Study on the upper current limit according to the anode dissolution in a high throughput electrorefiner

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Abstract

A high throughput electrorefiner developed in KAERI was designed to continuously recover uranium from the reduced metal of the electrolytic reduction process with a 20 kgU/day throughput. In order to achieve the throughput, the applied current to the electrorefiner has to be controlled. In the electrorefiner, the anode basket is located at the periphery of the reactor with a capacity of 50 kg metal feeding. As the electrorefining of uranium progressed, the surface area of anode decreased due to the anode dissolution and the voltage of it increased. According to the cut-off voltage of the anode, the upper current limit should be taken into account. The current-potential curves were measured with respect to the metal charge of the anode basket and the concentration of UCl_3. The upper current limit was evaluated according to the metal charge and the concentration of UCl_3 in a LiCl-KCl salt. From the results, the controlled current which can be applied maximally to the electrorefining system was suggested for the recovery of 20kgU/day. According to the upper current limit, the uranium electrodeposition was carried out with respect to the current densities.

Introduction

Recently researches for pyroprocess have been extensively investigated. Pyroprocess was proposed as an alternative solution for treating spent fuel. An electrorefining process is one of the key processes among the pyroprocesses [1]. By using electrorefining process, uranium is selectively recovered from a reduced metal which is produced from an electrolytic reduction process for treating spent oxide fuel.

The throughput of the uranium recovery of an electrorefiner is determined by the total ampere-hour which is applied to the cell. As an applied current increases, the throughput increases. But, in order to prevent transition metals and a structural material of the anode from dissolution and recover pure uranium, the anodic voltage should be controlled below the cut-off voltage. And a current density should be controlled in order to deposit uranium as a dendritic form at the cathode [2]. In order to enhance the throughput of an electrorefiner with controlling the anodic voltage, the surface of the electrodes and the concentration of UCl_3 in the LiCl-KCl eutectic salt should be increased. From these constraints, the upper current limit can be deduced for maximum throughput of the electrorefiner.

At Korea Atomic Energy Research Institute (KAERI), a high-throughput electrorefiner with a capacity of 20 kgU/batch has been developed for enhancement of the throughput and scale up to the engineering scale [3,4]. In this work, the current-potential curves have been obtained according to the electrode surface and the UCl_3 concentration. From these curves, the upper current limits of the cell have been able to be determined due to the cut-off voltage. Along with the upper current limit, the operational conditions to achieve the throughput of the electrorefiner were investigated. And the uranium recovery by electrorefining has been carried out with respect to the current density and the characteristics of the uranium deposition have been discussed.

Experiment

A lab-scale electrorefiner with a capacity of 20 kgU/batch was installed in a glove box filled with high-purity Ar gas as shown in Figure 1. The uranium metal was fed into an anode basket. The annular anode basket module consists of four parts with a cartridge type for easy replacement of anode basket. For enhancement of mass transfer during electrolysis, anode basket module rotated. The cathode as the working electrode was made of graphite for self-scarping. The graphite cathodes were located at the core part of the refiner. An Ag/AgCl reference electrode was used for measuring the cathode and anode potential during the electrolysis. High-purity LiCl-KCl eutectic salt (58.8-41.2 mol.%, T_m = 355°C) from the Sigma-Aldrich was used as an electrolyte. For stabilised initial cell voltage of the electrorefining, uranium trichloride (UCl_3) was prepared by two reactions: a reaction between gaseous chlorine and liquid cadmium to form $CdCl_2$ in a cadmium metal phase, and a reaction between uranium metal and $CdCl_2$ to form UCl_3 in a LiCl-KCl eutectic salt phase. The concentration of UCl_3 was adjusted in the range from 2.7 to 6 wt.% of salt. The electrochemical experiments were carried out at 500°C with a WonATech potentiostat with a capacity of 400 A. Electrochemical data were collected by a computer system.

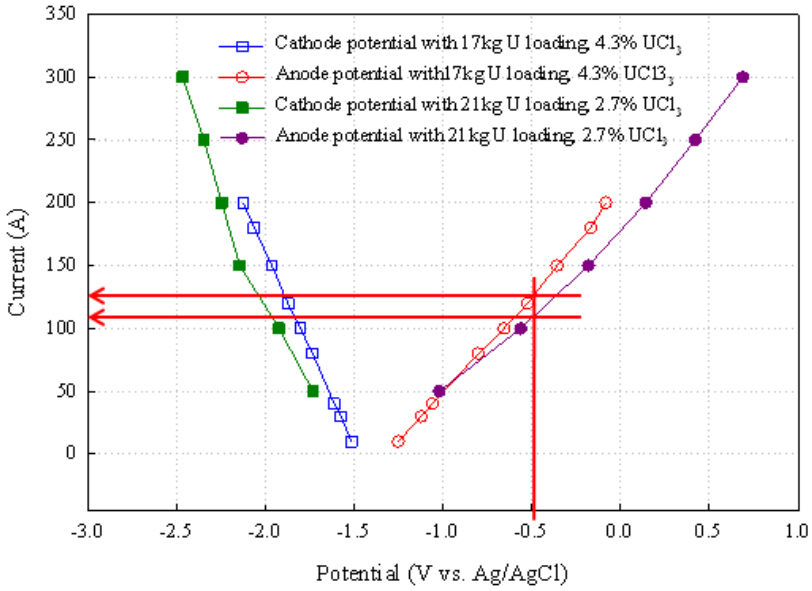
Figure 1: High throughput electrorefiner

Results

It is important to secure the upper current limit for uranium electrodeposition, because the throughput of the uranium recovery depends on total ampere-hour which is applied to the electrorefining cell. The upper current limit is maximum current which is able to apply to an electrochemical cell according to the cut-off voltage. It is deduced from the current-potential curve and is function of the amount of metal loaded at the anode and the concentration of UCl_3. The amount of metal loaded at the anode is directly related to the surface area of the anode.

Figure 2 shows current-potential curves for the uranium electrodeposition with respect to the amount of anodic loading and the UCl_3 concentration. As shown in Figure 2, in the condition of 17 kg U metal loaded into the anode basket and 4.3% UCl_3 concentration, the upper current limit was about 125 A from the current-potential curve according to the cut-off voltage (-0.5 V vs. Ag/AgCl). And in the condition of 21 kg U metal loaded and 2.7% UCl_3 concentration, the upper current limit was about 110 A. Compared these results of two conditions, as the concentration of UCl_3 in the salt increased, the upper current limit increased in spite of decreasing the amount of metal loaded into the anode basket. Therefore, if the anode basket is fully loaded with about 50 kg U metal and the concentration of UCl_3 in the salt increases to 9%, it is expected that the upper current limit could be increased.

Figure 2: Current-potential curves for U deposition with respect to the amount of anodic loading and the UCl_3 concentration



Uranium electrodeposition was carried out with chronopotentiommetry in the condition of 21 kg U loading and 2.7% UCl_3 concentration. The applied current to the electrorefiner was determined to 100 A from the current-potential curve shown in Figure 2. Figure 3 shows a chronopotentiogram of uranium electrodeposition with 100 A applied current at 500°C. The electrodepostion of uranium was carried out for 4 hours. The anode and cathode potential were about -0.35 and -1.5 V, respectively. The cell potential was 1.15 V. The current density was 70 mA/cm^2 in the cathode basis. From the result of the uranium deposition, the recovered uranium deposit at the graphite cathodes was like Figure 4(a). The uranium dendrite was formed. Then, the applied current was elevated to 150 A at the same conditions. Figure 4(b) shows the recovered uranium deposit at the cathode. The current density was 104 mA/cm^2. As shown in Figure 4(b), the uranium dendrite was also formed like the former, but the length of the dendrite was shortened. As the current density increased, the particle size of the dendrite decreased. The amount of the salt in the uranium deposit with 100 and 150 A applied currents were about 20%

Figure 3: Chronopotentiogram of uranium electrodeposition with 100 A applied current

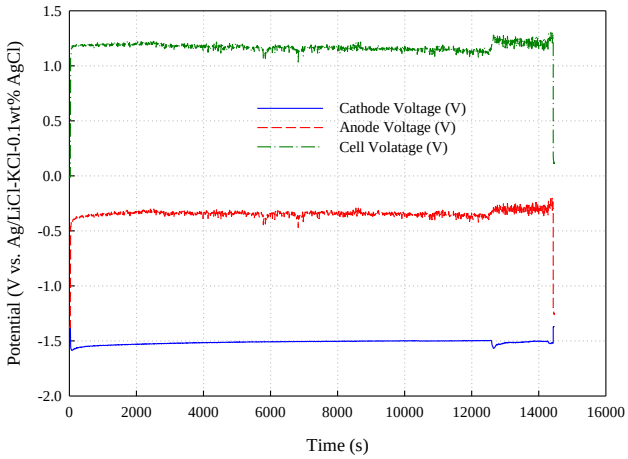
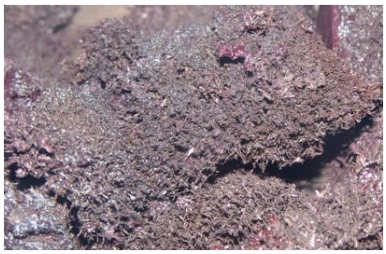


Figure 4: Recovered uranium deposit with respect to the applied current

(a) 100 A



(b) 150 A

and 35%, respectively. As the particle size of the dendrite decreased, the amount of the salt increased. From these results, the morphology of the uranium deposit of 100 A was more advantageous than that of 150 A in order to easily treat the uranium deposit in the cathode process. Thus, optimum current density should be maintained for effective uranium recovery during the electrorefining process.

Conclusion

The upper current limit was investigated with current-potential curves with respect to the anodic loading and UCl_3 concentration by using a high throughput electrorefiner which was developed at KAERI. The higher the UCl_3 concentration was, the higher the upper current limit became. From the results of uranium electrodeposition with chronopotentiomery, as the current density increased, the particle size of the uranium dendrite decreased and the amount of salt in the deposit increased. The optimum conditions of uranium recovery in the view of the throughput should be secure in further study.

Acknowledgements

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