FY-16 Technology Gap Study Technical Report: Analysis of Undissolved Anode Materials of Mark-IV Electrorefiner

Fuel Cycle Research & Development

Prepared for U.S. Department of Energy
Material Recovery and Waste Form Development
(MRWFD) Campaign

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SUMMARY

The Mark-IV electrorefiner contains an electrolyte/molten cadmium system for refining uranium electrochemically. Typically, the anode batch of the Mark-IV electrorefiner consists of the chopped sodium-bonded metallic driver fuels, which have been primarily U-10Zr binary fuels. The undissolved anode materials after electrorefining has been sampled and submitted for chemical analysis. The estimation of the undissolved anode materials based on individual chemical analysis results has been challenging due to inherently high sampling errors associated with heterogeneous undissolved material compositions. Investigation of chemical analysis data as a whole reveals noticeable trends in the compositions of the primary phases and materials. Based upon this observation, an empirical model is proposed in explaining the mass of the undissolved anode materials.

This report fulfills the Level 3 Milestone No. M3FT-17IN030106024 titled, “FY16 Technology Gap Study” within Work Package No. FT-17IN03010602 titled, Technology Gap Study - INL" (Rev. 1).

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ACRONYMS

ANL	Argonne National Laboratory
ARMTE	Adjusted Relative Mass To Explain
EBR-II	Experimental Breeder Reactor II
ER	Electrorefiner
FCF	Fuel Conditioning Facility
FCR&D	Fuel Cycle Research and Development
FY	Fiscal Year
HFEF	Hot Fuel Experiment Facility
INL	Idaho National Laboratory
Mk-IV	Mark-IV
MRWFD	Material Recovery and Waste Form Development
MTE	Mass To Explain
RMTE	Relative Mass To Explain

FCR&D MRWFD
Technology Gap Study Technical Report: Analysis of Undissolved Anode Materials of Mark-IV Electrorefiner

1. INTRODUCTION

The EBR-II is a sodium cooled fast reactor developed at ANL [Chang 1989; Tomczuk et.al. 1992]. The used fuels from the EBR-II are currently being treated in the FCF at the INL [Benedict and McFarlane 1998]. 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 LiC1-KCl eutectic with approximately 5 wt% UCl_3. However, at present, after having treated approximately 1.3 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 UCl_3 concentration, which is periodically replenished. The Mk-IV ER operating temperature is typically 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.

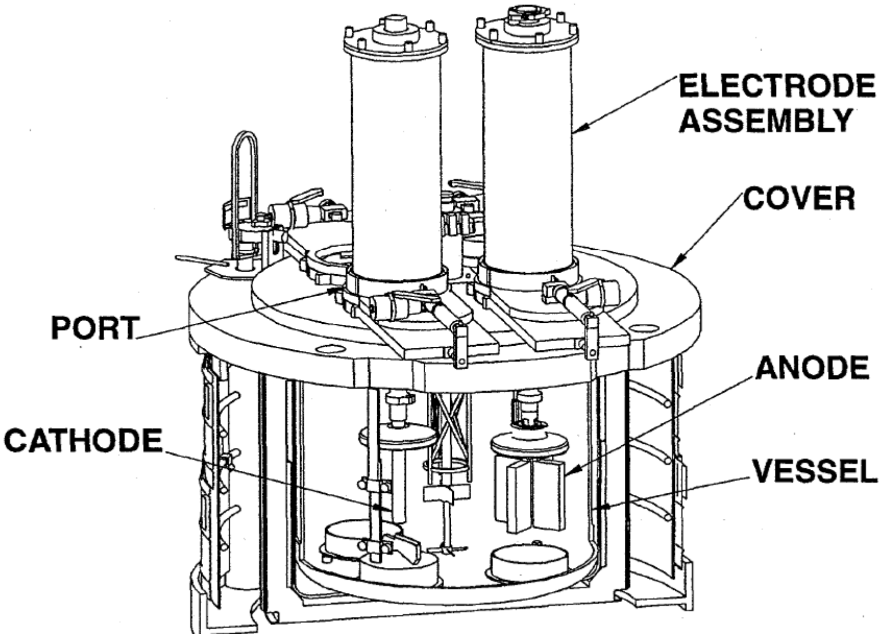

Figure 1: The Mk-IV electrorefiner schematic

The stainless steel anode baskets hold the chopped spent 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 reports to the electrolyte. Noble metals are mostly retained in the cladding hulls. Varying quantities of Zr are retained in the cladding hulls depending on the operational conditions of the Mk-IV ER.

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.

Since 2000, a new mission, called inventory operation, 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. By the end of 2006, the inventory operation processed 32 batches. 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 [Li et.al. 2005] 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.

Throughout these operations, 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 undissolved fuels, stainless steel cladding, and adhering electrolyte. A couple of hulls are retrieved for chemical analysis and used for estimating the composition of the entire undissolved anode materials. The mass balance attempt based on this practice of estimating the undissolved anode materials has been a challenge due to inherently high sampling errors associated with heterogeneous undissolved material compositions [Yacout et.al. 1999].

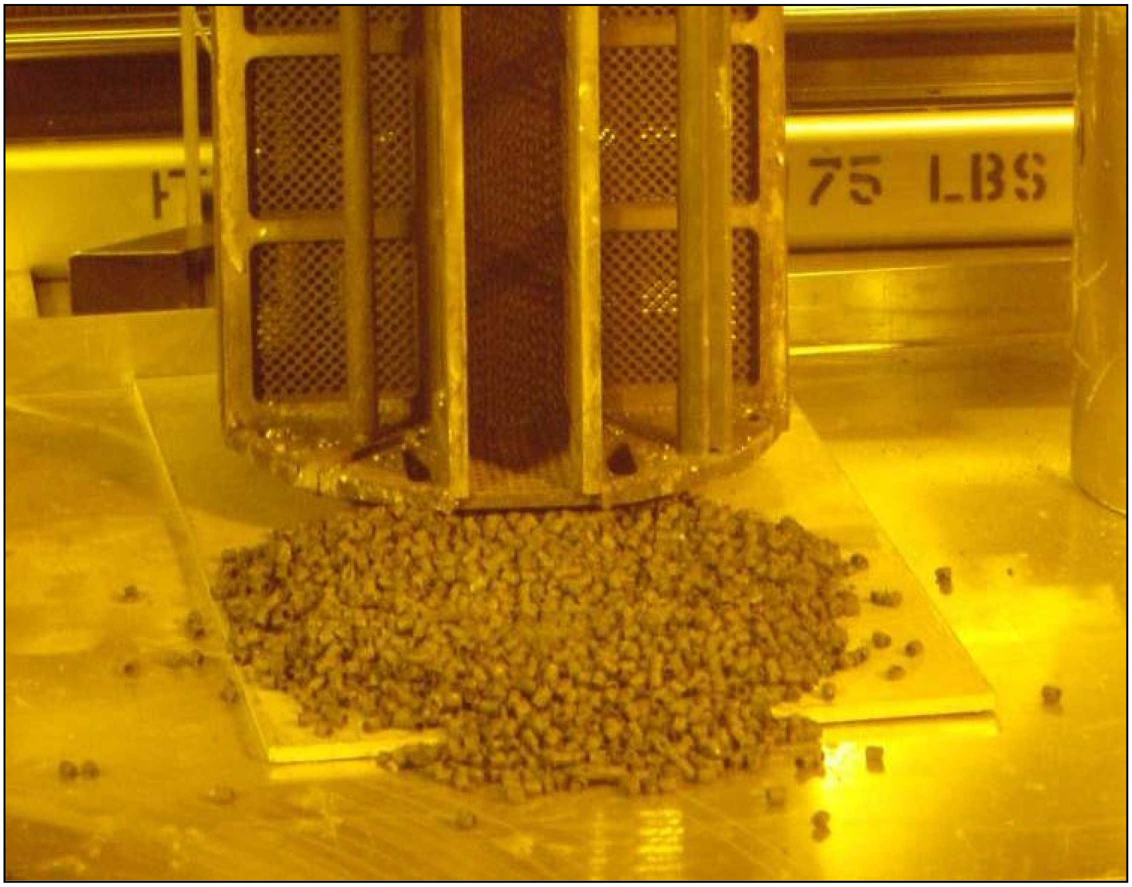

Figure 2: Undissolved anode materials removed from the Mk-IV ER

Responding to the prescribed challenge, this report investigates chemical analysis data as a whole and finds noticeable trends in the compositions of undissolved anode material samples with respect to the mass of the whole undissolved anode materials. Based upon this discovery, an empirical model is proposed.

2. MASS MEASUREMENTS AND CHEMICAL ANALYSIS OF UNDISSOLVED ANODE MATERIALS

Upon the completion of the dissolution process, the undissolved anode materials are removed from the Mk-IV ER and weighed. Then, the removed materials are stored for subsequent metal waste form processing. The EBR-II driver fuels adopted stainless steels of published compositions as the cladding materials. Thus, a credible calculation on material mass excluding the cladding materials can be performed. The mass to explain is denoted by MTE and is defined for each batch as below where m_{anode} is the weighed undissolved anode material mass and m_{clad} is the published cladding material mass:

$$MTE = m_{anode} - m_{clad} \tag{1}$$

The relative mass to explain with respect to m_{clad} is denoted by RMTE and is a dimensionless parameter defined as below:

$$RMTE = \frac{MTE}{m_{clad}} \tag{2}$$

As mentioned previously, a couple of hulls from the undissolved anode materials have been removed and subjected to chemical analyses. The anode baskets contain approximately 8,000 driver hull segments in the four compartments. Typically, 10 hulls from each compartment are collected for a total of 40 samples per batch for the demonstration operations. In order to reduce chemical analysis loads, during the inventory operation, the 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 analyses. The hull samples are weighed, washed in water to dissolve the adhering electrolyte, washed in acid to dissolve the undissolved fuel, dried, and reweighed. It is assumed that all of the adhering electrolyte and the fuel residuals are dissolved during the water and acid washing steps. The water and acid wash solutions are analyzed for a suite of elements and isotopes. Then, the composition of the entire materials removed from the Mk-IV ER was estimated from the resulting analyses.

The expected primary contributors to the MTE are the undissolved fuels and the adhering electrolyte. The undissolved fuels are mainly consist of uranium and zirconium, whose relative masses with respect to m_{clad} are denoted by $m_{U/clad}$ and $m_{Zr/clad}$, respectively. Formally, $m_{U/clad}$ and $m_{Zr/clad}$ are defined as below:

$$m_{U/clad} := \frac{m_U}{m_{clad}} \text{ and } m_{Zr/clad} := \frac{m_{Zr}}{m_{clad}} \tag{3}$$

Similarly, $m_{salt/clad}$ defines the relative mass of the adhering electrolyte with respect to m_{clad}:

$$m_{salt/clad} := \frac{m_{salt}}{m_{clad}} \tag{4}$$

The quantities, $m_{U/clad}$, $m_{Zr/clad}$, and $m_{salt/clad}$ are not known but can be estimated via the analyses of the hull samples. The mass of Zr in the sample, sm_{Zr} is measured and primarily from the undissolved fuels. The electrolyte mass, sm_{salt}, is estimated from Li and K measurements in the sample and the available bulk electrolyte composition estimate. The mass of U in the sample, sm_U, is calculated with U measurements and adjustment accounting U^{3+} in the electrolyte. The cladding mass of the samples, sm_{clad}, is also measured after dissolving the undissolved fuels and the adhering electrolyte with acid and water solution. Adjustments are made to compensate the dissolved cladding materials by examining Fe and Cr in acid and water solution. Then the following relative masses with respect to the cladding mass in the samples can be defined:

$$sm_{U/clad} := \frac{sm_U}{sm_{clad}};\ sm_{Zr/clad} := \frac{sm_{Zr}}{sm_{clad}};\ sm_{salt/clad} := \frac{sm_{salt}}{sm_{clad}} \qquad (5)$$

Figure 3 shows various relative masses of the hull samples explaining the RMTE. One can observe that the relative mass combining U, Zr, and the electrolyte provide a primary explanation of the RMTE.

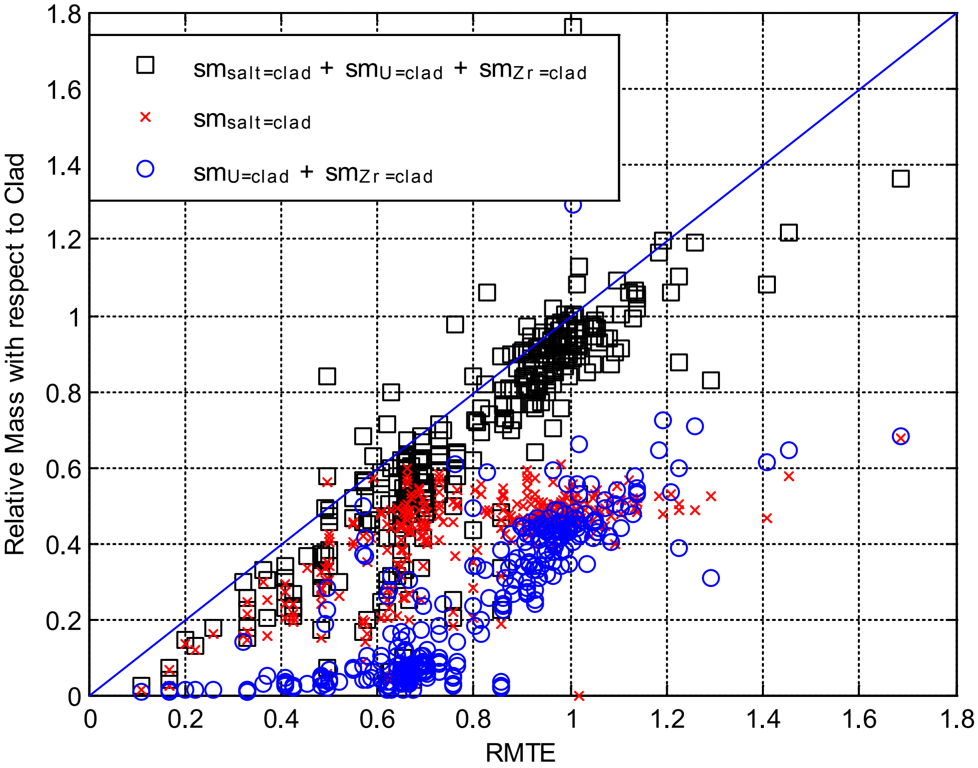

Figure 3: Undissolved anode materials removed from the Mk-IV ER

There are secondary materials expected to be in the undissolved anode. Notable ones include the noble metal fission products such as Mo, Tc, and Ru. Chemical analyses of the undissolved anodes show a high retention of these noble metal fission products in the undissolved anode [Li et.al. 2005; Li et.al. 2005a]. Another element that may deserve an attention is Cd. The transport mechanism of Cd from the bottom Cd pool to the anode structure was conjectured in [Yoo et.al. 2013]. In particular, the quantity of Cd in the undissolved anode materials is non-negligible during the inventory operation because of the adopted high-speed anode rotation.

3. MODELS FOR UNDISSOLVED ANODE MATERIALS

The prescribed secondary materials in the undissolved anode materials are qualitatively justified but nontrivial to quantify. An alternative approach for the quantification of the secondary material contributions is to estimate the unexplained relative mass from data itself presented in Fig.3. The average biases are calculated for the demonstration and inventory operations. The calculations conditioned on the operations are attempted as the expected Cd quantities in the undissolved anode materials for the demonstration and inventory operations are significantly different [Yoo et.al. 2013].

The average bias of $sm_{salt/clad} + sm_{U/clad} + sm_{Zr/clad}$ against the RMTE is 0.0907 for the demonstration operation while 0.1684 for the inventory operation. The RMTE is adjusted to reflect these biases and the ARMTE is defined as below:

$$ARMTE = \begin{cases} RMTE - 0.0907 & \text{for demonstration operation} \\ RMTE - 0.1684 & \text{for inventory operation} \end{cases} \tag{6}$$

Figure 4 shows various relative sample masses explaining the ARMTE. One can observe that the relative sample mass combining U, Zr, and the adhering electrolyte provide an excellent explanation of the ARMTE collectively. Thus, the equation (7) is proposed where $\widehat{m}_{salt/clad}$, $\widehat{m}_{U/clad}$, and $\widehat{m}_{Zr/clad}$ represent the models of $sm_{salt/clad}$, $sm_{U/clad}$, and $sm_{Zr/clad}$, respectively.

$$ARMTE = \widehat{m}_{salt/clad} + \widehat{m}_{U/clad} + \widehat{m}_{Zr/clad} \tag{7}$$

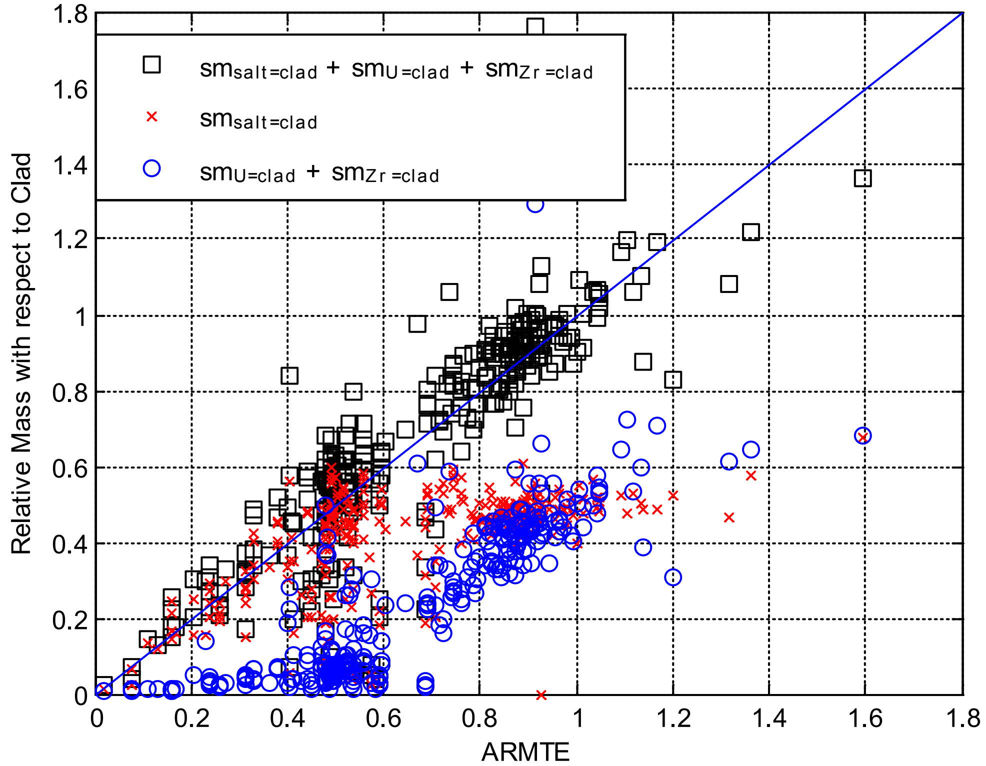

Figure 4: Explained masses with adjustment factors

The samples where $sm_{salt/clad} + sm_{U/clad} + sm_{Zr/clad}$ is away from the diagonal line in Fig. 4 are non-representative in terms of explaining the ARMTE of the entire batch. It is important to account those samples away from the diagonal line for assessing the heterogeneity of the residual anode materials. However, the purpose of this report is in identifying data patterns and proposing a model explaining the emerged patterns. Thus, for the sake of visual clarity, only samples appropriately explaining the whole batches are selected in the following manner (8) and plotted in Fig. 5.

$$\left\|\frac{ARMTE - sm_{salt/clad} - sm_{U/clad} - sm_{Zr/clad}}{ARMTE}\right\| < 0.1 \qquad (8)$$

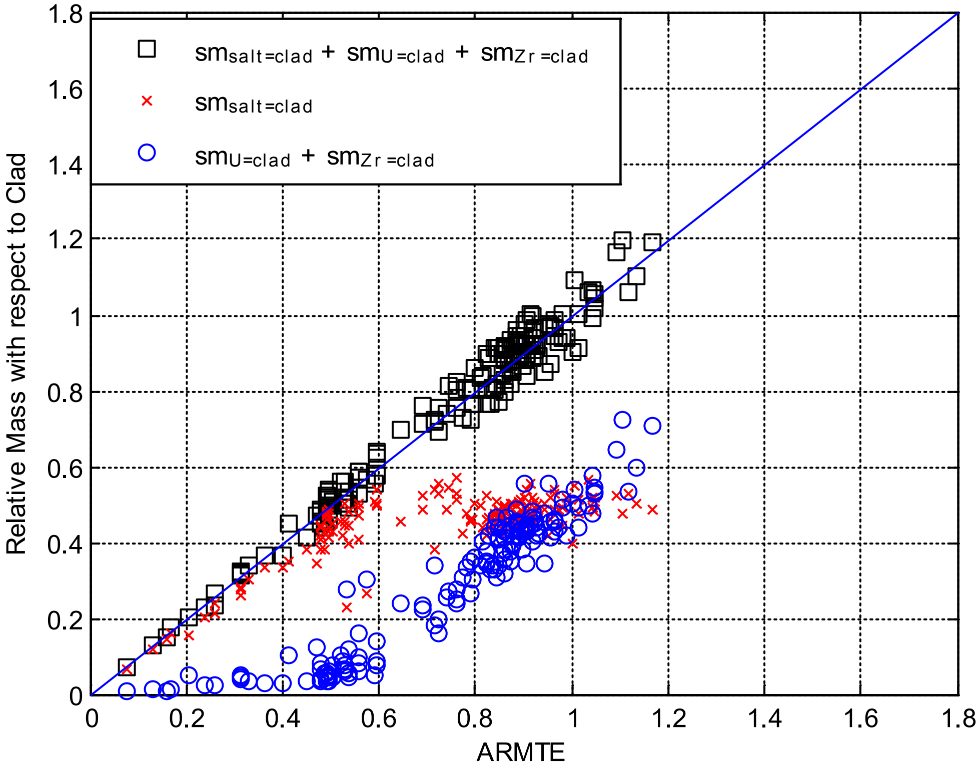

Figure 5: Explained masses with selected samples

Given these samples selected with the criteria in (8), Fig. 6 shows only the relative electrolyte mass with respect to the ARMTE. One can observe that relative electrolyte mass increases linearly until the ARMTE reaches around 0.6 and saturates after. Independent regressions over the prescribed two ARMTE regions are conjoined to give the relative electrolyte mass model below. The blue lines in Fig. 6 represent the model:

$$\widehat{m}_{salt/clad} = \begin{cases} 0.865\,ARMTE & ARMTE < 0.57 \\ 0.493 & o.w. \end{cases} \qquad (9)$$

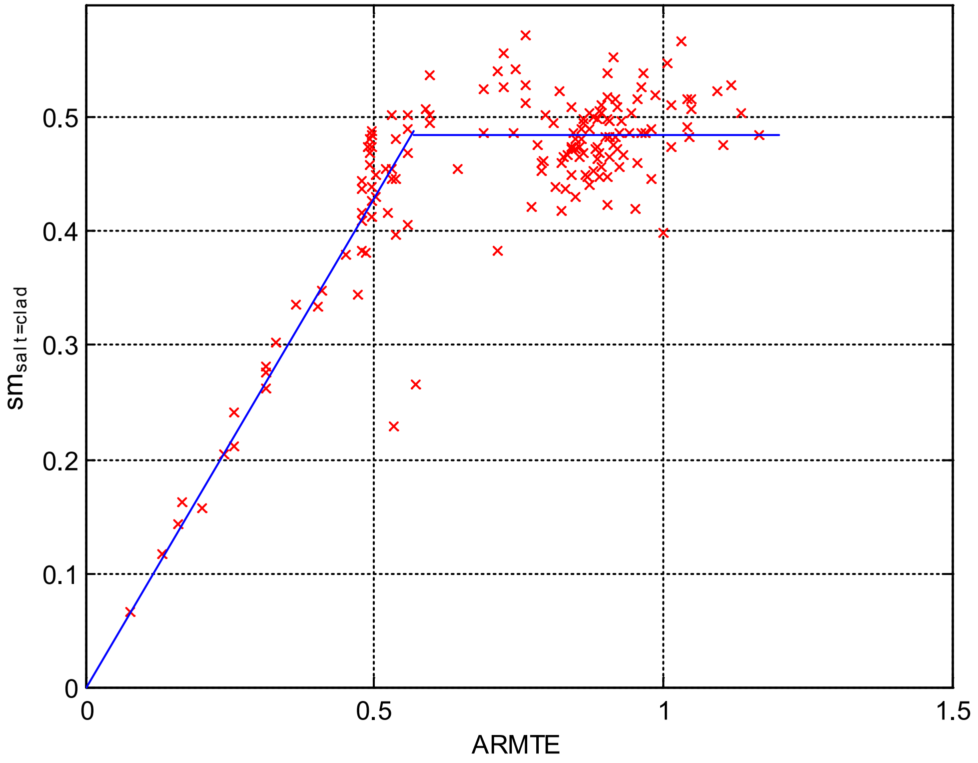

Figure 6: Relative electrolyte masses

From (7), we get

$$\widehat{m}_{Zr/clad} + \widehat{m}_{U/clad} = ARMTE - \widehat{m}_{salt/clad} \tag{10}$$

Thus, a good selection of the function $\widehat{m}_{salt/clad}$ should result in a proportional relationship between the terms, $sm_{U/clad} + sm_{Zr/clad}$ and $ARMTE - \widehat{m}_{salt/clad}$, as is shown in Fig. 7.

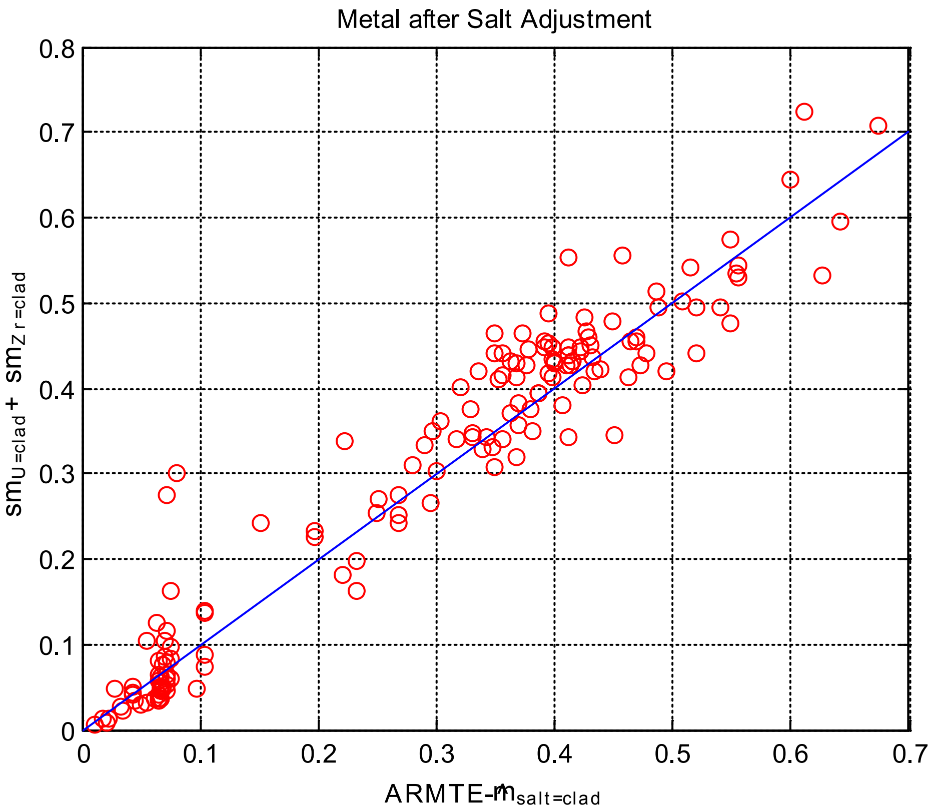

Figure 7: Relative metal masses after salt accounting with the model

Figure 8 shows the trends of $sm_{Zr/clad}$ and $sm_{U/clad}$ with respect to $ARMTE - \widehat{m}_{salt/clad}$. For $sm_{Zr/clad}$, a linear trend is observed until $sm_{Zr/clad}$ reaches around 0.35. Beyond 0.35, $sm_{Zr/clad}$ seems saturated. The observed Zr mass saturation may come from the constraint that the relative mass of the typical initial Zr feed mass with respect to m_{clad} is around 0.35. The samples manifesting Zr saturation may correspond to the batches where nearly all Zr metals are retained within the undissolved anode. On the contrary, $sm_{U/clad}$ samples show two linear trends joined around $sm_{U/clad}{\sim}0.15$. The steeper linear trend covering $sm_{U/clad} > 0.15$ corresponds to the region where $sm_{Zr/clad}$ reaches its saturation value 0.35 and the remaining mass is explained with $sm_{U/clad}$. Given these observations, we give the relative mass models for U and Z as below:

$$\widehat{m}_{Zr/clad} = \begin{cases} 0.7\left(ARMTE - \widehat{m}_{salt/clad}\right) & ARMTE - \widehat{m}_{salt/clad} < 0.5 \\ 0.35 & o.w. \end{cases} \tag{11}$$

$$\widehat{m}_{U/clad} = \begin{cases} 0.3\left(ARMTE - \widehat{m}_{salt/clad}\right) & ARMTE - \widehat{m}_{salt/clad} < 0.5 \\ ARMTE - \widehat{m}_{salt/clad} - 0.35 & o.w. \end{cases} \tag{12}$$

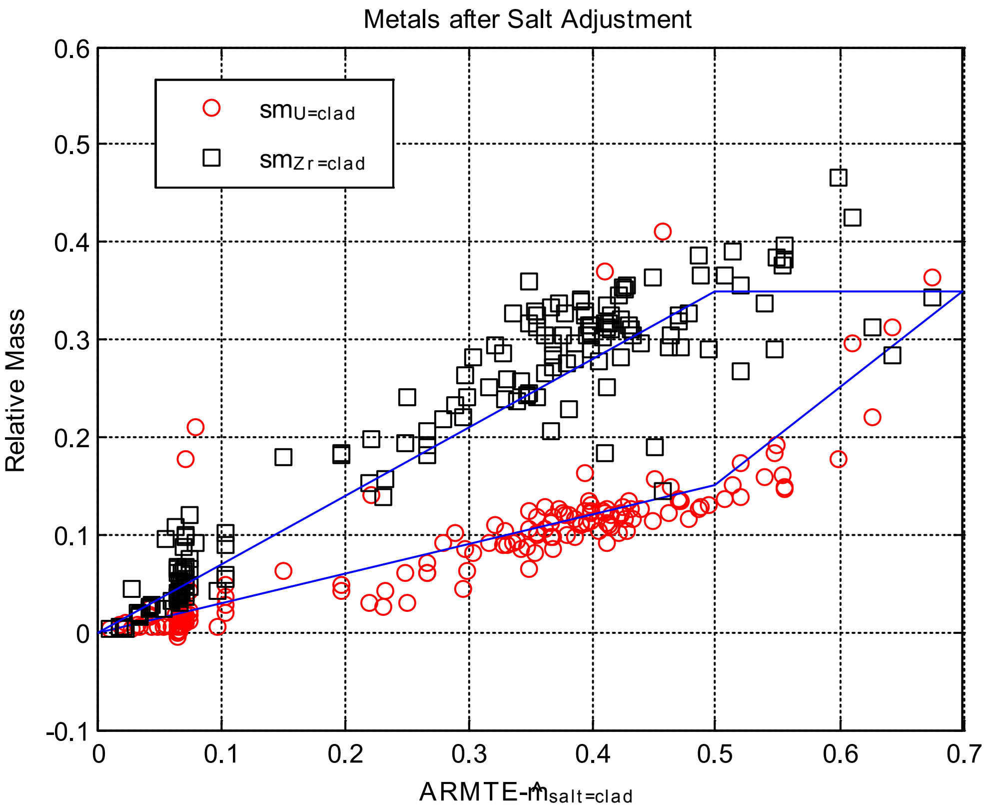

Figure 8: Breakdown of relative metal masses after salt accounting with the model

4. DISCUSSIONS

Observing the EBR-II cladding hull data set as a whole revealed that the ARMTE may provide a tool for predicting the composition of the undissolved anode materials. This option is extremely attractive as the ARMTE is *obtainable with relatively simple weighing operations* and done without long delay.

The research nature of the EBR-II driver fuel processing has incurred frequent changes of the operational parameters of the MK-IV electrorefiner. Also, limited quantity of hull samples and the highly heterogeneous material compositions of the undissolved anode materials deter accurate estimation of the whole undissolved anode material composition. Thus, it has long been considered that the metal waste operations consolidating the whole undissolved anode materials and the chemical analysis of the representative sample should be performed in order to have a high fidelity estimation of the whole undissolved anode material composition. At present, INL is active in operating the metal waste furnace in the HFEF and multiple chemical analysis requests for the composition of the metal waste ingots consolidating the undissolved anode materials have been submitted. The analysis results are expected to be available in FY17. Once the results are available and examined, the hull composition (e.g, U and Zr) and the condensates can be quantified and used for the verification of the model.

Without credible a priori composition information on the undissolved anode materials, determining the quantity of the supplementary materials (typically Zr to approximate Fe-Zr eutectic) for the metal waste process can be difficult. The residual anode material sample analyses provide a rough estimation for Zr contents and are useful for determining the supplementary materials. The proposed model in this report may also give similarly useful information and even can be used for rejecting chemical analysis results that may not be representative of the whole batch and be used as a tool to estimate composition instead.

At present, the fissium fuel processing campaign is in progress with the Mk-IV ER. It is remained to be seen if a similar result described in this report can be obtained for the undissolved anode materials of the fissium fuel processing. A positive confirmation may imply a possibility of cutting back sampling requirements for the undissolved anode materials of the fissium fuel processing campaign.

Further charting efforts revealing mass contributions from the major phases to the MTE may be performed in a controlled experimental condition. An option is to perform a set of experiments varying the level of fuel dissolutions for each fuel segment rather than the entire batch consisting of thousands of segments. A feasibility of scaling the small scale experiment results would be an enabling discovery.

Metallic U and Zr are primary in accounting the undissolved anode material mass. Though minor in terms of quantities, the undissolved anode materials include transuranic elements. These elements have been the subject of chemical analyses throughout the processing campaigns. From thermodynamic perspectives, these elements are expected to be in the salt phase. However, various causes including interface passivation and the migration of transuranic elements to the cladding are expected to hinder the complete partition of transuranic materials to the salt phase. Efforts are expected to be given to identify a transuranic material distribution pattern in the cladding hull during FY-17.

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