Removal of Salt-Soluble Fission Products from the Metal Product of the Electrolytic Reduction Process – 14063

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ABSTRACT

The metal product from the electrolytic reduction of oxide spent fuel in $LiCl–Li_2O$ molten salt retains about 20 wt% of electrolyte. In addition, during the electrolytic reduction, some salt-soluble fission products such as Cs, Sr, and Ba accumulate in the $LiCl-Li_2O$ salt bath as chlorides. In order to separate the residual salt from the metal product of electrolytic reduction, vacuum distillation equipment was developed. With this equipment, the LiCl was evaporated and could be recovered in a fine white powder form. The evaporation rate of the LiCl molten salt was considerably decreased by the addition of $BaCl_2$, $SrCl_2$, and Li_2O. For LiCl and CsCl, the complete removal of the salts from the evaporator was accomplished by reducing the pressure to less than 13.3 Pa and heating to 900 ℃. However, for $BaCl_2$ and $SrCl_2$, only about 30% were vaporized at 900 ℃. $BaCl_2$ and $SrCl_2$ were not vaporized by their own single component, but could be vaporized through a co-vaporization with LiCl salt. Evaporation efficiencies of 100% were achieved by heating above 1,000 ℃.

INTRODUCTION

The pyrochemical process on the basis of molten salt electrolysis is a technology that converts oxide nuclear fuel to metal and recovers valuable resources from spent fuel [1, 2]. The process involves the conversion of a spent oxide fuel to a metal by electrolytic reduction and separation of the actinides by means of electro-refining. The metal product from the electrolytic reduction of oxide spent fuel in $LiCl–Li_2O$ molten salt retains about 20 wt% of electrolyte including some salt-soluble fission products such as Cs, Sr, and Ba[3, 4]. The residual salts in the uranium metal product will cause the formation of UO_2 and change the salt composition of the next process. It is therefore important to remove the residual salt from the metal product during the electrolytic reduction process, and the removal of salt-soluble fission products is one of the main concerns with respect to waste management as well as nuclear material accountancy. In this study, vacuum distillation equipment was developed for the purpose of separating the residual salt from the reduced metal product and reusing it in electrolytic reduction, and the evaporation behaviors of the LiCl and salt soluble chlorides were investigated. The evaporation rates of LiCl and salt-soluble chlorides were measured using distillation equipment and thermogravimetric analyses(TGA). Experiments with surrogate molten salts ($LiCl-Li_2O$ salt including CsCl, $BaCl_2$, and $SrCl_2$) to evaluate the evaporation rate of each element in the molten salt were performed.

METHODS

Figure 1 shows the schematic diagram and the photograph of the experimental set-up. Distillation equipment was installed in an argon atmosphere glove box where oxygen and moisture were controlled to be 5 ppm. The equipment consists of an evaporator in which the reduced metal product is contained and exposed to a high temperature and reduced pressure, a receiver, and a vertically oriented condenser that operates at a temperature below the melting point of lithium chloride. The lowest part is the evaporator in which LiCl is vaporized, and it is

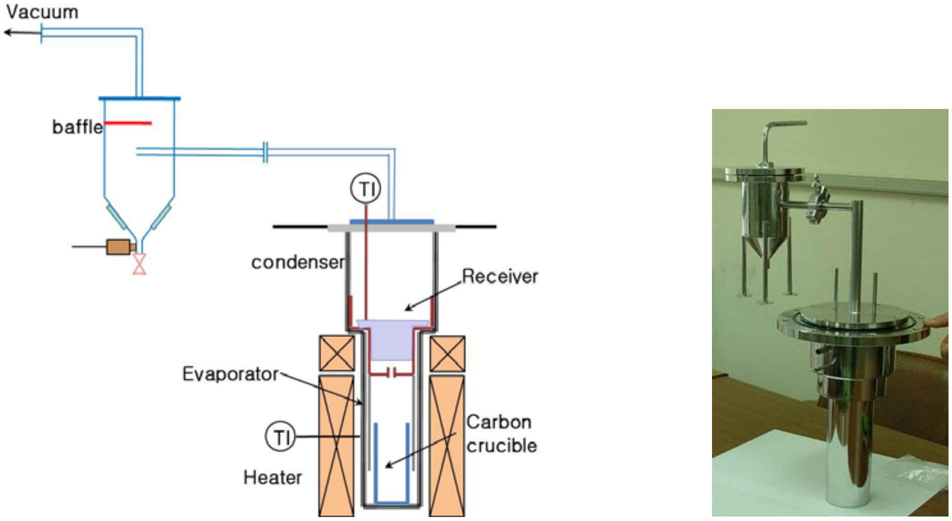

Fig.1. Salt distillation equipment.

surrounded by the heating furnace. The Kanthal super heating element is used for the heater, which can heat the furnace up to 1,200 ℃. Thermocouples are installed in the furnace region of the evaporator and at the bottom of the receiver to measure the process temperature. The insulator is disposed at the bottom of the receiver to block heat generated from the evaporator. The insulator makes a large temperature difference between the evaporator and the receiver to condense evaporated LiCl vapor so that condensed fine powder of LiCl can be collected on the receiver. A carbon crucible is used for a molten salt container in the evaporator. A vacuum system, which can reduce the system pressure to <1.33 Pa, is connected to the outlet of the condenser.

The evaporation rates of LiCl and salt-soluble chlorides were measured using this equipment and TGA analyses. About 10 grams of molten salt samples were put into a glassy carbon crucible and placed in the heating zone of the evaporator. The evaporator was heated with a heating rate of 5 ℃/min. After reaching the target temperature, the inside pressure of the evaporator was reduced by a vacuum pump to evaporate the molten salts, and a vacuum degree of <13.3 Pa was maintained. After finishing the evaporation, the equipment was cooled down to room temperature. The remaining salt in the evaporator and the evaporated salt in the receiver was collected and recovered. The weight of salts was measured, and if necessary, the collected sample was analyzed.

DISCUSSION

It is anticipated that, unlike LiCl, the evaporation of some salt-soluble chlorides will be difficult. The melting point and the boiling point of CsCl are similar to those of LiCl, and thus CsCl is expected to evaporate well with LiCl. But, evaporation of $BaCl_2$ and $SrCl_2$ is expected to be difficult because the melting points of them are much higher than that of LiCl. The difficulty of evaporating $BaCl_2$ and $SrCl_2$ is also anticipated in terms of the vapor pressure. Figure 2 shows the vapor pressure curves for the chloride salts which are calculated by using thermodynamic data[5]. $BaCl_2$ and $SrCl_2$ have very low vapor pressures compared with LiCl and CsCl, thus they do not seem to evaporate well with LiCl.

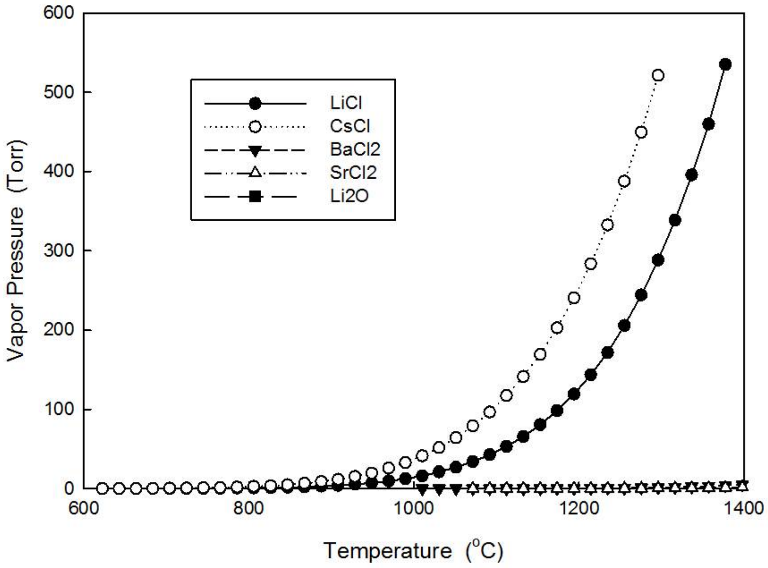

Fig.2. Vapor pressures of Chlorides.

The evaporation characteristics of salt chlorides were investigated using salt distillation equipment. Ten grams of each salt chloride was put into the glassy carbon crucible and evaporated for 2 hours. The experimental vacuum pressures were < 13.3 Pa and temperatures were 700 ~ 900 ℃. The results showed that CsCl and LiCl were completely evaporated at temperatures above 800 ℃. But $BaCl_2$ and $SrCl_2$ were evaporated very little even at high temperature 900 ℃. Li_2O did not evaporate at all in this temperature range. The evaporation rates of CsCl and LiCl at atmospheric conditions were also measured using TGA analyses. Fig.3 shows the evaporation rates of CsCl and LiCl which were obtained from the evaporation experiments at reduced pressure as well as at atmospheric pressure. The evaporation rate of CsCl is higher than that of LiCl, and this result confirms that the evaporation rate of molten salt depends largely on vapor pressure.

The experiments were carried out for the binary mixtures which were composed of LiCl and each single salt-soluble chloride. The compositions of binary mixtures were 10 g of LiCl and 1g of respective salt-soluble chloride (CsCl, $BaCl_2$, and $SrCl_2$). For LiCl-Li_2O binary mixture, 0.1 g of Li_2O was mixed with 10 g of LiCl which was the same composition as the molten salt used in the electrolytic reduction process(LiCl-1 wt% Li_2O). The experimental temperatures were 850 ~ 1000 ℃ for 2 hours, and the experimental method was the same for the single component evaporation. The results showed that CsCl was evaporated completely. $BaCl_2$ and $SrCl_2$ were evaporated 13 and 8 % respectively at 850 ℃. $BaCl_2$ and $SrCl_2$ were not evaporated for single component at this temperature, but they were evaporated about 10 % for binary component with LiCl. Evaporation experiments for the binary salt mixture were carried out repeatedly with increasing the evaporation temperature. As the heating temperature increases above 850 ℃, the amount of vaporized salt increases linearly with temperature, and almost 100% of LiCl-$BaCl_2$ and LiCl-$SrCl_2$ are evaporated at 1000 ℃. Li_2O, whose melting point is 1,570 ℃, is also evaporated 40% at 1000 ℃. This might be due to the entrainment with LiCl vapor which co-evaporates $BaCl_2$ and $SrCl_2$, and Li_2O in the binary mixture.

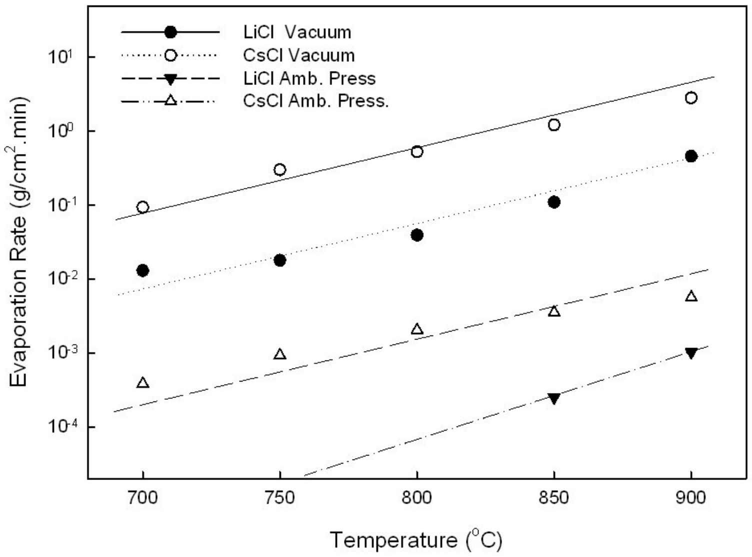

Fig. 3. Evaporation rate of LiCl and CsCl.

CONCLUSIONS

The evaporation behaviors of LiCl and salt-soluble chlorides were studied using vacuum distillation equipment. The evaporation rate of the LiCl molten salt was considerably decreased by the addition of $BaCl_2$ and $SrCl_2$, and Li_2O. For LiCl and CsCl, the complete removal of the salts from the evaporator was accomplished by reducing the pressure to less than 13.3 Pa and heating to 900 ℃. Evaporation efficiencies of nearly 100% were achieved, and more than 98% of the salts were recovered from the receiver. However, for $BaCl_2$ and $SrCl_2$, only about 30% were vaporized at 900 ℃. $BaCl_2$ and $SrCl_2$ were not vaporized by their own single component, but could be vaporized through a co-vaporization with LiCl salt. In general, the extent of evaporation increases with an increase in the operating temperature.

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