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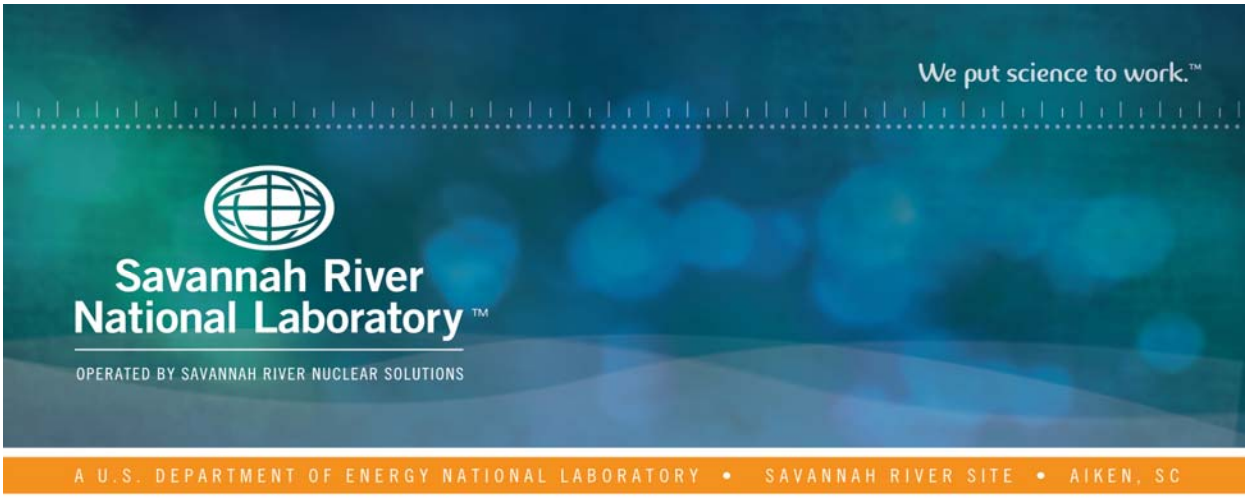


# Characterization of DWPF Recycle Condensate Tank Materials

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April 2015

SRNL-STI-2014-00603, Revision 1

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# EXECUTIVE SUMMARY

A Defense Waste Processing Facility (DWPF) Recycle Condensate Tank (RCT) sample was delivered to the Savannah River National Laboratory (SRNL) for characterization with particular interest in the concentration of I-129, U-233, U-235, total U, and total Pu. Since a portion of Salt Batch 8 will contain DWPF recycle materials, the concentration of I-129 is important to understand for salt batch planning purposes. The chemical and physical characterizations are also needed as input to the interpretation of future work aimed at determining the propensity of the RCT material to foam, and methods to remediate any foaming potential. According to DWPF the Tank Farm 2H evaporator has experienced foaming while processing DWPF recycle materials. The characterization work on the RCT samples has been completed and is reported here.

The composition of the Sludge Batch 8 (SB8) RCT material is largely a low base solution of 0.2M $NaNO_2$ and 0.1M $NaNO_3$ with a small amount of formate present. Insoluble solids comprise only 0.05 wt.% of the slurry. The solids appear to be largely sludge-like solids based on elemental composition and SEM-EDS analysis. The sample contains an elevated concentration of I-129 (38x) and substantial 59% fraction of Tc-99, as compared to the incoming SB8 Tank 40 feed material. The Hg concentration is 5x, when compared to Fe, of that expected based on sludge carryover. The total U and Pu concentrations are reduced significantly, 0.536 wt.% TS and 2.42E-03 wt.% TS, respectively, with the fissile components, U-233, U-235, Pu-239, and Pu-241, an order of magnitude lower in concentration than those in the SB8 Tank 40 DWPF feed material.

The radioactive waste sample retrieved from the DWPF RCT was evaluated for foaming. In all test cases the RCT samples foamed. The higher the solids content in the test sample the more the sample foamed. In all cases, the concentration of 5 ppm polydimethyl siloxane antifoam (Xiameter AFE-1010 reagent) was effective at collapsing preformed foams and stopping foam formation from recurring.

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| | |
|---|---|
| AD | Analytical Development |
| AR | Aqua Regia (Digestion) |
| BSD | Backscattered Electron Detector |
| CSEM | Contained Scanning Electron Microscopy |
| CVAA | Cold Vapor Atomic Absorption |
| DI | Deionized |
| dpm | Disintegrations Per Minute |
| DWPF | Defense Waste Processing Facility |
| EDS | Energy Dispersive Spectroscopy |
| HLW | High Level Waste |
| IC | Ion Chromatography |
| ID | Inner Diameter |
| ICP-AES | Inductively Coupled Plasma – Atomic Emission Spectroscopy |
| ICP-MS | Inductively Coupled Plasma – Mass Spectrometry |
| PF | Peroxide Fusion (Digestion) |
| ppm | Parts Per Million |
| PSIG | Pounds per Square Inch Gage |
| RCT | Recycle Condensate Tank |
| RSD | Relative Standard Deviation |
| SB8 | Sludge Batch 8 |
| SCCM | Standard Cubic Centimeters per Minute |
| SE | Secondary Electron (Detector) |
| SEM | Scanning Electron Microscopy |
| SRNL | Savannah River National Laboratory |
| SRS | Savannah River Site |
| TICTOC | Total Inorganic Carbon – Total Organic Carbon |
| TS | Total (Dried) Solids |
| TTQAP | Task Technical and Quality Assurance Plan |
| TTR | Technical Task Request |

## 1.0 Introduction

A Defense Waste Processing Facility (DWPF) Recycle Condensate Tank (RCT) sample was delivered to the Savannah River National Laboratory (SRNL) for characterization with particular interest in the concentrations of I-129, U-233, U-235, total U, and total Pu. Since a portion of Salt Batch 8 will contain DWPF recycle materials, the concentration of I-129 is important to understand for salt batch planning purposes. The chemical and physical characterizations are also needed as input to the interpretation of work aimed at determining the propensity of the RCT material to foam, and methods to remediate any foaming potential. The Tank Farm 2H evaporator has experienced foaming while processing DWPF recycle materials. This work was requested in a Technical Task Request (TTR)[1], and a Task Technical and Quality Assurance Plan (TTQAP)[2] was prepared. The characterization work on the RCT samples has been completed and is reported here.

The waste water recycle stream from the Defense Waste Processing Facility (DWPF) is returned to the H-area tank farm for processing in the evaporators. The processing of the waste water in the evaporator is a critical step for removing excess water from radioactive waste supernates. This evaporation process minimizes the volume of High Level Waste (HLW) requiring storage. Recent operational issues associated with radioactive material breakthrough into the off-gas treatment systems were believed to be associated with foaming of the waste during evaporation. As a result, DWPF requested that foaming studies be conducted at the SRNL to confirm whether sample foaming could occur and evaluate the effectiveness of an antifoam reagent (Xiameter AFE 1010) at collapsing any foams observed. Traditional methods for measuring the degree to which a liquid sample foams include the use of porous glass frits to introduce gas bubbles into a sample contained within a cylindrical column.[3] The radioactive waste sample retrieved from the Defense Waste Processing Facility (DWPF) Recycle Collection Tank (RCT) was evaluated with regard to the tendency to foam during air sparging.

The foaming tests were conducted on the DWPF SB8 RCT Composite sample using the same methods, apparatus design, and Quality Assurance Plan[4] recently used for 2H Evaporator Samples.[5]

## 2.0 Experimental

### 2.1 Sample Receipt and Consolidation

Five, 200 mL doorstops were received at SRNL on July 25, 2014. The doorstops were combined into a single 1-L wide mouth, high density, polyethylene storage bottle. One doorstop was extremely full, so a small portion was lost upon transfer to the composite bottle. The mass of transferred material was 919.14 g. The slurry was allowed to settle overnight and upon doing so it developed approximately ⅓ – ½ inch of black solids. Rinsing the doorstops with supernatant liquid did not increase the amount of consolidated material, i.e., initial transfers were complete.

### 2.2 Analytical Preparations

Weight percent solids[6] and density[7] were measured on both the slurry and supernate. The supernate was collected by filtering slurry through a 0.5µm filter cup.

Approximately 5 g of supernate was diluted to 50 mL in a volumetric flask with 1M nitric acid and subsamples submitted to Analytical Development (AD) for inductively coupled plasma – atomic emission spectroscopy (ICP-AES). Approximately 2 g of slurry was diluted to 50 mL in a volumetric flask with

deionized water (DI $H_2O$), with subsamples submitted for total inorganic carbon – total organic carbon (TICTOC) and total base/free $OH^-$/other bases analyses. Separately, approximately 5 g of slurry was diluted to 50 mL with DI $H_2O$, filtered through a 0.5 μm filter cup, and subsamples submitted for ion chromatography (IC) anion analysis.

Slurry was subjected to three separate digestions: aqua regia (AR),[8] peroxide fusion (PF),[9] and I-129 special preparation.[10] The AR and PF digestions target 0.25 g of total solids diluted to 100 mL while the I-129 preparation used 0.13 g of total solids diluted to 36.5 mL. The AR digestions were submitted for elemental analysis by ICP-AES and inductively coupled plasma – mass spectrometry (ICP-MS), and Hg analysis by cold vapor atomic absorption (CVAA) spectroscopy. The PF digestions were submitted for elemental analysis by ICP-AES, Pu-238/241, and U-233/234/235/236. The radiochemical separations and counting methods have been described elsewhere in great detail.[10]

Solids collected and air dried following the preparation of supernate were sampled twice and submitted to AD for scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS). All data has been recorded in the SRNL E-Notebook system.[11,12]

## 2.3 Test Apparatus for Foaming Study

The two foam test vessels used in the RCT foaming study were used in previous foaming studies of SRS radioactive waste.[3],[13] **Figure 2-1** shows one of the test vessels operating inside the SRNL shielded cells. The only difference between the two vessels was the fact that one vessel had been exposed to anti-foam reagent during previous testing while the other vessel had only contacted waste supernate solution. Antifoam tests with the RCT samples were conducted in the vessel which had been used previously for antifoam tests with other samples.

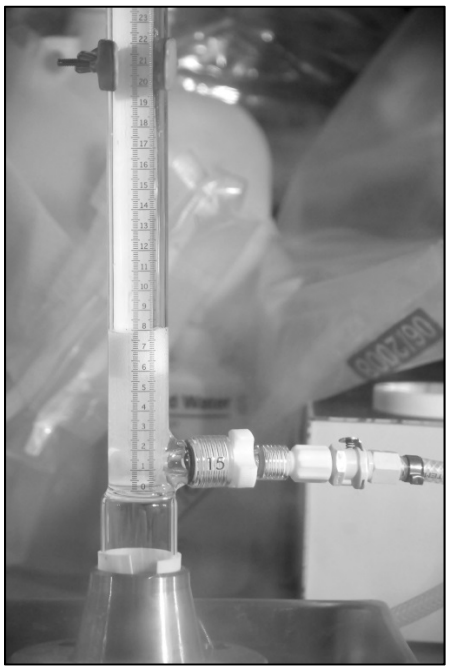

**Figure 2-1 Foam Test Apparatus used for RCT Foaming Evaluations**

The test vessels were prepared from approximately 1 inch inside diameter (ID: 26.4 mm) borosilicate glass tubing with one end closed to form a column for sample containment. Most of the tubing length was graduated with a millimeter scale, with the zero point positioned at the bottom of the column to allow for measurement of the liquid and liquid plus foam heights. A false bottom was added to the outer portion of the closed end of the cylinder to raise the vessel and facilitate easier reading of the fluid height. A stainless steel stand was constructed with a Teflon® sleeve to hold the cylinder in an upright position. A gas dispersion tube with a 1 cm outside diameter, coarse, glass frit was positioned in a horizontal orientation in the bottom of the column such that ~1 cm of liquid would be present below the frit when a test sample was transferred to the vessel. The gas dispersion tube was attached and sealed to the cylinder using threaded #7 and #15 Teflon® bushings with Viton® O-rings. The tube was removable and replaceable. The tube was adjusted to center the frit in the middle of the vessel prior to each test. The fritted glass portion of the dispersion tube was approximately 16 mm in length. Introduction of air through the frit resulted in the production of a plume of bubbles rising vertically through the liquid column and rapid release of bubbles across the upper surface of the liquid. Figure 2-2 is a design sketch of the Foam Test Apparatus.

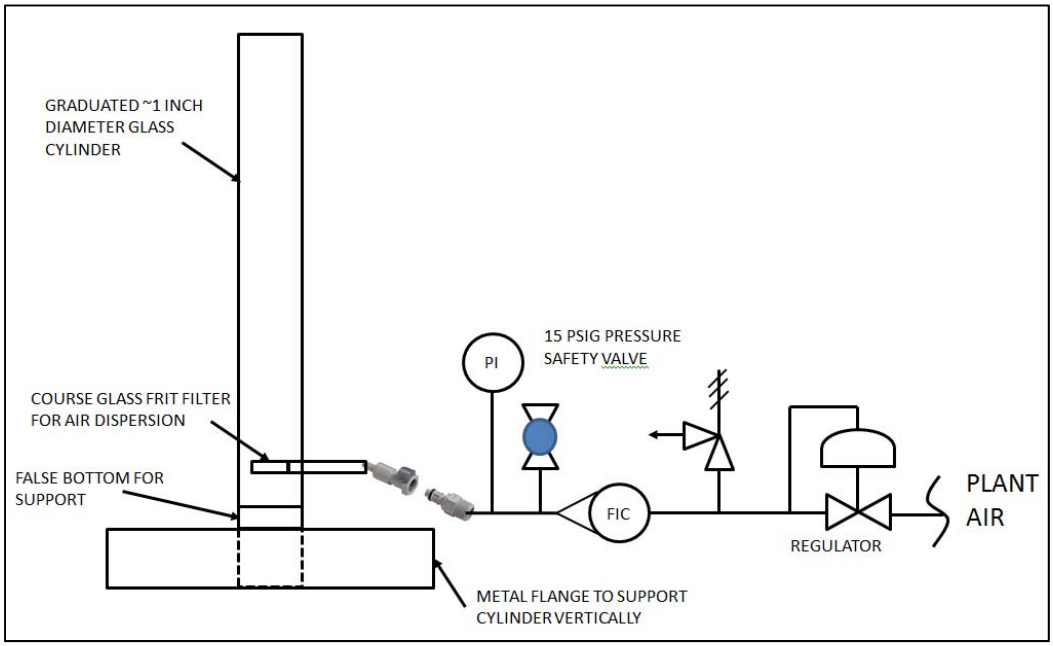


**Figure 2-2 Foam Test Apparatus Design Sketch**

House air supply in the SRNL shielded cells facility was used for air sparging. Air was introduced through a manifold including a pressure regulator, a calibrated pressure safety valve set to release air at 15 PSIG, and a flow shut off and vent valve. Air flow to the system was controlled using a mass flow device. Air was introduced into the cells through a standard KAPL plug penetration containing a 1 PSIG check valve. Air flow rates ranging from 50 to 150 mL/min (SCCM) were used for the sample foaming evaluations.

2.4 Test Methodology for Foaming Study

The testing methodology used for the RCT samples was identical to that used for the 2H Evaporator samples except that testing was only conducted with 50 mL of sample (previous testing[2] also included foaming evaluations with 35 mL of sample). Approximately 50 mL test samples (volume range: 49.0-51.2 mL) were evaluated to determine the effect air flow rate had on foam volume. The standard test sequence, which included constant and variable flow rate conditions, is provided below.

1. Transfer 50 mL of supernate into the test vessel and record the liquid height in the vessel.
2. Turn on the air sparge at a constant flow rate of 100 mL/min for 20 minutes with foam height data collection at 5 minute intervals.
3. Increase the air sparge to a constant flow rate of 125 mL/min and maintain this flow rate for 20 minutes with data collection at 5 minute intervals.
4. Turn off the flow and record the time required for the foam column to completely collapse.
5. Expose the sample to the following variable flow rate sequence and record the foam height after 5 minutes at each flow before adjusting the flow rate to the next target value: 50, 75, 100, 125, 150, 125, 100, 75, 50 mL/min.

This measurement sequence was intended: 1) to determine a steady state foam height over a 20 minute time scale at two intermediate flow rates (100 and 125 mL/min) known to produce measureable foam heights for most samples, and 2) to determine if there were significant hysteresis effects using sequential variable air flow rates. All tests were conducted at ambient temperature (21-27 ºC).

2.5 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

## 3.0 Results and Discussion

3.1 Analytical Characterization

The analytical results for the analyses conducted on the SB8 RCT sample appear in the following tables. Table 3-1 provides the weight percent solids[14] and density information collected on the sample. The insoluble solids settle rapidly, but comprise a small portion of the total solids present. Due to the small amount of insoluble solids the value given is at best an approximation due to limitation in the measurement of these trace insoluble solids levels. The closeness of the slurry and supernate densities is consistent with a low insoluble solids content. When settled they appear black, and comprise a layer of about ⅓ to ½ an inch at the bottom of a 1 L poly bottle.

**Table 3-1 Weight Percent Solids and Density for the SB8 RCT Sample [Number of Replicates Included in the Average]**

| Property | SB8 RCT | %RSD* |
|---|---|---|
| **Slurry Density** (g/mL) | 1.03 [4] | 0.97 |
| **Supernate Density** (g/mL) | 1.02 [4] | 0.26 |
| **Total Solids** (Wt.% in Slurry) | 3.03 [4] | 4.25 |
| **Dissolved Solids**[a] (Wt.% in Supernate) | 2.98 [4] | 2.60 |
| **Insoluble Solids** (Wt.% in Slurry) | 0.050 | NA |
| **Soluble Solids**[b] (Wt.% in Slurry) | 2.98 | NA |

NA ≡ not applicable
* Parenthetical %RSD values are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.
[a] Also known as Uncorrected Soluble Solids
[b] Also known as Corrected Soluble Solids

Table 3-2 provides the results from the supernate analyses conducted on the SB8 RCT sample for the analytes listed in column 1 by the method listed in column 6. Columns 2 and 3 provide the results on a supernate basis in moles/L (M), while columns 4 and 5 provide the results on a slurry basis in mg/kg. The IC data was obtained from weighted dilutions of slurry which were then filtered prior to analysis. The ICP-AES results were obtained from supernate dilutions into acid, as previously described in Section 2.2. The sample is mostly comprised of sodium nitrate and nitrite salts along with some measurable formate. The nitrite to nitrate ratio is more than 2X on a molar basis. The measurable metal ions, i.e. those above the detection limits, are provided in the Table 3-2. The detection limits are dependent upon the dilutions submitted. Sodium dominates, with measurable levels of other metal ions in the following order of abundance, but all orders of magnitude below the concentration of Na:

$$Al > S > Si > U > B > P > Li > Ca \approx Cr$$

**Table 3-2 Supernate Analyses for SB8 RCT Sample [Number of Samples Included in Average]**

| 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|
| **Analyte** | **SB8 RCT (%RSD*) Mol/L super. Wt'd Dil. Slurry** | **SB8 RCT (%RSD*) Mol/L super. Wt'd Dil. Super.** | **SB8 RCT (%RSD*) mg/kg slurry Wt'd Dil. Slurry** | **SB8 RCT (%RSD*) mg/kg slurry Wt'd Dil. Super.** | **Method** |
| $NO_3^-$ | 0.0855 (1.7) [3] | NA | 5170 (1.7) [3] | NA | IC |
| $NO_2^-$ | 0.186 (0.69) [3] | NA | 8340 (0.69) [3] | NA | IC |
| $SO_4^{2-}$ | <0.00103 | NA | <95.5 | NA | IC |
| $PO_4^{3-}$ | <0.00104 | NA | <95.5 | NA | IC |
| $Br^-$ | <0.00124 | NA | <95.5 | NA | IC |
| $Cl^-$ | <0.00279 | NA | <95.5 | NA | IC |
| $CHO_2^-$ | 0.0179 (0.82) [3] | NA | 787 (0.82) [3] | NA | IC |
| $C_2O_4^{2-}$ | <0.00112 | NA | <95.5 | NA | IC |
| $F^-$ | <0.00520 | NA | <95.5 | NA | IC |
| Al | NA | 0.00194 (2.2) [4] | NA | 50.9 (2.2) [4] | ICP-AES |
| B | NA | 0.00140 (2.3) [4] | NA | 14.8 (2.3) [4] | ICP-AES |
| Ca | NA | 0.0000141 (11) [4] | NA | 0.552 (11) [4] | ICP-AES |
| Cr | NA | 0.0000102 (8.8) [4] | NA | 0.520 (8.8) [4] | ICP-AES |
| Li | NA | 0.000330 (2.7) [4] | NA | 2.23 (2.7) [4] | ICP-AES |
| Na | NA | 0.401 (4.4) [4] | NA | 8980 (4.4) [4] | ICP-AES |
| P | NA | 0.000151 (1.0) [4] | NA | 4.55 (1.0) [4] | ICP-AES |
| S | NA | 0.00133 (9.4) [4] | NA | 41.6 (9.4) [4] | ICP-AES |
| Si | NA | 0.00135 (1.7) [4] | NA | 37.1 (1.7) [4] | ICP-AES |
| U | NA | 0.000131 (1.9) [4] | NA | 30.4 (1.9) [4] | ICP-AES |

NA ≡ not measured
* Parenthetical %RSD values are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.

Table 3-3 provides the TICTOC results for the SB8 RCT sample. There were equal amounts of inorganic and organic carbon based on the results. However, the sample blank had the unusual situation of having about 80% of the inorganic carbon found for the sample; there is currently no explanation for this observation. The dilutions submitted for base analysis (total base, free hydroxide, and other base excluding carbonate) gave no measurable readings, so it would appear that the sample is not highly caustic.

**Table 3-3 Carbon Analysis for SB8 RCT Sample [Number of Samples Included in Average] (mg C/kg slurry)**

| **Analyte** | **Slurry Wt'd Dilution SB8 RCT (%RSD*)** |
|---|---|
| Total Inorganic Carbon | 238 (5.4) [4] |
| Total Organic Carbon | 235 (5.4) [4] |
| Total Carbon | 474 (4.5) [4] |

Table 3-4 provides the elemental composition of the SB8 RCT material based upon the total digestions performed by AR and PF. The analyses were obtained from ICP-AES analysis unless indicated otherwise in the table footnotes. Once again Na dominates at nearly 31 wt.% of total solids. The relative abundance of elements is:

$$Na >> Fe > Hg \approx Al > Mn > U > Si > Ni > Ca > S > Th \qquad \text{SB8 RCT}$$

The ratio of U to Th is roughly 5:1 in the RCT sample which is close to the 4.5:1 found for Tank 40 SB8 material.[15] The composition is reminiscent of dilute sludge components with an increased ratio of Hg to the other elements:

$$Fe > Na > Al > Mn > U > Hg > Ni > Si > Ca > Th \qquad \text{SB8 Tank 40}$$

**Table 3-4 Elemental Concentration in SB8 RCT Sample in Wt. % of Total Dried Solids (%RSD**) [Number of Samples Included in Average]**

| Element | SB8 RCT | Element | SB8 RCT |
|---|---|---|---|
| Al | 1.09 (2.4) [3] | Mn | 0.802 (5.3) [6] |
| B | 0.0624 (5.7) [6] | Mo | <0.016 |
| Ba | 0.0113 (5.3) [6] | Na | 30.9 (2.9) [3] |
| Be | <0.00013 | Ni | 0.251 (10) [6] |
| Ca | 0.163 (9.2) [3] | P | 0.0322 (6.4) [3] |
| Cd‡ | 0.00269 (6.7) [3] | Pb‡ | 0.00506 (4.7) [3] |
| Ce‡‡ | 0.0313 (2.6) [3] | S | 0.148 (1.4) [3] |
| Co | 0.00137 (1.0) [3] | Sb | <0.038 |
| Cr | 0.0205 (7.2) [3] | Si | 0.363 (11) [3] |
| Cu | 0.0204 (4.1) [3] | Sn | <0.076 |
| Fe | 2.27 (7.0) [6] | Sr | 0.00518 (4.1) [3] |
| Gd‡ | 0.0121 (5.4) [3] | Th‡‡ | 0.106 (5.8) [3] |
| Hg^ | 1.20 (2.1) [3] | Ti | 0.00186 (6.8) [3] |
| K | 0.0959 (8.6) [3] | U‡‡ | 0.536 (3.0) [3] |
| La‡ | 0.00764 (5.7) [3] | V | <0.00028 |
| Li | 0.0104 (4.4) [3] | Zn | 0.00507 (2.7) [3] |
| Mg | 0.0362 (6.6) [6] | Zr‡‡‡ | 0.0329 (12) [3] |

* ICP-AES data unless specified otherwise. ^ Calculated from CV-AA data.
** Parenthetical %RSD values are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.
‡ Calculated from MS data for Cd: Cd-112, Cd-114; La-139; Gd: Gd-155, Gd-156, Gd-157, Gd-158, Gd-160; Pb: Pb-206, Pb-207, Pb-208; and Th-232; respectively.
‡‡ Calculated from the sum of MS data for Ce: Ce-140 and Ce-142; U: U-233, U-234, U-235, U-236, and U-238.
‡‡‡ Zr may be biased low based upon the value obtained for the ARG standard.

The concentration of Hg is lower than that found for the incoming SB8 Tank 40 feed, 1.86 wt.% TS, but still significant considering the DWPF processing to remove it that has occurred. The ratio of Hg:Fe in SB8 is 0.11, while in the RCT material it is 0.53, or five times as much as would be expected from sludge carryover.

Table 3-5 gives the activities, expressed as μCi/g total dried solids (TS), and concentrations, expressed as wt.% TS, of select radionuclides[1] found in the SB8 RCT sample. If the activities provided for U in the table are converted to a wt.% TS basis with the specific activities of each isotope[16] and summed, the value is 0.535 wt.% TS, essentially the same value determined for U in Table 3-4. Since both measurements came from separate digestions, i.e. those in Table 3-5 from PF and those in Table 3-4 from AR, and were analyzed by different instruments, this agreement significantly improves the reliability of this data.

In a similar manner, if the specific activities of the Pu isotopes are employed to convert the Pu isotope activities to the mass of each Pu isotope and then summed, the total Pu is not more than 2.42E-03 wt.% TS – the uncertainty arises from the detection limit value for Pu-242.

The concentration of I-129 is increased about 38x over that found for the incoming SB8 Tank 40 feed to DWPF (1.15E-03 wt.% TS).[10] This would seem to point to a significant portion not being incorporated into the glass. The concentration of Tc-99 decreased over that found in SB8 Tank 40 feed (2.02E-03 wt.% TS)[10], but a substantial 59% fraction on a wt.% TS basis is in the RCT material and this appears to be mostly soluble since there was little difference between the digestion replicates for this isotope as compared to species expected to be in the insoluble solids. The U-233, U-235, Pu-239, and Pu-241 fissile component concentrations are an order of magnitude lower than those found for SB8 Tank 40 feed[10]. The values reported previously were 6.20E-04, 2.50E-02, 1.25E-02, 4.19E-05 wt.% TS, respectively.

**Table 3-5 Activities of Select Radionuclides for the SB8 RCT Sample in μCi/g of Total Dried Solids**

| Radionuclide | Specific Activity (Ci/g) | Wt.% of Total Solids | Activity (μCi/g TS) | %RSD* | Replicates | Method |
|---|---|---|---|---|---|---|
| Tc-99 | 1.695E-02 | 1.20E-03 | 2.03E-01 | 2.7 | 4 | ICP-MS |
| I-129 | 1.765E-04 | 4.32E-02 | 7.62E-02 | 11 | 4 | I-129 |
| U-233 | 9.680E-03 | 8.19E-05 | 7.93E-03 | 6.0 | 3 | U – ICP-MS |
| U-234 | 6.248E-03 | 9.73E-05 | 6.08E-03 | 7.8 | 3 | U – ICP-MS |
| U-235 | 2.161E-06 | 3.49E-03 | 7.54E-05 | 5.4 | 3 | U – ICP-MS |
| U-236 | 6.469E-05 | 2.27E-04 | 1.47E-04 | 5.7 | 3 | U – ICP-MS |
| U-238 | 3.362E-07 | 5.31E-01 | 1.79E-03 | 5.2 | 3 | U – ICP-MS |
| Pu-238 | 1.712E+01 | 1.21E-04 | 2.08E+01 | 8.2 | 3 | Pu-238/-241 |
| Pu-239 | 6.216E-02 | 1.72E-03 | 1.07E+00 | 5.7 | 3 | ICP-MS |
| Pu-240 | 2.279E-01 | 1.13E-04 | 2.58E-01 | NA | NA | Calculated from Pu-238/-241 |
| Pu-241 | 1.030E+02 | 4.36E-06 | 4.49E+00 | 7.9 | 3 | Pu-238/-241 |
| Pu-242 | 3.818E-03 | <4.57E-04 | <1.74E-02 | NA | 3 | ICP-MS |

* Values in the %RSD column are relative to the true calculated averages of the quantities in the table, while the average values reported have been rounded off to a reasonable number of significant figures.

Solids obtained during the collection of supernate were air dried and analyzed by SEM-EDS. Figure 3-1 provides an example of the SEM images that were obtained from these air dried solids.

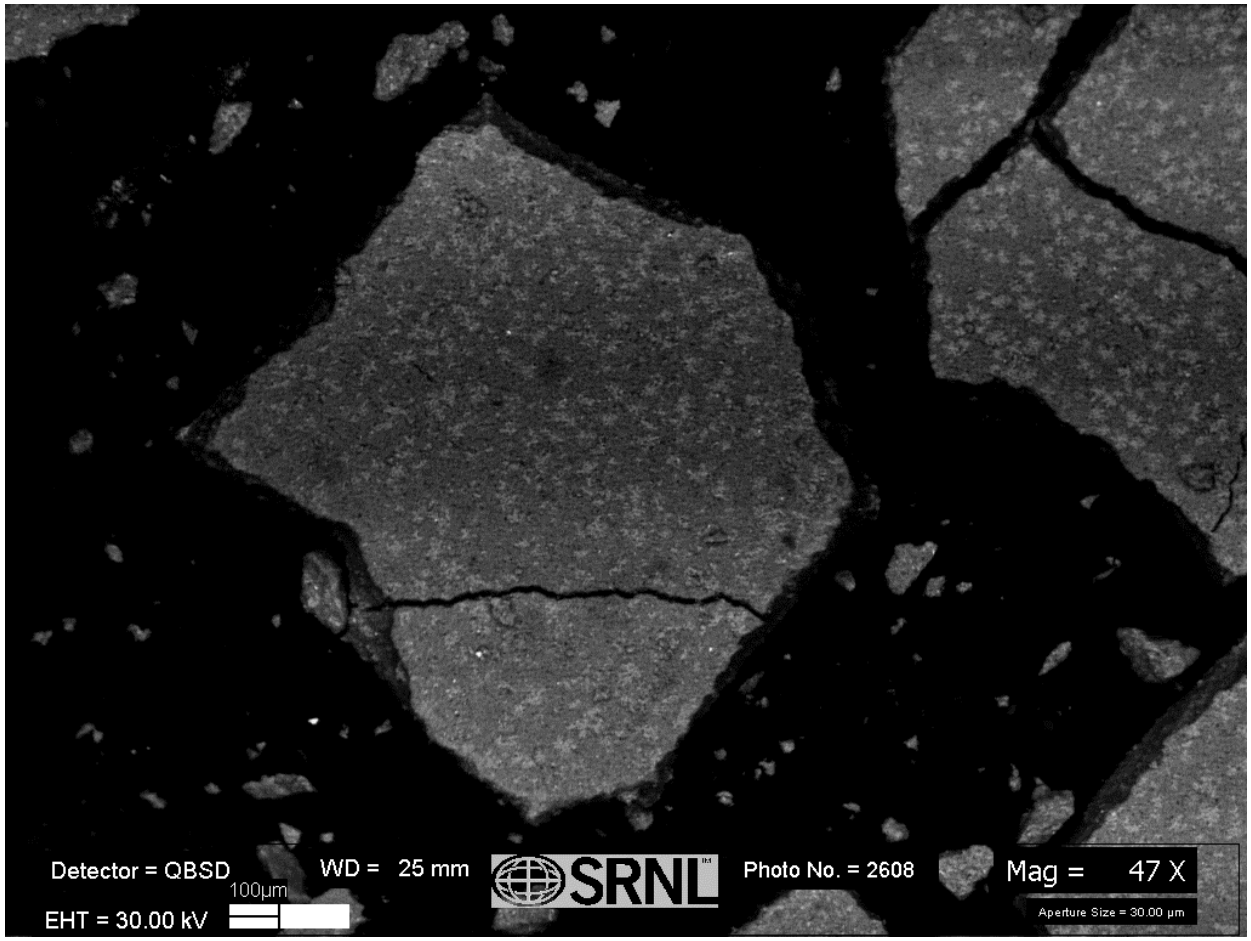


**Figure 3-1 SEM Image 2608 of SB8 RCT Solids**

The image shows a solid surface that is mottled with lighter and darker areas. As will be shown later, the EDS spectral analysis showed that the lighter areas contained U, as well as other elements, while the darker areas did not contain U.

Figure 3-2 shows two raster areas analyzed by EDS and marked "1" and "2". Both areas gave the same analysis, which is shown in Figure 3-3 for area 1, and represents a characteristic overall analysis for both samples that were examined by SEM.

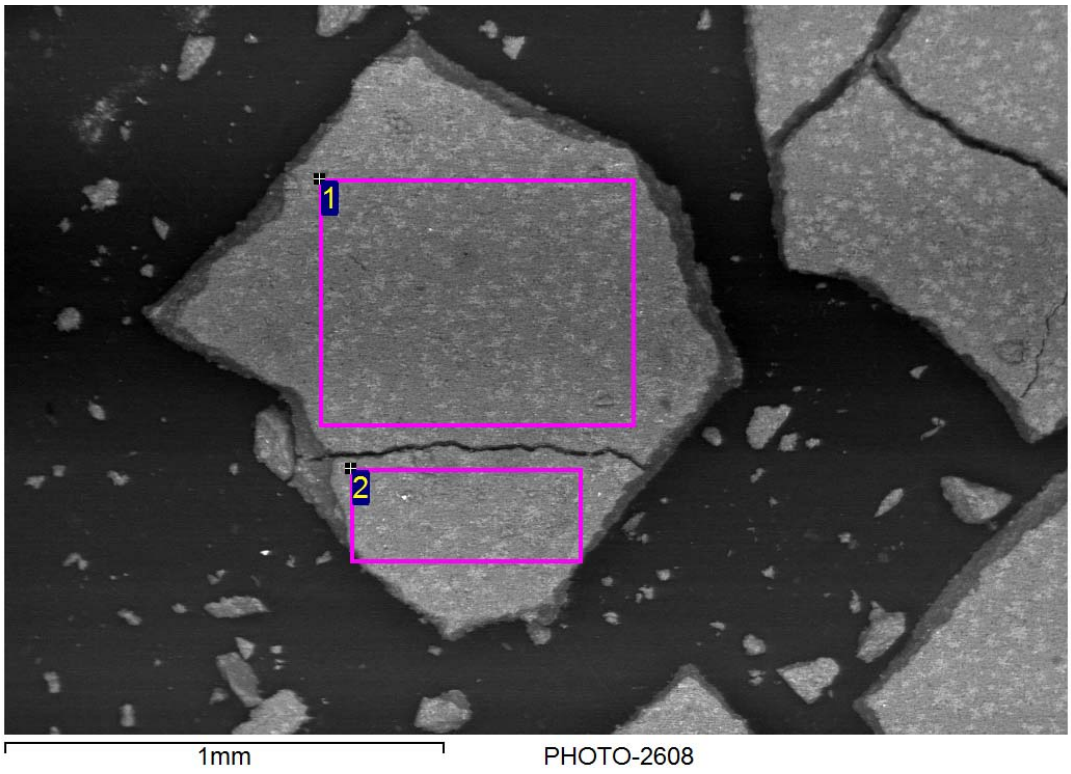


**Figure 3-2 SEM Image 2608 Showing Areas of Raster Scan for EDS Analysis**

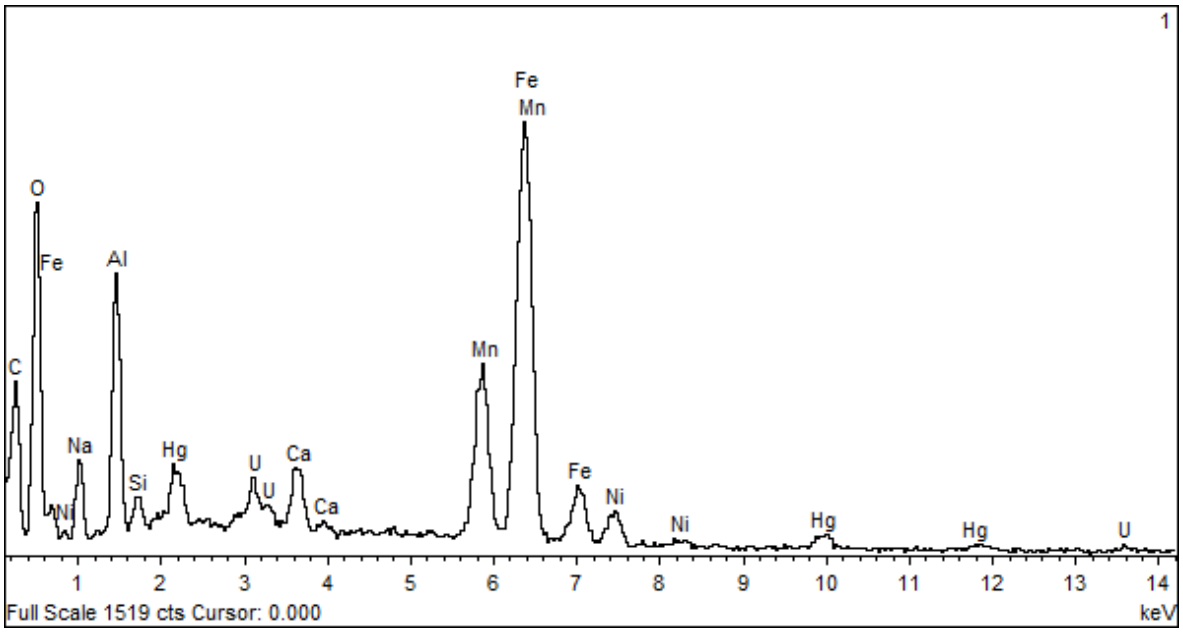


**Figure 3-3 EDS Spectra for Raster Area 1 in Image 2608**

The composition of elements matches that listed above as determined from ICP-AES, ICP-MS, and CVAA analysis of the digested material (Table 3-4). There is less Na since that is largely in solution, but

Hg, Al, Mn, U, Si, Ni, and Ca are clearly present. Closer examination of individual areas reveals the S and Th components.

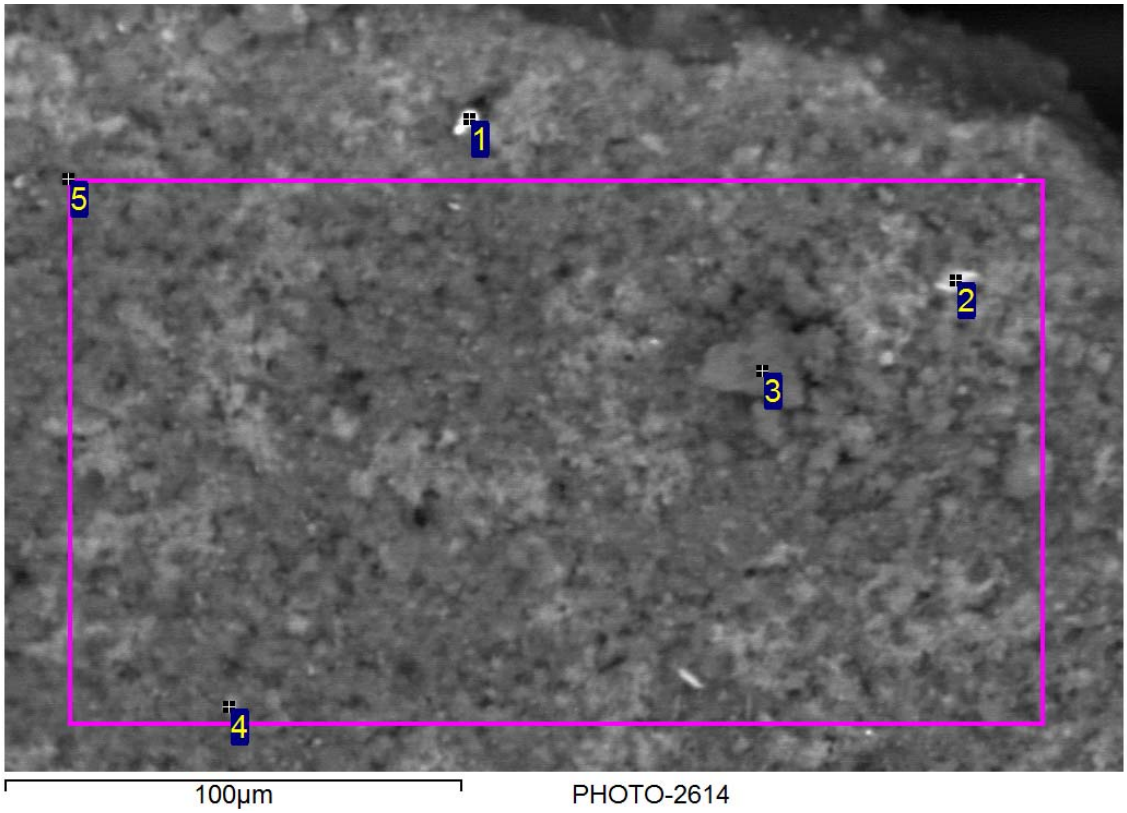


**Figure 3-4 SEM Image 2614 Showing Raster Area and Select Spots for EDS Analysis**

The EDS spectra of Spot 1 and 4 is shown in Figure 3-5. Spot 1 clearly shows the presence of Hg along with the other sludge components. There is likely some elemental Hg or Hg compounds present in the RCT solids. Spot 4 indicates the presence of Th distinct from the signal for U which does not show up at this spot. The spectrum for Spot 2 is not given since it was similar to that shown for Spot 4. Overall, as has been stated, there is about a 5:1 ratio of U:Th, but the Th can be selectively found with the SEM analysis.

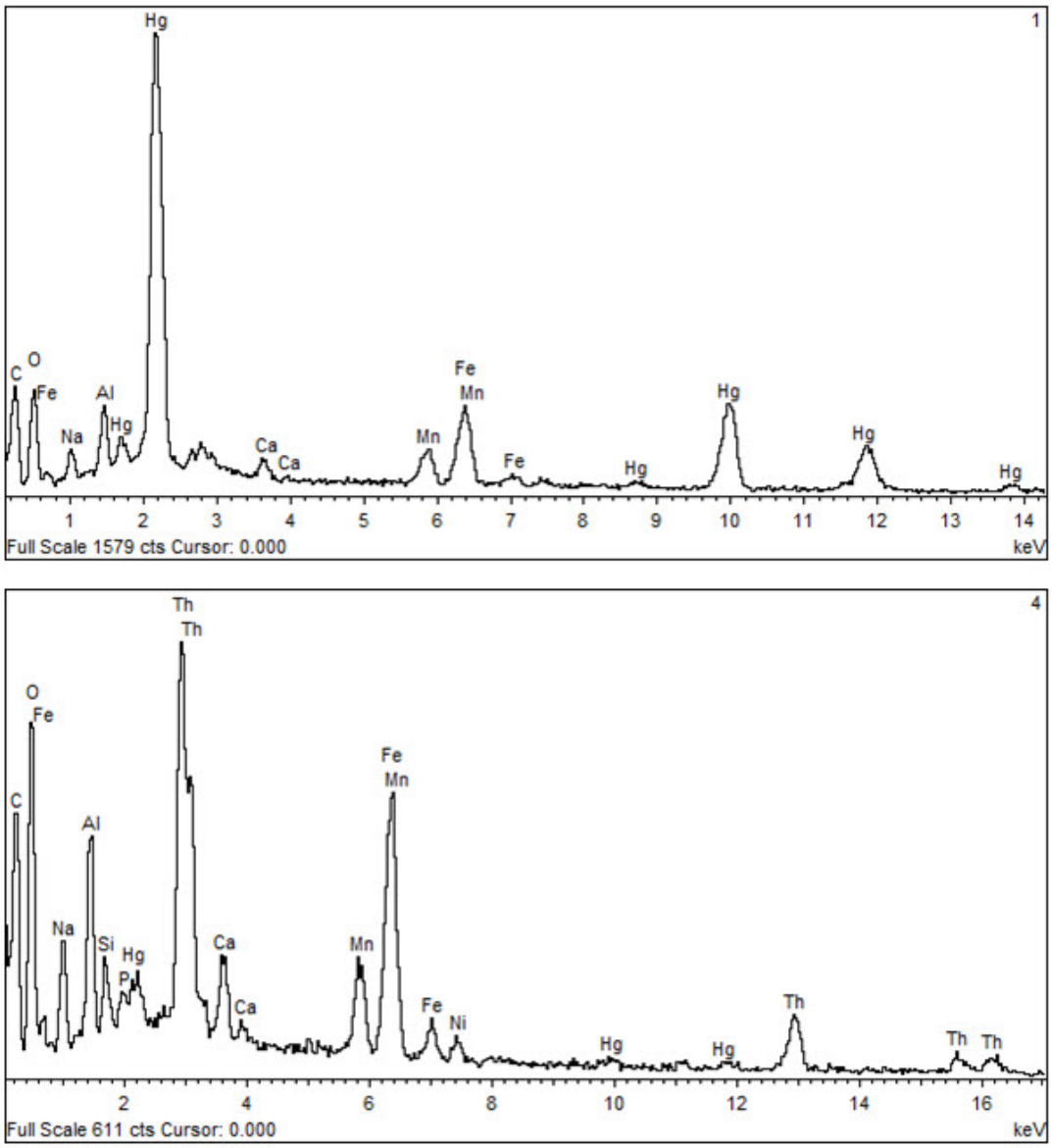


**Figure 3-5 EDS Spectra of Spots 1 and 4 in Image 2614 of SB8 RCT Solids**

Figure 3-6 provides the EDS spectra obtained for Spot 3 and Raster Area 5 in Figure 3-4. Both Spot 3 and Raster Area 5 show the usual sludge elemental components: Al, Si, Hg, Ca, Mn, Fe, Ni, and Th. Note, the keV window size is larger for the raster area, going from 0 – 14 keV, rather than 0 – 10 keV, so this makes the spectra appear slightly different. Additionally, the U signal at 3.0 – 3.4 keV is not labeled for Spot 3. The smaller raster area spectra collected here is nearly identical to that shown in Figure 3-3.

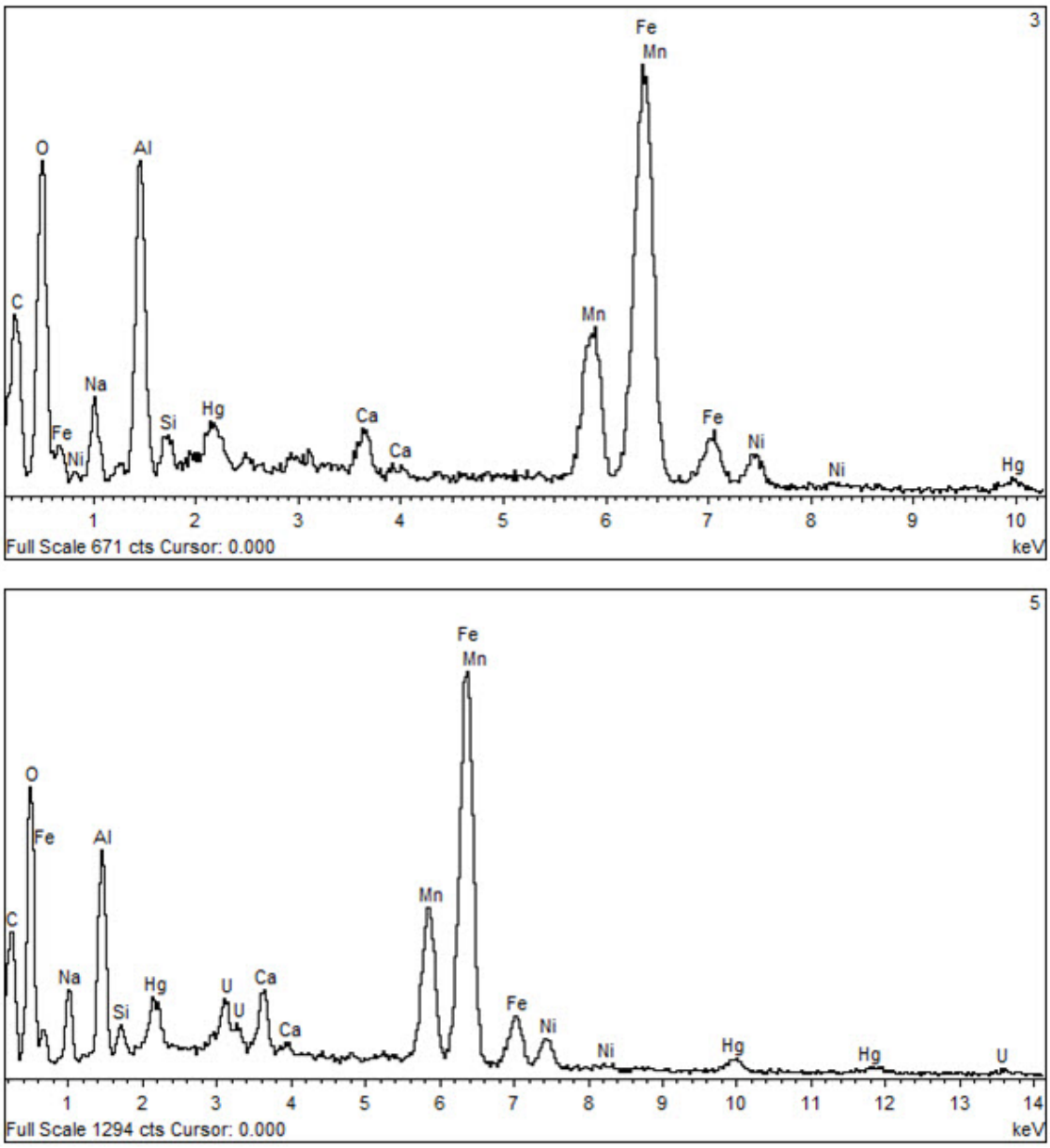


**Figure 3-6 EDS Spectra of Spot 3 and Raster Area 5 in Image 2614 of SB8 RCT Solids**

3.2 Sample Foaming Evaluations

**Figure 3-7** is a picture of the as-received RCT radioactive sample showing the solids which had settled to the bottom of the container after several days without agitation.


**Figure 3-7 Solids Settled in the RCT Sample**

The solids in the RCT sample were slow settling. When the sample was well mixed, the solution became very dark due to the suspended solids. The solids did not settle within a few hours, however the solids settled after being left undisturbed overnight. **Figure 3-8** is a comparison of the RCT sample with settled solids (on the left) with the same RCT sample after mixing (on the right).


**Figure 3-8 Settled Solids vs Well Mixed**

Foam tests were conducted to mimic three (3) different potential processing scenarios within the Receipt Collection Tank:

1) Supernate only - The supernate sample was obtained by mixing the RCT sample (approximately 700 mL), pouring off approximately 350 mL of well-mixed slurry, and allowing the solids to settle. The supernate solution was decanted into a separate container and was not filtered, but no visible solids were observed in the sample.
2) As-received sample – This was the original RCT sample containing entrained solids (0.050 wt. % insoluble solids).
3) High solids - The supernate from a portion of the as-received sample was decanted into a separate container after overnight settling (see supernate discussion above). The remaining concentrated slurry sample contained approximately 0.3 wt. % insoluble solids based on the original and final slurry volumes and the known wt. % insoluble solids content of the original sample. This high-solids condition would be expected at the bottom of the RCT and might be representative of a processing scenario in which the tank was not full of supernate, but still contained significant residual solids.

The RCT test samples were found to foam in all three test cases (supernate only, as-received, and high solids). As shown in **Figure 3-9**, the higher the solid content in the test sample, the larger the foam volume. Higher air flow rates also resulted in larger foam volumes (as would be expected).

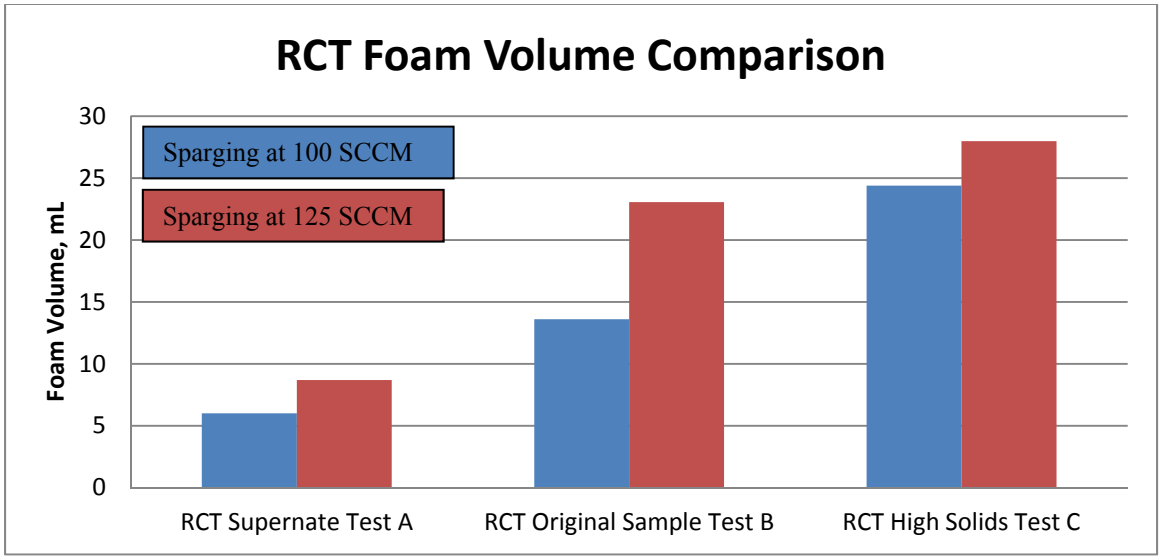


**Figure 3-9 Foam Volumes Measured for 50 mL RCT Test Samples during Air Sparging at Constant Air Flow Rates of 100 and 125 SCCM (average of 4 measurements collected over 20 minutes).**

The foam volume data measured for each sample is provided in Table 3-6. In general, the foaming behavior of the samples was somewhat erratic in that the foam height tended to pulse with time, making it difficult to measure a steady foam height in the vessel. Nonetheless, close inspection of the data reveals that there was general agreement between the constant and variable flow rate data, except for the original RCT sample. In this case, the variable flow rate data was offset towards higher foam volumes relative to the previously measured constant flow rate data. This phenomenon has been observed during foam testing of other sample types and indicates a steady increase on foam volume during the testing period (hysteresis effect).

**Table 3-6 Foam Volume Data Collected for Each RCT Sample**.

| Air Flow (SCCM) | Foam Volume (mL) Supernate | As-Received | High Solids |
|---|---|---|---|
| 100 | 6.4 | 14.1 | 23.7 |
| 100 | 5.3 | 12.5 | 26.4 |
| 100 | 5.9 | 13.8 | 23.7 |
| 100 | 6.4 | 14.1 | 23.7 |
| 100 (average) | 6.0 | 13.6 | 24.4 |
| 125 | 7.6 | 17.5 | 31.4 |
| 125 | 8.7 | 18.0 | 28.7 |
| 125 | 8.7 | 28.4 | 25.9 |
| 125 | 9.8 | 28.4 | 25.9 |
| 125 (average) | 8.7 | 23.1 | 28.0 |
| 50 | 1.9 | 10.7 | 8.2 |
| 75 | 4.2 | 17.3 | 9.4 |
| 100 | 6.4 | 26.1 | 21.5 |
| 125 | 9.2 | 28.4 | 25.9 |
| 150 | 10.4 | 36.1 | 28.2 |
| 125 | 9.2 | 31.1 | 25.9 |
| 100 | 8.1 | 25.6 | 21.5 |
| 75 | 5.3 | 20.0 | 18.7 |
| 50 | 3.0 | 15.0 | 10.9 |

In all cases the antifoam reagent provided by DWPF (Xiameter AFE-1010, Dow Corning) quickly (in less than 1 minute) dissipated all foaming in the waste samples. In the 50 mL test samples, only one drop of diluted anti-foam (discussed below) was required to prevent foaming. The antifoam reagent was very effective at destroying pre-formed foams and minimizing the formation of new foam.

Prior to adding antifoam, 0.25 g of as-received antifoam reagent (nominally 10 wt. % polydimethyl siloxane) was diluted with 4.75 g of deionized water to produce a 1:20 (by mass) diluted reagent solution, as has typically been done prior to reagent use in the tank farm. This diluted antifoam reagent solution was added to the sample to evaluate the impact on foaming. A drop is equivalent to 0.05 mL (assuming 20 drops per mL). This indicates that the addition of 1 mL of antifoam reagent, diluted as described above, per liter of RCT sample is sufficient to stop sample foaming. This is equivalent to a polydimethyl siloxane (active antifoam ingredient) concentration of 5 ppm. Based on the results, it is expected that the addition of diluted antifoam at this concentration (1 mL diluted reagent to 1 L of waste) would prevent foaming in the 2H evaporator when processing the recycle from DWPF. The data also suggests that if the solids were removed from the DWPF recycle before processing in the 2H Evaporator, foaming may be less of a concern. Given the small amount of anti-foam required to collapse the foam, the formation of hazardous organomercury species in the evaporator system is expected to be minimal.

## 4.0 Conclusions

The composition of the SB8 RCT material is largely a low base solution of 0.2M $NaNO_2$ and 0.1M $NaNO_3$ with a small amount of formate present. Insoluble solids comprise only 0.05 wt.% of the slurry. The solids appear to be largely sludge-like solids based on elemental composition and SEM-EDS analysis. The sample contains an elevated concentration of I-129 (38x) and substantial 59% fraction of Tc-99, as compared to the incoming SB8 Tank 40 feed material. The Hg concentration is 5x, when compared to Fe, of that expected based on sludge carryover. The total U and Pu concentrations are reduced significantly, 0.536 wt.% TS and 2.42E-03 wt.% TS, respectively, with the fissile components, U-233, U-235, Pu-239, and Pu-241, an order of magnitude lower in concentration than those in the SB8 Tank 40 DWPF feed material.

All of the RCT samples that were evaluated produced foam during air sparging. The higher the solids content of the test sample, the more the sample foamed. Xiameter AFE-1010 antifoam was very effective at collapsing preformed foams and stopping foam formation as sparging of the test samples continued. It was found that the foaming was stopped by addition of only 5 ppm polydimethyl siloxane to the RCT samples.

## 5.0 Future Work

No further work anticipated now that the foaming task has been completed.

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