10].

For a successful reuse of a LiCl-KCl eutectic waste salt in an electrorefining process, the eutectic ratio and the impurity concentration of the recovered salt must be within an acceptable range. When considering a rare earth separation as well as a successful reuse of a LiCl-KCl eutectic waste salt, it is difficult to employ a precipitant addition method because the eutectic ratio of the salt may be changed or a by-product may be formed due to a side reaction of the metal chlorides with a precipitate agent. Furthermore, the addition of an excess amount of a precipitate agent to achieve a complete precipitation reaction may cause the same problems.

To solve the above mentioned problems, as a new attempt, a precipitation by a reaction with oxygen and a successive distillation method could be used. In this process, pure oxygen is sparged into a molten salt containing rare earths to react with them, and then the oxides or oxychlorides which are insoluble in the molten

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doi:10.1016/j.jnucmat.2008.11.020

salt are formed. When these rare earth precipitates are completely settled down, the upper pure salt phase is separated from the precipitate phase which includes precipitates (i.e. oxychlorides or oxides) and a salt residue. After that, the remaining salt residue in the precipitate phase is distilled away from the precipitate by a vacuum distillation method. For a convenience of solidification process, among separated rare earth precipitates, rare earth oxychlorides are converted to their oxide form (RE_2O_3) in a high temperature and in an oxygen present condition by oxidation and de-chlorination reaction. In this oxidation and de-chlorination process the form of rare earth oxides is not changed. Finally, these rare earth oxides are treated to fabricate final waste form by solidification/immobilization process such as a ceramization or a vitrification process [22].

Among these processes, a precipitation of the rare earth elements is the most important process. So in the present study the precipitation characteristics of some rare earth chlorides by a reaction with oxygen are investigated. Identification of the form of the rare earth precipitates and the effects of the temperature and sparing time on the precipitation ratio are also investigated. Furthermore, thermodynamic equilibrium calculations have been carried out in order to predict the most stable species formed by a reaction between oxygen and rare earth elements at different temperatures and oxygen concentrations.

2. Experimental

The apparatus for the oxidative precipitation of the rare earth chlorides is composed of a cylindrical stainless-steel column, an electric ceramic heater with a thermocouple and a temperature controller, an oxygen sparger for an oxygen distribution into the molten salts and a crucible of 0.06 m in inner diameter and 0.16 m in height as shown in Fig. 1. To overcome a corrosion problem due to a high temperature and oxygen atmosphere, the oxygen sparger and crucible were made from alumina materials. As a representative of the rare earth elements, four anhydrous rare earth chlorides (Ce, Pr, Eu, Nd) were premixed with 500 g of a LiCl-KCl solid salt with a purity of 99.9% (LiCl: 44.2 wt.%, eutectic point: 360 °C) in an alumina crucible. The oxidative precipitation reaction of rare earth chloride by a reaction with oxygen was operated in gas (oxygen)–liquid (molten salt) two-phase flow system. In this flow system, the optimum flow rate was very important experimental variable. Ordinarily, in a vertical two-phase flow system, a flow regime with gas flow rate is developed from a homogeneous bubble flow to a slug or annular flow [21]. If an oxidation reaction is initiated at slug or annular flow regime, salts or oxidation products can be entrained due to the resultant large and fast rising bubbles or slugs. So the oxidation reaction by using oxygen sparging must be operated in a bubble or bubble slug flow regime. In the preliminary experiments when the oxygen sparging rate was smaller than 2 l/min, a dispersed bubble flow regime was maintained and salt entrainment was minimized. So, oxygen sparged into molten salt bed through an alumina sparger of 0.007 m inner diameter which has eight 2 mm I.D.(inner diameter) holes around the end (sparging) point with a 1.5 l/min of sparging rate in whole experiments.

The crucible containing the mixture of solid eutectic salt and rare earth chlorides was heated up to a given temperature (400–650 °C) and when the temperature reached the operating temperature, oxygen was sparged into the molten salt via an oxygen sparger. During the oxygen sparging process, to detect a conversion of the rare earth elements to insoluble precipitates with time, about 9 g of the molten salt was taken into a quart tube at regular time intervals. Molten salt samples were weighted and dissolved in 500 ml of distilled water then the concentrations of the rare earth ions in the solutions were analyzed by an ICP (Inductively Coupled Plasma)-atomic emission spectrometry. After completing the experiments, the alumina crucible was lifted from the stainless-

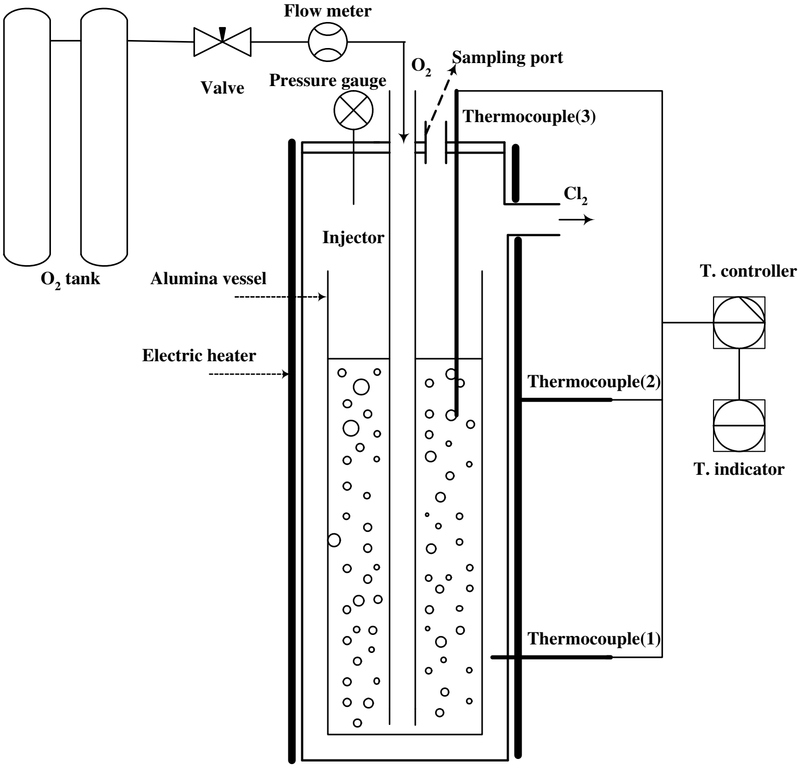

Fig. 1. Schematic diagram of the experimental apparatus.

Table 1
Detailed experimental conditions.

Rare earth chloride	Temperature	Amount of eutectic salt	Amount of rare earth chloride
$CeCl_3$ $NdCl_3$ $PrCl_3$ $EuCl_3$	400-650 °C	500 g (LiCl – 221 g KCl – 279 g)	16 g (each 4 g)

steel column and then slowly cooled. The entire cooled salt was dissolved in a cold distilled water vessel, where the insoluble rare earth precipitates formed as a result of a reaction between the rare earth ions and oxygen were precipitated. The insoluble precipitates were filtered off, washed several times with distilled water and dried in a dry oven at 200 °C which was maintained as an argon atmosphere. The dried precipitates were collected and then analyzed by means of an X-ray powder differential analysis for their structure and SEM–EDS (Scanning Electron Microscope–Energy Dispersive Spectroscopy, Leo 1455VP; KBSI) and EPMA (Electron Probe Micro-Analyzer) for their elemental weight composition. Detailed experimental conditions are listed in Table 1.

Before performing any oxygen sparging experiments, the theoretical equilibrium compositions of the rare earth compounds during an oxygen sparging process were predicted by thermodynamic equilibrium calculations by using HSC Chemistry software [11]. HSC Chemistry software makes conventional thermodynamical calculations based on a minimization of the Gibbs free energy in order to simulate the chemical reaction equilibrium and the processes [12].

3. Results and discussion

3.1. Thermodynamic equilibrium calculation

To predict possible solid products between rare earth chlorides and oxygen, the thermodynamic equilibrium composition was predicted by using thermodynamic calculation software (HSC Chemistry [11]) in the rare earth chlorides–oxygen system. Oxygen, four rare earth chlorides (i.e. $CeCl_3$, $PrCl_3$, $NdCl_3$ and $EuCl_3$) and their oxides (RE_2O_3 or REO_2) and oxychlorides (REOCl) as a possible molten salt-insoluble solid products formed by reaction between rare earth chlorides and oxygen were used as the considered species. In this calculation, the thermochemical data of rare earth ion state in LiCl-KCl eutectic salts are supposed to those of in water since only the thermochemical date of rare earth ion in aqueous state are available in HSC Chemistry. When assuming the same mole ratio (0.1 kmol) of the rare earth chlorides and a sufficient oxygen supply condition, Fig. 2(a) shows the equilibrium amounts of the rare earth compounds with the temperature ranging from 400 to 700 °C. As shown in Fig. 2(a), the calculation results of the equilibrium amounts indicate that an oxychloride (REOCl) for Pr, Eu and Nd, and an oxide (REO_2) for Ce are the dominant species formed in this study. In the case of praseodymium (Pr), at a higher temperature than 500 °C, not only an oxychloride but also an oxide appeared as a stable species. Fig. 2(b) shows the effect of the oxygen concentration on the equilibrium amount of the rare earth species, where the calculation conditions are 600 °C for the temperature and the others are the same as those of the Fig. 2(a) case. At a deficient oxygen concentration condition (below 0.3 kmol of an oxygen concentration), for the Ce case, the dominant species is an oxychloride not an oxide and for the Pr, Eu and Nd cases they are oxychlorides. When the oxygen concentration exceeds 0.3 kmol there is no change in the dominant species formed and these results are the same as those of the Fig. 2(a) case. Based on the these results, at a sufficient oxygen concentration condition, the reaction equation between the rare earth chlorides used in this experiment and oxygen can be represented as follows:

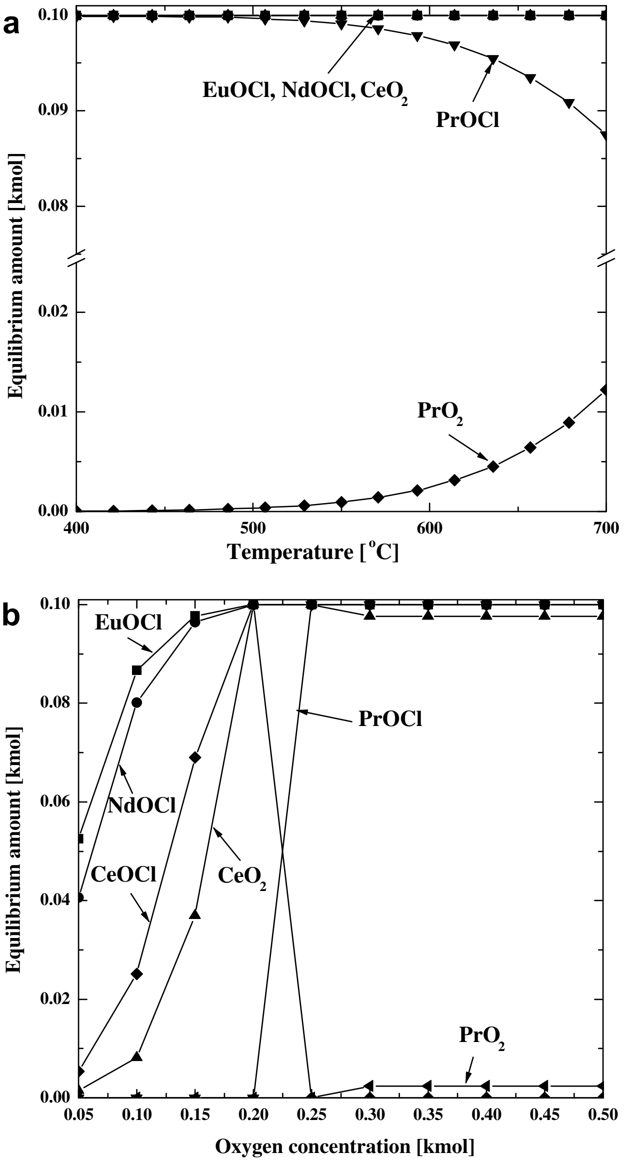

Fig. 2. Thermochemical estimations of the equilibrium compositions of the rare earth compounds in the presence of oxygen and rare earth elements.

$$RECl_3 + 0.5O_2 \rightarrow REOCl + Cl_2 \tag{1}$$

$$RECl_3 + O_2 \rightarrow REO_2 + 1.5Cl_2 \tag{2}$$

where Nd and Eu are applied to Eq. (1) and Ce is to Eq. (2). In the case of Pr, both Eqs. (1) and (2) are applied.

3.2. Precipitate form

When oxygen is sparged into a molten salt bed containing rare earth chlorides, precipitates which are nearly insoluble in molten salts are formed. It has generally been accepted that oxide (REO_2 or RE_2O_3) or oxychloride (REOCl) forms are a stable chemical form of a product by a reaction between a rare earth ion (RE^{3+}) and an oxygen ion (O^{2-}) in a molten salt condition, where the form of the rare earth precipitates is affected by the oxygen concentration/pressure and its formation enthalpies [13]. Casterillejo et al. [14] have reported that the stable species by a reaction between RE^{3+} and O^{2-} in a LiCl-KCl molten salt condition are rare earth oxychlorides (RE = La, Ce, Pr, Nd). Katayama et al. [6] showed that among the rare earth elements, the rare earth elements which have a smaller ionic radius to that of gadolinium are apt to precipitate as an oxychloride form by a reaction with oxygen.

Fig. 3 shows the X-ray diffraction (XRD) patterns of the mixture of rare earth precipitates obtained from this experiment with the molten salt temperature. The XRD patterns of the rare earth oxychlorides reveal no significant changes. Holsa et al. [19] reported that the X-ray powder diffraction patterns showed no significant changes between the individual rare earth oxychloride samples and as the reflection positions moved smoothly from the lower 2θ angles toward the higher ones the rare earth ionic radius decreased. As shown in Fig. 3, the rare earth precipitates are a mixture of oxychlorides, i.e. EuOCl, NdOCl, PrOCl and oxides, i.e. CeO_2, PrO_2, which are nearly identical to the thermochemical calculation results (Fig. 2) The effect of the molten salt temperature on the form of the rare earth precipitates is negligible that is the precipitate forms of the rare earth chlorides are independent of the molten salt temperature. In the thermochemical calculation results when the temperature exceeded about 500 °C, PrO_2 was formed but in this experiment for the full experimental temperature range (400–650 °C) both PrOCl and PrO_2 existed in the precipitates.

The morphologies of the precipitates are presented in the SEM picture in Fig. 4. The rare earth precipitates formed by a reaction with oxygen are two separate structures: a small cubic fluorite structure and a large plate-like (tetragonal) structure. From the EDS and EPMA result it was found that for the cubic structure precipitates no chloride element existed and for the plate-like structure no cerium element existed. Table 2 is EPMA analysis results of plate-like (tetragonal) precipitates. This result is nearly same to that of ideal case ($(NdEuPr)O_3Cl_3$). So it is estimated that the small cubic shape precipitates are oxide mixture (i.e. $(PrCe)O_2$) and the large plate-like shape precipitates are oxychloride mixture (i.e. $(NdEuPr)O_3Cl_3$). These estimations coincide well with other researches: CeO_2 and PrO_2 have a cubic fluorite structure [15–17] and PrOCl, NdOCl and EuOCl have a tetragonal structure [18,19].

3.3. Precipitation reaction

A typical example of a weight change of the rare earth chlorides in a molten salt with the oxygen sparging time at 550 °C is shown in Fig. 5, where the rare earth concentration in the molten salt with the sparging time was calculated using the rare earth ion concentration analyzed by ICP-AES for the salt samples. The weight of the four rare earth chlorides in the molten salts was decreased with an increasing oxygen sparing time, which means that the dissolved rare earth chlorides in the molten salt were converted to their molten salt-insoluble precipitates, oxides or oxychlorides. From the rare earth concentration data we calculated the conversion efficiency to their insoluble precipitates with the sparing time and the molten salt temperature.

Fig. 6 shows the effects of the sparging time on the conversion efficiency of the rare earth elements in a constant molten salt temperature condition (450 °C and 650 °C), where the conversion efficiency increased with the sparging time. At 650 °C of the molten salt temperature condition, when the sparging time exceeded about 360 min, the conversion efficiencies of the four rare earth elements showed nearly an asymptotic value, over 99.9%. As shown in Fig. 6, the best reactive rare earth element is Ce, which can be explained by the Gibbs free energy of the reactions of Eqs. (1) and (2). As shown in Fig. 3, at a constant temperature, CeO_2 is the most stable when compared to the others.

The molten salt temperature is a key parameter for the rare earth precipitation reaction. The conversion efficiency was increased with the molten salt temperature (Fig. 7). However, the conversion efficiency of Ce was nearly constant with an increase of the molten salt temperature, when the sparging time exceeded 240 min. Since the diffusion phenomena of the oxygen into the rare earth element could be eliminated due to an oxygen sparging process, the oxidative precipitation reaction in a molten salt by a

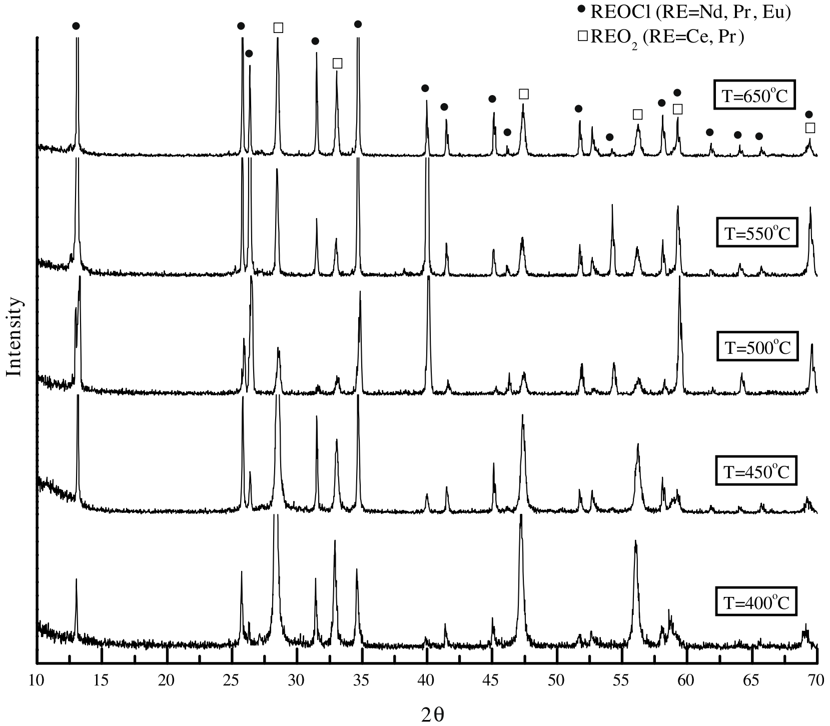

Fig. 3. XRD patterns of the precipitates by a reaction between a rare earth element and oxygen in a molten salt condition.

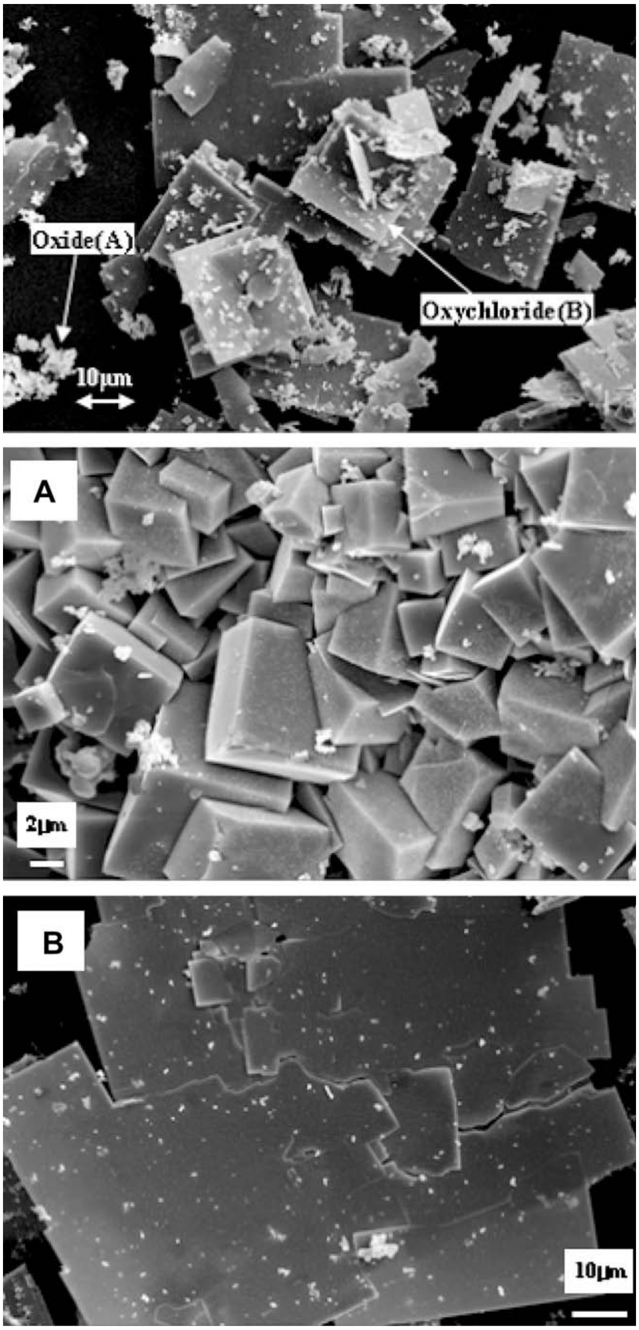

Fig. 4. SEM photography of the precipitates from the oxygen sparing process.

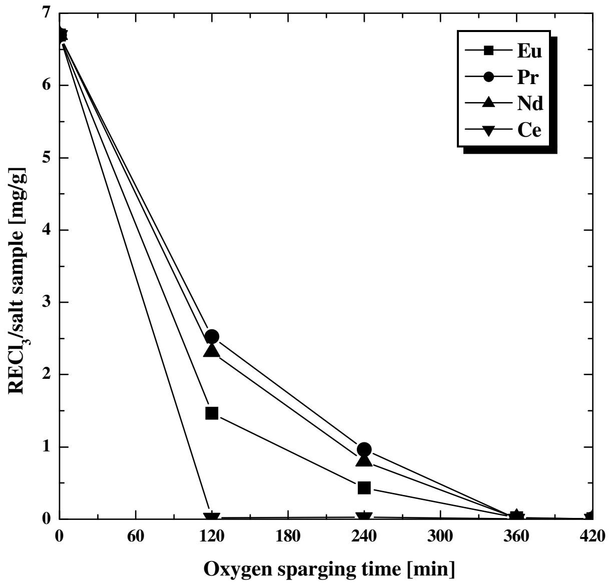

Fig. 5. A typical example of a weight change of the rare earth chlorides in a molten salt with the oxygen sparging time.

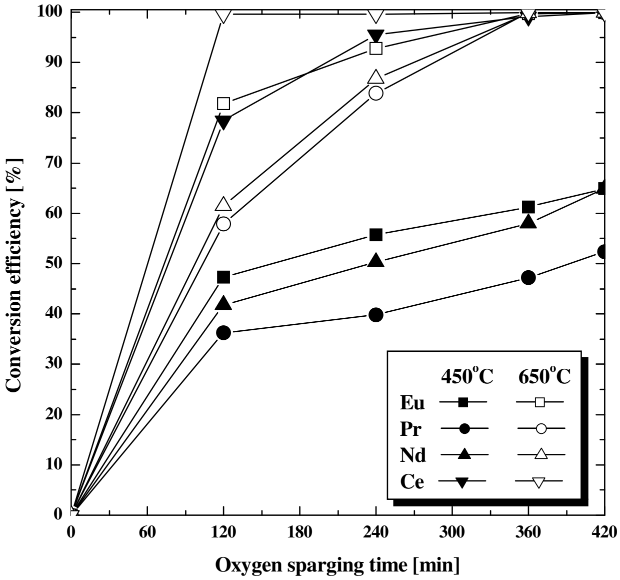

Fig. 6. Effects of the sparging time on the precipitation efficiency.

Table 2
EPMA results of plate-like (tetragonal) precipitates.

Element	Weight fraction	Mole fraction (Mole ratio)
O	8.376	0.524 (3.154)
Cl	18.072	0.510 (3.071)
Pr	24.210	0.172 (1.035)
Eu	25.225	0.166 (1.000)
Nd	24.117	0.167 (1.007)

reaction between a rare earth element and oxygen is governed by two factors: the oxygen solubility in a molten salt and the reaction rate. In case of a reaction rate with temperature, Cho et al. [21] reported that the oxidation reaction of $LaCl_3$ in LiCl-KCl eutectic molten salts by reaction with a oxygen is a pseudo-first-order reaction and the rate constant of the reaction increases with the increasing molten salt temperature. Therefore, a higher molten salt temperature causes a faster oxidation reaction. It is well known that gases are soluble in a molten salt at a high temperature. It is possible to distinguish between a reactive and inert gas solubility by observing their temperature dependency. For the former, its solubility decreases with an increasing temperature, while for the latter it increases [20]. Oxygen is inert in a LiCl-KCl eutectic molten salt. Therefore, it is postulated that the increasing trend of the conversion efficiency with the temperature is due to an increasing oxygen solubility in the molten salt with the temperature. Fig. 8 shows the final conversion efficiency result for the conditions of 420 min sparging time and 1.5 l/min sparging rate. When molten salt

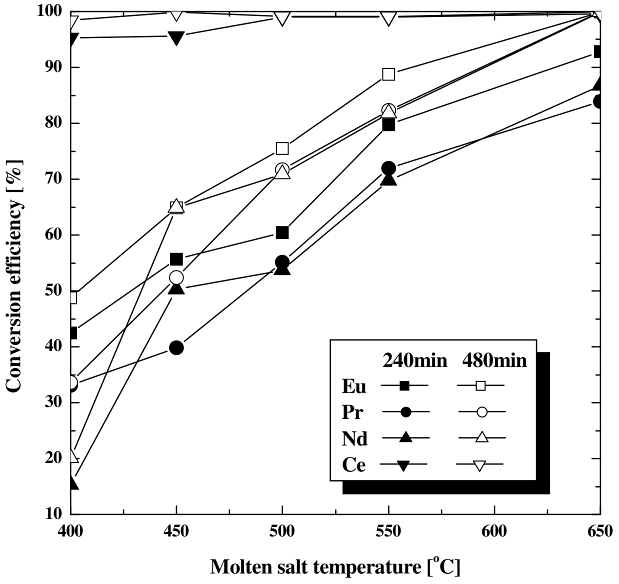

Fig. 7. Effects of the molten salt temperature on the precipitation efficiency.

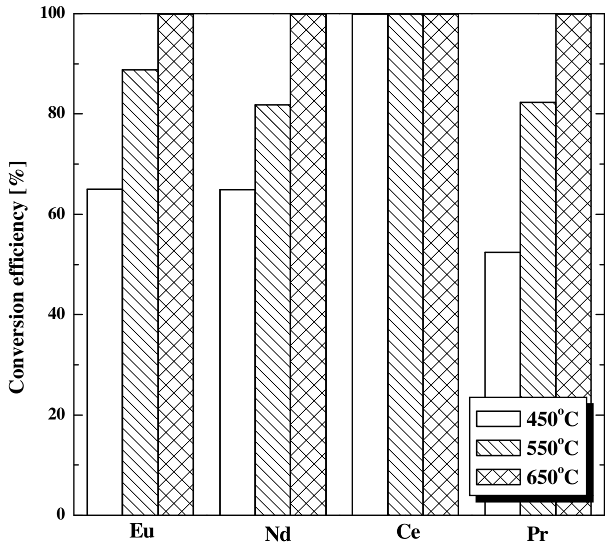

Fig. 8. Conversion efficiency of rare earth chlorides used in this experiment.

temperature was 650 °C, the conversion efficiency of the rare earth elements used in this experiments are all over 99.9% by a reaction with oxygen. Therefore, it is concluded that the rare earth elements involved in a LiCl-KCl eutectic waste molten salt from an electrorefining process can be effectively removed by reaction with oxygen.

4. Conclusion

For a minimization of a waste salt delivered from an electrorefining process of spent oxide fuel, an oxidative co-precipitation of four rare earth chlorides (Ce/Pr/Nd/$EuCl_3$) in a LiCl-KCl eutectic molten salt has been carried out by using an oxygen sparging method. In the oxygen sparging method, oxygen is sparged into the molten salt bed to react with the free rare earth elements and then the resultant oxides or oxychlorides which are insoluble in the molten salt are precipitated. In this study, regardless of the sparging time (max. 420 min) and the molten salt temperature (400–650 °C), oxychlorides (EuOCl, NdOCl, PrOCl) and oxides (CeO_2, PrO_2) were formed as a precipitates by a reaction with oxygen. The conversion efficiency of the rare earth elements to the insoluble precipitates increases with the sparging time and the molten salt temperature. In the conditions of 650 °C of a molten salt temperature and 420 min of a sparging time, the values of the conversion efficiency of the used rare earth chlorides were over 99.9%. The oxygen sparging method is effective for a precipitation of rare earth chlorides in eutectic molten salts without changing the eutectic composition of the salts and there is no formation of byproducts.

Acknowledgment

This project has been carried out under the Nuclear R&D Program by the Ministry of Education, Science and Technology.

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