

CsCl Separation From a LiCl-CsCl Mixture by Using a Crystallization Approach

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ABSTRACT

Separation of CsCl and SrCl₂ from LiCl was carried out by using a noble separation technology, the Czochralski crystallization method. It was experimentally confirmed that Cs as well as Sr could be simultaneously separated from a LiCl molten salt by the suggested crystallization process without any kind of additive or adsorption media. The concentrations of Cs and Sr in the LiCl were decreased from 1.53 wt% and 4.18 wt% in the initial salt to a minimum of 114 ppm and 135 ppm in the grown LiCl crystal respectively. The separation mechanism of Cs and Sr is described by the solubility difference of the solutes between the molten and the solid states. It is expected that the total amount of salt waste could be drastically decreased, because most of the LiCl could be recovered for recycling to the electroreduction process.

INTRODUCTION

In a pyrochemical process of spent oxide fuel, the electrochemical reduction of uranium oxide to uranium metal takes place in a LiCl-Li₂O molten salt [1-3]. This pyroprocessing includes a voloxidation, electroreduction, electrorefining and a waste treatment process. Spent fuel pellets are oxidized at around 500 °C under an air-blowing atmosphere in the voloxidation process which is introduced to pulverize the pellets as well as to remove volatile fission products (VFPs) such as I, Kr, and Xe. The metal oxide powder is loaded into a cathode basket for the following electrolytic reduction. The oxygen of the metal oxides is removed from the cathode as ions which release electrons at the anodes in a LiCl-Li₂O molten salt cell. The electrorefiner recovers pure uranium in LiCl-KCl eutectic molten salt from the metallic spent fuel produced by electrolytic reduction process. A portion of the salt is discharged and replaced by a fresh molten salt regularly to control the reaction, because alkali-metal, alkaline earth and some of the rare-earth fission products accumulate in the molten salts as the chloride salts dissolve. Among the fission products in a spent fuel, Cs and Sr are burdensome elements, due to their characteristic of high heat generation. Most of the Cs and Sr can be removed during a voloxidation process, however, a small amount of the Cs and significant of the Sr can be remained in the fuel. Hence, the Cs and Sr is solved in the molten salt, LiCl-Li₂O mixture, as a chloride form in the electroreduction process. This is the main reason that the molten salt is replaced with a fresh one at a certain time when the

temperature of the salt becomes uncontrollable. To reduce the high level waste volume, the molten salt is recycled so that the Cs or Sr in the molten salt is separated. The conventional salt regeneration process comprises an occlusion and ion exchange by zeolite [4,5]. However, this process generates a large quantity of waste and the absorption capacity of the ions is limited although it allows the salt to be reused. Hence, a noble purification technology has been investigated to separate Cs and Sr from the molten LiCl without any kind of additives or adsorption media. The Czochralski crystallization process which is one of the conventional crystallization methods [6, 7] was applied to separate the Cs and Sr from the molten salt for the first time, and the separation yield was calculated. The effect of the processing parameters such as the melt temperature and extraction rate on the purity of the LiCl crystal was also investigated.

EXPERIMENTAL PROCEDURES

The Czochralski crystallization experiments were performed, and the electrolyte used in this study was an anhydrous 99.6% purity LiCl from Acros Chemical and a 99.9% purity CsCl and a 99% purity SrCl₂ from Kojundo Chemical Lab Co. Ltd. A schematic diagram of the crystal growth of the molten salt is depicted in Fig. 1 a). The LiCl, SrCl₂ and CsCl with a predefined composition were added into the alumina crucible and then the crucible was heated gradually by a resistance furnace up to a certain temperature. When the temperature reached to a programmed value, extraction bar was immersed in the molten salt after a 30 min holding for a stabilization. Once the formation of meniscus was confirmed visually, crystallization process was started by drawing up the extraction bar. Molten salt samples for a chemical analysis were taken with a quartz tube before and after the crystallization experiments and the impurity level of the LiCl crystal was also measured by an inductively coupled plasma atomic emission spectrometry (ICP-AES) and/or an atomic absorption spectroscopy (AAS). As for the chemical analysis of the LiCl crystal, each crystal was divided into five parts and the five lumps of LiCl were analyzed separately.

RESULTS AND DISCUSSION

The separation mechanism of Cs and Sr from a LiCl molten salt comes from the fact that each element doesn't have a solid solubility below a liquidus temperature. This phenomenon can also be expressed by an equilibrium partition ratio as follows [6];

$$k = \frac{C_S}{C_L} \quad (\text{Eq. 1})$$

where k =equilibrium partition ratio, C_S =concentration of a solute in a solid, C_L =concentration of a solute in a liquid. If CsCl and SrCl₂ don't form a solid solution, the C_S should be very low. This means that CsCl and SrCl₂ prefer to stay at a liquid phase rather than becoming incorporated

in the LiCl crystal. The binary phase diagrams of CsCl-LiCl and SrCl₂-LiCl are available elsewhere, where as only limited data is available for the phase equilibria of CsCl-SrCl₂-LiCl. Unknown phase diagrams have been successfully constructed by a numerical package based on a thermodynamic data base. Fig. 1 b) shows the calculated pseudo binary diagram of LiCl-3.2wt%SrCl₂-CsCl by a commercial database, FACTSage [8]. There is an eutectic point at

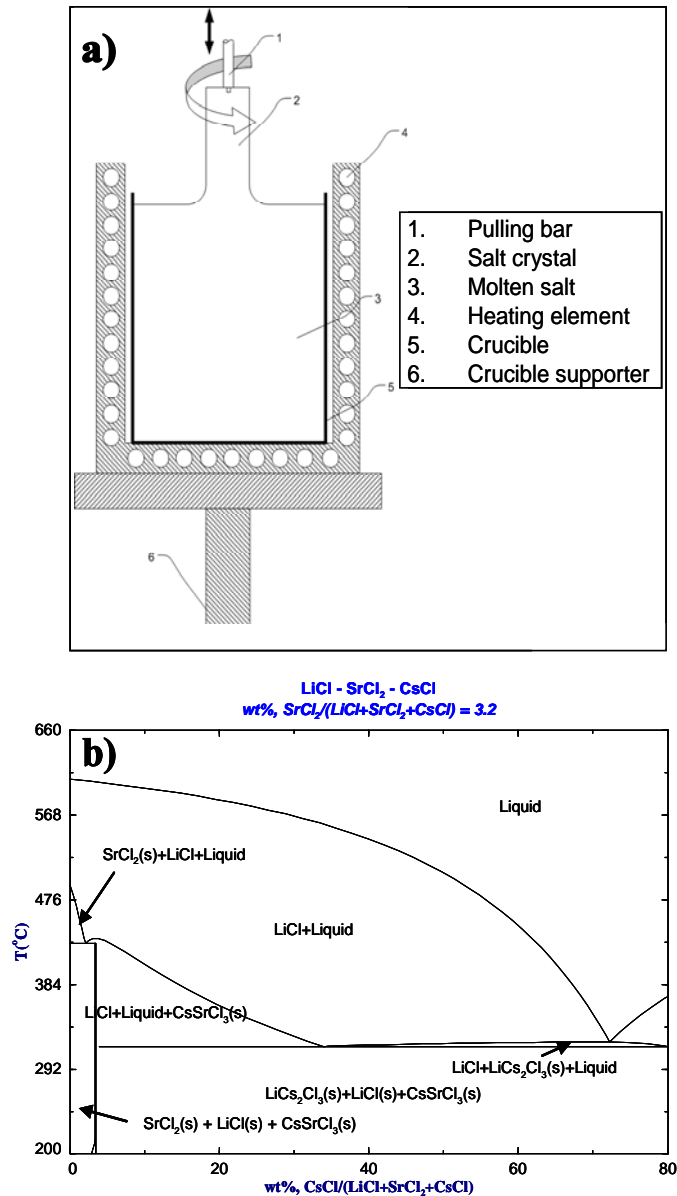


Fig. 1. Schematic diagram of the crystal growth of the molten salt (a) and the calculated pseudo binary phase diagram of the LiCl-SrCl₂-CsCl by FACTSage (b).

~72wt% of CsCl with ~300 °C of an eutectic temperature, and no solid solution is observed even though SrCl₂ and CsSrCl₃ solid phases start to form below ~480 °C in a LiCl rich area. This

means pure LiCl can be attained when an appropriate condition is provided.

Preliminary experimental result for the separation of CsCl from the molten LiCl is presented in Table I. The initial concentration of Cs is 5.9 wt%. The LiCl crystal was divided into five parts

Table I. Variation of the Cs concentration in LiCl before and after a crystallization process (Surface temperature: 610 °C, pulling rate : 20 mm/hr, rotation rate of pulling bar : 10 rpm).

Sample no.	Initial salt	1(Top)	2	3	4	5(Bottom)
Cs Conc., wt%	5.9	1.43	0.7	0.62	0.7	0.71

which are numbered as 1~5 from the top to the bottom of the crystal. The Cs content was measured as somewhat high at the top of the crystal while it decreased in all the samples. Hence the possibility of a Cs separation from the LiCl molten salt was experimentally confirmed. The

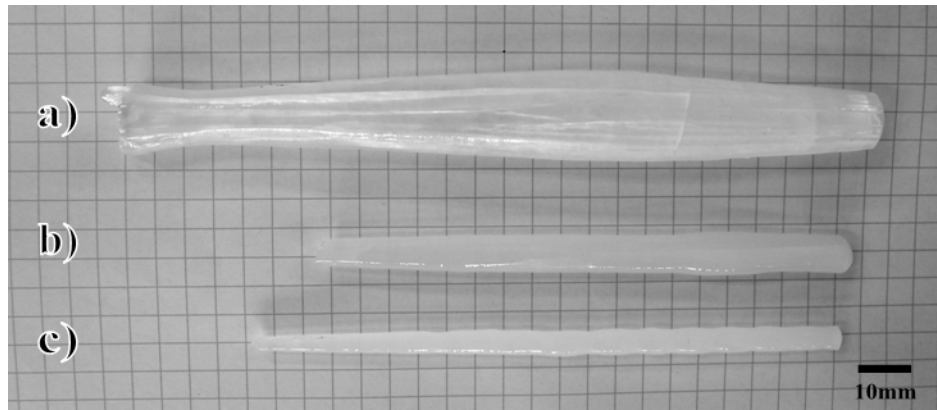


Fig. 2. Photographs of salt crystals prepared with different extraction rates.

(Surface temperature : 610 °C, rotation rate of the extraction bar : 10 rpm)

a) 5 mm/hr b) 20 mm/hr c) 40 mm/hr

crystal growth was performed on a ternary LiCl-CsCl-SrCl₂ system to observe the simultaneous separation behavior of Sr as well as Cs. Fig. 2 shows photographs of the salt crystals prepared with different extraction rates with a constant surface temperature of 610 °C and a rotation rate of the extraction bar of 10 rpm. It was clearly seen that the diameter of the crystals drastically changed with extraction rate. The mean diameters of the crystals were 14 mm, 7 mm and 4 mm for 5 mm/hr, 20 mm/hr and 40 mm/hr of pulling rate respectively. It has been reported that the maximum pulling rate is inversely proportional to the square root of the crystal radius as described in Eq. (2) [7].

$$V_{P_{Max}} = \frac{1}{LN} \sqrt{\frac{2\sigma\epsilon k_M T_M^5}{3r}} \quad (\text{Eq. 2})$$

Where, $V_{P_{Max}}$ is the maximum extraction rate, L is the latent heat of fusion, N is the density of a

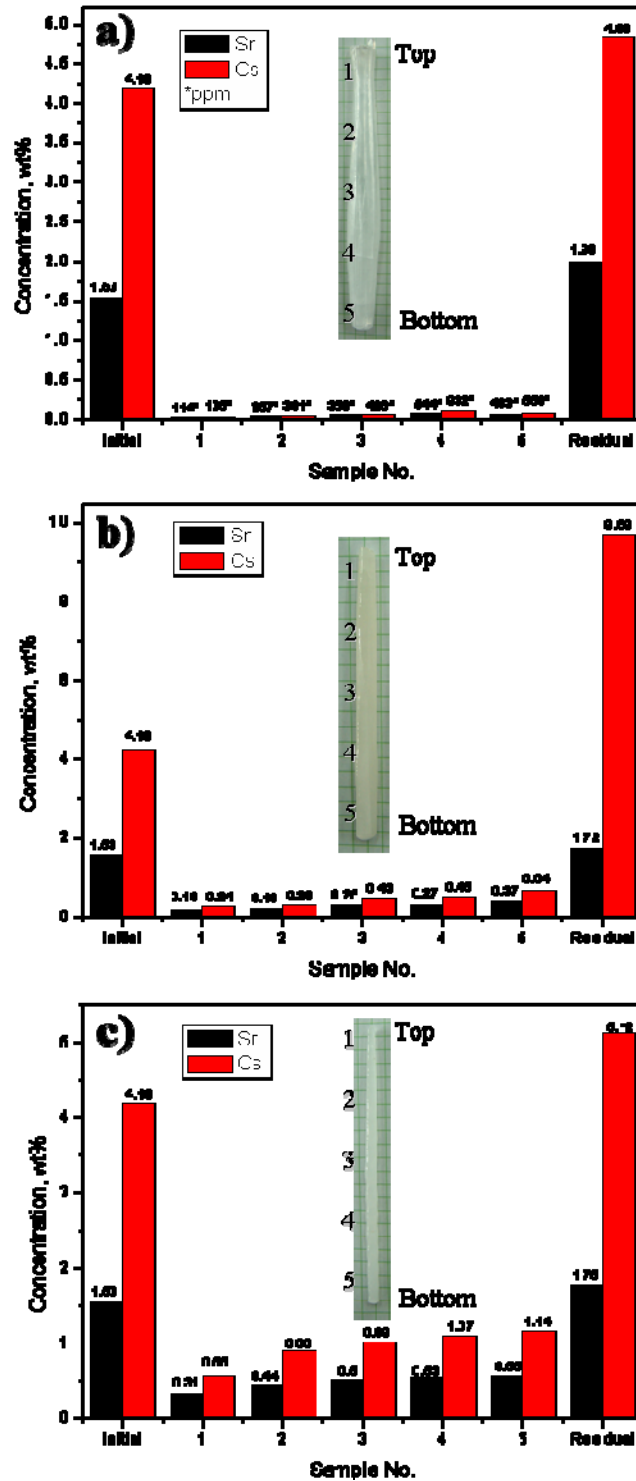


Fig. 3. Concentrations of Cs and Sr in the LiCl crystal with the extraction rate at different locations. (Surface temperature : 610 °C, rotation rate of pulling bar : 10 rpm)

a) 5 mm/hr

b) 20 mm/hr

c) 40 mm/hr

solid, σ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ W/m}^2\text{K}^4$), ε is the emissivity, k_M is the

thermal conductivity at a melting point, T_M : melting point, r is the radius of a crystal. Hence, the tendency of a diameter increase of the LiCl crystal agrees well with Eq. 2.

The effect of the extraction rate on the separation was observed by chemically analyzing the concentration of Cs and Sr in a crystal. Five samples were taken at difference places along a crystal as shown in Fig. 3. In the case of 5 mm/hr of an extraction rate, the concentrations of Cs and Sr ranged from 135 to 932 ppm and 114 to 544 ppm respectively as shown in Fig. 3 a). Compared to the initial concentrations of Cs and Sr, a maximum of ~300 and ~100 times the purification degrees were achieved. When the extraction rate increased to 20 mm/hr, the concentrations of Cs and Sr in the LiCl crystal were increased as shown in Fig. 3 b). Further increases in the extraction rate significantly decreased the purity of the LiCl crystal as shown in Fig. 3 c). These results are summarized in Fig. 4. It is clearly seen that the mean concentrations of

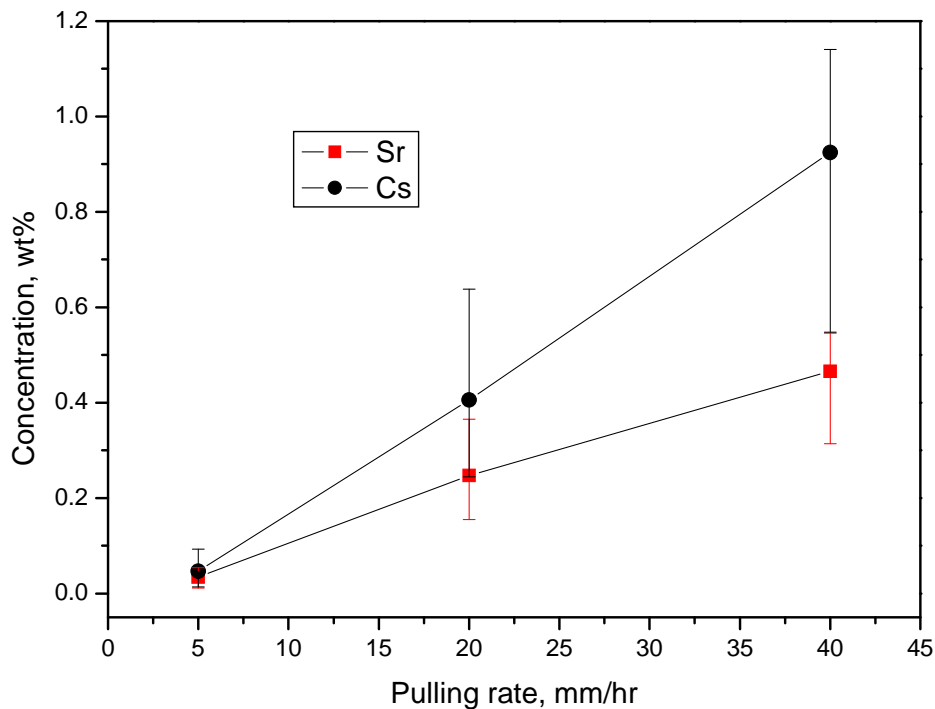


Fig. 4. Mean concentration of Cs and Sr in LiCl crystal with the pulling rate.
(Surface temperature : 610 °C, rotation rate of pulling bar : 10 rpm)

Cs and Sr in the LiCl crystal linearly increase with the extraction rate. The separation mechanism suggested in this study originated from a macro segregation of the solute components as described in Eq. 1. This means that the purity of the LiCl crystal is dependent on not only the partition ratio but also the movement rate of the solid-liquid interface and the diffusion rate of the solute. This phenomenon is represented well by Burton et al equation as follows [6];

$$k' = k / [k + (1 - k) \exp(-R\delta / D_L)] \quad (\text{Eq. 3})$$

Where, k' is the effective partition ratio, R is the movement rate of a solid-liquid interface, δ is the boundary layer thickness, D_L is the solute diffusion coefficient. During the crystallization of LiCl, the Cs and Sr rejected into the liquid are transported by a diffusion and so an enriched boundary layer forms. When the diffusion layer thickness is large, the effective partition ratio increases which means the solute concentration would also increase in the LiCl crystal. The effective partition ratio is also proportional to the movement rate of the solid-liquid interface as described in Eq. 3. This also agrees well with the decreases of the Cs and Sr concentrations in the LiCl crystal with a decrease of the extraction rate as shown in Fig. 4. This is a very promising result which could enhance the competitiveness of pyroprocessing technology, because the electrolyte could be recycled without generating any secondary waste. Also, we believe that the molten salt crystallization method could be an effective way to separate Cs and Sr from a LiCl molten salt produced during the pyroprocessing of a spent nuclear fuel, provided that the processing parameters such as the rotation rate of the crystal, the extraction rate and the melt temperature are optimized.

CONCLUSION

The main heat generating elements such as Cs and Sr were successfully separated by the Czochralski crystallization process from a molten LiCl salt as a simulated spent salt from a pyroprocessing procedure. The separation efficiency was dependent on the extraction rate and the highest purity of the LiCl crystal was attained at 5 mm/hr of extraction rate. The dependency of the extraction rate on a variation of a crystal's diameter and its purity agree well with the reported equations. The adopted crystallization process to remove the Cs and Sr from a molten salt has the benefits of a higher removal efficiency, a simpler process, and no more solvent addition when compared with the conventional separation processes. Finally the total waste volume to be disposed could be drastically decreased, provided that the small amount of the salt residue is treated by reported vitrification methods.

Acknowledgments

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