

Investigation of Various LiCl Waste Salt Purification Technologies

Yung-Zun Cho, Hee-Chul Yang, Han-Soo Lee and In-Tae Kim

*Nuclear Fuel Cycle Development, KAERI, 105, Dukjin-Dong, Yuseong, 305-353, Korea
choyj@kaeri.re.kr*

Abstract Various purification research of LiCl waste molten salt generated from electroreduction process were tested. The purification of the LiCl waste salt very important in a various aspects, where the purification means separation of cesium and strontium from LiCl salt melts. In this study, for the separation of cesium and strontium from LiCl salt melts, precipitant agent addition techniques such as sulfate and carbonate addition method and, as a new attempt, zone freezing technique for concentration of cesium and strontium elements was investigated. As a results of this research, only strontium was carbonated by reaction with Li_2CO_3 (cesium did not react with Li_2CO_3). In case of sulfate addition method, both cesium and strontium were converted their sulfate that is $\text{Cs}_2\text{S}_2\text{O}_6$ and SrSO_4 and maximum sulfate efficiency of cesium and strontium were about 72% and 95%, respectively. Cesium and strontium involved in LiCl molten salt were could be concentrated in the molten salt by using zone freezing method.

INTRODUCTION

Spent nuclear fuel can be reprocessed by a pyroprocessing, which has the advantages of a low cost and proliferation-resistant. Generally, a pyroprocessing of spent oxide fuel includes several steps : disassembly and decladding of the oxide spent fuel, electroreduction process to convert the spent oxide fuel to a metal, actinide separation by an electrorefining and a manufacturing of the resulting actinides mixture to a suitable fuel for use in an advanced reactor[1,2]. During a pyroprocessing, amounts of waste salts (LiCl-KCl eutectic-electrorefining, LiCl-eletrorredution) containing some fission product (e.g. alkali, alkaline-earth, rare-earth or tracer amounts of TRUs) are generated. These fission products are highly radioactive. Thus, they must be disposed of as durable waste forms which are compatible with the environment inside of a geologic repository for thousands of years. It has been generally believed that the decontamination of waste salts from fission products (i.e., removal of fission products from waste salts) and the recycling of this salt to a main process are crucial from the standpoint of an economical as well as an environmental aspect.

Various researches have been undertaken to remove the fission products from a waste molten salt by using dry methods[3]; ion-exchange column method by a zeolite-A column, oxide precipitation method by an oxidant addition or an oxygen sparging, and a phosphate precipitation method. Cesium can be removed from a LiCl-KCl eutectic waste molten salt by an

ion-exchange process. In the case of rare earth elements, using the oxide, phosphate precipitation method or oxygen sparging process, they can be separated easily from a LiCl-KCl eutectic waste salt. In case of alkaline earth elements, a phosphate precipitation method by the addition of sodium(NaCl-KCl eutectic case) or lithium(LiCl-KCl eutectic case) phosphate was carried out[3]. But relatively little research has been carried out in LiCl molten system containing alkali and alkaline-earth elements.

In this study, therefore, for the purification of the LiCl waste salt namely separation of alkali(cesium) and alkaline-earth(strontium) from LiCl molten salts, precipitant agent addition methods such as sulfate and carbonate were carried out. Furthermore, as a new attempt, zone freezing method for concentration of cesium and strontium elements was investigated.

EXPERIMENTS

Precipitant Addition Method

For separation of cesium and strontium, carbonation method was tested. For this, Li_2CO_3 injection tests were carried out in LiCl molten salt by using an electric furnace equipped with an Ar gas(purity 99.999 %) sparger and a temperature controller. The carbonate reactions were performed by changing the injection ratio of the carbonate agent in 750 °C. Anhydrous cesium and strontium chlorides were premixed with about 150g of LiCl solid salt with a purity of 99.9 % in an alumina crucible of 0.055 m in

inner diameter and 0.16 m in height. Fig. 1 shows a schematic diagram of the experimental apparatus used in this experiment. The alumina crucible containing the mixture was heated up to an operating temperature in a stainless-steel column and when the temperature reached the operating temperature, carbonate agent (Li_2CO_3) was injected into the molten salt bed. To maintain nearly perfect mixing and inert atmosphere conditions, during the carbonate reaction, argon gas was continuously sparged into molten salt bed through alumina tube sparger.

Sulfate addition method was carried out similar to carbonate addition method. As a sulfate agent, Li_2SO_4 was used. Temperature and injected Li_2SO_4 molar ratio were ranged from 650 to 750 °C and from 1 to 2, respectively.

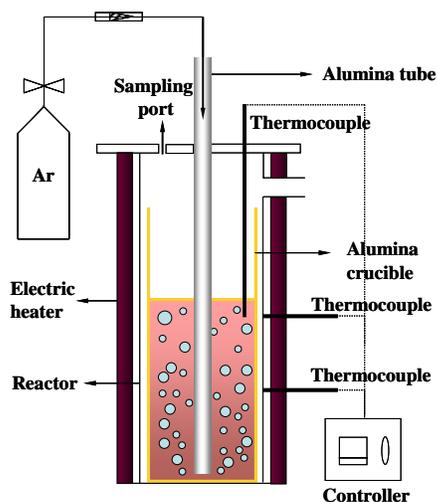


Fig. 1. Schematic diagram of experimental apparatus for Ba and Sr carbonation in molten salt by carbonate agent injection

Zone Freezing Method

Anhydrous cesium and strontium chlorides with a purity of 99.99 % were premixed with about 160g of LiCl-KCl solid salt in an alumina crucible (40mm I.D., 170mm H.). The initial weight % of Cs and Sr chlorides in LiCl-KCl salt was ranged from 2.4 to 4.8. The lower furnace was used as a heating zone and controlled at 660 °C, which was about 50 °C higher than the melting point of LiCl salt.

The possibility of the concentration of Cs and Sr elements involved in LiCl salt was tested by using the vertical Bridgman method. Fig. 2 shows the apparatus for the concentration of Cs and Sr, which has two electric furnaces

controlled independently, and ascending /descending velocity controller. In this feasibility testing procedure, unlike the common Bridgman process used for pure crystal growing, the seeding step was omitted

Temperatures of the cooling zone (upper furnace) and adiabatic zone were maintained at about 300 °C and 400 °C, respectively. The crucible containing feed mixture was heated in an electric furnace for a complete melting of the mixture, and then the concentration (or purification) process was driven by moving the crucible upward at a rate of 1.67 ~ 5.8 mm/hr. After completion of the purification experiment, the crucible was cooled down to the room temperature. The cooled salt solid was equally sliced into six parts along with the axial direction, and then the concentration of Cs and Sr in each sliced salt was analyzed by an ICP-AES analyzer.



Fig.2. Testing apparatus for Cs/Sr concentration by zone freezing (vertical Bridgman) method.

RESULTS AND DISCUSSION

Precipitant Addition Method

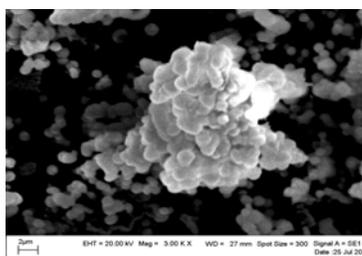
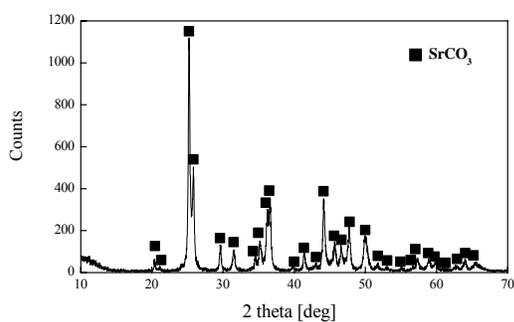
Addition of Li_2CO_3 to the LiCl molten salt containing SrCl_2 resulted in the formation of SrCO_3 as a carbonate. The results of powdered XRD pattern analysis and the SEM-EDS analysis of the strontium carbonate obtained after the Li_2CO_3 injection into the LiCl molten salt are shown in Fig. 2. In this figure, except for oxygen, the composition values of each element are larger than the theoretical values. This is because the SEM-EDS analysis of the precipitation product was carried in carbon coating condition. But, there is no element except for C, O and Sr, and

the analyzed value of the ratio of Sr and O elements, 1.82, is nearly identical to the theoretical value, 1.73.

Both results indicate that the following strontium carbonation reaction occurs exclusively in the SrCl₂-LiCl molten salt condition by an addition of excess Li₂CO₃.



Additionally, an ICP analysis of the salt sample was performed to confirm the content of Sr remaining in the LiCl salt after a completion of the carbonation reaction. Based on the analyzed concentration of Sr in the salt sample, the carbonation efficiency of SrCl₂ was calculated as a function of the molar ratio. As shown in Fig. 2 the carbonation efficiency increased from 45.5% to 90.1% as the molar ratio of the Li₂CO₃ against the SrCl₂ increased from 1 to 2. Over 99.5% conversion efficiencies were obtained from a Li₂CO₃/SrCl₂ molar ratio of 3 or more



[EDS result]	
Composition, [wt%]	
(Exp. / Theo.)	
C	11.53 / 8.13
O	28.09 / 32.52
Sr	60.38 / 59.35

Fig.2. XRD-pattern and SEM-EDS of the carbonated obtained from the Li₂CO₃ injection in the LiCl molten salt condition

When Li₂SO₄ was added in LiCl molten salt containing both cesium and strontium, they both were converted their sulfates that is Cs₂S₂O₆ and

SrSO₄. Fig. 4 shows XRD and SEM-EDS results of cesium and strontium sulfates. The sulfate efficiency of both cesium and strontium was increased with injected molar ratio of Li₂SO₄ and molten salt temperature. Fig. 5 shows the sulfate efficiency with experimental conditions. As shown the maximum sulfate efficiency of cesium and strontium was about 72% and 98%, respectively.

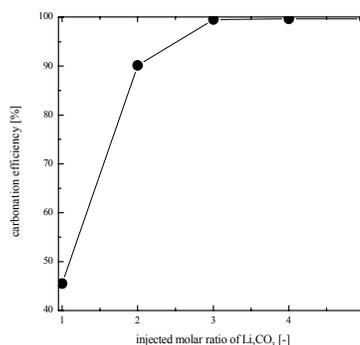
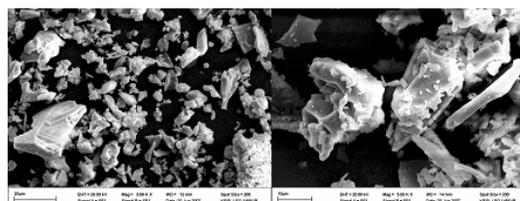
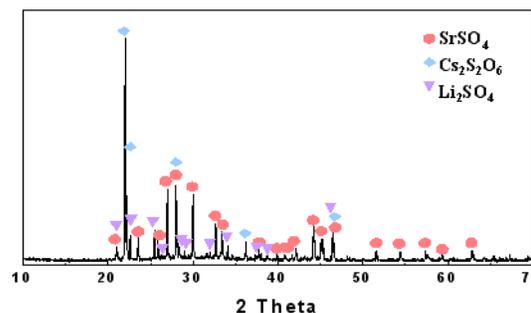


Fig. 3. Effects of injected molar ratio of Li₂CO₃ on carbonation efficiency of strontium in the LiCl molten salt condition



SEM-EDS result	
element	wt%
O	34.67
S	15.27
Cs	38.52
Sr	11.12

Fig. 4. XRD and SEM-EDS analysis result of cesium and strontium sulfate

Zone Freezing Method

Zone refining is a technique used to reduce the level of impurities in certain metals, alloys, semiconductors, and other materials where purification takes place by recrystallization. It is based on the phenomena that the solubility of an impurity may be different in the liquid and solid phases of a material. To take advantage of this observation, a narrow molten zone is moved along the length of a specimen of the material, with the result that the impurities are segregated at one end of the bar and the pure material at the other[4,5].

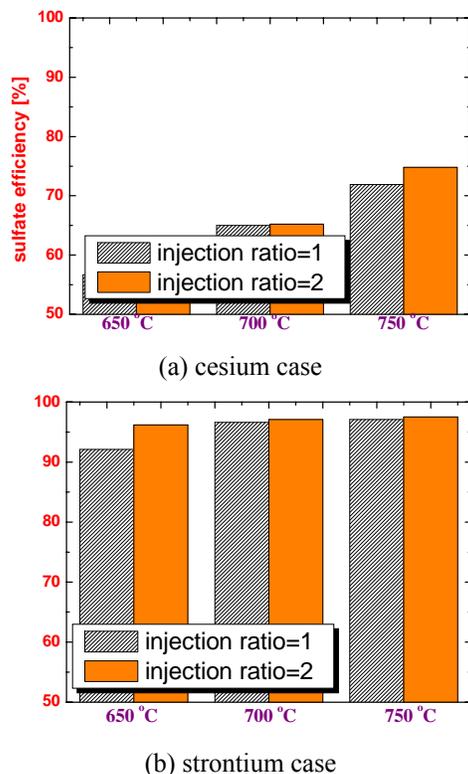


Fig. 5. Sulfate efficiency of Cs and Sr in LiCl molten salt with experimental conditions.

Fig. 6. shows the progressive view of zone freezing process with time. Fig. 7 shows the cumulative concentration fraction of cesium and strontium chlorides with the height fraction of solidified salt. In the melt growing process, when an impurity is present with a segregation constant k and an initial concentration C_0 , the concentration of the material freezing when a fraction g of the ingot has frozen, C , is given by:

$$C = kC_0(1-g)^{k-1} \quad (2)$$

This is called the normal freezing equation. If k is smaller than 1, it means the crystals get progressively richer in impurities down the ingot[5]

As shown in Fig. 7, when the rising velocity is 1.67 mm/hr, In the about 10 wt% of solid salt, about 90wt% of cesium and strontium present, which means cesium and strontium could be concentrated in LiCl molten salt by zone freezing method. So we concluded that LiCl waste molten salt containing alkali and alkaline-earth elements from electroreduction process can be purified by means of zone freezing method.

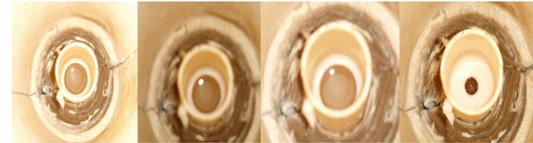


Fig. 6. crystallization feature in the vertical Bridgman method.

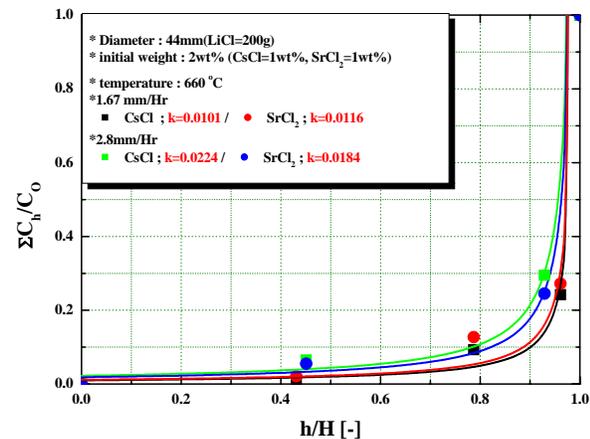


Fig. 7. Cumulative concentration of cesium and strontium ($\sum C_h/C_0$) with vertical height fraction (h/H).

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