Clean-up of LiCl-KCl Eutectic Salt in an Electrorefiner

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1. Introduction

It is needed to separate long-lived actinides from the rest of the spent nuclear fuel to recycle them in a transmutation process [1-2]. The long-lived actinides could be extracted and fabricated into a fuel for use in advanced reactors. In addition, the extraction of actinides from a spent fuel will significantly reduce the radioactivity of the spent fuel and the volume of the spent fuel to be buried in a repository.

Pyroprocessing has been developed for the separation of the long-lived elements due to its advantages of a compactness, nuclear proliferation resistance, and a reduction of the secondary waste generation [3].

Electrorefining is a key step in the pyroprocessing. Electrorefining process is generally composed of two recovery steps- deposit of uranium onto a solid cathode and then the recovery of the remaining uranium and TRU elements simultaneously by a liquid cadmium cathode. After the recovery step of actinides by the liquid cadmium cathode, there are TRU residues along with rare earth elements in the salt. The TRU residues are to be removed from the salt by a so-called draw down step before a salt regeneration step. One method for the draw down is an electrolysis of actinides with a solid cathode - catch pan and Li alloy anode system.

In this study, it was attempted to apply a solid cathode surrounded by a ceramic container (CASC; Container-Aided Solid Cathode) for the salt clean-up step. The cathode was used by Kwon et al. for replacing the liquid cadmium cathode [4].

2. Experimental

The experimental set-up is composed of an electrorefiner, a control system and a gas purification system. The electrorefiner is installed in the Ar gas filled glovebox. There is a cathode (CASC), an anode, an agitator and a reference electrode in the electorefiner as shown in Figure 1. The cathode system is a solid cathode surrounded by a ceramic container. Molybdenum rod with a diameter of 3mm was used as a solid cathode. The container is made of codierite with an inner diameter of 10 mm and a height of 75mm. There are 30 holes in the container. Glassy carbon rod with a diameter of 6mm was used as an anode.

LiCl-KCl eutectic salt was used as a medium of the electrorefiner. Uranium and cerium were used as solutes, where the uranium was used as a surrogate for the TRU elements. Cerium chloride (CeCl₃) in the glass ampoule was used as received without any further treatment. The

uranium chloride was prepared by oxidizing U –metal (Korea Atomic Energy Research Institute stock material) by adding CdCl₃ to the LiCl-KCl eutectic salt.

Electrolysis experiments were carried out at 500°C by passing the constant current between the anode and the cathode for the salt clean-up. Salt samples were taken by dipping a cold ceramic rod into the eutectic salt for the measurement of the solute contents during the electrolysis experiment. The salt samples were dissolved into the nitric acid and the solute contents were measured by using ICP spectroscopy.

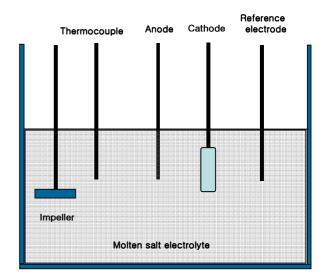


Figure 1. Experimental set-up for the electrolysis experiments.

3. Results and Discussion

Electrolysis experiments were carried out in the electrorefiner with a cathode surrounded by a perforated ceramic container. It was examined the effect of the initial solute concentration in the salt (The ratio of U to Ce wt % in the salt was varied from zero to 100).

In run #1, the initial concentration of uranium was 2.0 wt % and cerium was not used as solute. The initial cathode potential was about -1.7V and the potential was kept nearly constant until more than 99 percent of the uranium in the salt was removed during electrolysis. The electrolysis was terminated at 30 minutes after the cathode potential arrived at about -2.5V. The final uranium concentration was about 400ppm.

In run #2, the initial concentrations of uranium and cerium were 0.8 and 2.0 wt %, respectively. The current density was 60mA/cm₂.

The concentrations of uranium and cerium in the salt decreased with an increasing amount of the current passed. The final uranium concentration in the salt was dependent on the duration of the electrolysis (amount of current passed) and initial concentration. Electrolysis experiments were continued for about 7.5 hours and the final content of uranium in the salt was about 20ppm.

The potentials of the anode and the cathode were stable and no unusual phenomena were observed during all the electrolysis experiments even though there was a very low solute concentration in the salt. The electrorefiner was successfully operated and the uranium in the molten salt was effectively recovered onto the cathode and separated from the cerium successfully.

The color change of the salt sample was observed during an electrodeposition of the uranium. The color of the salt containing uranium chloride was dark purple initially. The color of the salt became lighter during the uranium deposition, and finally turned white, which is the color of a LiCl-KCl salt containing cerium chloride only at room temperature.

From the results of this study, it is expected that a salt clean-up could be possible with a system of a cathode of a solid cathode- perforated ceramic container and an anode of a glassy carbon.

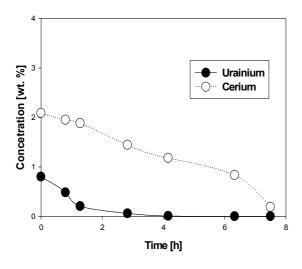


Figure 2. Concentration profiles of uranium and cerium in the salt during electrolysis

4. Summary

Salt clean-up experiments were carried out in a electrorefiner with a cathode surrounded by a perforated ceramic container. The uranium in the salt was transferred to the solid electrode and separated from the cerium successfully. The uranium concentration in the salt was 20ppm after the electrolysis provess. It was found that the CASC could be one of the candidates for a salt clean-up process to remove residual actinide

elements in the salt after the recovery step by using a liquid cadmium cathode.

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