FUEL CONDITIONING FACILITY ELECTROREFINER
SPECIAL NUCLEAR MATERIAL MASS ESTIMATION

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ABSTRACT

In one of the electrometallurgical process steps of the Fuel Conditioning Facility (FCF), the in-process nuclear material is dissolved in the electrorefiner tank in an upper layer of a mixture of liquid LiCl-KCl salt and a lower layer of liquid cadmium. To determine the mass of special nuclear material in the electrorefiner requires the estimation of the volume of fluid in the tank and the concentration of the special nuclear material together with the uncertainties in these estimates. Procedures are presented to compute these estimates under the unique conditions posed by the electrorefiner.

I. INTRODUCTION

Material control and accountancy of special nuclear material (SNM) in a nuclear facility, with process steps involving liquids, requires an accurate measurement of the liquid content of the process tanks, and of the density of the fluid. In the electrometallurgical refining process step of the Fuel Conditioning Facility (FCF), the in-process nuclear material is dissolved in the electrorefiner in an upper layer of liquid salt and a lower layer of liquid cadmium. Thus, to estimate the in-process inventory of special nuclear material in the electrorefiner requires the estimation of an equation, which relates the tank's measurement system, such as in the case of the electrorefiner the liquid level probe, to the volume of the liquid, and samples of the fluids to determine the concentration of SNM.

The electrorefiner tank, as most process tanks, is not a smooth right-circular cylinder for which a single linear volume calibration curve can be fitted over the whole height of the tank. Rather, the tank contains many internal components, as shown in Fig. 1, which cause systematic deviations from a single linear function. Thus, an important objective of the tank volume calibration is to identify those tank levels over which a single, preferably linear, function will suffice to define the volume versus height relation. The adverse consequences of the perturbations, due to tank internal structures, are expected to play an important role in the case of the electrorefiner. For one, the operating volume of the electrorefiner is generally smaller, by well over an order of magnitude, when compared, for example, to the volume of process or accountancy tanks in aqueous processes. The small size of the tank, therefore, will accentuate the contribution of structural imperfections to the estimated uncertainties. In addition, operational considerations constrain the size and number of incremental additions of liquid to the electrorefiner, and thereby, limit the resolution.
The density of the electrorefiner fluid can be estimated on the basis of the measured weight fractions and published densities of the components via the method of additive volumes.

II. ELECTROREFINER VOLUME CALIBRATION

The salt and cadmium, the operating liquids of the electrorefiner, are loaded into the electrorefiner in the argon cell in solid form. They are liquid at the operating temperature of about 500°C. This situation precludes multiple calibration runs at operating conditions. As a matter of fact, the measurements taken during the loading constitute the calibration data. Furthermore, because of the possibility of severe asymmetric thermal stresses on the tank during loading, the loading takes place at a temperature of 410°C, which is about 100°C below the operating temperature of the electrorefiner.

In order to overcome some of these short-comings, two calibrations were performed -- one, consisting of three runs, performed out-of-cell with water at room temperature, the other, consisting of one run, was performed in-cell with the operating fluids at 410°C. Although these two calibrations have some operational differences, we believe they are both, not only relevant, but necessary to the development of a robust measurement function for material accountancy in the Fuel Conditioning Facility.

The variation of the water data in two types of diagnostic plots -- profile plots and incremental slope plots -- was compared to that expected from the engineering design drawing of the electrorefiner tank. On the basis of these diagnostic plots four axial regions were selected for estimating the volume calibration function.

Table I. Estimated Calibration/Measurement Function Using Ordinary Least Squares Model for Out-of-Cell Volume Calibration Run #3 (Reference Temperature 20°C)

<table>
<thead>
<tr>
<th>Liquid Height, H (in.)</th>
<th>Number Data Points</th>
<th>Calibrated Volume, V (l)</th>
<th>Random Variance, ( \sigma^2_R ) (( \text{m}^2 ))</th>
<th>Systematic Variance, ( \sigma^2_S ) (( \text{m}^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00( \leq )H&lt;4.62</td>
<td>14</td>
<td>-1.96280 +17.9464xH</td>
<td>8.31013\times10^{-4}</td>
<td>6.1259\times10^{-2} - 2.87980\times10^{-3}xH + 6.85471\times10^{-3}xH^2</td>
</tr>
<tr>
<td>4.62( \leq )H&lt;6.75</td>
<td>14</td>
<td>-11.3153 +19.9846xH</td>
<td>1.03049\times10^{-3}</td>
<td>5.15948\times10^{-1} - 1.53021\times10^{-1}xH + 1.65253\times10^{-2}xH^2</td>
</tr>
<tr>
<td>8.5( \leq )H&lt;15.75</td>
<td>11</td>
<td>-13.9485 +20.3193xH</td>
<td>1.06530\times10^{-3}</td>
<td>1.66336\times10^{-1} - 2.15882\times10^{-2}xH + 1.19884\times10^{-3}xH^2</td>
</tr>
<tr>
<td>17.5( \leq )H&lt;21.25</td>
<td>21</td>
<td>-15.6185 +20.3905xH</td>
<td>1.06903\times10^{-3}</td>
<td>1.60881 - 1.51891\times10^{-1}xH + 4.22053\times10^{-3}xH^2</td>
</tr>
</tbody>
</table>

III. ESTIMATION OF THE CALIBRATION FUNCTION AND CALIBRATION UNCERTAINTY

Although during calibration the volume of liquid added is the controlled variable and the liquid height the measured quantity, we shall follow common practice and use the following model

\[ V_i = \alpha + \beta h_i + \epsilon_i, \]

where \( V_i \) is the volume in liters after the \( i \)-th incremental volume addition, \( h_i \) the liquid level measurement, in inches and \( \epsilon_i \) the error. This form of the calibration function is also the measurement function, and consequently inversion is not necessary.

A variety of statistical error models and fitting methods are found throughout the literature. Since the tank is filled in incremental additions, any errors associated with previous additions of liquid can, in principle, affect the error in the total amount. In such cases, for example, the error model chosen for the calibration is a cumulative model. The cumulative error model appears to be the most frequently chosen model, both for statistical reasons and computational implications. Based on the analysis of different possible models and the fact that at the high operating temperature of the electrorefiner measurement error is sure to be larger, we choose Ordinary Least Squares as the estimation method.

The estimated calibration functions, based on run three data, together with the estimates of the random and systematic error variances for the linear segments, are shown in Table I.
IV. ELECTROREFINER VOLUME CALIBRATION BASED ON SALT AND CADMIUM AT 410°C

We now compare the data collected during the loading of the electrorefiner with the working fluids -- salt and cadmium, and the associated calibration estimates -- to the results based on measurements with water at room temperature. Since loading the electrorefiner with salt and cadmium precludes multiple runs, the three calibration runs with water at room temperature are an important compliment to the inferences based on salt and cadmium data. As such, every effort is made to incorporate the information in the water data into the final salt and cadmium calibration and measurement functions.

In Fig. 2 we show the salt-cadmium residuals, relative to the regression curve based on the water data, over the full height of the salt-cadmium volume in the electrorefiner. It is clear that a measurement function based on the salt-cadmium data will systematically predict a greater liquid volume than one based on the water calibration data. Moreover, when viewed from a slightly different perspective as in Fig. 3, where the salt-cadmium measurements and the water measurements are subtracted from a common arbitrary regression line over the height of the electrorefiner, the difference between the two data increases with liquid level. The rate of increase is greater for the cadmium additions than for the salt additions. The systematic nature of this difference suggests that there may be a dominant component.

It has been noted by the operators, that during the initial incremental additions of the cadmium to the electrorefiner, there was some "splashout" of salt. Furthermore, there occurred some spillage of cadmium during the removal of the bulk loader after the second increment (i.e., for the third increment). We quantify and bound these possibilities in the light of the measurements. To this end, Fig. 4 demonstrates, for the salt level measurements, the effect of including the maximum estimate for each anomaly -- a splashout of 1 kg of salt at each of the first two cadmium incremental additions (1.2 kg total), and a spillage of 0.5 kg of cadmium after the second increment. These adjustments remove the slope discrepancy for the first five of the nine cadmium increments.

V. ESTIMATION OF THE MEASUREMENT FUNCTION AND THE MEASUREMENT UNCERTAINTY

Of interest to material accountancy in the electrorefiner are the cadmium volume and the salt volume. These are determined, via measurement functions, by the two liquid levels -- the top of the cadmium and the top of the salt. The current operating levels are a minimum, and are expected to slowly increase as operation proceeds until drawdown of the electrorefiner. It is, therefore, sufficient to focus the estimates on the expected ranges of the liquid levels over that period.

Fig. 2. Volume Residuals, Relative to Water Calibration Regression Line, for Salt Level (o) Measurements for all Salt and Cadmium Increments and for Water Level (•) Measurements of Water Calibration
Fig. 3. Volume Residuals, Relative to Arbitrary "Calibration" (V=0+20\(\times\)H) Line, for Salt Level (\(\circ\)) Measurements for all Salt and Cadmium Increments and for Water Level (\(\ast\)) Measurements of Water Calibration

Fig. 4. Volume Residuals, Relative to Water Calibration Regression Line, for Salt Level (\(\circ\)) Measurements for all Salt and Cadmium Increments Assuming Maximum Estimates for Observed Splash/Spill Losses (Salt Loss of 0.6 \(\ell\) at each Cadmium Increment #1 and #2 and Cadmium Loss of 0.5 \(\ell\) at Cadmium Increment #3)
A. Top of the Salt

The estimate is based on liquid level measurements in the range 13.3 in. to 16.4 in. We estimate that in the range of liquid levels from 13.3 in. to 17.5 in. the following measurement function is appropriate:

\[
V_{sc} = 21.9016 + 21.2383 \cdot h_{TS}
\]  
(3)

where \(V_{sc}\) is the salt and cadmium volume in liters and \(h_{TS}\) the top of salt liquid level in inches. The associated estimated random error for the volume estimate in liters is \(\sigma_s = 0.214\). The estimate of the systematic error in liters is given by

\[
\sigma_s = (1.80 - 0.231 \cdot h_{TS} + 0.00746 \cdot h_{TS}^2)^{1/2}
\]  
(4)

B. Top of the Cadmium

The estimate is based on liquid level measurements in the range 2.0 in. to 4.0 in. We estimate that in the range 2.0 in. to 4.65 in. the following measurement function for the cadmium volume \(V_c\) in liters is appropriate:

\[
V_c = 0.3828 + 17.4334 \cdot h_{TC},
\]

\(h_{TC}\) is the cadmium liquid level in inches.

C. Volume of Salt

The volume of salt between the levels \(h_{TS}\) and \(h_{TC}\) is given by the difference of Eqs. (4) and (5),

\[
V_s = V_{sc} - V_c = 21.5188
+ 21.2383 \cdot h_{TS} - 17.4334 \cdot h_{TC}.
\]

\(V_s\) is the volume of salt in liters. The associated random error is \(\sigma_r = 0.597\) liters. The systematic error is given by

\[
\sigma_s = (2.498 - 0.411 \cdot h_{TC} - 0.231 \cdot h_{TS} + 0.0619 \cdot h_{TC}^2 \cdot h_{TS}^2)^{1/2}.
\]

(7)

VI. ESTIMATION OF THE DENSITY OF THE ELECTROREFINER SALT

The density of the mixture of salt and SNM in the electrorefiner fluid is estimated by the method of additive volumes. This method, given by Eq. (9), is a weighted average of the volumes of the constituent components,

\[
\frac{1}{\rho_{mix}} = \frac{w_s}{\rho_s} + \frac{w_a}{\rho_a}
\]

(9)

where \(\rho_{mix}\) is the density of the mixture of components \(s\) and \(a\), and \(w_s, \rho_s\) and \(w_a, \rho_a\) are the weight fractions and densities of the respective individual components, such as LiCl/KCl eutectic and SNM.

The approach is to measure the weight fractions by sampling the electrorefiner fluid, and estimate the constituent densities, at operating conditions, from published data. To this, end, the critical component is the expression for the density of the LiCl/KCl eutectic which is estimated as

\[
\rho_s = 1.95 - 0.177w - 0.000559T + 0.000110wT
\]

where \(w\) is the weight fraction of LiCl in the mixture and \(T\) the temperature.

The random error component in gm/l for an estimate of the fluid density using Eq. 10 is given by the root mean square error. Thus,

\[
\sigma_r = 0.00234.
\]

The systematic component, the standard error of the mean, varies as a function of the explanatory variables. Of interest here are the conditions during calibration (weight fraction of LiCl of about 0.44 and a fluid temperature of 410\(^\circ\)C) and those at operation (weight fraction of LiCl of about 0.44 and a fluid temperature of 500\(^\circ\)C). At these conditions the systematic error estimates are

\[
\sigma_{s,cal} = 0.00065
\]

at calibration, and

\[
\sigma_{s,op} = 0.00045
\]

at operation.

The random error associated with the estimate of \(\rho_{mix}\) in Eq. 9 is given by the familiar expression

\[
\text{Var}(\rho_{mix}) = \left(\frac{\partial \rho_{mix}}{\partial w_s}\right)^2 \sigma_w^2 + \left(\frac{\partial \rho_{mix}}{\partial T}\right)^2 \sigma_T^2
\]

\[
+ \left(\frac{\partial \rho_{mix}}{\partial w_a}\right)^2 \sigma_w^2 + \left(\frac{\partial \rho_{mix}}{\partial T}\right)^2 \sigma_T^2
\]

\[
+ 2 \left(\frac{\partial \rho_{mix}}{\partial w_s} \frac{\partial \rho_{mix}}{\partial w_a}\right) \sigma_w \sigma_w + 2 \left(\frac{\partial \rho_{mix}}{\partial T} \frac{\partial \rho_{mix}}{\partial T}\right) \sigma_T
\]

(14)
The uncertainties relevant to this expression are given in Table II. The random error in the density of the operating fluid at reference conditions is estimated to be

\[ \sigma_r = 0.00848 \]  

\[ (15) \]

Table II. Uncertainty Estimates for Reference Conditions\(^1\) (1\(\sigma\))

<table>
<thead>
<tr>
<th>Weight fraction: (^2)</th>
<th>( w_3 )</th>
<th>0.005</th>
</tr>
</thead>
<tbody>
<tr>
<td>( w_4 )</td>
<td>7 x 10(^{-4})</td>
<td></td>
</tr>
</tbody>
</table>

| Density:                | \( \sigma_{p_3} \) | 2.34 x 10\(^{-3}\) |
|-------------------------| \( \sigma_{p_4} \) | 2.60 x 10\(^{-2}\) |

| Covariances:            | \( \sigma_{w_3 w_4} \) | -7 x 10\(^{-5}\) |
|-------------------------| \( \sigma_{p_3 p_4} \) | 0 |

| Temperature:            | \( \sigma_T \) | \( \sim 10^\circ\)C |

1. Reference conditions are 500\(^\circ\)C fluid temperature, 0.44, 0.93, and 0.07 are respectively the weight fractions of LiCl in LiCl/KCl, LiCl/KCl in salt with uranium, uranium in the salt.

2. Reference 1

3. Reference 1

4. Perfect correlation assumed since \( w_3 + w_4 = 1 \)

5. No correlation assumed

Due, at present, to the lack of measurements on the density of the operating fluid, we derive the systematic error on the basis of the salt density only. This error has two components: one because a regression equation is used to predict the density of the salt, the other, because additive volume is used to predict the density of the mixture. From the estimates of these components the computed systematic error in the estimate of the density of the operating fluid is

\[ \sigma_s = 0.000791 \]  

\[ (16) \]

REFERENCES

1. R. D. Mariani, Argonne National Laboratory, personal communication (1994).


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