METHOD FOR REMOVAL OF HEAVY METAL FROM MOLTEN SALT

E. C. Gay, W. E. Miller, and J. J. Laidler
Argonne National Laboratory
Chemical Technology Division
9700 South Cass Avenue
Argonne, Illinois 60439-4837 U.S.A.

ABSTRACT

The pyrometallurgical process for recycling spent metal fuels from the Integral Fast Reactor (IFR) involves electrorefining spent fuel in a molten salt electrolyte (LiCl-KCl-U/PuCl₃) at 500°C. At some point, the concentrations of alkali, alkaline earth, and rare earth fission products in the salt must be reduced to lower the amount of heat generated in the electrorefiner. The heavy metal concentration in the salt must be reduced before removing fission products from the salt. The operation uses a lithium-cadmium alloy anode that is solid at 500°C and a solid mandrel cathode. In tests conducted in an engineering-scale electrorefiner (10 kg uranium per cathode), good separation was achieved while removing uranium and rare earths from the salt. Only 13% of the rare earths was removed, while 99.9 % of the uranium in the salt was removed; subsequently, the rare earths were also reduced to low concentrations.

INTRODUCTION

Electrorefining is a key step in the pyrometallurgical process that was developed to recover uranium, plutonium, and minor actinides from spent metal fuel (1,2) from the Integral Fast Reactor (IFR). The IFR is an advanced reactor concept that was developed at Argonne National Laboratory. It has these distinguishing features: It is a sodium-cooled, pool-type reactor; that is, all the major components, reactor core, pumps, and heat exchangers are in a large sodium-filled pot (3). It employs a metallic fuel, a U-Pu-Zr alloy clad with a stainless steel alloy. It has an integral fuel cycle, whereby discharged core and blanket materials are processed and refabricated in an on-site facility.

We previously have reported experiments using an engineering-scale electrorefiner (4). The electrorefiner consisted of a cadmium anode or anodic dissolution baskets, solid and liquid cathodes, and a molten salt electrolyte (LiCl-KCl) at 500°C. A dual cathode approach was adopted where uranium is recovered on a solid cathode
mandrel and uranium-plutonium is recovered in a liquid cadmium cathode. In the engineering-scale electrorefiner, we have demonstrated the following: electrotransport of uranium from the cadmium anode to a solid cathode in 10-kg batches; anodic dissolution of 10-kg batches of chopped fuel (U-10 wt % Zr); and recovery of 4 kg of heavy metal using the liquid cadmium cathode.

EXPERIMENTAL EQUIPMENT

Electrorefiner Assembly

An engineering-scale electrorefining facility that can support 10 kg of uranium on a single solid cathode was constructed to demonstrate the electrolytic transport of uranium at plant-scale levels and to measure the dissolution rate of clad segments of uranium-zirconium alloy. The electrorefiner assembly is enclosed by a 42-cubic-meter, argon-filled glovebox (with ovens, transfer locks, wells, and lifting systems), that is equipped to control gas pressure, temperature, and gas purity.

Schematic of Drawdown Operation

A schematic representation of the drawdown operation is shown in Fig. 1. A lithium-cadmium alloy (5.8 wt % lithium) that is solid at 500°C is loaded into the anodic dissolution baskets and rotated at 75 rpm; current is driven from the anodic dissolution baskets to a solid mandrel cathode, that has a ceramic catch crucible below to collect product that falls off of the solid cathode. Salt and cadmium mixers are operated at 150 and 50 rpm, respectively. The possible drawdown reactions include (1) electrotransport of lithium to the solid cathode and lithium reduction of the uranium and rare earth chlorides at the solid cathode and (2) lithium reduction of the uranium and rare earth chlorides at the anode and electrotransport of the uranium and rare earths to the solid cathode. The design criteria that had to be met for the drawdown equipment include the following: (1) control of the reduction rate by lithium, (2) good separation between uranium and rare earths, and (3) the capability to collect uranium and rare earths over a wide range of salt concentrations.

EXPERIMENTAL RESULTS

The concentrations of uranium in the cathode deposits from the drawdown runs were found to fall into three ranges: low (<0.1 wt %), medium (31.8-39.2 wt %) and high (70-89.3 wt %). The results are summarized in Table I.
Table I. Summary of Data from Drawdown Operations in the Engineering-Scale Electrorefiner

|                      | U in Cathode Deposit, wt % | U in Salt, wt % | Run | Rare Earths in Cathode Deposit, wt % |
|----------------------|-----------------------------|-----------------|-----|-------------------------------------|
| **High**             |                             |                 |     |                                     |
| 89.3                 | 4.33                        | 65              |     | <0.01                               |
| 79.5                 | 1.75                        | 71              |     | 1.2                                 |
| 73.2                 | 6.68                        | 58              |     | <0.01                               |
| 70.0                 | 2.98                        | 70              |     | 1.1                                 |
| **Medium**           |                             |                 |     |                                     |
| 39.2                 | 0.72                        | 75              |     | 1.8                                 |
| 32.4                 | 0.14                        | 76              |     | 2.7                                 |
| 31.8                 | 1.3                         | 72              |     | 2.8                                 |
| **Low**              | <0.1                        | 0.015           | 77  | 31.8                                |

**High Uranium Concentration**

The average uranium concentrations in the salt during drawdown Runs 58, 65, 70, and 71 ranged from 6.68 to 1.75 wt %, while the concentrations of uranium in the cathode deposits from these runs ranged from 70.0 to 89.3 wt %. These data are plotted in Fig. 2. The concentrations of rare earths (cerium, neodymium, and yttrium) in the cathode deposits were low (1.2 wt % or less). These results are shown in Fig. 3.

**Medium Uranium Concentration**

The range of average uranium concentrations in the salt during drawdown Runs 72, 75, and 76 was 0.14 to 1.30 wt %. The range of uranium concentrations in the cathode deposits from these runs ranged from 31.8 to 39.2 wt %. These results are plotted in Fig. 2. The concentrations of rare earths in the cathode deposits from Runs 72, 75, and 76 were 2.8, 1.8, and 2.7 wt %, respectively. These results are shown in Fig. 3. Over this range of uranium concentration in the salt, the concentrations of rare earths in the cathode deposits were still low (1.8 to 2.8 wt %, as shown in Fig. 3).
Low Uranium Concentration

The average concentration of uranium in the salt during drawdown Run 77 was 0.015 wt %, and the concentration of uranium in the cathode deposit from this run was <0.1 wt %. This result is also plotted in Fig. 2. The concentration of rare earths in the deposit was 31.8 wt %, which is shown in Fig. 3.

CONCLUSIONS

Good separation can be achieved while removing uranium and rare earths in the salt from the engineering-scale electrorefiner. Only 13% of the rare earths were removed, while 99.9% of the uranium in the salt was removed. The uranium and rare earth concentrations in the salt were reduced to <0.01 wt %, using the in-situ drawdown techniques described in this paper.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Nuclear Energy Research & Development Program, under Contract W-31-109-Eng-38 at Argonne National Laboratory (ANL). The authors also wish to acknowledge the contributions of the staff and support groups in the Chemical Technology and Reactor Engineering Divisions at ANL. We also appreciate the managerial support of Dr. Yoon Chang and Dr. James E. Battles.

REFERENCES

1. L. Burris, R. Steunenberg, and W. E. Miller, AIChE Symposium Series, No. 254, 83, pp. 135-142 (1987).

2. L. Burris, Chemical Engineering Progress, 82(2), pp. 35-39 (February 1986).

3. C. Till and Y. Chang, "Evolution of the Liquid Metal Reactor: The Integral Fast Reactor (IFR) Concept," in Proceedings of the American Power Conference, Illinois Institute of Technology: Chicago, April 24-26, 1989.
4. J. E. Battles, W. E. Miller, and E. C. Gay, "Pyrometallurgical Processing of Integral Fast Reactor Metal Fuels," in Proceedings of the Third International Conference on Nuclear Fuel Reprocessing and Waste Management, RECOD '91, Sendai, Japan, April 14-18, 1991.
Fig. 1. Schematic of Electrorefiner Drawdown

Fig. 2. Uranium Concentration in the Salt vs. Uranium Concentration in the Cathode Product
Fig. 3. Concentration of Uranium in the Salt vs. Concentration of Rare Earths in the Product