ELECTROREFINING OF URANIUM AND PLUTONIUM FROM LIQUID CADMIUM

by

Z. Tomczuk, D. S. Poa, W. E. Miller, and R. K. Steunenberg
Chemical Technology Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

The separation of fission-product elements from uranium and plutonium by electrorefining is a key step in the proposed pyrometallurgical process for the recovery of fuel and blanket materials from the Integral Fast Reactor. Electrorefining in a molten-salt electrolyte was selected for this process because it has proven successful for the preparation of high-purity uranium and plutonium. In the IFR electrorefining process, the anode is a liquid cadmium solution, uranium and plutonium are co-transported, and the product is collected as a solid deposit.

The feasibility of electrodepositing uranium from a molten-salt electrolyte onto various cathode materials such as carbon, molybdenum, uranium, and stainless steel was investigated. These small-scale (10 g U) tests were conducted at 485-500°C using molten LiCl-KCl-UC1₃ as the electrolyte. The uranium deposits were generally adherent on the cathode material and were of a dendritic nature.

Small-scale tests were then conducted on the electrotransport of uranium, using a liquid cadmium anode containing dissolved uranium, LiCl-KCl-UC1₃ electrolyte, and a molybdenum rod cathode. These tests showed that (1) a smaller potential difference was required to transport the uranium when the cadmium and electrolyte phases were agitated, (2) the uranium deposit was more uniform laterally when the cathode was rotated, and (3) the deposits consisted of interwoven clusters of fine crystals.
Experiments were then conducted with 300-400 g U to evaluate the feasibility of a larger-scale operation and to determine whether separations of certain fission-product elements would occur as expected from theoretical considerations. A low-carbon steel crucible (15 cm dia. x 30 cm high) was used as the containment vessel, and mixing was provided by a steel agitator in the salt and metal phases. The electrolyte was molten LiCl-KCl eutectic containing 9.1 wt % UC\textsubscript{3} and the metal phase was 15.0 kg of cadmium. The temperature was 480-500°C, the stirring rate was 0-100 rpm, and the cathode was rotated at 50 rpm. A reference electrode (Ag/AgCl) was used to monitor the anode and cathode potentials individually. The results were as follows:

1. About 96% of the total uranium was found on the cathode. This value was obtained by chemical analysis of the residual uranium in the cadmium.
2. Agitation of the cadmium and electrolyte was required to provide a mass-transport rate sufficient to support the electrochemical reduction rate at the cathode. Under the same experimental conditions, 8% of the uranium was transferred without stirring; this value increased to about 80% with the agitator rotating at 100 rpm. The reference electrode measurements showed that the rate-limiting effect occurred at the anode.
3. The amount of uranium transferred decreased with increasing current rate. At a 4-A rate (current density, \(-25\) mA/cm\textsuperscript{2} at the anode and \(-39\) mA/cm\textsuperscript{2} at the cathode), essentially all of the uranium was removed from the anode. Again, the anode proved to be the limiting electrode when the current density was increased.
4. When inactive fission-product elements were added to the system, the noble metals remained in the cadmium anode and cerium was transferred to the electrolyte, as expected from theory. The behavior of zirconium was not well-defined; it was found both in the anode and in the electrodeposited uranium.
To make the electrorefining operation compatible with the other steps of the IFR process, the electrolyte must contain BaCl$_2$ and CaCl$_2$. Also, LiCl is added to lower the melting point and NaCl is formed from the sodium thermal bond in the fuel. Several electrorefining experiments were conducted, using BaCl$_2$-CaCl$_2$-LiCl (7.2-28.8-54.0 mol %) and BaCl$_2$-CaCl$_2$-LiCl-NaCl (14.9-38.3-34.0-12.8 mol %), both of which are eutectic compositions. Both salts contained a small concentration of UCl$_3$ to permit uranium transport between the electrodes. Good uranium deposits were obtained on the cathode in both cases.

The feasibility of electrorefining plutonium was then investigated, using pure plutonium initially and plutonium-uranium mixtures later. The electrolyte in these tests was the LiCl-NaCl-CaCl$_2$-BaCl$_2$ eutectic, which contained about 3 wt % PuCl$_3$, and the temperature was 485-490°C. The following results were obtained with the pure plutonium: (1) No deposition of plutonium occurred when the molybdenum rod cathode was rotated at rates greater than 24 rpm; however, good deposits were obtained when the cathode was stationary. (This result is attributed to the deposition of plutonium at the bottom of the cathode and subsequent mechanical loss from the deposit due to the stirring action. (2) The cell-voltage curves indicated that the potential difference for the deposition of plutonium was smaller and more stable than that for uranium. (3) The plutonium deposits differed from the uranium deposits; instead of a needle-like crystalline structure, the plutonium deposits were fine-grained and did not adhere as well to the molybdenum cathode. (4) The coulombic efficiency for plutonium transport was high -- a value of 97% was obtained in one experiment. The typical values, however, were lower, due either to poor adherence of the deposit or to partial short circuits resulting from contact between the deposit and the anode.
The electrorefining of uranium-plutonium mixtures was investigated, using a uranium to plutonium ratio of 4:1, with the following results:

(1) No deposition occurred when the cathode was rotated at speeds higher than 36 rpm. Good deposits were obtained when the cathode was stationary or rotated slowly (<10 rpm). (2) The morphological characteristics of the deposit were intermediate between those obtained with pure uranium and pure plutonium; some dendrites were visible, but the deposit consisted mainly of lumped crystals. (3) The best deposits were obtained when a low-carbon steel rod was substituted for the molybdenum cathode. (4) The potential difference during the transport of uranium and plutonium was intermediate between those required for the individual metals.

Throughout these series of tests, there was no observable corrosion of the steel or molybdenum cell components. This is particularly noteworthy in the case of the larger-scale electrorefining experiments, where the steel electrorefining cell was in contact with the liquid cadmium and the electrolyte at 400-500°C for about four months.


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