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Electrorefining Experience for Pyrochemical Processing of Spent EBR-II Driver Fuel

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ABSTRACT

Pyrochemical processing has been implemented for the treatment of spent fuel from the Experimental Breeder Reactor-II (EBR-II) at Idaho National Laboratory since 1996. This report summarizes technical advancements made in electrorefining of spent EBR-II driver fuel in the Mk-IV electrorefiner since the pyrochemical processing was integrated into the AFCI program in 2002. The significant advancements include improving uranium dissolution and noble metal retention from chopped fuel segments, increasing cathode current efficiency, and achieving co-collection of zirconium along with uranium from the cadmium pool.

KEYWORDS:

Advanced Fuel Cycle Initiative, pyrochemical processing, electrorefining, molten salt, spent fuel, uranium dissolution, zirconium, noble metal fission product retentions,

I. INTRODUCTION

Pyrochemical processing may play an important role in development of next generation nuclear reactors and closed nuclear fuel cycle technology. At the Idaho National Laboratory (INL), a pyrochemical process has been implemented for the treatment of spent fuel from the Experimental Breeder Reactor (EBR-II). A successful demonstration of the technology was performed from 1996 to 1999 for the Department of Energy (DOE) [1]. And now processing of the spent fuel and associated research and development activities have been integrated into DOE's Advanced Fuel Cycle Initiative (AFCI) program since 2002. Electrorefining can be considered to be the signature or central technology for pyrochemical processing. This report summarizes recent experience and results in electrorefining, specifically focusing on the treatment of spent EBR-II driver fuel in the Mark-IV electrorefiner.

II. EQUIPMENT AND PROCESS DESCRIPTIONS

The experiments and results reported here were performed in the Mk-IV electrorefiner (ER). The ER is located in the hot cell of the Fuel

Conditioning Facility at the Materials and Fuels Complex (MFC) of the Idaho National Laboratory.

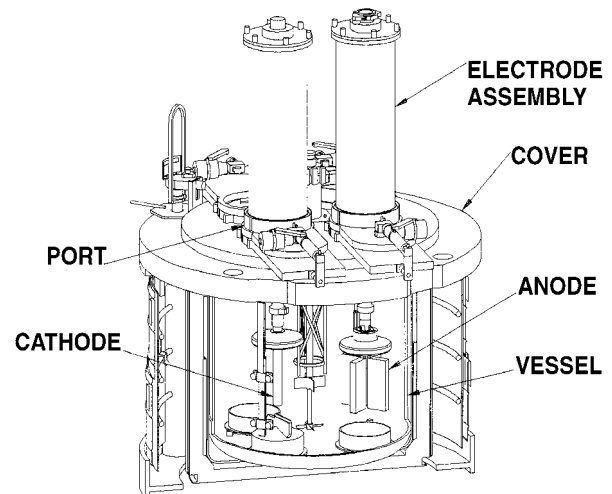


Figure 1. Schematic of Mk-IV electrorefiner

The major components of the ER are illustrated in Figure 1. The ER vessel is made of stainless steel (2.25 Cr-1 Mo) with an inside diameter of 1.0 m and height of 1.0 m. The vessel contains a

nominal 10 cm thick bottom layer of molten cadmium and a 32 cm thick top layer of molten LiCl-KCl eutectic containing <10 wt% UCl_3 . The ER operating temperature is at 500°C. A stirrer is used to continually mix the cadmium, while no mixer is installed in the salt phase. The salt is agitated during the electrorefining process by rotating the cathode and anode assemblies. Four ports on the top of the ER are available for inserting anode and cathode assemblies.

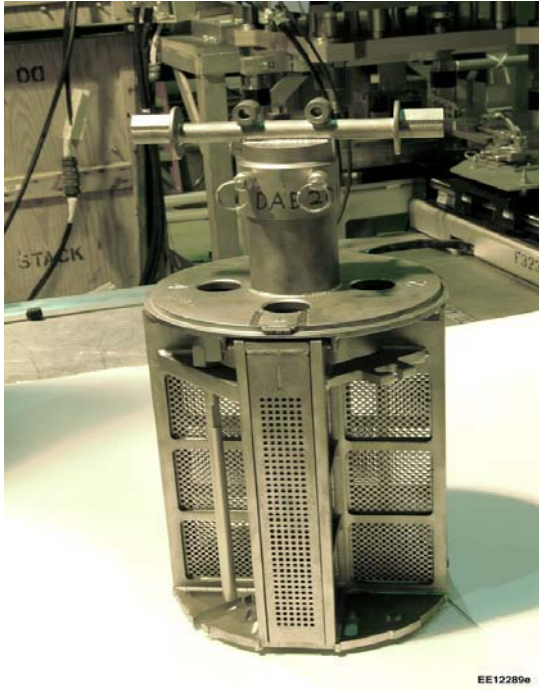


Figure 2. Anode Dissolution Basket

The EBR-II driver fuel is a highly enriched, metallic uranium-zirconium alloy in stainless steel cladding. Sodium metal was placed within each fuel element to serve as a thermal bond between the fuel and cladding in the reactor. The spent driver fuel also contains fission products. Prior to electrorefining, the fuel pins were removed from their respective assemblies, chopped into 0.64 cm long segments, and placed into perforated anode dissolution baskets (Figure 2). Each anode dissolution basket contains the segments from three chopped spent fuel assemblies or 12.3 kg heavy metal. The cathode is a mild steel mandrel, 6.67 cm in diameter, with an active length of approximately 23 cm in the electrolyte. Electrorefining is typically performed by a process called direct transport when uranium is dissolved from an anode basket

and deposited to a solid cathode. Occasionally the cadmium pool is electrically configured as the anode after accumulating uranium metal which dropped from the cathode. Electrorefining of the dissolved uranium from the cadmium pool to a solid cathode is called deposition.

Once the basket loaded with chopped fuel segments is inserted into the molten salt electrolyte, the bond sodium and active metal fission products undergo redox reactions with UCl_3 from the molten salt. Sodium chloride and fission product chlorides are formed, while some of the U is reduced to metallic form. Uranium in the fuel segment is then electrochemically transported from the anode to the cathode. Ideally, zirconium and noble metal fission products are retained within the cladding hulls in the anode baskets. The overall process has been described in more detail elsewhere [1].

III. EXPERIMENTS, OBSERVATIONS, RESULTS, AND DISCUSSIONS

The purpose of the electrorefining is to separate and recover uranium from the other components in spent fuel. To date, approximately 800 kg of spent driver fuel has been processed in the ER. The following describes significant advancements.

1. Extent of Uranium Dissolution from Chopped Fuel Segments

During the EBR-II spent fuel treatment demonstration project (1996 -1999), the goal for the electrorefining of spent driver fuel was to achieve total noble metal retention in the cladding hulls. Achieving a high extent of U dissolution was also considered desirable, but noble metal retention was not sacrificed for the sake of improving U dissolution. The uranium dissolution was reported to be 96 wt% when greater than 85 wt% of noble metal was retained. Under the guidance of the AFCI program, more of an emphasis has been placed on achieving complete uranium dissolution. Mk-IV ER operating parameters have, thus, been adjusted to meet this goal. Table 1 lists dissolution results of spent driver fuel from recent electrorefining runs under the modified operating conditions. The data shown in the table are the weight percentages of elements dissolved from the anode baskets after the electrorefining process. The percentages of the elements dissolved were determined by the ratio of the elements or

Table 1. Uranium and Noble Metal Dissolution from Spent EBR-II Driver Fuel (wt%)

Batch ID	U	La	Ce	Nd	Zr	Tc	Mo	Ru
ERBF005	99.82	100.00	100.00	100.00	87.37	47.18	49.87	52.66
ERBF006	99.50	100.00	100.00	100.00	83.77	10.98	17.82	13.36
ERBF007	99.73	100.00	100.00	100.00	88.69	0.34	17.80	10.64
ERBF008	99.94	99.12	99.86	99.79	97.54	40.23	43.52	49.11
ERBF009	99.82	98.42	99.84	99.93	94.86	44.59	38.54	43.93
ERBF010	99.89	99.34	99.82	99.75	93.01	18.11	23.50	25.42
ERBF011	99.81	100.00	100.00	100.00	74.10	13.48	22.44	17.81
ERBF012	99.68	100.00	100.00	100.00	87.47	13.52	13.01	9.19
ERBF013	99.61	100.00	100.00	100.00	82.88	34.02	34.83	34.91
ERBF014	99.84	100.00	96.52	100.00	94.13	38.12	45.14	43.53
ERBF015	99.53	100.00	100.00	100.00	82.23	10.28	12.44	5.13
ERBF016	99.45	100.00	100.00	100.00	88.15	10.14	8.93	6.36
Average	99.72	99.74	99.67	99.96	87.85	23.42	27.32	26.02
STDV	0.16	0.51	0.99	0.09	6.55	16.20	14.32	17.92

isotope left in the cladding hulls in relation to their original quantities in the feed. The quantity of an element left in the cladding hulls was determined through specific sampling and analytical techniques.

The data in Table 1 indicate that an average 99.7 wt% uranium dissolution has been achieved through adjusting operational parameters. As expected, approximately 88 wt% of Zr was dissolved under the operating conditions to dissolve all the uranium from the fuel [2]. Nevertheless, on average, approximately 77% of Tc, 73% of Mo, and 74% of Ru were retained in the cladding hulls when 88% of Zr was dissolved. The results given in Table I demonstrate that the electrorefining process can dissolve nearly all the uranium from the spent driver fuel while retaining approximately three quarters of noble metal fission products within the cladding hulls. The dissolved Zr can be electrochemically recovered subsequently from the ER. The experimental results of Zr co-collection are discussed in Section III.3 of this report.

2. Current Efficiency

The morphology of uranium product collected on a solid cathode in a high temperature molten salt electrolyte is dendritic in general [3, 4, 5]. The dendritic material is easily dislodged from the

cathode as the rotating mass grows out toward the scrapers located on the interior sidewalls of the ER. This results in low current efficiency for the cathode process. Current efficiency is defined as the ratio of the actual amount of uranium deposited to the theoretical maximum based on time-integrated current (A-h). The average current efficiency observed during the three year demonstration project was approximately 50%.

Significant improvements in current efficiency have been achieved since 2003. The current efficiency has been in the range from 65% to 76% for recent electrorefining runs. In addition, no massive drop of cathode dendrite has been detected during a run, as deduced by monitoring voltage/current data. The system attribute that is believed to be directly tied to the improvement is salt mixing or agitation.

Salt agitation is imperative to an electrorefining process in a molten salt electrolyte [4]. As mentioned previously, the Mk-IV ER does not have a salt mixer installed. However, salt agitation is provided by rotating the anode (5 rpm) and cathode (5 rpm) during a direct transport, and by rotating the cathode only (5 rpm) during a deposition. The formation of loose dendritic deposits, which tended to fall from the cathode and result in low current efficiency, may be caused by inadequate mixing in the salt phase.

Therefore, tests were conducted to improve the salt mixing conditions during deposition runs. Four deposition tests were performed. During each test, two empty anode dissolution baskets were transferred into the ER and rotated in the salt phase at 25rpm to 50 rpm during the electrotransport. The experimental conditions and results are listed in Table 2. The average results of 25 deposition runs, without the extra salt mixing and under otherwise similar conditions, are also listed in Table 2 for comparison. The cathode was rotated at 5 rpm for all the tests.

Table 2. Impact of Salt Mixing on Cathode Current Efficiency

Test No.	1	2	3	4	*DP run average
Basket rpm	25	25	50	50	No salt mixing via basket
Total A-h	2943	2650	2541	2387	2437
Cathode, kg	6.3	4.9	5.4	4.9	3.5
Current efficiency	62%	53%	64%	58%	42%

* 25 deposition runs under the same operating conditions

The effect of salt mixing is readily evident. The average cathode current efficiency was increased by more than 40% through using anode baskets as salt mixers. Rotating the baskets during a deposition run would enhance the mass transfer process in the electrolyte. And a more compact deposit would form, which tends to hold onto the cathode. Subsequently, the cathode current efficiency would increase.

Based on the salt mixing test results, rotation of an anode basket at 50 rpm has been used as a fixed operating parameter for all the direct transport and deposition runs in the Mk-IV ER since 2003. The adhesion of the uranium deposits has expectedly been improved since then. The average current efficiency for direct transport has been increased from 50% (demonstration) to 70%. Figure 3 is a photo of a uranium cathode deposit produced from a recent direct transport run (Batch ERBF016). Consequently, no deposition run has since been required for the ER operations, because no significant amount of uranium dendrites has fallen into the cadmium pool. The electrorefining process has become more stable

and predictable. The ER throughput has been increased as well.



Figure 3. A cathode removed from Mk-IV ER, 10.1 kg

3. Zirconium Co-collection

Zirconium, which is a major component of spent EBR-II driver fuel (U-10Zr alloy) and accounts for 10 wt% of the spent fuel, has complicated chemistry in the electrorefining system. Approximately 88.0 wt% of the Zr in the spent fuel is electrochemically dissolved in order to achieve greater than 99.7 wt% uranium dissolution. A large portion of the dissolved Zr accumulates in the cadmium pool. It is estimated that more than 30 kg of Zr metal have accumulated in the ER since 1996. In order to lower the Zr inventory, experiments were performed in the Mk-IV ER to co-collect zirconium along with uranium.

The experiment involved configuring a mild steel mandrel as the cathode and the Cd pool was configured as the anode, i.e. a deposition run. An Ag/AgCl reference electrode was used to monitor the voltage changes at the salt/Cd interface [2]. Uranium dissolved in the Cd pool was depleted prior to the co-collection experiments. This was verified by reference electrode voltage readings.

The co-collection experiments were performed with a constant current mode. Once the current was energized, the observed voltage (reference electrode reading) at the salt/Cd interface quickly reached to $\sim 0.35V$ above the uranium voltage, and then remained relatively unchanged during the run. This was an indication that zirconium was being electrochemically dissolved from the cadmium pool. The morphology (see Figure 4) of the resulting cathodes indicated that the collected material was a mixture of uranium and zirconium with adhering salt [6]. Four co-collection experiments were conducted. The collected material was combined and run through the cathode processor (CP) and casting furnace (CF). Pin samples were taken to confirm the amount of Zr recovered.

At the cathode processor, due to the Zr content in the material, a higher temperature ($1350^{\circ}C$) and additional depleted uranium were used to assure the consolidation of the electrorefining products into a homogeneous ingot. High salt fractions (>50 wt %) were observed for the high Zr content dendrites. Normal operating conditions were performed at the casting furnace.

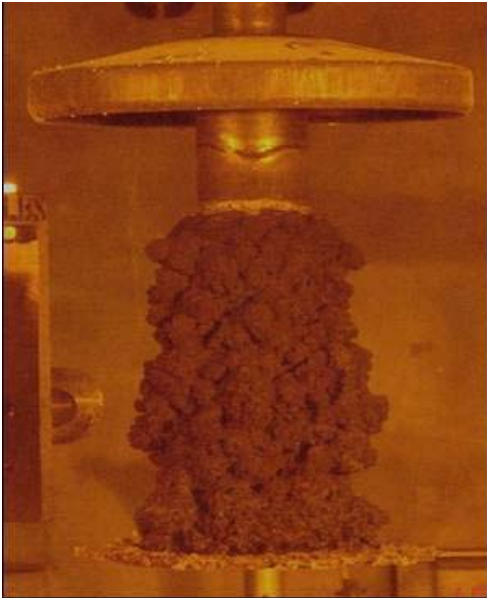


Figure 4. High zirconium content cathode collected by solid cathode

The casting pin sample analysis results indicated that the Zr concentration in the cathode deposit produced by the co-collection tests was up to 14

wt%. For comparison, the cathode deposit produced at normal ER operating conditions, where no Zr ions are presented in the electrolyte, contain 0.43-0.86 wt% of Zr. The experiment results confirmed that electrochemically recovering zirconium together with uranium was feasible in the absence of zirconium ions in the salt prior to the test. An initial Zr concentration in the salt phase by chemical oxidation is not necessary to recover Zr from the Cd pool by co-deposition with uranium.

Mk-IV salt samples were taken after the Zr recovering experiments. Analytical results showed that the salt contained 0.1 wt% Zr and 6.4 wt% U. This was a good indication that uranium was completely depleted and zirconium was being electrochemically transferred from the cadmium pool. It is believed that both Zr^{4+} and Zr^{2+} are stable species and co-exist in molten LiCl-KCl eutectic at $500^{\circ}C$ [7].

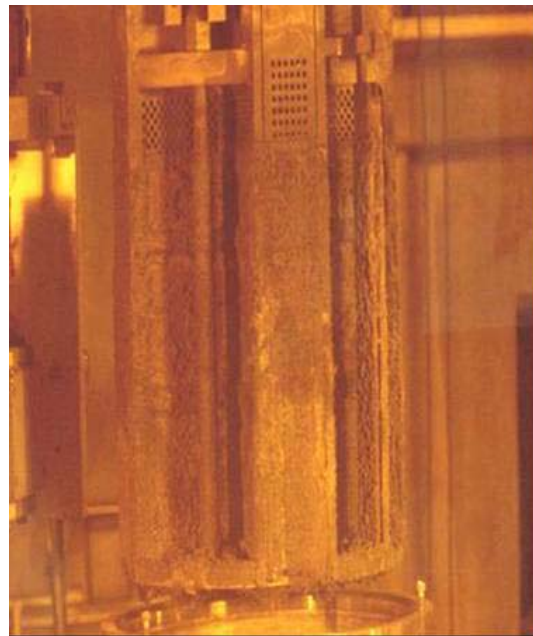
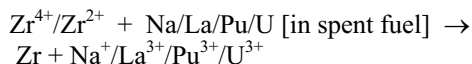


Figure 5. Anode basket loaded with spent fuel segment covered by a metal layer

Directly after taking the post-Zr co-collection salt sample, an anode basket loaded with chopped spent fuel segments (12.3 kg heavy metal) was inserted in the salt phase. The segment-loaded basket was held in the salt for ~ 12 hours and then removed from the electrorefiner.

Figure 5 is a picture taken after the basket was removed from the ER. It is clear that the basket was covered by a layer of metal. Apparently the zirconium in the salt phase reacted with Na, Pu, active metal fission products, or even uranium in the spent fuel by the following redox reaction:



One salt sample was taken after the anode basket was removed. Analysis of the salt indicated that no zirconium remained in the salt, which provided additional confirmation that all of the zirconium ions in the salt phase were reduced to zirconium metal by the active elements in the spent fuel. The reduced Zr metal chemically deposited on the surface of the basket.

IV. SUMMARY

To date, 800 kg of sodium-bonded and highly enriched spent EBR-II driver fuel has been processed in the Mk-IV ER, and research and development continues in an effort to improve the process. U dissolution of greater than 99.7 wt% has been demonstrated, compared to 96 wt% in early demonstration tests. The current efficiencies for both direct transport and deposition have been significantly improved (from 50% to 70% for direct transport and from 42% to 61% for deposition). Zirconium has been successfully co-collected with U on the cathode (up to 14 wt% Zr in the cathode deposit). When combined, these results support the claim that pyroprocessing can be an efficient technology for closing the nuclear fuel cycle.

ACKNOWLEDGEMENT

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