

Oxidative precipitation of some rare-earth chlorides in LiCl-KCl salt melts

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1. Introduction

Spent nuclear fuel can be reprocessed by pyroprocessing, which has advantage of low cost, proliferation-resistant and low impact to the environment from the final disposal[1-3]. During the electrorefining process, amounts of waste salts are generated containing some metal chloride species such as rare earths and actinide chlorides. In the electrorefining process, the reuse of the waste salts is very important from the standpoint of an economical as well as environmental aspect. In this study, oxidative precipitation of the some rare earth chlorides in a LiCl-KCl eutectic molten salt has been carried out using the oxygen sparging method. Identification of form of rare earth precipitates and effects of temperature and sparging time on precipitate ratio are carried out. Furthermore, thermodynamic equilibrium calculations have been carried out in order to predict the most stable species formed during oxygen sparging process at different temperature.

2. Methods and Results

2.1 Prediction of equilibrium composition

Figure 1 shows the thermochemical estimation of equilibrium compositions of the rare earth species in the presents of oxygen and rare earth chlorides(Ce/Pr/Nd/EuCl₃) from 400 °C up to 640 °C. The calculation results of equilibrium composition indicates that oxychloride for Pr, Eu and Nd, and oxide for Ce are the domain species formed by reaction with oxygen and there is no gaseous species. At higher than 500 °C small amount of PrO₂ are stable species.

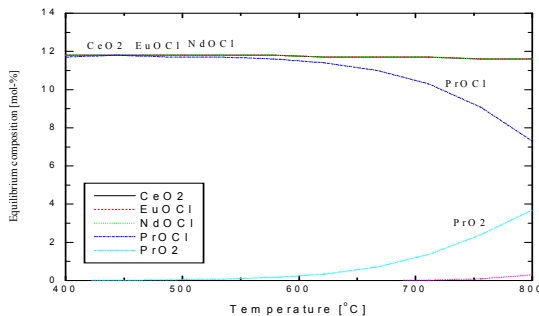


Figure 1. Predicted equilibrium composition by thermodynamical calculation results

2.2 Precipitates of rare-earth chlorides

When oxygen is sparged into the molten salt bed containing rare-earth chlorides, precipitates which are nearly insoluble to the molten salts are formed. It has been generally accepted that oxide or oxychloride are stable chemical forms of the product by the reaction of rare-earth ion(RE³⁺) and oxygen ion(O²⁻) in the molten salt, where the form of precipitates is affected by oxygen concentration and their formation enthalpies[4-6]. Figure 2 shows XRD patterns of precipitates obtained from this experiments. The precipitates are mixture of oxychlorides, i.e. NdOCl, PrOCl and oxides, i.e. CeO₂, Eu₂O₃, PrO₂. Except of Eu and Pr, XRD results shows similar results to thermodynamical calculation results. From the XRD analysis of precipitates Eu is precipitates as a form of oxide(Eu₂O₃) but oxides(EuOCl) from thermodynamical calculation results. And at 400 °C of molten salt temperature Pr is precipitates as a PrOCl and PrO₂. The precipitate forms of rare earth chlorides are independent to molten salt temperature and sparging time.

Based on the experimental results, the stoichiometry of the precipitation reaction of rare-earth chlorides by an oxygen sparging in the molten salt can be represented as follows it is postulated that the reaction between oxygen and rare-earth ion can be represented as follows :

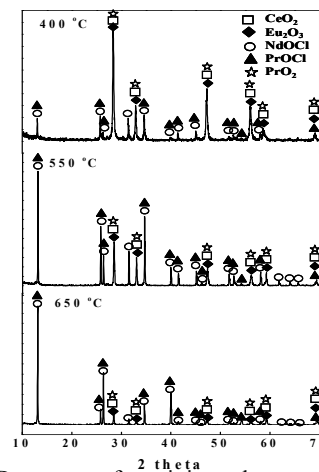
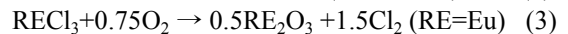
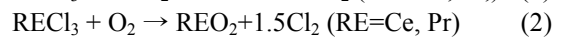
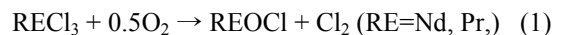


Figure 2. XRD patterns of precipitates by reaction between rare-earth and oxygen in molten LiCl-KCl eutectic salt condition

2.3 Precipitation ratio

Figure 3 shows the effects of sparging time and molten salt temperature on the conversion ratio. The conversion ratios increased exponentially with sparging time. For CeCl_3 , when sparging time was reached about 120min, the value of conversion ratio showed asymptotic value, over 99.9%, in 550 °C of molten salt temperature condition. The temperature of the molten salt is the key parameter of the precipitation of the rare-earth chlorides. The conversion ratio was increased with molten salt temperature in the constant sparging time of 120 min. However, the conversion ratio of the cerium chloride was nearly constant with the molten salt temperature, which indicates that CeCl_3 is easily converted to the precipitate in a low temperature condition compared to others.

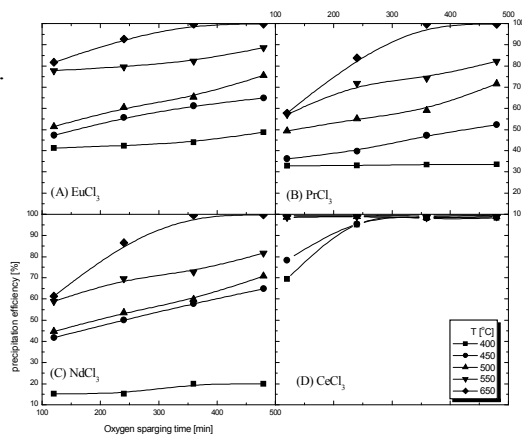


Figure 3. Effects of sparging time and molten salt temperature on the precipitation efficiency.

3. Conclusion

The oxidative-precipitation of some rare-earth chlorides in the LiCl-KCl molten salt were successfully carried out by oxygen gas sparging without using oxygen agents. From the results obtained from thermodynamical calculations it may be concluded that, from a thermodynamic point of view, the most stable rare-earth compounds during oxygen sparging process are oxychlorides (PrOCl , NdOCl) and oxides (CeO_2 , Eu_2O_3 , PrO_2). In this study, regardless of sparging time and temperature, oxychlorides and oxides are formed as a precipitant by reaction between rare-earth ion and oxygen ion, respectively. The conversion of rare-earth chlorides into the insoluble precipitates was described using conversion ratio. The conversion ratios were increased with sparging time and temperature. In the conditions of 650 °C of molten salt temperature and 420min of sparging time, the final conversion ratios were over 99.9% in all experimented rare-earth chlorides.

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