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Fuel Conditioning Facility Electrorefiner Model Predictions versus Measurements

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Abstract: Electrometallurgical treatment of spent nuclear fuel is performed in the Fuel Conditioning Facility (FCF) at the Idaho National Laboratory (INL) by electrochemically separating uranium from the fission products and structural materials in a vessel called an electrorefiner (ER). To continue processing without waiting for sample analyses to assess process conditions, an ER process model predicts the composition of the ER inventory and effluent streams via multi-component, multi-phase chemical equilibrium for chemical reactions and a numerical solution to differential equations for electro-chemical transport. The results of the process model were compared to the electrorefiner measured data.

Keywords: Electrochemical processing, electrorefiner, process modeling

INTRODUCTION

The Fuel Conditioning Facility (FCF) at the Idaho National Laboratory (INL) treats spent nuclear fuel from the Experimental Breeder Reactor-II (EBR-II) via an electro-chemical process. Uranium in the spent fuel is separated from the fission products and structural materials (cesium, sodium, steel cladding, etc.) in an electrorefiner (ER) (1,2). Having process knowledge of the ER inventory prior to sample analysis is essential for timely operations and material accountability. A way to obtain this knowledge is to predict the mass and composition of the ER inventory and the composition of the effluent streams without waiting for sampling and analysis, which are time-consuming for FCF and the Analytical

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Laboratory. To serve this purpose, an ER process model was developed to perform these predictions for the ER inventory and its effluent streams using multi-component, multi-phase chemical equilibrium and electrochemical transport from the anode(s) to the cathode(s). The chemical equilibrium portion of the model was discussed in a previous article (3). This paper covers mostly the electrochemical transport portion of the process model in addition to the modeling of the isotopic mixing that occurs during chemical equilibrium and electrochemical transport. Comparing the predicted and measured data is an indication of how well the ER process model mimics reality based on the measured data.

EXPERIMENTAL SYSTEM

Figure 1 shows a schematic of the electro-chemical spent fuel treatment process currently operating in the Fuel Conditioning Facility at Idaho National Laboratory. For processing EBR-II spent fuel, it uses two element choppers, two electrorefiners, one cathode processor, and one casting furnace. The equipment details are briefly described below.

Element Choppers

The element choppers (EC) chop the lower section, or fuel region, of incoming fuel elements into small segments (6.3 mm [0.25 inches] long

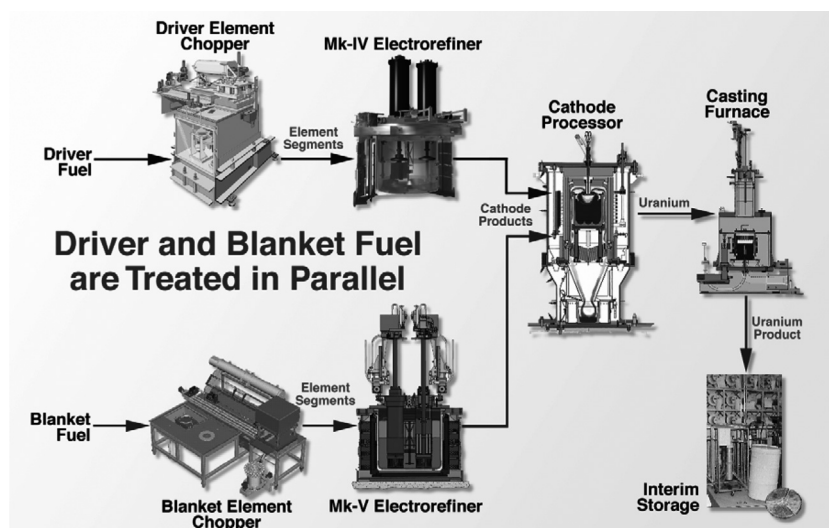


Figure 1. Electro-chemical processing at the fuel conditioning facility.

for driver fuel and 18.3 mm [0.72 inches] long for blanket fuel) for processing in the electrorefiners. The upper section, called the plenum, does not contain fuel and is placed in a container, called a can, for processing as metal waste. The mass and composition of the fuel elements entering the element chopper were modeled values from the Physics Analysis Database (PADB) (4). The PADB was derived from reactor codes and irradiation history of nuclear fuel used in the EBR-II to predict an axial profile of nuclides in the individual fuel elements. During element chopping, a small portion of the fuel segments accumulates in the EC inventory with each chop. The EC process model assigns a modeled mass and composition to the EC inventory, anode baskets, segment samples, fission gases released to the argon cell, and the plenum can during the chopping operation. Measured weights were obtained for the anode baskets and the can holding the plenums. The EC process model then compares the modeled weight to the measured weight for the anode baskets and the plenum can. The modeled mass and composition of the anode baskets and plenum can are scaled to equal their respective measured masses. The difference between the measured mass and modeled mass is placed in the EC inventory. Upon exiting the EC, the anode baskets and plenum have both a measured total mass and a modeled composition.

Electrorefiners

The electrorefiners take advantage of chemical and electro-chemical differences between elements to separate uranium and transuranics from the steel cladding and fission products. Both electrorefiners are steel vessels one meter tall with a one-meter inside diameter maintained at 500°C. The driver electrorefiner contains around 440 kg of molten salt and 530 kg of liquid cadmium. The blanket electrorefiner contains around 610 kg of molten salt. The molten salt in both electrorefiners is mostly LiCl-KCl near its eutectic composition of 45 wt% LiCl.

Cathode Processor

The cathode processor (CP) employs high temperature vacuum distillation to separate the salt from the metal in the product harvested from the mandrels exiting the electrorefiner. Adding depleted uranium lowers the uranium enrichment to reduce its attractiveness level, a nuclear non-proliferation term. The consolidated metal ingot then travels downstream to the casting furnace for further processing. The amount of salt distilled in the CP determines the fraction of distillate or the salt fraction of the material exiting the electrorefiner (ER). The electrorefiner process model

uses the measured salt fraction to adjust the salt-metal composition of material leaving the ER.

Casting Furnace

The casting furnace (CF) is another high temperature vacuum furnace that uses quartz-tube molds to injection cast metal sample pins. One or two metal pins were cast for sample analysis with each batch of product. Adding depleted uranium in the CF lowers the uranium enrichment to produce a low enriched uranium (LEU) ingot.

ELECTROREFINER PROCESS MODEL

The ER process model tracks both chemical reactions between the salt and metal phases and electro-chemical transport from the anode(s) to the cathode(s). For the chemical reactions, the process model uses the stoichiometric method (5) to minimize the total Gibbs free energy by adjusting the extent of reaction ($d\epsilon_r$) incrementally (e.g., Newton-Raphson) for each chemical reaction r and using the ν_{er} terms in the stoichiometric matrix \mathbf{V} to determine the n_e values that minimize G^t , as shown in Equation 1.

$$\begin{aligned} &\text{Determine } \delta\epsilon_r \text{ from } \left(\frac{\partial^2 G^t}{\partial \epsilon_r^2} \right)_{T,P} \cdot \delta\epsilon_r = - \left(\frac{\partial G^t}{\partial \epsilon_r} \right)_{T,P} \text{ to obtain} \\ &\left(\frac{\partial G^t}{\partial \epsilon_r} \right)_{T,P} = \sum_a^A \sum_e^E (\nu_{ear} \cdot \mu_{ea}) = 0 \quad r = 1, 2, \dots, R \text{ reactions} \\ &\text{where } n_{ea} = n_{ea} + dn_{ea} = n_{ea} + \sum_r (\nu_{ear} \cdot \delta\epsilon_r) \end{aligned} \quad (1)$$

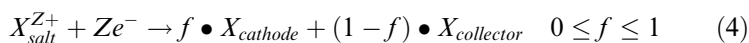
For a chemical reaction in the form $\nu_a A + \nu_b B \leftrightarrow \nu_c C + \nu_d D$, the upper-case letters are the chemical species involved in the chemical reaction and the ν terms are the stoichiometric coefficients that balance the chemical reaction. For multiple reactions occurring in a system, the stoichiometric coefficients form the stoichiometric matrix \mathbf{V} with a sign convention where ν_{er} is negative for reactants and positive for products.

For the isotopic exchange during chemical reactions, Equation 1 determines dn_{ez} , the change in moles of element n_{ez} due to chemical reaction. Because isotopes with the same atomic number behave the same chemically, isotopic exchange during chemical reaction is shown in Equation 2.

$$dI_{iez} = \frac{I_{iz}(\text{mass})}{n_{ez}(\text{moles})} dn_{ez} \quad \begin{array}{ll} i = 1, 2, \dots, I \text{ isotopes of element } e \\ e = 1, 2, \dots, E \text{ elements} \\ \alpha = 1, 2, \dots, \Pi \text{ phases} \end{array} \quad (2)$$

In Equation 2, dI_{iez} is the change in mass of isotope i with the same atomic number as element e in phase α .

For the electro-chemical transport, the ER process model performs numerical integration of a simple differential equation that represents oxidation from the anode to the salt and reduction from the salt to the cathode. The oxidation and reduction reactions for metal X with valance Z are shown in Equations 3 and 4, respectively.



Which metals electro-transport depends on the potential applied between the anode and the cathode. The potential is set to transport uranium and sometimes zirconium. Metals such as iron, nickel, and chromium will not transport unless the potential is set to a value to transport those metals. The X in Equation 4 represents only the metals that electro-chemically transport. Material reducing at the cathode adheres to the cathode or falls into the cadmium pool (driver ER) or to the product collector (blanket ER). The factor f in Equation 4 represents the fraction of material adhering to the cathode, or sticking coefficient. The process model determines the sticking coefficient via a Simplex algorithm using the integrated current, measured cathode mass and measured cathode salt fraction. The mass balance equations representing electro-chemical transport are derived from the general mass balance equation shown in Equation 5.

$$\text{accumulation} = \text{in} - \text{out} + \text{generation} - \text{destruction} \quad (5)$$

In Equation 5, accumulation is the change in mass per amp-hour in a particular container or location. The *in* term is the mass per amp-hour entering the container or location. The *out* term is the mass per amp-hour exiting the container or location. If Equation 5 was used for fission products, the generation and destruction terms represent the generation and destruction, respectively, of nuclides due to radioactive decay. Ignoring the generation and destruction terms for now, the mass balance equations for the containers undergoing electro-chemical transport are shown in Table 1, where ε represents the amp-hours passed during electro-transport. The term M represents the mass of material undergoing electro-chemical transfer in a container or location. The term A represents

Table 1. Electro-chemical transport equations

Container or location	Change in mass	Change in amp-hours
Anode	$\frac{dM_a}{d\varepsilon} = -\left(\frac{M_a}{A_a}\right)$	$\frac{dA_a}{d\varepsilon} = -1$
Electrolyte	$\frac{dM_e}{d\varepsilon} = \left(\frac{M_a}{A_a}\right) - \left(\frac{M_e}{A_e}\right)$	$\frac{dA_e}{d\varepsilon} = 0$
Cathode	$\frac{dM_c}{d\varepsilon} = f_c \left(\frac{M_e}{A_e}\right)$	$\frac{dA_c}{d\varepsilon} = f_c$
Product collector or Cadmium pool	$\frac{dM_p}{d\varepsilon} = (1 - f_c) \times \left(\frac{M_e}{A_e}\right)$	$\frac{dA_p}{d\varepsilon} = 1 - f_c$

the amp-hours required to transfer all the material undergoing electro-transport from the container. The subscripts *a*, *e*, *c*, and *p* represent the anode, electrolyte, cathode, and product collector/cadmium pool, respectively. The expression (*M_i/A_i*) represents the rate material is entering or leaving a phase per amp-hour passed. To maintain the charge balance in the electrolyte, the integrated current or amp-hours for oxidation equals the integrated current or amp-hours for reduction, which means the change in amp-hours in the electrolyte is zero, as shown in Table 1. The process model performs a numerical integration of the equations listed in Table 1. For isotopic exchange during electro-transport, the numerator of the (*M_i/A_i*) term is the mass of the isotope, and the denominator still represents the amp-hours required to transfer all the material undergoing electro-transport from the container.

RESULTS

Using the known or measured mass of input and output streams, and the measured salt fractions from the cathode processor runs, the ER process model predicted the volume and composition of the ER inventory and the composition of the output streams. Level probes and volume calibration equations determined the measured volume in the electrorefiners. Samples taken from the electrorefiners were analyzed to measure the composition in the electrorefiners. This paper discusses the predicted volume and composition of the ER inventory to the measured volume and composition. The effluent streams predictions were not compared to the measurements because the measured mass and measured salt fractions of the effluent streams were used in the process model to predict the ER inventory and composition.

Figure 2 compares the predicted volumes to the measured volumes in the two FCF electrorefiners. The relative percent deviation (RPD) of the predicted value from the measured value was used to determine the accuracy of the ER process model. For the driver ER cadmium volume, the average RPD is 16.23% with a standard deviation of 7.50%. This positive bias is due to cadmium vapor escaping from the driver ER during processing, for which the ER process model does not compensate. For the driver ER salt, the average RPD is 2.24% with a standard deviation of 1.80%. Places to check are the anode baskets leaving the ER with adhering salt. If more salt is leaving via the anode baskets than predicted, then the predicted salt volume would be higher than the measured salt volume. For the blanket ER salt, the average RPD is -4.09% with a standard deviation of 4.21%. A possible explanation for this deviation pertains to the removal of uranium product from a blanket product collector (BPC). When harvesting a uranium product from a BPC, not all of the material is removed. The BPC returns to the blanket ER for more processing. The amount of salt in this BPC holdup is unknown. After several blanket ER runs, the BPC holdup has grown to a significant amount requiring removal of the holdup using a bake-out oven or kiln. This removed holdup material is sent to the cathode processor, which determines the salt fraction of the BPC holdup at the blanket ER operation prior to BPC holdup removal. More work is necessary in this area to mitigate the impact of the BPC holdup on the ER process model.

Figures 3 and 4 compare the modeled concentrations of uranium, plutonium, and sodium to their respective measured concentrations in the driver ER salt and blanket ER salt, respectively. The ER process model correctly predicts the accumulation of plutonium and sodium in

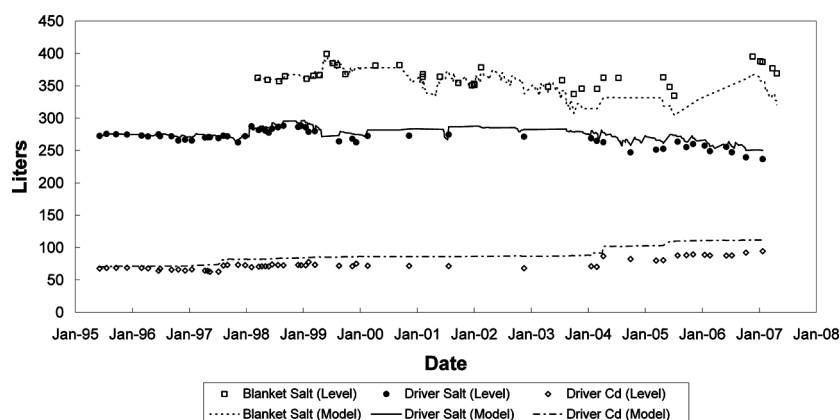


Figure 2. Electrorefiner volume-modeled versus measured.

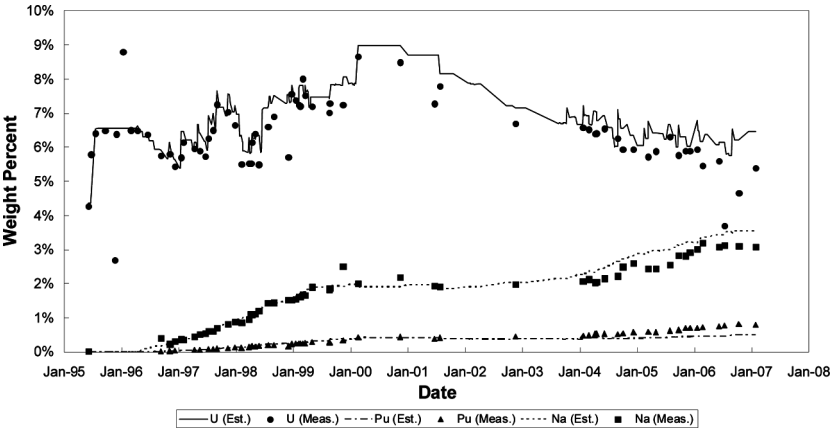


Figure 3. Driver electrorefiner salt composition—modeled versus measured.

the salt as fuel is processed. An explanation of the deviations from measured values could be the element and blanket chopper models. More work is necessary to study the chopper model and the mass and composition of its effluent streams entering the electrorefiners.

For modeling isotopic mixing, depleted uranium at an enrichment of 0.2% (0.2 atoms of ²³⁵U per 100 atoms of uranium) was initially loaded into the driver electrorefiner. As driver fuel with an enrichment of approximately 63% was processed in the ER, the salt enrichment increased to a steady state value around 63%. When blanket fuel with an enrichment of 0.2% ²³⁵U was processed, the salt enrichment decreased to around 10%. As driver fuel and

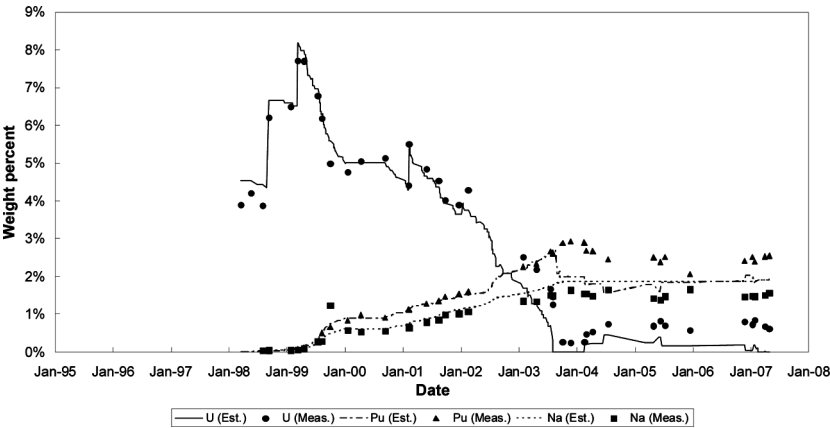


Figure 4. Blanket electrorefiner salt composition—modeled versus measured.

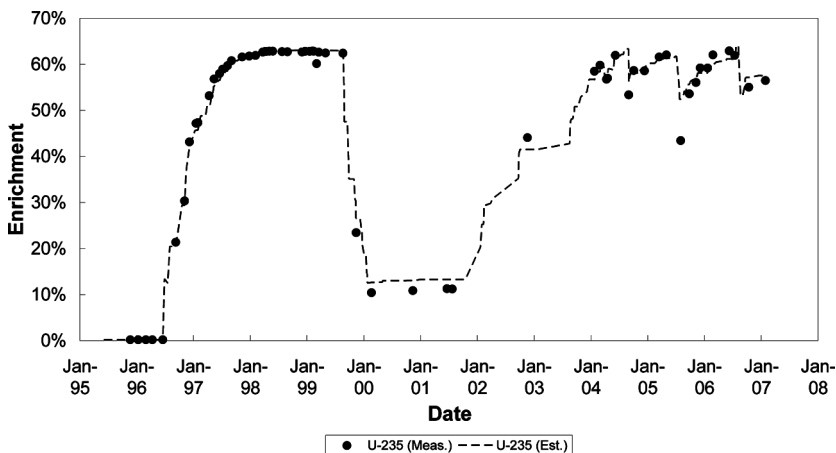


Figure 5. Driver electrorefiner salt enrichment—modeled versus measured.

blanket fuel were periodically processed in the driver ER, numerical integration of the electro-chemical transport algorithm predicted the change in enrichment, as shown in Fig. 5.

Figure 6 is a comparison of the modeled and measured ^{235}U enrichment in the blanket electrorefiner. Even though the blanket electrorefiner

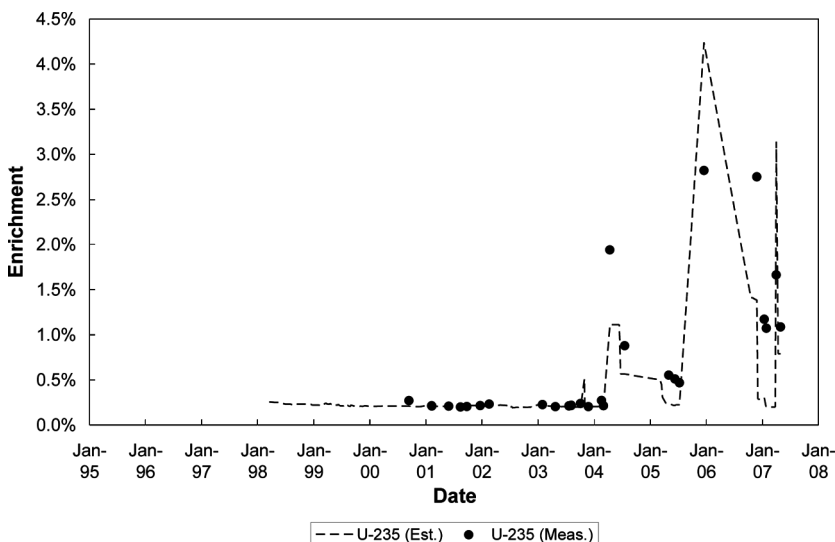


Figure 6. Blanket electrorefiner salt enrichment—modeled versus measured.

only processed fuel with a 0.2% enrichment, the process model and analysis of salt samples produced enrichments greater than 0.2%. The reason for this is related to the cathode processor, which processes cathodes from both the driver and blanket electrorefiners. When a driver cathode is processed in the CP, the condensate is returned to the driver ER. When a blanket cathode is processed in the CP, that condensate is returned to the blanket electrorefiner. Salt holdup in the CP from processing a driver cathode will enrich the condensate in a subsequent CP blanket processing operation. That condensate returned to the blanket electrorefiner will increase its enrichment. Work is required to improve the CP process model to handle cross-contamination of driver and blanket cathode processing in the cathode processor. The impact of driver condensate tainted with blanket salt is insignificant compared to the impact of blanket condensate tainted with driver salt.

CONCLUSIONS

Predicting the electrorefiner inventory allows for continuing spent fuel treatment without waiting for sample analysis. The ER process model is adequate for predicting the composition of the electrorefiner inventories and effluent streams to allow such processing to continue. Improving the ER process model requires an investigation of individual unit operation models (e.g., choppers and cathode processor). It also requires mitigating the accumulation of material during processing having no known composition between ER operations (e.g., blanket product collectors). Work is continuing to improve the electro-transport algorithm. Improving the cathode processor process model would help better predict the enrichment in the blanket electrorefiner.

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