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# Study on a recovery of rare earth oxides from a LiCl–KCl–$RECl_3$ system

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ABSTRACT

Radioactive rare earth chlorides in waste LiCl–KCl molten salts have to be separated as a stable form to minimize waste volume and to achieve stable solidification. In this work, thermal behavior of rare earth chlorides ($CeCl_3$, $GdCl_3$, $NdCl_3$, $PrCl_3$) was investigated in an oxygen condition to recover rare earth oxides from a LiCl–KCl–$RECl_3$ system. The rare earth chlorides in the LiCl–KCl molten salts were smoothly converted to an oxychloride form at a higher temperature than 650 °C, except for $CeCl_3$. $CeCl_3$ was totally converted to an oxide from at a higher temperature than 450 °C. The rare earth oxychlorides (GdOCl, NdOCl, PrOCl) were effectively converted to oxide forms at a higher temperature than 1100 °C. It was confirmed that rare earth oxides can be recovered from a LiCl–KCl–$RECl_3$ system without impurity generation.

## 1. Introduction

The pyrochemical process has many advantages such as compactness, economy, radiation resistance, nonproliferation and less secondary wastes when compared to the existing commercial process [1,2]. This process is to electrochemically partition the fission products from spent nuclear fuels in a molten salt bath [3–5]. In this process, the electrorefining process using LiCl–KCl molten salts is a main process and it exhausts considerable amounts of waste salts containing some metal chlorides such as rare earth chlorides or actinide chlorides [6,7]. These waste salts are classified as high-level wastes (HLW) because they exceed both the standard decay heat and radioactivity levels. Thus, it is required to separate the rare earth nuclides from the salt wastes for minimizing the HLW volume. To resolve the problem, various studies on the nuclides precipitation by injecting a chemical agent such as $Li_2O$ or $V_2O_5$ or Li(or K)$_3PO_4$ were performed [1,8,9]. Particularly, it is reported that the phosphate precipitation method was very effective for removing the nuclides from the salt wastes [1]. However, the method has a problem that the composition of the LiCl–KCl molten salts can be changed by byproduct generation according to the agent injection, and this means that it may be difficult to reuse the salt and to reduce the salt wastes. Thus, it is needed to separate the nuclides from the salt wastes without the composition change to minimize the salt wastes and to reuse the salts. Also, it is needed to convert the rare earth nuclides to oxide forms for achieving a stable solidification as a final waste form because the rare earth nuclides existing as chloride forms in the salt wastes have some chlorine elements and the chlorine elements can be an obstructive factor [10–12].

In this study, thermal behavior characteristics of the rare earth chlorides were investigated for recovering rare earth oxides from a LiCl–KCl–$RECl_3$ system. For this aim, thermo-gravimetric analysis (TGA) of the rare earth chlorides was performed. Based on the TGA results, a dechlorination and oxidation test of a rare earth chloride in LiCl–KCl molten salts and a conversion test of rare earth oxychloride to oxide form were carried out.

## 2. Experimental and methods

### 2.1. TGA of rare earth chlorides

A TGA of rare earth chlorides under an oxygen-rich condition was performed by using a thermo-gravimetric analyzer (SDT 2960; TA Instrument Co.). Before doing the TGA test, the rare earth chlorides used in this study as anhydrous agents were treated to remove hydration water in them at 70 °C under a nitrogen-rich condition in the analyzer when the mass of them is kept constant. Sample mass was fixed at about 15 mg. The temperature of the furnace was programmed to rise from room temperature to a set temperature. The heating rate was fixed at 5 °C/min. The set temperature was 1400 °C. To maintain the oxygen-rich condition, high purity (>99.999%) oxygen gas was injected during a TGA test of the rare earth chlorides. After a test, the residues were characterized to observe a thermal behavior of a rare earth chloride by using XRD patterns.

### 2.2. Dechlorination and oxidation test of rare earth chloride in LiCl–KCl molten salts

The experimental apparatus (0.2 kg/batch) for a dechlorination and oxidation test of a rare earth chloride in LiCl–KCl molten salts consists of a cylindrical stainless-steel column, an electric heater,

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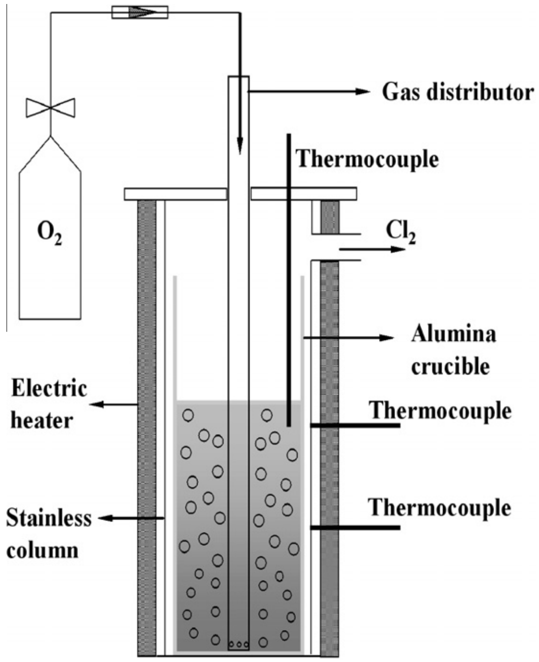


**Fig. 1.** A schematic apparatus for a dechlorination and oxidation test of a rare earth chloride in LiCl–KCl molten salts.

an $O_2$ gas distributor and an alumina crucible. Fig. 1 shows a schematic diagram of the apparatus. Before the dechlorination and oxidation test, rare earth chlorides and LiCl–KCl salts were dried to remove residual hydration water in them at about 100 °C for 48 h. An anhydrous rare earth chloride ($PrCl_3$, $CeCl_3$, $NdCl_3$, $GdCl_3$) with a purity of 99.99% was premixed with a LiCl–KCl salt with a purity of 99.9% (LiCl: 44.2 wt.%, eutectic point: 360 °C) in the alumina crucible. The mixture consists of 5 wt.% of a rare earth chloride and 95 wt.% of the LiCl–KCl salt. The alumina crucible containing the mixture was heated up to an operating temperature (450–750 °C) in the stainless-steel column and when the temperature reached the given temperature, $O_2$ was sparged into the eutectic salt at the flow rate of 1.0 L/m through the gas distributor. After the dechlorination and oxidation test, the alumina crucible was cooled and then the contents in the alumina crucible were dissolved in distilled water at room temperature, where the insoluble precipitates were characterized by using XRD patterns.

### 2.3. Conversion test of rare earth oxychloride to oxide

A conversion test of rare earth oxychlorides was performed by using an electric furnace. The tested samples were GdOCl, NdOCl and PrOCl generated from the dechlorination and oxidation test of a rare earth chloride in LiCl–KCl molten salts. The sample mass was about 10 g. The sample was put into an alumina crucible and then the crucible was charged into the electric furnace. The temperature of the furnace was programmed to rise from room temperature to a set temperature in 2 h. After heating for 2 h, the furnace temperature was fixed at a set temperature for 2 h. The set temperatures were 900 °C, 1000 °C, 1100 °C and 1200 °C. This test was also performed under an oxygen-rich condition. To maintain the condition, high purity (>99.999%) oxygen gas was injected during the conversion test. After the test, the residues were identified to observe chemical deformation of the rare earth oxychloride by using XRD patterns.

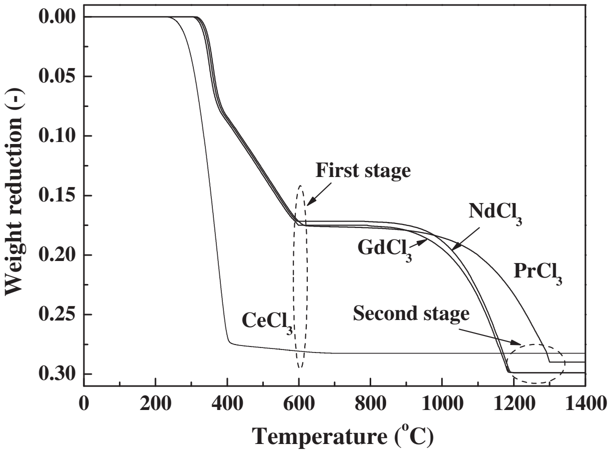


**Fig. 2.** Thermal mass reductions of rare earth chlorides with temperatures in an oxygen condition.

## 3. Results and discussion

### 3.1. Thermal behavior of rare earth chlorides in an oxygen-rich condition

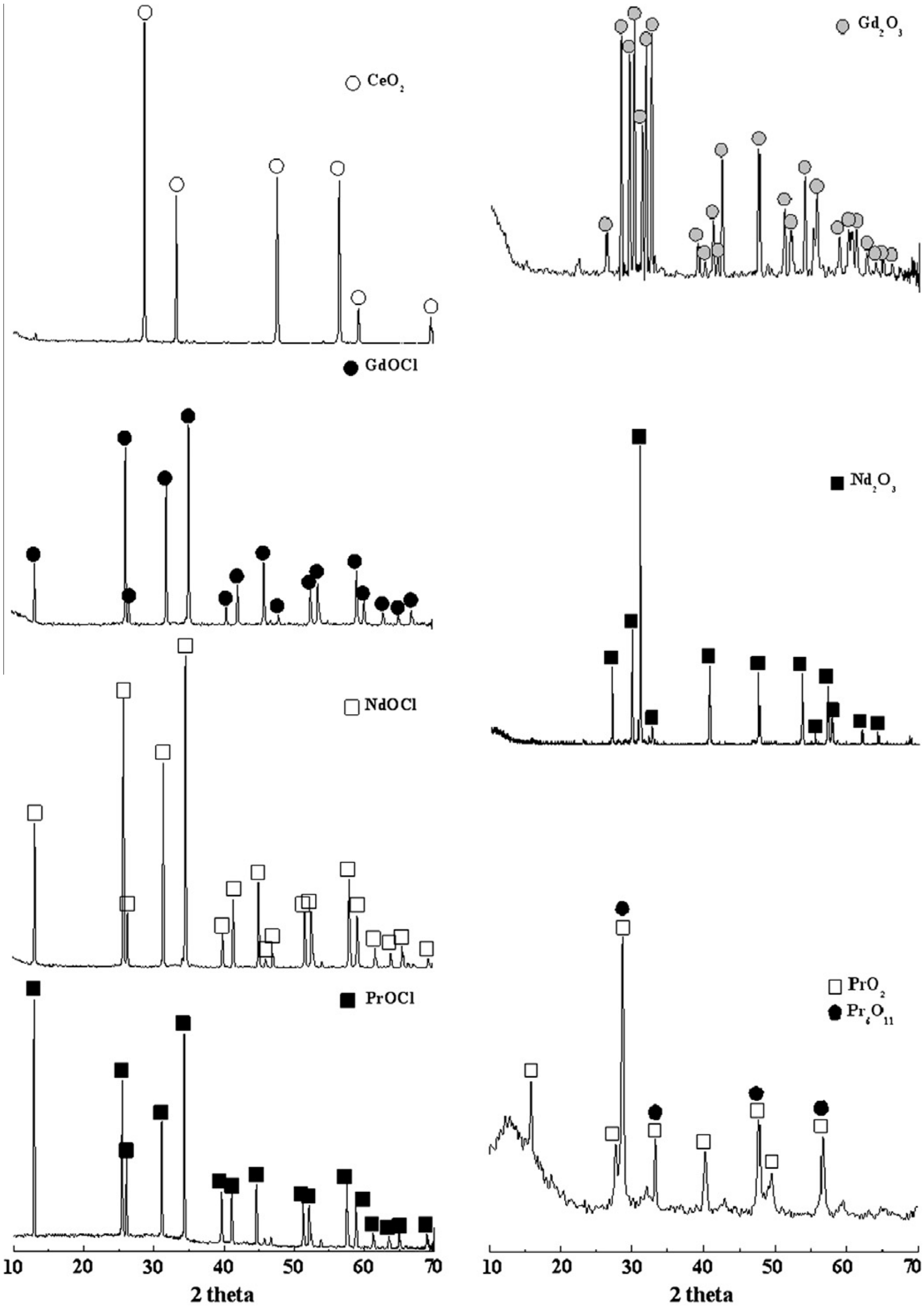
TGA of rare earth chlorides was performed to investigate thermal behavior of them under oxygen-rich conditions before doing a dechlorination and oxidation test of rare earth chloride in LiCl–KCl molten salts and a conversion test of rare earth oxychloride to an oxide form. Generally, a rare earth chloride is melted at a constant temperature and is vaporized as a gas phase of a rare earth chloride under an inert condition. This means that the chemical form of rare earth chloride is not changed under inert conditions. A vapor pressure difference between a rare earth chloride and lithium chloride (or potassium chloride) is not large. This is the reason that makes it difficult to separate rare earth chlorides from LiCl–KCl molten salts. However, rare earth chloride, which is present as trivalent ions, is easily converted to an oxychloride form or an oxide form insoluble in the salts under oxygen conditions. In a previous study, it is reported that a rare earth oxychloride is easily formed by heating hydrated rare earth chloride in air conditions at around 300 °C [8]. This was also confirmed from the calculation results of Gibb's free energy for a reaction between a rare earth chloride and oxygen [13]. The calculation results are expressed in Table 1. Fig. 2 shows thermal mass reductions of rare earth chlorides ($CeCl_3$, $GdCl_3$, $NdCl_3$, $PrCl_3$). As shown in Fig. 2, thermal mass reductions of the rare earth chlorides under an oxygen-rich condition occurred through two stages with temperatures, except for $CeCl_3$. The first mass reduction of them was completed at about

**Table 1**
Gibbs free energy (kcal/mole) of the reaction calculated by HSC 5.1 Chemistry software with temperature [12].

| Reaction eq. | T (°C) | | | | | |
|---|---|---|---|---|---|---|
| | 250 | 350 | 450 | 550 | 650 | 750 |
| $CeCl_3 + O_2(g) \rightarrow CeO_2 + 3/2Cl_2(g)$ | −13.742 | −14.517 | −15.225 | −15.869 | −16.454 | −19.979 |
| $GdCl_3 + 1/2O_2(g) \rightarrow GdOCl + Cl_2(g)$ | −2.893 | −4.276 | −5.613 | −6.907 | −7.616 | −7.662 |
| $NdCl_3 + 1/2O_2(g) \rightarrow NdOCl + Cl_2(g)$ | −2.630 | −3.142 | −3.474 | −3.659 | −3.676 | −3.720 |

600 °C and the next stage was terminated between 1200 °C and 1300 °C. The thermal mass reduction of $CeCl_3$ happened through only one stage and it was terminated at about 400 °C. The residue taken in each mass reduction stage was characterized to observe a thermal behavior of a rare earth chloride by using XRD patterns, and the results are expressed in Fig. 3. According to Fig. 3, the rare earth chlorides ($GdCl_3$, $NdCl_3$, $PrCl_3$) were converted to oxychloride forms (REOCl) at the first stage, and the oxychlorides were converted to oxide forms ($RE_2O_3$ or $REO_2$ or $RE_6O_{11}$) at the second stage. This means that they react with oxygen gas and are converted to oxychloride forms after chlorine elements are dissociated and are released out from the rare earth chlorides below about 600 °C, and then the conversion of the oxychlorides to the oxides occurs at a temperature between 900 °C and 1300 °C. Unlike these results, $CeCl_3$ was directly converted to the stable oxide form, $CeO_2$. It was considered that its mass was not changed and was kept constant at a higher temperature than about 400 °C regardless of a temperature increase because of this. This indicates that the reaction of $CeCl_3$ with $O_2$ is more active than that of other rare earth chlorides, and it agrees with the calculations expressed in Table 1.

Based on the above results, it was found that the thermal mass reductions of the rare earth chlorides in Fig. 2 show less than



(a) First stage (b) Second stage

**Fig. 3.** XRD patterns of the residues taken in each mass reduction stage of Fig. 2.

theoretical mass reductions of them during their conversion to oxychloride or oxide forms. It was considered that the differences between the thermal mass reductions and the theoretical mass reductions resulted in an experimental error generated by dealing with traces of the samples.

Through the TGA results of the rare earth chlorides, it was found that two methods would be possible to obtain the rare earth oxides from the LiCl–KCl–$RECl_3$ system. One is to keep an operation temperature at a higher temperature than 1000 °C, and the other is to pass through the two stages. In this study, the latter is more appropriate because a considerable amount of the LiCl–KCl–$RECl_3$ molten salts can be vaporized at a higher temperature than 900 °C [14,15]. Thus, it was thought that an appropriate operating temperature range is from 500 °C to 700 °C for a dechlorination and oxidation test of rare earth chlorides in the LiCl–KCl molten salt.

### *3.2. Dechlorination and oxidation of rare earth chlorides in LiCl–KCl molten salts*

For a dechlorination and oxidation test of rare earth chlorides in LiCl–KCl molten salts as a gas–liquid reaction contact efficiency between rare earth chlorides and oxygen gases as well as operation temperature is an important factor, and it depends on the gas distributor design and the gas flow rate [16–19]. Vaporization of molten salts can be facilitated by large sizes of gas bubbles and that can cause problems in the experimental apparatus operation. Thus, it is required to determine an appropriate gas distributor design and gas flow rate for obtaining effective contact efficiency between rare earth chlorides and oxygen gases and lowering molten salt vaporization. To conduct this, three types of oxygen gas distributors, as shown in Fig. 4, were tested with changing gas flow rates before performing a dechlorination and oxidation test of rare earth chlorides in LiCl–KCl molten salts. The tested distributors made of alumina tubes had the same inner diameter (7 mm). As shown in Fig. 4, distributor 1 did not have holes and the oxygen gas was sparged through the 7 mm of the inner hole. Distributor 2 and 3 had 2 mm holes and 1 mm holes near the bottom, respectively. In the case of these, oxygen gas was sparged through the 2 mm holes and 1 mm holes. According to previous papers, small bubbles and a uniform distribution are effective in improving mixing characteristics [16,19]. In these tests, bubble sizes were relatively small and bubble size distribution was the most uniform when oxygen gas was sparged through the distributor 3 at about 0.5 L/min. However, an appropriate flow rate was determined at 1.0 L/min. The reason was as follows. Insoluble particles (rare earth oxychlorides or oxides) as products were generated and were precipitated to the bottom of the molten salts in the dechlorination and oxidation test of rare earth chlorides in LiCl–KCl molten salts. In this condition, an effective mixing state was not kept at a flow rate below 1.0 L/min because it was not easy to fluidize the particles, and salt vaporization was facilitated at a flow rate above 1.0 L/min because large sizes of bubble distributions became greater with an increase in flow rate [17].


(a) distributor 1 (b) distributor 2 (c) distributor 3

**Fig. 4.** Tested oxygen gas distributors.

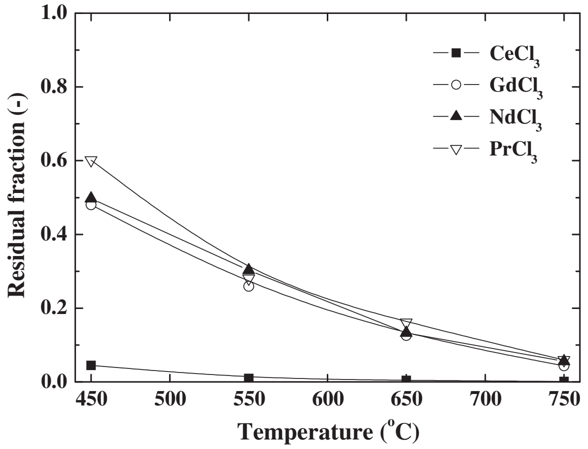


**Fig. 5.** Residual fraction of rare earth chlorides in the LiCl–KCl molten salts during a dechlorination and oxidation test.

The dechlorination and oxidation tests of rare earth chlorides in the molten salts were performed with temperatures at an oxygen gas flow rate of 1.0 L/min by using the distributor 3 with 1 mm holes, and the results are expressed in Fig. 5. According to Fig. 5, residual fraction of $CeCl_3$ was the lowest in the rare earth chlorides and it was converted to an oxide form ($CeO_2$). This indicates that $CeCl_3$ was the most active in the reaction with oxygen gas, and this result agreed with the TGA results. The dechlorination and oxidation of the other rare earth chlorides were effective at a higher temperature than 650 °C, and they were converted to their oxychloride forms. The effective test temperature was higher than that obtained from the TGA tests. This can be explained by using contact efficiency of the rare earth chlorides and oxygen gas. The contact efficiency in the dechlorination and oxidation test was lower than that in the TGA test because the TGA test was a directly contacting reaction of the rare earth chlorides and oxygen gas and the dechlorination and oxidation test was not. This resulted in requiring the higher operation temperature than that obtained from the TGA tests. The efficiency of the dechlorination and oxidation of the other rare earth chlorides was evaluated by using a residual fraction of the rare earth chlorides in the molten salt. The residual fraction is defined as:

$$E = \frac{W_t}{W_i} \tag{1}$$

where $E$ is the conversion ratio of the rare earth chlorides to the precipitates, $W_i$ is the weights of the rare earth chlorides in the molten salts at the initial, and $W_t$ is the weights of the rare earth chlorides in the molten salts after the test is terminated. The residual fractions of the rare earth chlorides were about 0.05 at 750 °C, and they were converted to rare earth oxychlorides or oxides insoluble in the molten salts. This means that it would be possible to recover more than 95 wt.% of rare earth in the molten salts without impurity generation by using this process. The rare earth oxychlorides or oxides generated from the dechlorination and oxidation tests can be easily separated from the molten salts by using a vacuum distillation process without changing their chemical forms [14,20].

### *3.3. Conversion of rare earth oxychloride to oxide*

In an equilibrium state, conversion of rare earth oxychloride to oxide is not easily performed below 1500 °C. According to Gibb's

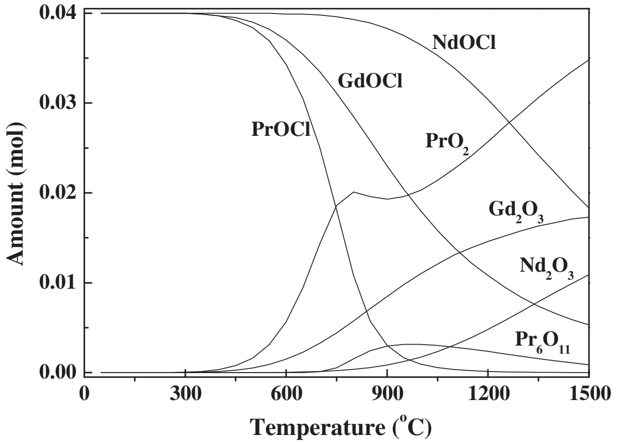


**Fig. 6.** Equilibrium compositions of the conversion of the rare earth oxychlorides (GdOCl, NdOCl, PrOCl) to oxides in the experimental condition by using HSC-Chemistry software.

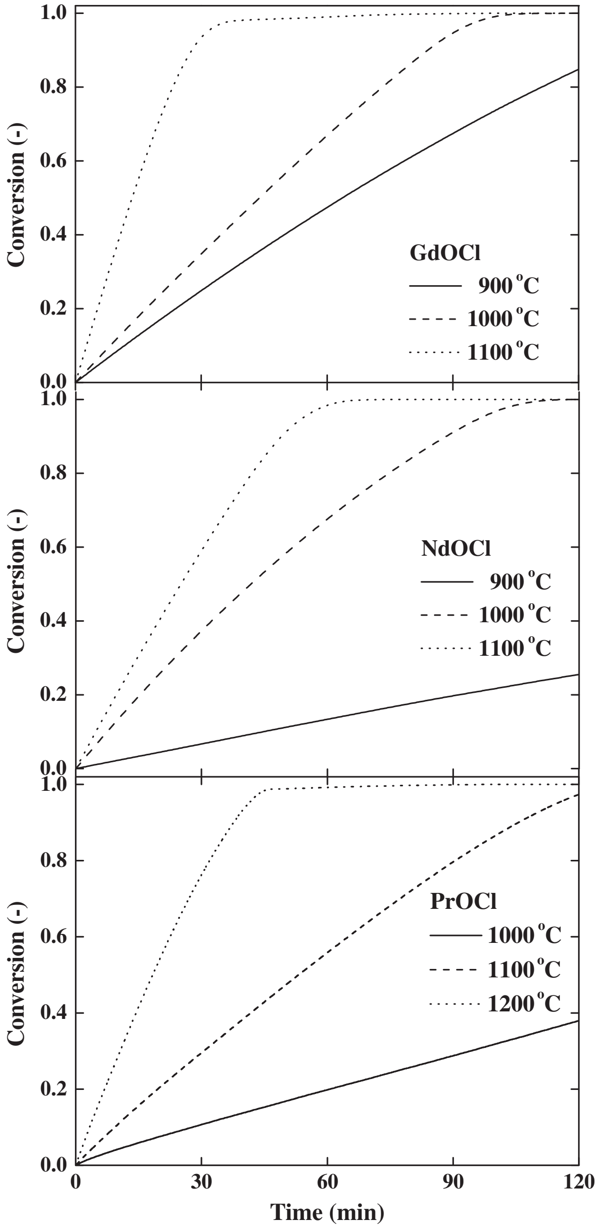


**Fig. 7.** Conversion ratios of the rare earth oxychlorides to oxides.

free energy calculated by HSC-Chemistry software, conversion of NdOCl to $Nd_2O_3$ is possible at about 2200 °C in an equilibrium condition [13]. However, it was confirmed that the conversion of the rare earth oxychlorides (GdOCl, NdOCl, PrOCl) to oxides was progressed effectively below 1300 °C as shown in Fig. 2. To observe this tendency, equilibrium composition of the conversion was calculated by using the software in the conversion test condition described in Section 2.3 (amount of rare earth oxychloride: 10 g (=0.04 mol), oxygen flow rate: 5 L/min), and the results were expressed in Fig. 6. According to Fig. 6, it was found that the conversion of NdOCl to $Nd_2O_3$ is possible at a higher temperature than 800 °C in the conversion test condition. The conversion test condition was an oxygen-rich state unlike the equilibrium condition. This means that the conversion temperature can be lowered in an oxygen-rich state like the conversion test condition. Because of that, it was considered that the conversion of the rare earth oxychlorides to oxides was generated below a temperature calculated in an equilibrium state.

According to the TGA results, mass reduction was generated during a conversion of rare earth oxychloride to oxide, and a conversion ratio can be checked by observing the mass reduction. Fig. 7 shows the conversion ratios of the rare earth oxychlorides to oxides, the conversion ratios were calculated by using a mass reduction generated during the conversion, and the equation was defined as:

$$X = \frac{W_F - W_T}{W_F} \tag{2}$$

where $X$ is the conversion ratio of the rare earth oxychlorides to oxides, $W_F$ is the totally reduced mass after the conversion is terminated, and $W_T$ is the reduced mass after a constant time, respectively. As shown in Fig. 7, the conversion of GdOCl and NdOCl was effective at a higher temperature than 1000 °C, and the conversion of PrOCl was effective at a higher temperature than 1100 °C. These results agreed well with the TGA results. The conversion ratios show that the mass were reduced constantly with time at a temperature. This indicates that the supply of oxygen gas and the removal of chloride gas was accomplished by diffusion through the porous rare earth oxychloride particles and this diffusion occurred simultaneously with a conversion of oxychlorides to oxides [14]. Yang et al. [21] reported that dechlorination and oxidation of GdOCl agrees well with a linear-contacting boundary reaction model. It was thought that the constant mass reduction with time results from that. The conversion ratios also had distinct slopes with temperatures. This means that activation energy in the conversion was constant with temperatures, and Yang et al. [21] announced a similar trend. Thus, the conversion would be effective at a higher temperature than 1100 °C by controlling the supply of oxygen gas and the vent of chlorine gas smoothly, and a conversion progress would be predicted by using the slopes with temperatures.

## 4. Conclusion

To recover rare earth oxides from a LiCl–KCl–$RECl_3$ system, thermal behavior of the rare earth chlorides ($CeCl_3$, $GdCl_3$, $NdCl_3$, $PrCl_3$) was investigated in an oxygen condition. According to TGA tests of the rare earth chlorides, rare earth oxides could be obtained at a higher temperature than 1000 °C in an oxygen condition. However, a considerable amount of the LiCl–KCl–$RECl_3$ molten salts can be vaporized at a higher temperature than 900 °C. Thus, the rare earth chlorides as rare earth oxychloride or oxide forms have to be separated from the molten salts at a lower temperature than 900 °C and then the conversion of rare earth oxychlorides to oxides must be performed at a higher temperature than 1000 °C. The rare earth chlorides in the LiCl–KCl molten salts were converted to an oxychloride form at a higher temperature than 650 °C, except for $CeCl_3$. $CeCl_3$ was totally converted to an oxide from at a higher temperature than 450 °C. The rare earth oxychlorides (GdOCl, NdOCl, PrOCl) were effectively converted to oxide forms at a higher temperature than 1100 °C. It is thought that rare earth oxides can be recovered effectively from LiCl–KCl–$RECl_3$ system without impurity generation through the two processes.

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## References

[1] V.A. Volkovich, T.R. Griffiths, R.C. Thied, J. Nucl. Mater. 323 (2003) 49–56.
[2] M. Matsumiya, H. Matsuura, J. Eletroanal. Chem. 579 (2005) 329–336.
[3] O. Shirai, M. Iizuka, T. Iwai, Y. Arai, Anal. Sci. 17 (2001) 51–57.
[4] J.P. Ackerman, Ind. Eng. Chem. Res. 30 (1991) 141.
[5] T. Kato, T. Inoue, T. Iwai, Y. Arai, J. Nucl. Mater. 357 (2006) 105–114.
[6] Y.J. Cho, H.C. Yang, H.C. Eun, E.H. Kim, I.T. Kim, J. Nucl. Sci. Technol. 43 (10) (2006) 1280–1286.
[7] H.C. Eun, Y.J. Cho, H.C. Yang, H.S. Park, E.H. Kim, I.T. Kim, J. Radioanal. Nucl. Chem. 274 (3) (2007) 621–624.
[8] Y. Katayama, R. Hagiwara, Y. Ito, J. Electochem. Soc. 142 (7) (1995) 2174–2178.
[9] D.M. Smith, M.P. Neu, E. Garcia, V.R. Dole, J. Alloys Compd. 319 (2001) 258.
[10] I.W. Donald, B.L. Metcalfe, S.K. Fong, L.A. Gerrard, D.M. Strachan, R.D. Scheele, J. Nucl. Mater. 361 (2007) 78–93.
[11] P. Bhunia, A. Pal, M. Bandyopadhyay, J. Hazard. Mater. 141 (2007) 826–833.
[12] M.Y. Wey, K.Y. Liu, T.H. Tsai, J.T. Chou, J. Hazard. Mater. B137 (2006) 981–989.
[13] A. Roine, Outokumpu HSC Chemistry for Windows, Pori, Finland, 2002.
[14] H.C. Eun, H.C. Yang, Y.Z. Cho, H.S. Park, H.S. Lee, I.T. Kim, J. Radioanal. Nucl. Chem. 280 (3) (2009) 643–649.
[15] B. Westhphal, K.C. Marsden, J.C. Price, D.V. Laug, Nucl. Eng. Technol. 40 (3) (2008) 163–174.
[16] P. Wongsuchoto, T. Charinpanitkul, P. Pavasant, Chem. Eng. J. 92 (2003) 81–90.
[17] A.A. Mouza, G.K. Dalakoglou, S.V. Paras, Chem. Eng. Sci. 60 (2005) 1465–1475.
[18] Y.K. Doshi, A.B. Pandit, Chem. Sci. J. 112 (2005) 117–129.
[19] G. Li, X. Yang, G. Dai, Chem. Eng. Sci. 64 (2009) 5104–5116.
[20] H.C. Eun, H.C. Yang, H.S. Lee, I.T. Kim, J. Nucl. Mater. 395 (2009) 58–61.
[21] H.C. Yang, Y.J. Cho, H.C. Eun, E.H. Kim, I.T. Kim, J. Therm. Anal. Cal. 90 (2007) 379–384.