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PYROPROCESSING OF FAST FLUX TEST FACILITY NUCLEAR FUEL

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Used nuclear fuel from the Fast Flux Test Facility (FFTF) was recently transferred to the Idaho National Laboratory and processed by pyroprocessing in the Fuel Conditioning Facility. Approximately 213 kg of uranium from sodium-bonded metallic FFTF fuel was processed over a one year period with the equipment previously used for the processing of EBR-II used fuel. The peak burnup of the FFTF fuel ranged from 10 to 15 atom% for the 900+ chopped elements processed. Fifteen low-enriched uranium ingots were cast following the electrorefining and distillation operations to recover approximately 192 kg of uranium. A material balance on the primary fuel constituents, uranium and zirconium, during the FFTF campaign will be presented along with a brief description of operating parameters. Recoverable uranium during the pyroprocessing of FFTF nuclear fuel was greater than 95% while the purity of the final electrorefined uranium products exceeded 99%.

I. INTRODUCTION

Following the successful demonstration of irradiated testing in the Fast Flux Test Facility (FFTF) in the late 1980's with sodium-bonded U-10Zr metallic fuel¹, the fuel was recently transferred from FFTF to the Idaho National Laboratory for pyroprocessing in the Fuel Conditioning Facility (FCF). The inventory of used fuel included six intact assemblies (MFF-2, MFF-3, MFF-4, MFF-5, MFF-6, and MFF-8A) and over 200 loose elements from various assemblies (IFR-1, IFR-1B, IFR-1C, and MFF-1). Of the total 1200+ elements, over 900 were treated by pyroprocessing while the balance was retained for post-irradiation examinations and characterizations.

Pyroprocessing includes disassembly and removal of fuel elements, fuel chopping, electrorefining, cathode processing, and casting to separate transuranics and fission products from recovered uranium²⁻³. In addition to recovery, the bond sodium is neutralized by the electrorefining salt and the uranium products are down-

blended to low-enriched uranium during the casting step. During electrorefining, the sodium, fission products, and transuranics are separated as the fuel is oxidized (dissolved) at an anode and refined uranium is reduced (deposited) on a cathode⁴. The highly dendritic electrorefined cathode products with adhering salt require a distillation operation for removal of the salt and consolidation of uranium at a temperature of 1200°C under vacuum conditions⁵. The consolidated cathode processor ingot is diluted with depleted or natural uranium to an enrichment of less than 20% U-235 and sampled at the casting furnace while molten for chemical analyses.

The scope of the paper is to summarize the pyroprocessing of FFTF nuclear fuel by performing a material balance of select constituents on the operations and provide recovery and purity information during the processing of FFTF fuel. Starting with the incoming composition of the FFTF fuel, material control and accountancy is maintained throughout the process via sampling efforts, mass measurements, volume calibrations, and process knowledge where applicable.

II. OPERATIONAL

Since electrorefining and cathode processing are the primary separational steps in the pyroprocess, a brief description of their operating conditions follows. Equipment descriptions, schematics, and more detailed operating parameters for the electrorefiner and cathode processor operations can be found elsewhere⁴⁻⁵. The element chopping and casting operations are the head-end and product preparation steps, respectively, in the process, and as such their operating conditions are not considered significant to this discussion.

For electrorefining, 24 batches (fuel basket loadings) of FFTF used fuel were processed in the Mk-IV electrorefiner (ER). The following process steps were performed per batch:

- Direct transport wherein uranium is transported from the fuel basket to the mandrel,
- Anodic dissolution wherein uranium is transported from the fuel basket to the vessel,
- Deposition wherein uranium is transported from the vessel to the mandrel,
- Cathode stripping wherein uranium is transported from the mandrel to the vessel, and
- CdCl_2 addition wherein pellets of CdCl_2 are added to the electrolyte to react with available uranium metal and replace UCl_3 that reacts with active metals (bond sodium, transuranics, and fission products from Group I and II and the lanthanides).

A typical process sequence during electrorefining is multiple direct transports, followed by anodic dissolution and depositions, then CdCl_2 addition, and finally cathode stripping. Cathodes are harvested following the direct transport and deposition operations. Typical photographs of harvested cathodes are shown in Figures 1 and 2 for direct transport and deposition, respectively.

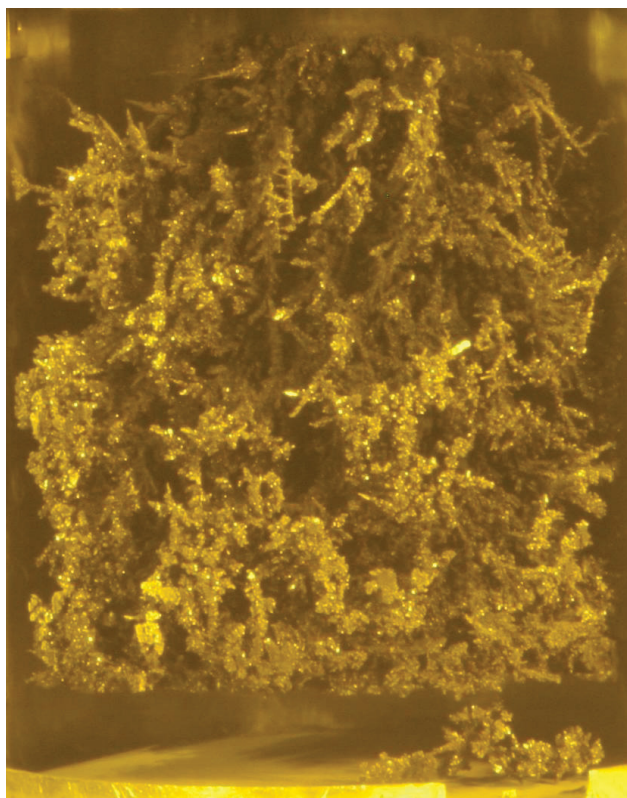


Fig. 1. Photograph of typical direct transport cathode



Fig. 2. Photograph of typical deposition cathode

For the sixty-seven harvested cathodes from electrorefining, sixteen distillation operations were performed at the cathode processor by combining cathodes from like or adjacent batches. Distillation conditions, for the most part, were consistent; heating to 1200°C or above under a vacuum of less than 10 Torr. Following an initial evacuation and isolation period to minimize cadmium migration, a re-evacuation of the vacuum system is performed for salt distillation. A temperature hold of approximately one hour is performed at 1100°C to assure complete salt removal from the metallic uranium. Slight variations to the hold times (up to three hours) at 1100°C and the maximum temperatures (up to 1350°C) were performed during the processing of FFTF fuel to determine their effect on radiation readings of the uranium products. The radiation measurements are not completed and the results are pending. The sixteen cathode processor ingots were cast into fifteen uranium products and sampled for chemical analyses.

III. RESULTS

Shown in Figure 3 is a simplified diagram of material flow during the pyroprocessing of FFTF nuclear fuel. A more detailed description of the process flow streams and

mass balance area are given elsewhere⁶. Briefly, fuel elements or feed are sized at the element chopper (EC) for electrorefining (ER), cathode processing (CP), and casting (CF) to produce uranium products. Following electrorefining, cladding hulls with adhering salt and residual fuel are removed from the anode baskets in preparation for metal waste operations⁷. Dross streams are produced from both the cathode processing and casting operations as a result of a uranium reaction with the crucible materials, either zirconia or yttria, depending on the operation, respectively.

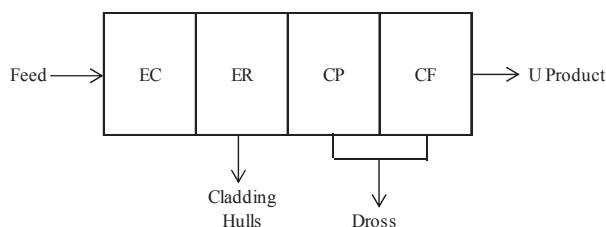


Fig. 3. Simplified material flow during pyroprocessing

Since the two primary constituents in used FFTF fuel are uranium and zirconium (U-10Zr alloy), a mass balance of these elements has been performed during the pyroprocessing operations. Presented in Table 1 are the process streams shown in Figure 3 with either an X or a Y to indicate known or unknown values, respectively. Although modeled, the feed stream is well defined as confirmed by previous sampling⁸. The amount of uranium and zirconium in the cladding hulls following electrorefining is unknown and justifies the processing of metal waste to quantify these constituents. Also unknown is zirconium in the electrorefiner since it is noble to the salt and should report to the cadmium pool although it is found throughout the electrorefiner⁹. On the other hand, uranium in the electrorefiner is monitored by periodic salt sampling and is thus, well known. The cathode processor and casting dross streams are not routinely sampled but have been established from process knowledge of random samples. Every uranium product from pyroprocessing is routinely sampled at multiple locations and is thus, compositionally, well characterized, especially considering the homogeneity of the molten metal.

Table 1. Mass balance data depicting known (X) and unknown (Y) values.

Metal	Feed	Cladding Hulls	Electro- refiner	CP/CF Drosses	Uranium Product
U	X	Y	X	X	X
Zr	X	Y	Y		X

Values for the mass balance of uranium and zirconium are shown in Table 2. The natural uranium added for dilution of the FFTF fuel to less than 20% enrichment has been excluded from the table to allow a more direct calculation of uranium recovery. The unknown uranium value for cladding hulls was determined by difference of the other known uranium values. At least 75% of the uranium associated with the cladding hulls is residual metal as opposed to a salt species based on process knowledge of adhering salt and its composition. Thus, the amount of uranium metal in the cladding hulls is significant and reaffirms the need to process metal waste in order to completely account for fissile materials in the process. An assumption that 80% of the zirconium is retained in the cladding hulls was made based on previous research to allow the estimation of zirconium in the electrorefiner⁴. Again, this will be confirmed by metal waste processing.

Table 2. Mass balance values for the streams of interest related to uranium and zirconium.

	Feed	Cladding Hulls	Electro- refiner	CP/CF Drosses	Uranium Product
Metal	(kg)	(kg)	(kg)	(kg)	(kg)
U	212.6	10.2	5.6	4.5	192.2
Zr	29.8	23.8	4.3		1.7

The recovery of uranium as products was greater than 90%, by mass, and in excess of 95% if salt associated with the electrorefiner and hulls is included since the uranium in the salt as UCl_3 can easily be converted to metallic uranium. The amount of uranium associated with the dross streams is just over 2% of the total, slightly lower than earlier operations due to the use of ceramic-lined crucibles¹⁰. In order to retain a significant amount (~80%) of zirconium in the cladding hulls for metal waste, a minor amount of uranium must also be associated with the hulls. Reducing the uranium retention in the hulls would come with the consequence of reducing the zirconium retention in the hulls, i.e. the addition of trim zirconium for metal waste operations would be necessary. Approximately 6% of the total incoming zirconium ends up in the products due to electrochemical similarities with uranium.

The average zirconium content of the uranium products during the processing of FFTF fuel was 0.86 wt. % with a low of 0.09 wt. % and a high of 9.03 wt. %. Besides zirconium, the products contain less than 1000 ppm of other impurities, primarily from processing equipment. Steel constituents (Fe, Cr, and Mn), oxygen, carbon, and silicon are the typical process impurities in the uranium products. Fission product impurities are

generally too low for detection while the actinides, particularly plutonium, may be problematic if disposal or hands-on operations are desired of the products. However, pyroprocessing, as originally designed, was never intended to produce products for disposal nor be handled outside of a hot cell. In fact, the alloying of actinides with the uranium products for recycle was the intended goal of the Integral Fast Reactor program. It should also be noted that although a chlorine analyses is not performed on the uranium products, the indirect measurement for salt species indicates very little (<100 ppm) chlorine would be present in the uranium products. Thus, considering the zirconium and other impurity contents, the products are greater than 99 wt. % uranium.

An interesting observation was noted when the zirconium content of the uranium products was correlated with the salt fraction from distillation at the cathode processing, see Figure 4. As the zirconium concentrations increase, so do the salt fractions at the cathode processor. The benefits of this observation are that the isotopic uranium enrichment can be better controlled at the casting furnace and if high zirconium is expected, the casting temperature can be increased accordingly to ensure sufficient temperature for isotopic mixing.

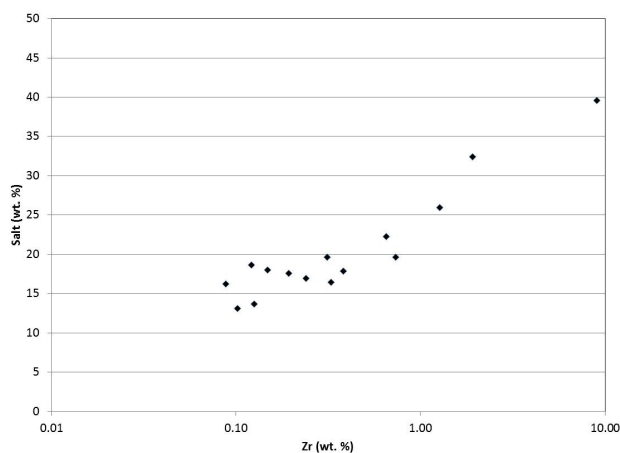


Fig. 4. Correlation of zirconium content of uranium products with salt fraction from cathode processor

IV. CONCLUSIONS

Brief operating conditions for the two key pieces of equipment, electrorefiner and cathode processor, for the pyrometallurgical processing of FFTF fuel have been presented along with a mass balance of the primary constituents in the uranium products. The recovery and purity of the uranium products has also been discussed in context with the fuel matrix zirconium.

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REFERENCES

1. A.L. PITNER and R.B. BAKER, "Metal Fuel Test Program in the FFTF," *J. Nucl. Matl.* **204**, 124 (1993).
2. C.E. TILL and Y.I. CHANG, *Plentiful Energy – The Story of the Integral Fast Reactor*, CreateSpace, Charleston, SC (2012).
3. Y.I. CHANG, "The Integral Fast Reactor," *Nucl. Tech.*, **88**, 129 (1990).
4. S.X. LI and M.F. SIMPSON, "Anodic Process of Electrorefining Spent Driver Fuel in Molten LiCl-KCl-UCl₃/Cd System," *Min. Metall. Process.*, **22**, 193 (2005).
5. B.R. WESTPHAL, K.C. MARSDEN, J.C. PRICE, and D.V. LAUG, "On the Development of a Distillation Process for the Electrometallurgical Treatment of Irradiated Spent Nuclear Fuel," *Nucl. Eng. Tech.*, **40**, 163 (2008).
6. D. VADEN and G.L. FREDRICKSON, "Material Control and Accountability Experience at the Fuel Conditioning Facility," *Proc. Global 2007*, Boise, ID, September 2007, p. 170, ANS (2007).
7. B.R. WESTPHAL et al., "Characterization of Irradiated Metal Waste from the Pyrometallurgical Treatment of Used EBR-II Fuel," *Met. Trans. A.*, pending publication.
8. R.D. MCKNIGHT, B.J. TOPPEL, and J.R. KRSUL, "Characterization of Spent EBR-II Driver Fuel," *Proc. DOE Spent Nucl. Fuel Fissile Matl. Mgt.*, Charleston, SC, September 1998, p. 67, ANS (1998).
9. T.S. YOO et al., "Analysis of Cadmium in Undissolved Anode Materials of Mark-IV Electrorefiner," these proceedings.
10. B.R. WESTPHAL, K.C. MARSDEN, and J.C. PRICE, "Development of a Ceramic-Lined Crucible for the Separation of Salt from Uranium," *Met. Trans. A*, **40A**, 2861 (2009).