

# Analysis of Cadmium in Undissolved Anode Materials of Mark-IV Electrorefiner

**GLOBAL 2013**

Tae-Sic Yoo  
Guy L. Fredrickson  
DeeEarl Vaden  
Brian Westphal

October 2013

The INL is a  
U.S. Department of Energy  
National Laboratory  
operated by  
Battelle Energy Alliance



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint should not be cited or reproduced without permission of the author. This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, or any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use, or the results of such use, of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights. The views expressed in this paper are not necessarily those of the United States Government or the sponsoring agency.

# ANALYSIS OF CADMIUM IN UNDISSOLVED ANODE MATERIALS OF MARK-IV ELECTROREFINER

Tae-Sic Yoo, Guy L. Fredrickson, DeeEarl Vaden, and Brian Westphal

Separation Department, Materials and Fuels Complex, Idaho National Laboratory  
{tae-sic.yoo,guy.fredrickson,deeearl.vaden,brian.westphal@inl.gov}

*The Mark-IV electrorefiner (Mk-IV ER) contains an electrolyte/molten cadmium system for refining uranium electrochemically. Typically, the anode of the Mk-IV ER consists of the chopped sodium-bonded metallic driver fuels, which have been primarily U-10Zr binary fuels. Chemical analysis of the residual anode materials after electrorefining indicates that a small amount of cadmium is removed from the Mk-IV ER along with the undissolved anode materials. Investigation of chemical analysis data indicates that the amount of cadmium in the undissolved anode materials is strongly correlated with the anode rotation speeds and the residence time of the anode in the Mk-IV ER. Discussions are given to explain the prescribed correlation.*

## I. INTRODUCTION

The Experimental Breeder Reactor-II (EBR-II) is a sodium cooled fast reactor developed at Argonne National Laboratory (ANL) (Refs. 1 and 2). The used fuels from the EBR-II are currently being treated in the Fuel Conditioning Facility (FCF) at the Idaho National Laboratory (INL) (Ref. 3). The Mk-IV ER is a unit process in the FCF, which is primarily assigned to treating the used driver fuels. Figure 1 illustrates the major components of the Mk-IV ER. The primary vessel is cylindrical (1.0 m diameter and 1.0 m tall) and made from 2.25Cr-1Mo alloy (ASME SA-387). The molten cadmium layer on the bottom of the vessel is approximately 10 cm thick and the electrolyte layer is approximately 30 cm thick. The electrolyte began its life as a mixture of LiCl-KCl eutectic with approximately 5 wt%  $\text{UCl}_3$ . However, at present, after having treated approximately 1.2 MTHM of used fuel, the electrolyte is a complex mixture of metal chlorides from the fission products, transuranics, and bond-sodium that accumulate in the electrolyte at the expense of  $\text{UCl}_3$  concentration, which is periodically replenished. The Mk-IV ER operating temperature is typically at 500°C with the exception of some early runs conducted at 450°C. The anode and cathode assemblies rotate during the electrorefining process and stir/mix the two liquids. There are four ports (25.4 cm diameter) in the lid for inserting anode and cathode assemblies.

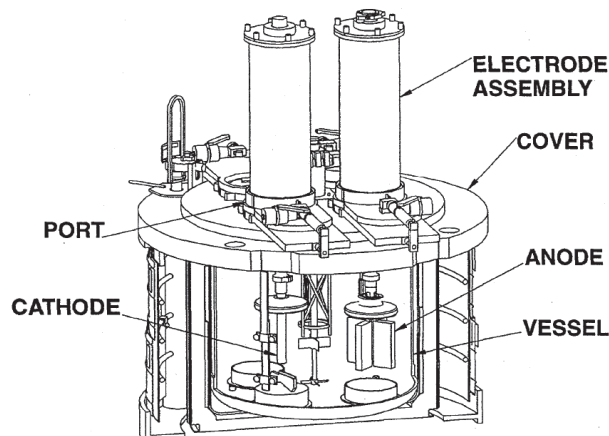


Fig. 1: The Mk-IV electrorefiner schematic

The stainless steel anode baskets hold the chopped used driver fuel segments. During electrorefining, the anode baskets are immersed into the electrolyte and the used fuel is dissolved electrochemically. Perforated sides and bottoms allow the flow of the electrolyte into and out of the anode baskets. The steel cathode is also immersed into the electrolyte and collects the reduced products. The active metal contents in the used fuel (e.g., Cs, Sr, lanthanides, Pu, etc.) reacts with uranium cations in the electrolyte and progressively decreases the concentration of uranium cations in the electrolyte. Periodically, batches of  $\text{CdCl}_2$  are added to the electrolyte to increase the uranium cation concentration via the reaction below, which results in a gradual increase of cadmium inventory in the vessel.



The undissolved anode materials (see Fig. 2) are removed from the anode baskets and stored for metal waste form processing. These undissolved materials typically include fuel residual (~25 wt%), stainless steel cladding (~50 wt%), and adhering electrolyte (~25 wt%). Chemical analyses show that nontrivial amounts of cadmium are reporting to these undissolved anode materials.

Tracking Cd is important from the perspective of waste stream management as Cd is one of the Resource Conservative and Recovery Act (RCRA) metals. The objective of this article is to investigate the chemical analytical data of the undissolved anode materials and to explain the mechanisms of cadmium accumulation on these materials in terms of the operating parameters of the Mk-IV ER.



Fig. 2: Undissolved anode materials from the Mk-IV ER

## II. CADMIUM IN THE UNDISSOLVED ANODE MATERIALS DURING DEMONSTRATION OPERATION

The demonstration operation for driver fuel processing refers to the period between 1993 and 1999. During this period, the Mk-IV ER processed 25 batches of irradiated driver fuel. The primary purpose was to demonstrate the expected material partitioning, whereby uranium is transported from the anode to the cathode, noble metals including zirconium are retained in the anode basket, and active metals are dissolved to the electrolyte. Thus, operating conditions were identified to maximize the retention of noble metals while dissolving uranium and active metals as much as possible.

The anode baskets used for the demonstration operation have perforated sides and bottoms (~0.4 cm diameter holes and 46% open area) allowing the flow of the electrolyte into and out of the anode baskets. The initial period of the demonstration operation examined various rotation speeds (5, 25, and 75 rpm) of the anode baskets. Eventually 5 rpm was used for the majority of the anode batches for the demonstration operation. Figure 3 plots estimated cadmium mass in each basket with respect to the immersion time of the anode in the Mk-IV ER during the demonstration operation. Data are marked with respect to the anode rotation speeds. One can observe a wide variability of immersion time between 3 to 17 days.

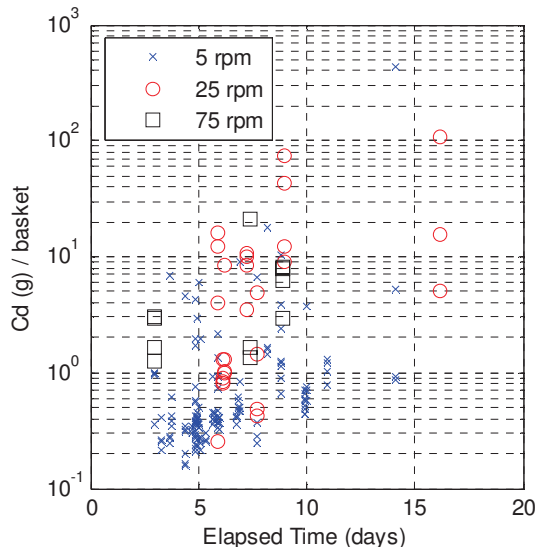


Fig. 3: Operational parameters and cladding hull analysis for the demonstration operation

The amount of cadmium removed from the Mk-IV ER was estimated using the chemical analysis of the undissolved anode materials. The anode baskets contain approximately 8,000 driver hull segments in four compartments. Typically, 10 hulls from each compartment are collected for a total of 40 samples per batch. Segments are known to be extremely inhomogeneous (Ref. 4) and subject to a sampling uncertainty. The hull samples are weighted, washed in water to dissolve adhering electrolyte, washed in acid to dissolve fuel residual, dried, and reweighted. It is assumed that all of the adhering electrolyte and fuel residual are dissolved during the water and acid washing steps. The water and acid wash solutions are analyzed for a suite of elements and isotopes.

The variability of cadmium concentrations from the chemical analyses of the hulls are known to be too large (up to three orders of magnitude difference) to draw a conclusion on the concentration of cadmium in the undissolved anode materials. However, regardless of the difficulty of quantifying the cadmium concentration in these materials, the cladding hull analyses do confirm that a nontrivial amount of cadmium reports to the undissolved anode materials and is removed from the Mk-IV ER at the end of each batch when the hulls are removed from the anodes baskets.

## III. CADMIUM IN THE UNDISSOLVED ANODE MATERIALS DURING INVENTORY OPERATION

Since 2000, a new mission was given to EBR-II driver fuel processing to demonstrate a higher process throughput. Thus, Mk-IV ER operations were conducted to give fast and complete dissolution of uranium while

less attention was given to noble metal retention, in particular zirconium. During these operations, more than 80% of the zirconium escaped from the anode baskets and the major portion this zirconium has accumulated in the Mk-IV ER vessel. A high (50 rpm) anode rotation speed was adopted to achieve higher current efficiency (Ref. 5) by providing the greater electrolyte agitation with the faster anode rotation. The anode baskets were redesigned to accommodate more chopped fuel and have increased perforations on the sides; 12 kg versus 8 kg HM, and 50% versus 46% open area. In order to reduce number of chemical analyses required, hulls from the 4 cruciform anode baskets were all mixed into one pile and 10 hulls from the whole pile were collected for elemental/isotopic analysis.

Figure 4 plots estimated cadmium mass in each basket with respect to the immersion time of the anode in the Mk-IV ER during the inventory operation.

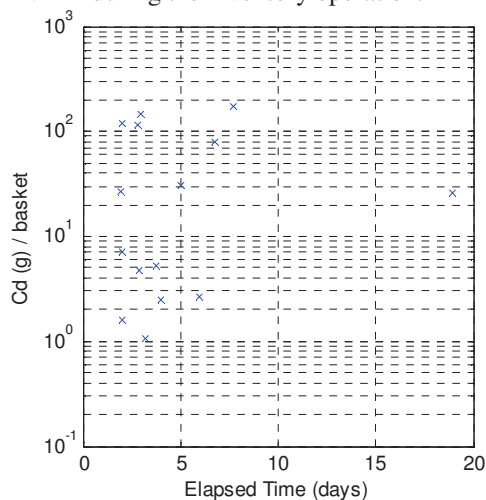


Fig. 4: Operational parameters and cladding hull analysis for the inventory operation

#### IV. DISCUSSIONS

The examination of the composition analyses of the undissolved anode materials from the Mk-IV ER shows that nontrivial amounts of cadmium are deposited on these materials and removed along with the hulls. The estimated quantity of cadmium varies significantly from less than 1 g/batch to more than 1 kg/batch.

The Mk-IV ER environment is reducing to  $\text{Cd}^{+2}$  as metallic uranium and zirconium are abundant in the vessel. Thus, it is unlikely to have electrochemical oxidization of cadmium to  $\text{CdCl}_2$  and incur deposition at the anode by the electrochemical reduction. Another source of cadmium is the electrolyte is dissolved cadmium at a concentration of approximately 40 ppm (Ref. 6). However, the amount of adhering electrolyte removed along with the undissolved anode materials is

typically less than 400g/basket. In turn, one can see that the amount of dissolved cadmium expected to be present in the adhering electrolyte ( $< 0.02 \text{ g/basket}$ ) is far less than the estimated cadmium deposited to these materials. Another possibility is the formation of stable species among cadmium and the undissolved anode materials that are insoluble in the electrolyte.

Major constituents of the undissolved anode material are uranium and zirconium from the fuel matrix and iron from the cladding materials. Cadmium shows no intermetallic formation between uranium and iron at  $500^\circ\text{C}$ . However, the Cd-Zr phase diagram shows various intermetallic formations. In particular, Ref. 7 confirmed  $\text{Cd}_3\text{Zr}$ ,  $\text{Cd}_2\text{Zr}$ , and  $\text{CdZr}_2$  phases and Ref. 8 reported a  $\text{CdZr}$  phase.

The phase diagram study suggests that the residual zirconium in the anode may act as a cadmium getter via the formation of Cd-Zr intermetallics. Typical Mk-IV ER environments are abundant of metallic zirconium and cadmium while bulk electrolyte samples show only ppm levels of zirconium and cadmium concentrations. Thus one can infer that the solubility of Cd-Zr intermetallics to the electrolyte should be minimal. The amount of cadmium dissolved in the entire electrolyte of the Mk-IV ER (approximately 400 kg) is expected to be about 15 g. The formation of Cd-Zr intermetallics in the anode may strip cadmium from the electrolyte while cadmium is dissolved to the electrolyte from the molten cadmium pool ( $> 500 \text{ kg}$ ) at the bottom of the Mk-IV ER vessel. Thus, cadmium deposits to the anode can be sustained.

The observed cadmium quantities in the undissolved anode materials suggest that equilibrium is not yet reached as the expected intermetallic composition is  $\text{Cd}_3\text{Zr}$  in an environment with excess cadmium, which is the case in the Mk-IV ER as a result of the cadmium pool on the bottom of the vessel. Thus, the amount of cadmium in the hulls for typical Mk-IV operation is considered to be kinetically limited. In view of the assumed mechanism of cadmium deposit to the anode, the rate of cadmium deposit is expected to be correlated positively with the electrolyte flux to the anode. A strong correlation is expected between the electrolyte flux and the rotation speed of the anode. Thus, one can examine the rotation of speed of the anode and the duration of the immersion of the anode to the electrolyte to estimate and predict the amount of cadmium deposits to the anode assuming the dissolution of cadmium from the bottom molten cadmium pool to the electrolyte is not a rate-limiting step.

Arguably, the data presented in Figures 3 and 5 supports the assumed cadmium deposit mechanism as the higher anode rotation speed and the longer immersion



time tend to result in the higher estimated amount of cadmium deposit in general.

The wide variability on the amount of cadmium deposit and the past sampling practice on the residual anode materials invite a large uncertainty on the estimate of cadmium deposits to the anode. One way of minimizing this statistical uncertainty is to aggregate the samples under similar operating conditions to simulate the larger size samples. Table 1 classifies the operations and attempts to draw a clearer picture. One can observe that the lowest anode speed operation (5 rpm) incurs the least amount of cadmium deposit to the anode in the sense of average. The demonstration operation with 75rpm anode rotation speed shows the lower amount of average cadmium deposit compared to those of the lower anode rotation speed operations. This is against the expectation that the higher anode rotation speed should promote the more electrolyte flow into the anode and entail the higher amount of cadmium deposit. However, in the defense of the proposed mechanism of cadmium deposit to the anode, only 3 anode batches were processed with 75 rpm anode rotation speed. Thus, quantitative arguments with these sample sets are subject to high statistical uncertainty and not reliable given the wide variability of the amount of cadmium deposits among the samples. A research project is in progress to obtain data without the prescribed statistical uncertainty and confirm Cd deposition mechanism argued in the paper, which will be published elsewhere upon the completion of the project.

Table 1: Operations performed in the Mk-IV ER

Operation	Anode Speed (rpm)	# of Baskets Sampled	Average Elapsed Time (day)	Average Cd (g/basket)
Demo.	5	123	6.24	4.06
Demo.	25	28	8.46	14.83
Demo.	75	7	6.33	5.33
Inventory	50	56*	4.88	51.03

\*Batch was sampled instead of each basket

Inventory runs were performed with a high anode rotation speed (50 rpm) and the slightly larger perforated areas on the sides and bottoms of the baskets. Also the baskets used for the inventory operation hold 50% more anode materials than those of demonstration runs. These factors are expected to promote Cd deposit to the anode and chemical analyses of the residual anode materials of the inventory operation show the higher cadmium deposit than those of the demonstration operation with the lower anode rotation speeds.

It has been argued the benefit of a high speed anode rotation as a mean to promote the electrolyte agitation,

which enhance the current efficiency and predictability of electrorefiner operation (Ref. 5). Chemical analysis data for the residual anode material composition, however, suggests that the benefits may come with the expense of increased cadmium deposit to the anode and potentially to the cathode of high zirconium composition.

Regardless of operation parameters, it seems that the downstream processes such as metal waste process for the residual anode materials and cathode process for the cathode materials should deal with varying quantities of cadmium. Thus, further researches on understanding cadmium behaviors at the downstream processes are recommended.

## ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, under DOE Idaho Operations Office contract DE-AC07-05ID14517

## REFERENCES

1. Y.I. CHANG, "The Integral Fast Reactor," *Nucl. Technol.*, **88**, 129 (1989).
2. Z. TOMCZUK, J.P. ACKERMAN, R.D. WOLSON, and W.E. MILLER, "Uranium Transport to Solid Electrodes in Pyrochemical Reprocessing of Nuclear Fuel," *J. Electrochem. Soc.*, **139**, 12, 3523 (1992).
3. R.W. BENEDICT and H.F. MCFARLANE, "EBR-II Spent Fuel Treatment Demonstration Project Status," *Radwaste Magazine*, **5**, 23 (1998).
4. A.M. YACOUT, R. G. BUCHER, R. D. MCKNIGHT, R. D. MARIANI, D. VADEN, B. WESTPHAL, T. BATTISTI, AND J. KRSUL, "Nuclear Material Estimation and Uncertainties for the Spent Fuel Treatment at FCF," *Proc. 40<sup>th</sup> Annual Meeting of the Institute of Nuclear Material Management*, Phoenix, AZ, July, 1999, p. 25 (1999).
5. S.X. LI, T.A. JOHNSON, B.R. WESTPHAL, K.M. GOFF, and R.W. BENEDICT, "Electrorefining Experience for Pyrochemical Processing of Spent EBR-II Driver Fuel," *Proc. Of GLOBAL 2005*, Tsukuba, Japan, Oct.9-13, 2005.
6. K.M. GOFF, A SCHNEIDER, and J.E. BATTLES, "Cadmium Transport Through Molten Salts in the Reprocessing of Spent Fuel for the Integral Fast Reactor," *Nucl. Tech.*, **102**, 331 (1993).
7. ARUNSINGH and B. DAYAL, "A New Inter-Diffusion Technique for Preparing Alloys of Cd-Zr System," *Zeitschrift fur Metallkunde*, **60**, 7, 610 (1969).
8. W. ROSSTEUTSCHER and K. SCHUBERT, "Über einige T-Zn- und T-Cd-Legierungssysteme," *Z. Metallkd.*, **56**, 730 (1965).