Removal of adhered salt from uranium deposits in the pyroprocess

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Abstract

Pyroprocessing has been developed for the recovery of actinide elements from spent fuel due to its advantages like compactness, nuclear proliferation resistance, and reduction of a secondary waste generation [1-2]. In this study it was proposed to produce the required throughput for the salt removal process by the separation of the liquid salt prior to the distillation of the LiCl-KCl eutectic salt from the uranium deposits. The feasibility of liquid salt separation was examined by salt separation experiments on a stainless steel sieve. It was found that the amount of salt to be distilled could be reduced by liquid salt separation prior to salt distillation. It was found that the liquid salt can be separated from the uranium dendrites above 500^{0}C. The residual salt remained in the uranium deposits after the liquid salt separation was successfully removed by vacuum distillation. The temperature distribution of the experimental distillation tower was calculated by the code of ANSYS CFX. The calculation results confirmed that the salt vapour could be transported to the bottom of the salt recovery vessel without condensing before arrival at the vessel.

Introduction

The cathode deposit in the pyroprocess is uranium dendrites coated with eutectic salt loaded with fission product chlorides. The purpose of the solid cathode processor is to remove entrained salt from the electrodeposited uranium and to consolidate the dendritic deposits. The cathode process has two separate steps of salt separation and consolidation of uranium deposits at the Korea Atomic Energy Research Institute.

A physical separation process, such as distillation separation, is more attractive than a chemical or dissolution process because physical processes generate much less secondary process. Distillation process was employed for the cathode processing due to the advantages of minimal generation of secondary waste, compact unit process, simple and low cost equipment [7]. The basis for vacuum distillation separation is the difference in vapour pressures between a salt and uranium. A solid cathode deposit is heated in a heating region and salt vaporises, while non-volatile uranium remains behind.

Some studies have reported on the vacuum evaporation of the salt or cadmium in the pyroprocess [3-5]. The efficiency of vacuum distillation depends on evaporation rate, transportation of vapour, condensation and solidification. In addition, vacuum level, material of crucible, heating and cooling cycles play a major role in deciding optimum distillation process parameters.

The salt separation process is a crucial step since the process could be a bottle neck of the pyroprocess. It is very important to increase the throughput of the salt separation system due to the high-uranium content of spent nuclear fuel and high salt fraction of uranium dendrites. The evaporation rate of the LiCl-KCl eutectic salt in a vacuum distiller is not high enough to develop the generation capacity of the uranium dendrites in the electro-refiner. An increase in the distiller throughput could be made possible by the wide evaporation area or high distillation temperature. But the realisation of the wide evaporation area or high distillation temperature is limited by various factors such as material or structure of a distiller.

Kwon *et al.* has proposed a combined process to produce the required throughput for the salt removal process by the separation of the liquid salt prior to the distillation of the LiCl-KCl eutectic salt from the uranium deposits [4].

In this study, it was proposed to produce the required throughput for the salt removal process by the separation of the liquid salt prior to the distillation of the LiCl-KCl eutectic salt from the uranium deposits to reduce the burden of the following vacuum distillation step.

Experimental

The solid-liquid separation experiments were carried out at various temperatures on the sieve with a stainless steel mesh. Figure 1 shows a photograph of a sieve assembly including a stainless steel mesh, a stand and a bottom salt container for the solid-liquid separation. The effect of the mesh opening size was examined with mesh openings of 63, 100, and 150 μm. The liquid salt separation experiments were carried out with LiCl-KCl, LiCl-KCl-UCl_3(5 wt%) salt systems and uranium deposits, where the content of salt in the deposits was about 40 wt %.

The salt evaporation experiments were carried out after the liquid salt separation experiments in the bench scale vacuum distiller as shown in Figure 2. The distiller was composed of a distillation tower with an evaporator, a condenser, a control unit, and an off-gas treatment system. About 15 g of uranium deposit was placed in the crucible and heated at 900 °C for two hours. The weight of uranium deposits was measured before and

after distillation. The salt content of the uranium deposits was measured by dissolving the salt with water.

Figure 1: Photograph of a sieve assembly including a stainless steel mesh, a stand and a bottom salt container for the solid-liquid separation

Results and discussion

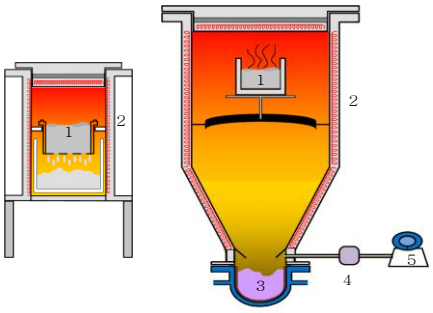
In the electro-refiner of the pyroprocess, the uranium deposits have more than 20 wt% of the electrolyte eutectic salt. The capacity of a salt distiller should be sufficiently large to develop the throughput of the uranium electro-refining process. To achieve a high throughput performance in the salt separation process Kwon *et al.* proposed a method to combine liquid salt separation and vacuum distillation as shown in Figure 2. The salt separation system is composed of a liquid salt separation column and a vacuum distiller. In the combined process, the adhered salt is separated by heating on the sieve at a relatively low temperature compared to the operation temperature of the vacuum distiller, and then the residual salt is evaporated in a salt distiller at an elevated temperature.

In this study the salt removal system of the combined process was devised for the process equipment design of the pyroprocess as shown in Figure 3. The salt separation system is composed of a liquid salt separation column and a vacuum distiller. The adhered salt in the uranium deposits is separated in a solid-liquid separation column at a low temperature, and the resulting uranium deposits are transferred to the vacuum distiller for further removal of the remaining salt. The final salt removed uranium deposits can be fed to the following uranium casting process for ingot preparation.

The feasibility of the combined process of a liquid salt separation and a vacuum distillation was examined. The solid-liquid separation experiments were carried out on a stainless steel mesh with an opening of 150 μm. Lumps of LiCl-KCl eutectic salt (about 100g) were placed on the mesh and heated at 450^{0}C for 0.5 hr. Figure 3 shows a photograph of a frozen LiCl-KCl salt collected in the bottom container. As shown in Figure 3, most of the LiCl-KCl eutectic salt flowed down through the mesh because of gravity. However, the salt melted on the sieve, but did not flow through the mesh at 400^{0}C.

The meshes with openings of 63, 100, and 150 μm were used to examine the effect of the mesh opening size. About 100 g of the LiCl-KCl eutectic salt was heated on each type of mesh at 450^{0}C for 1 hr. It was observed that most of the LiCl-KCl eutectic salt flowed down through the mesh and no difference between the mesh openings was observed. Therefore a mesh opening of 150 μm was used for the liquid salt experiments. Generally, the uranium deposits (dendrites) on the solid cathode are much larger than 150 μm.

Figure 2: Schematic of the salt separation system composed of (a) liquid salt separation column and (b) vacuum distiller



Note: 1: uranium deposit, 2: heater, 3: recovered salt, 4: filter, 5: vacuum pump

The separation of LiCl-KCl-UCl_3 was also tested since the residual salt in cathode deposits contains uranium chloride. For the experiment of uranium chloride containing salt, lumps of the salt (about 50 g) were heated on the sieve during 0.5 hr at 450^{0}C. The uranium chloride containing salt melted on the mesh but more than 98 wt% of the initial salt remained on the sieve after heating at 450^{0}C. This phenomenon was probably caused by the viscosity of the uranium chloride containing salt. In the experiment of heating at 500^{0}C during 0.5 hr, less than 1.0 wt% of the initial salt remained on the mesh surface as a thin film as shown in Figure 4.

Figure 3: Photograph of a frozen LiCl-KCl salt collected in the bottom container after liquid salt separation experiment

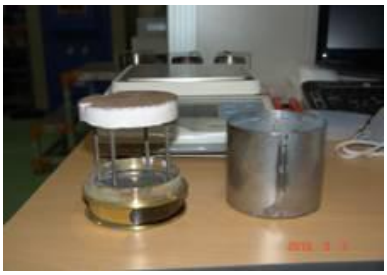
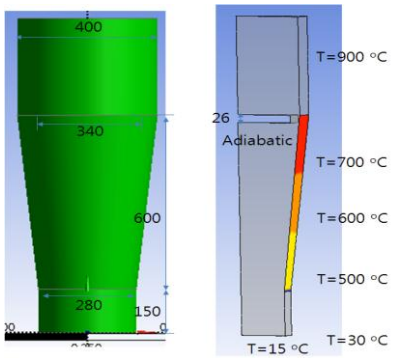


Figure 4: Photograph of a LiCl-KCl-UCl_3 (5 wt%) salt after heating at 500^{0}C during 0.5 hr

The temperature distribution of the experimental distillation tower was calculated by the code of ANSYS CFX as shown in Figure 5. The tower has cylindrical shape with a 40 cm of inner diameter in the evaporation zone and a conical shape in the condensing zone. The wall temperature of the evaporation zone is 900°C. The wall temperature of the condensing

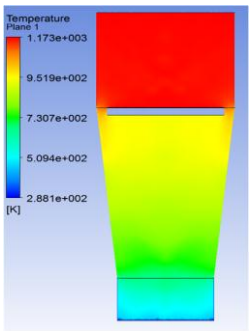
zone decreased from 700 to 500°C. The temperature under the salt recovery vessel, which was cooled by cold water, is 15°C.

Figure 5: Geometry and wall temperature of the experimental distillation tower



The temperature in the evaporation zone is almost constant due to the heat shield and it decreases smoothly in the condensing zone as shown in Figure 6. From the temperature profile it could be concluded that the salt vapour can be transported to the bottom of the salt recovery vessel without condensing before arrival at the vessel.

Figure 6: The temperature distribution of the experimental distillation tower calculated by the code of ANSYS CFX



Conclusion

In this study, it was proposed to produce the required throughput for the salt removal process by the separation of the liquid salt prior to the distillation of the LiCl-KCl eutectic salt from the uranium deposits of the solid cathode in an electro-refiner. The feasibility of liquid salt separation was examined by salt separation experiments on a stainless steel sieve. The adhered salt in uranium deposits was separated as a liquid by heating the deposits at a low temperature. Therefore, the amount of salt to be distilled can be reduced by liquid salt separation prior to salt distillation. It was found that the liquid salt can be separated from the uranium dendrites above 500°C. The temperature distribution of the experimental distillation tower was calculated by the code of ANSYS CFX. The calculation results confirmed that the salt vapour could be transported to the bottom of the salt recovery vessel without condensing before arrival at the vessel.

References

[1] S.T. Ali, N.R. Munirathnam, C. Sudheer, R.C. Reddy, T.L. Prakash (2004), *Material Letters,* 58, 1683.

[2] S.T. Ali, J.V. Rao, K.S. Varma, T.L. Prakash (2002), *Bull. Mater. Sci. 25,* 479.

[3] S. Dushman (1962), Scientific Foundations of Vacuum Technique, 2nd ed., John Wiley and Sons, New York.

[4] S.W. Kwon, J.Y. Kim, H.S. Lee, H.G. Ahn (2010), *J. Radioanal. Nucl. Chem.*, 284, 143.

[5] S.W. Kwon, K.M. Park, H.G. Ahn, H.S. Lee (2011), *J. Radioanal. Nucl. Chem.*, 288 789.

[6] Z. Tomczuk, R.D. Wolson, W.E. Miller, (1989), *Report ANL-IFR-119*, Argonne National Laboratory.

[7] B.R. Westphal, D. Vaden, T.Q. Hua, J.L. Willit, D.V. Laug (2002),"Recent Development at the Cathode Processor for Spent Fuel Treatment", *American Nuclear Society Fifth Topical Meeting,* Charleston, South Carolina, USA, 17-20 September.