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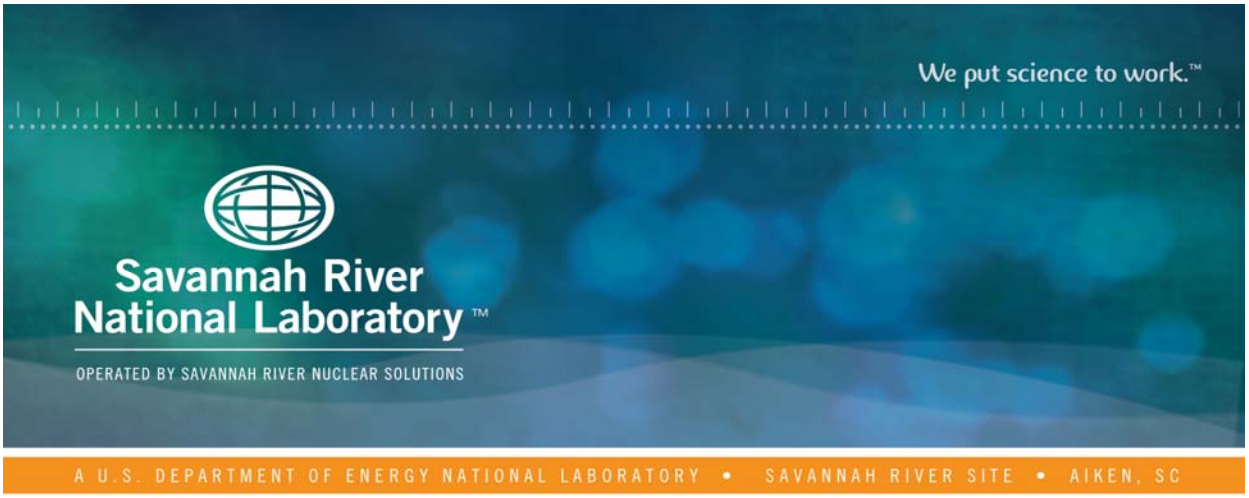


# Characterization of the March 2017 Tank 15 Waste Removal Slurry Sample (Combination of Slurry Samples HTF-15-17-28 and HTF-15-17-29)

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May 2017
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# EXECUTIVE SUMMARY

Two March 2017 Tank 15 slurry samples (HTF-15-17-28 and HTF-15-17-29) were collected during the second bulk waste removal campaign and submitted to SRNL for characterization. At SRNL, the two samples were combined and then characterized by a series of physical, elemental, radiological, and ionic analysis methods. Sludge settling as a function of time was also quantified. In summary, the results indicated that:

- the slurry density is 1.19 g/mL and the supernatant density is 1.16 g/mL
- the total solids content of the slurry is 22.5 wt% and the insoluble solids content of the slurry is 4.2 wt%
- the yield stress is 3.2 Pa and the plastic viscosity is 7.3 cP
- the dominant elemental constituents in the slurry solids (excluding oxygen, nitrogen, and hydrogen) are sodium, aluminum, mercury, iron, thorium, sulfur, and manganese, at concentrations of approximately 30, 10, 1.7, 1.6, 1.0, 0.4, and 0.3 wt% of the solids, respectively
- the primary alpha-emitting radionuclides in the slurry are Pu-238, Am-241, Pu-239, Pu-240, and Cm-244, at concentrations of approximately 3E-03, 3E-04, 1E-04, 6E-05, and 6E-05 Ci/L of the slurry, respectively (the total alpha concentration is significantly lower than the "low rem" limit of the inhalation dose potential determination)
- the primary beta-emitting radionuclides in the slurry are Sr-90, Y-90, and Cs-137, at concentrations of approximately 0.6, 0.6, and 0.3 Ci/L of the slurry, respectively (note that the Sr-90 and Y-90 concentrations were estimated from the measured concentrations of non-volatile beta and Cs-137)
- the primary gamma-emitting radionuclide in the slurry is Ba-137m, at a concentration of approximately 0.25 Ci/L of the slurry
- the total uranium content of the slurry solids is approximately 1.6E-02 wt%, with a U-235 enrichment of ~9%
- the total plutonium content of the slurry solids is approximately 8E-04 wt%, with Pu-240 comprising ~13% of the plutonium
- the supernatant sodium concentration is approximately 3.7 M and the dominant supernatant anions are free hydroxide, nitrite, nitrate, carbonate, and aluminate, at concentrations of approximately 1.4, 0.9, 0.8, 0.3 and 0.2 M, respectively
- the supernatant mercury concentration is approximately 60 mg/L
- moderately rapid sludge settling occurred over the first days, but the sludge settling rate declined significantly over the remainder of the settling period. (Over the first two days, the settled sludge volume dropped from 100 mL to ~74 mL. In contrast, the settled sludge volume was ~65 mL after a settling period of one week and ~59 mL after a settling period of four weeks.)

The characterization results reported in this document are consistent with expectations based upon waste type, process knowledge, comparisons between alternate analysis techniques, and comparisons with the characterization results obtained for the November 2016 Tank 15 slurry sample (the sample collected during the first bulk waste removal campaign).

# TABLE OF CONTENTS

# LIST OF TABLES



# LIST OF FIGURES

# LIST OF ABBREVIATIONS

| | |
|---|---|
| AD | Analytical Development |
| AR | Aqua regia |
| CVAA | Cold vapor atomic absorption |
| IC | Ion chromatography |
| ICP-AES | Inductively coupled plasma atomic emission spectroscopy |
| ICP-AES-S | ICP-AES axial sulfur method |
| ICP-MS | Inductively coupled plasma mass spectrometry |
| LSC | Liquid scintillation counting |
| MDL | Minimum detection limit |
| n | Number of determinations |
| PF | Peroxide fusion |
| RSD | Relative standard deviation |
| SRNL | Savannah River National Laboratory |
| SRR | Savannah River Remediation |
| TIC | Total inorganic carbon |

## 1.0 Introduction

Two 200 mL sludge slurry samples were collected from Savannah River Site Tank 15 on March 15, 2017. The sampling location was fifty-seven inches from the bottom of the tank and the sample identification numbers were HTF-15-17-28 and HTF-15-17-29. The estimated temperature of the waste at the time of sampling was between 50 and 60 °C.

The two samples were submitted to SRNL for characterization activities supporting determination of Inhalation Dose Potential and sludge batch planning purposes. The two samples were received at SRNL on March 16, 2017, and transferred from the samplers to a 500 mL polybottle where the two samples were combined and mixed.

The applicable scope of characterization work for this task is defined in Technical Task Request X-TTR-S-00050,[2] Task Technical and Quality Assurance Plan SRNL-RP-2016-00635,[3] and an email message from J. E. Occhipinti dated March 9, 2017 (see Attachment A).

## 2.0 Objectives

The specific objectives were to characterize:

a) densities of the slurry and supernatant;
b) the solids distribution of the slurry (total, dissolved, insoluble, and soluble solids);
c) the rheological properties of the slurry (yield stress and plastic viscosity);
d) elemental constituents in the slurry;
e) select radionuclides in the slurry;
f) primary supernatant ions;
g) supernatant mercury; and
h) sludge settling as a function of time.

## 3.0 Methodology

### 3.1 Laboratory Methods

*Densities*: Density measurements were conducted at a temperature of ~21 °C. This temperature was governed by the Shielded Cells conditions at the time of the measurements. Densities were measured using weight-calibrated balances and 8-9 mL volume-calibrated plastic test tubes. Three individual slurry aliquots and three individual supernatant aliquots were utilized in the measurements. Supernatant was generated as a filtrate by passing slurry through a 0.45 µm filtration membrane (note that this generation method was utilized for all of the supernatant analyses – not just those used for determining density). The density of a deionized water standard was determined along with the slurry and supernatant determinations, to demonstrate measurement accuracy.

*Solids Distribution*: Total solids and dissolved solids determinations were performed by driving water from slurry and supernatant aliquots (respectively) at a nominal temperature of ~110 °C. Three individual

slurry aliquots and three individual supernatant aliquots were utilized in the measurements. The mass of each aliquot was ~3.0 g. Insoluble and soluble solids concentrations were calculated based on the total solids and dissolved solids measurements. The dissolved solids content of a 15 weight percent sodium chloride solution was determined alongside the sample determinations, to demonstrate measurement accuracy.

*Rheological Properties of the Slurry*: Yield stress and the plastic viscosity measurements were performed by generating "flow curves" of shear stress as a function of shear rate. The data for the flow curves was acquired using the Haake RV-30 viscometer fitted with a MV1 rotor, at a temperature of 25º C. The shear rate was increased from 0-600/s over a five minute period, held at 600/s for one minute, and then reduced from 600-0/s over a five minute period. The yield stress was determined by extrapolating the linear portion of the flow curve back to the Y-axis. The plastic viscosity was determined by calculating the slope of the linear portion of the curve. For each sludge blend, duplicate rheology measurements were performed on a single 50-60 mL slurry sample aliquot. Note that the flows curves are given in Attachment B, whereas the yield stress and plastic viscosity results are reported in Section 4.0.

*Elemental Analysis of Slurry Solids*: In preparation for the elemental analyses (prior to submittal), three slurry aliquots were digested by the aqua regia (AR) method and three slurry aliquots were digested by the peroxide fusion (PF) method. Note that the AR method utilized a sealed vessel to prevent loss of volatile constituents. Applicable blanks were also processed through the digestion methods, and multi-element standards were submitted along with the digest solutions, where applicable, for quality assurance purposes. The total solids mass of each sample aliquot was ~0.25 g, and the volume of each final digest solution was 100 mL.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on both the AR and PF digest solutions, along with the applicable blanks and multi-element standard solution for quality assurance purposes. The ICP-AES measurements provided quantification of most of the elemental constituents reported in this document. The ICP-AES axial sulfur method (ICP-AES-S) was performed on the AR digest solutions for quantifying sulfur. Cold vapor atomic absorption (CVAA) spectroscopy was performed on the AR digest solutions (along with the AR blank) for the purpose of quantifying mercury. Inductively coupled plasma mass spectrometry (ICP-MS) was performed on the AR digest solutions (along with the AR blank) for the purpose of quantifying neodymium and uranium. Dilution-correction of the results was performed by Analytical Development (AD) prior to reporting.

The elemental results determined through ICP-AES analyses were based either solely on the AR digest solutions, solely on the PF digest solutions, or on both the AR and PF digest solutions, depending on the following factors: potential for interference, magnitude of "blank values," magnitude of minimum detection limits, consistency of data, and apparent anomalies. Note that applicable digestion method(s) feeding the results is identified in the table providing the results.

The elemental results determined through ICP-MS analyses were based on sums of specific isotope results. For neodymium, the isotope results that were summed were those associated with mass numbers 143-146, 148, and 150. For uranium, the isotope results that were summed were those associated with mass numbers 233-236 and 238.

*Radionuclide Analysis of the Slurry Solids*: The same PF and AR digestion methods that were used for the slurry elemental analyses were utilized for preparing the slurry aliquots for the select radioisotope analyses. The PF digest solutions were analyzed for radioisotopes by the following methods: a) gamma spectroscopy for Cs-137/Ba-137m; b) chemical separation coupled with gamma spectroscopy for Am-241; c) chemical separation coupled with alpha spectroscopy for Pu-238, Pu-239/240, Am-242m, and Cm-244; d) chemical separation coupled with liquid scintillation counting (LSC) for Pu-241; e) chemical separation coupled with low energy photon/X-ray, thin-windowed, semi-planar gamma spectroscopy for Cm-245; and f) LSC for total alpha and non-volatile beta. The AR digest solutions were analyzed by ICP-MS for Th-232, U-233, U-234, U-235, U-236, U-238, Np-237, Pu-239, and Pu-240. Dilution-correction of the results was performed prior to reporting. A sum of the primary alpha-emitting radionuclides was calculated to compare with the total alpha result. Two sigma upper bounds for the radionuclide concentrations were calculated based on the estimated analytical uncertainties associated with the radionuclide measurements.

*Elemental Analysis of the Supernatant*: In preparation for the elemental analyses (prior to submittal), three supernatant aliquots were each diluted by an average factor of ~26 (on a volume basis), using 0.5 M $HNO_3$. Use of the 0.5 M $HNO_3$ diluent resulted in a final solution pH of ~1, which was considered beneficial for minimizing loss of constituents through sorption to the walls of the sample submittal vessels and through potential precipitation reactions. An applicable "acid blank" and a multi-element standard were submitted along with the acidified/diluted supernatant, for quality assurance purposes.

ICP-AES and CVAA were performed on the acidified/diluted supernatant aliquots, to quantify elemental aluminum, mercury, potassium, and sodium (Al, K, and Na by ICP-AES, and Hg by CVAA). Note that prior to the supernatant mercury measurements, AD performed permanganate-persulfate digestions on the acidified/diluted sample aliquots. Dilution-correction of the results was performed prior to reporting.

*Anion Analysis of the Supernatant*: In preparation for the anion analyses (prior to submittal), three supernatant aliquots were each diluted by an average factor of ~27 (on a volume basis), using de-ionized water. Ion chromatography (IC) was performed on the diluted supernatant aliquots, to quantify bromide, chloride, fluoride, formate, nitrate, nitrite, oxalate, phosphate, and sulfate. Total inorganic carbon (TIC) analyses were performed to quantify carbonate, and base titration analyses were performed to quantify free hydroxide. Aluminate was quantified based on the ICP-AES supernatant aluminum concentration results, assuming 100% of the aluminum was present as aluminate. Dilution-correction of the results was performed prior to reporting.

*Monitoring of Sludge Settling*: Sludge settling was monitored as a function of time, using a 100 mL volume of the suspended slurry transferred to a specially-fabricated capped graduated cylinder. The inner diameter of the graduated cylinder was approximately 1.0 inch. Visual determinations of settled sludge volume were recorded over a 28 day period, with relatively frequent monitoring at the beginning of the settling period (when the settling rate was highest) and less frequent monitoring as the settling period progressed (when the settling rate declined). Results of the settled sludge volumes were plotted as a function of time, and a logarithmic relationship between the settled sludge volume and the settling time was determined.

### 3.2 Format of the Reported Results

Mean results, based on the average of all applicable analytical determinations, are reported in this document, along with the percent relative standard deviation (%RSD) and the number of determinations (n) feeding each mean. %RSD provides an indication of the measurement variation between replicate determinations, but is typically not an indicator of analytical accuracy. In general, the one sigma analytical uncertainty as reported by Analytical Development was 10%, although it was sometimes lower or higher. Specifically, the one sigma analytical uncertainties reported by AD were: a) ~10% for base titration, IC, ICP-AES, ICP-AES-S, ICP-MS, and TIC analyses; b) ~20% for CVAA analyses; and c) ranging from 5-20% for radionuclides quantified by counting methods (gamma spectroscopy, alpha spectroscopy, and liquid scintillation counting). As such, only one to two of the leading digits reported for the AD analysis results should be considered significant.

### 3.3 Assessment of the Results

Multiple approaches were used to assess the validity of the analytical data being reported. The primary goal of this was to demonstrate that the reported results were both reasonable and consistent with expectations. Focus areas of the assessment included: a) densities and solids distribution; b) dominant constituents in the slurry solids; c) key radionuclides; d) charge balance of the ions in the supernatant; e) dominant supernatant salts feeding the dissolved solids; and f) comparisons with characterization results for the November 2016 Tank 15 sample.[1] Discussion of the assessment approaches and results is included in Section 4.0. Note that when characterization results were compared, percent differences were calculated as follows:

% Difference = 100 × [(absolute value of the difference between results) ÷ (the average result)]

### 3.4 Quality Assurance

Standard laboratory quality assurance protocols were used to assure analytical data quality. This included use of blanks, standards, and replicate determinations.

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.

## 4.0 Results and Discussion

Photographs of the samplers placed in the Shielded Cells, the transfer of material from the samplers into the 500 mL laboratory polybottle, and the final combined slurry sample in the polybottle are given in Figure 4-1. The total combined slurry sample mass was measured to be 508 grams.

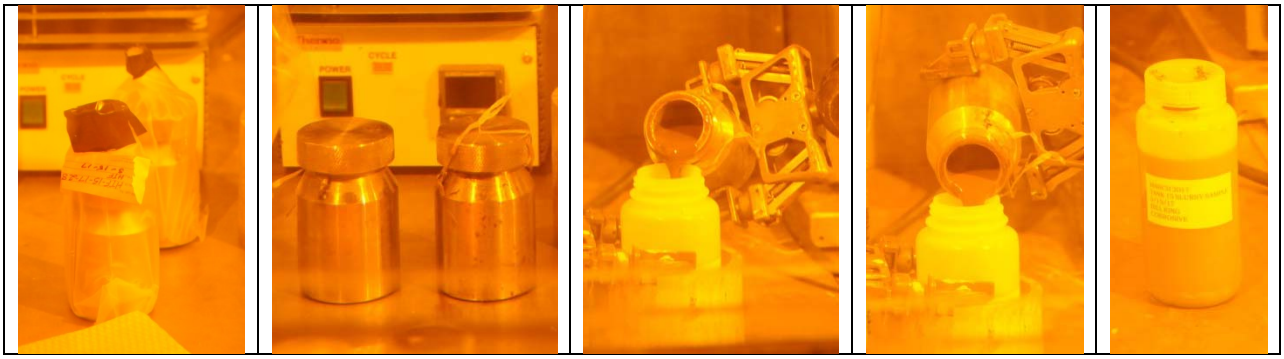


**Figure 4-1. Unopened Samplers in the Shielded Cell and Transfer of Material to the Polybottle**

During transfer of the samples to the polybottle, the slurry material was found to have the appearance of typical tank sludge, with a brown color, but somewhat thinner in consistency than the November 2016 Tank 15 slurry sample (HTF-15-16-100[1]). Whereas the November 2016 Tank 15 had the consistency of a thick syrup while being poured, the March 2017 sample had the consistency of a relatively thin oil.

Density, solids distribution, and rheology results for the March 2017 sample are given in Table 4-1. These results indicate that the March 2017 contains less soluble and insoluble solids than the November 2016 sample, as evidenced by the lower slurry and supernatant densities (1.19 g/mL and 1.16 g/mL, respectively), the lower total and dissolved solids contents (22.5 wt% of the slurry and 19.1 wt% of the supernatant, respectively), and the lower yield stress and plastic viscosity (3.2 Pa and 7.3 cP, respectively). Whereas the November 2016 slurry contained 22.5 wt% soluble solids and 7.9 wt% insoluble solids, the March 2017 slurry contained 18.3 wt% soluble solids and 4.2 wt% insoluble solids. The lower insoluble solids content and yield stress of the March 2017 slurry is consistent with the observation that the March 2017 sample appeared “thinner” in consistency than the November 2016 sample.

**Table 4-1. Densities, Solids Distribution, and Rheology**

| Measurement | Mean Result | %RSD (n) |
|---|---|---|
| Slurry density, g/mL | 1.19 | 0.5 (3) |
| Supernatant density, g/mL | 1.16 | 0.5 (3) |
| Total solids, wt% of slurry | 22.5 | 1.3 (3) |
| Dissolved solids, wt% of supernatant | 19.1 | 0.1 (3) |
| Insoluble solids (calculated value), wt% of slurry | 4.2 | N/A |
| Soluble solids (calculated value), wt% of slurry | 18.3 | N/A |
| Yield stress of the slurry, Pa | 3.2 | 1.5 (2) |
| Plastic viscosity of the slurry, cP | 7.3 | 0.2 (2) |

The relative magnitudes of the slurry and supernatant densities (1.19 and 1.16 g/mL, respectively) are consistent with expectations based on the relative magnitudes of the total solids and dissolved solids contents (22.5 and 19.1 wt%, respectively). Specifically, the amount that the density of the slurry exceeds that of water (~0.19 g/mL) is about 20% higher than the amount that the density of the supernatant exceeds that of water (~0.16 g/mL) – which closely matches the result of the total solids content being about 20% higher than the dissolved content (22.5 ÷ 19.1 ≈ 1.2). Based on this correlation, the density and solids distribution results certainly appear sound.

All of the RSDs for the densities and solids content measurements were low (≤ 1.5%), demonstrating high measurement precision and lack of any apparent shielded cells processing anomalies.

Concentrations of the elemental constituents in the slurry solids are given in Table 4-2, with concentrations greater than 0.1 wt% shaded for easy identification. (Note that this table contains analytical results for the primary elemental constituents measured by ICP-AES, mercury by CVAA, and neodymium and uranium by ICP-MS). As shown in the table, the dominant constituents in the solids include sodium, aluminum, mercury, iron, thorium, sulfur, and manganese, with concentrations of approximately 30, 10, 1.7, 1.6, 1.0, 0.4, and 0.3 wt%, respectively. In contrast, the uranium concentration in this slurry is relatively low (~0.016 wt%), which is consistent with the waste receipt history documented in Sludge 1.5.[4] Other constituents that were detectable, but less than 0.1 wt%, include nickel, chromium, lanthanum, calcium, neodymium, magnesium, barium, strontium, and zinc, with concentrations of approximately 0.057, 0.053, 0.046, 0.041, 0.039, 0.026, 0.013, 0.0078, and 0.0045 wt%. The relatively high aluminum, mercury, and thorium concentrations and the high aluminum to iron ratio are consistent with expectations based on the type of waste received into Tank 15.

Most of the RSDs for the elemental analyses were limited to ten percent or less, demonstrating normal analytical precision. In contrast, the RSDs applicable to calcium, strontium, and thorium, were higher, at 12, 12, and 15%, respectively. These higher RSDs give an indication that the propagated analytical uncertainties associated with these three constituents are likely higher than those of the other constituents.

Concentrations of select radioisotopes in the slurry solids are given on a slurry activity basis (Curies per liter of slurry) in Table 4-3. Pu-238, Am-241, Pu-239, Pu-240, and Cm-244 are the alpha emitters present at the highest activity concentrations (~3E-03, 3E-04, 1E-04, 6E-05, and 6E-05 Ci/L, respectively). In contrast, the activity concentrations of the other actinide isotopes are lower by up to four orders of magnitudes – this includes Th-232, the uranium isotopes, Am-242m and Cm-245. Comparison of the individual Pu-239 and Pu-240 results determined by ICP-MS (1.02E-04 and 6.00E-05 Ci/L, respectively) versus the combined Pu-239/240 result determined by alpha spectroscopy (1.21E-04 Ci/L) shows a 29% difference. Although a 29% difference may seem higher than expected, it is deemed reasonable, given that the one sigma analytical uncertainty of an individual ICP-MS measurement is approximately 10% and the one sigma analytical uncertainty of the counting method is approximately 22%.

The sum of the concentrations of the individually measured alpha emitters is ~4E-03 Ci/L, which is consistent with the total alpha result of <4.9E-03 Ci/L, where the measured alpha signal was biased high due to spillover of the much more dominant beta peak. Note that the estimated two sigma upper bound for the sum of the primary alpha emitters is ~4.6E-03 Ci/L, which is also consistent with the total alpha result (<4.9E-03 Ci/L). Clearly, the alpha concentration is significantly below the defined “low rem” limit (0.2247 Ci/L) associated with the inhalation dose potential determination.

**Table 4-2. Elemental Constituents in the Slurry (Shading Indicates Concentrations > 0.1 wt%)**

| Constituent | Digestion Method | Mean Result, wt% of solids | %RSD (n) |
|---|---|---|---|
| Ag | AR | <2.1E-03 | N/A |
| Al | AR/PF | 9.90E+00 | 2.5 (6) |
| B | AR | <1.5E-02 | N/A |
| Ba | AR | 1.33E-02 | 0.5 (3) |
| Be | AR | <6.5E-05 | N/A |
| Ca | AR | 4.10E-02 | 12 (3) |
| Cd | AR | <2.0E-03 | N/A |
| Ce | AR | <5.7E-03 | N/A |
| Co | AR | <2.2E-03 | N/A |
| Cr | AR/PF | 5.28E-02 | 10 (6) |
| Cu | AR | <1.4E-02 | N/A |
| Fe | AR/PF | 1.60E+00 | 0.6 (6) |
| Gd | AR | <1.6E-03 | N/A |
| Hg | AR | 1.73E+00 | 2.1 (3) |
| K | AR | <1.9E-01 | N/A |
| La | AR | 4.58E-03 | 4.2 (3) |
| Li | AR | <2.1E-03 | N/A |
| Mg | AR | 2.57E-02 | 2.6 (3) |
| Mn | AR/PF | 2.97E-01 | 0.7 (6) |
| Mo | AR | <2.4E-02 | N/A |
| Na | AR | 3.02E+01 | 0.5 (3) |
| Nd | AR | 3.88E-02 | 1.0 (3) |
| Ni | AR | 5.72E-02 | 1.2 (3) |
| P | AR | <6.1E-02 | N/A |
| Pb | AR | <2.8E-02 | N/A |
| S | AR | 4.23E-01 | 2.6 (3) |
| Sb | AR | <3.0E-02 | N/A |
| Si | PF | <8.8E-02 | N/A |
| Sn | AR | <1.8E-02 | N/A |
| Sr | AR/PF | 7.77E-03 | 12 (6) |
| Th | AR/PF | 9.84E-01 | 15 (6) |
| Ti | AR | <6.3E-03 | N/A |
| U | AR | 1.61E-02 | 2.8 (3) |
| V | AR | <8.3E-04 | N/A |
| Zn | AR | 4.52E-03 | 7.9 (3) |
| Zr | AR | <7.0E-02 | N/A |

**Table 4-3. Select Radionuclides in the Slurry**

| Radionuclide | Mean Result, Ci/L | %RSD (n) | 1σ Uncertainty, % | Mean Result + 2σ |
|---|---|---|---|---|
| Cs-137 | 2.60E-01 | 3.3 (3) | 5.0 | 2.86E-01 |
| Ba-137m | 2.46E-01 | 3.3 (3) | 5.0 | 2.71E-01 |
| Th-232 | 2.99E-07 | 1.2 (3) | 10.0 | 3.59E-07 |
| U-233 | 5.25E-06 | 3.1 (3) | 10.0 | 6.30E-06 |
| U-234 | 1.26E-06 | 3.0 (3) | 10.0 | 1.51E-06 |
| U-235 | 8.12E-09 | 4.3 (3) | 10.0 | 9.74E-09 |
| U-236 | 5.66E-08 | 1.3 (3) | 10.0 | 6.79E-08 |
| U-238 | 1.27E-08 | 2.8 (3) | 10.0 | 1.52E-08 |
| Np-237 | 5.81E-07 | 2.5 (3) | 10.0 | 6.97E-07 |
| Pu-238 | 3.34E-03 | 14 (3) | 9.9 | 4.00E-03 |
| Pu-239 | 1.02E-04 | 1.1 (3) | 10.0 | 1.22E-04 |
| Pu-240 | 6.00E-05 | 2.6 (3) | 10.0 | 7.20E-05 |
| Pu-239/240 | 1.21E-04 | 33 (3) | 21.9 | 1.74E-04 |
| Pu-241 | 6.20E-04 | 15 (3) | 14.1 | 7.95E-04 |
| Am-241 | 3.15E-04 | 21 (3) | 5.6 | 3.50E-04 |
| Am-242m | <1.1E-06 | N/A | N/A | N/A |
| Cm-244 | 6.07E-05 | 20 (3) | 12.1 | 7.54E-05 |
| Cm-245 | <4.3E-05 | N/A | N/A | N/A |
| Total alpha | <4.9E-03 | N/A | N/A | N/A |
| Non-volatile beta | 1.48E+00 | 11 (3) | 10.0 | 1.77E+00 |
| Primary alpha sum | 3.89E-03 | N/A | N/A | 4.64E-03 |

Notes: a) one sigma uncertainty values based on counting statistics only – reported values represent the maximum counting uncertainties for all replicates; and b) total alpha represents the sum of alpha contribution and beta spillover, where beta contribution is significant – uncertainty is not quantified in this case.

The total non-volatile beta concentration is ~1.5 Ci/L, which is assumed to be driven by beta emitters Sr-90, Y-90, and Cs-137 (Sr-90/Y-90 was not one of the requested analyses). Based on the measured Cs-137 concentration of ~0.3 Ci/L, the Sr-90 and Y-90 concentrations are each thought to be on the order of 0.6 Ci/L, although not specifically measured. Consistent with expectations, Pu-241 (~6E-04 Ci/L) is a very minor beta contributor, due to its initial small isotopic abundance coupled with its significant radiological decay occurring since production (Pu-241 half-life ≈ 14 years).

The Sr-90/Y-90 concentrations projected for the March 2017 sample (0.6 Ci/L) are about 55% of the Sr-90/Y-90 concentrations identified for the November 2016 sample (1.05 Ci/L). This makes sense, given that Sr-90/Y-90 are typically insoluble, and the insoluble solids content of the March 2017 sample (4.2 wt%) is about 55% that of the November 2016 sample (7.9 wt%).

The Cs-137 concentration for the March 2017 sample (0.26 Ci/L) is about 10% higher than that of the November 2016 sample (0.23 Ci/L). This difference is considered minor, given the magnitude of the total propagated sampling and analysis uncertainties, the differences between the March 2017 and November 2016 samples, and the high solubility of cesium which makes its distribution highly dependent on the supernatant transfer history. Due to the Cs-137 that is present, the primary gamma emitter is Ba-137m, which exists at a concentration of ~0.25 Ci/L (Ba-137m is the short-lived progeny of Cs-137).

A comparison of the uranium and plutonium mass concentrations is presented in Table 4-4. On a mass basis, the total uranium content is ~1.6E-02 wt% of the solids, with a U-235 enrichment of ~9%, and the total plutonium content is ~8E-04 wt% of the solids, with a Pu-240 fraction of ~13%. Enriched uranium and high-burn plutonium are consistent with expectations based on the waste receipt history of this tank. However, it should be noted that the U-235 enrichment value for the sample is significantly lower than the typical U-235 enrichment value identified for Tank 15 waste in the Sludge 1.5 database.[4] Investigation into the source of this difference may be warranted.

**Table 4-4. Mass Concentrations of Uranium and Plutonium Isotopes**

| Radionuclide | Mean Result, wt% of Solids | Isotopic Distribution, Mass % of Element |
|---|---|---|
| U-233 | 2.02E-04 | 1.3 |
| U-234 | 7.53E-05 | 0.5 |
| U-235 | 1.40E-03 | 8.7 |
| U-236 | 3.27E-04 | 2.0 |
| U-238 | 1.41E-02 | 87.6 |
| Total U | 1.61E-02 | |
| Pu-238 | 7.30E-05 | 9.3 |
| Pu-239 | 6.11E-04 | 77.8 |
| Pu-240 | 9.84E-05 | 12.5 |
| Pu-241 | 2.25E-06 | 0.3 |
| Total Pu | 7.85E-04 | |

Conversion of the isotopic Th-232 activity concentration given in Table 4-3 to a Th-232 mass concentration yields a value of 1.02E+00 wt% of solids. Comparison of this value with the elemental thorium value given in Table 4-2 (0.984 wt% of solids) shows very good agreement, with the two values differing by only about 4%. This relatively small difference provides confidence that the isotopic measurements of ICP-MS and the elemental measurements of ICP-AES are accurate.

Molar concentrations of the primary supernatant ions are given in Table 4-5. Also given in Table 4-5 are the corresponding equivalence concentrations allowing a charge balance comparison of the pertinent cations and anions. The pertinent cations include sodium, with a measured concentration of 3.65M, and potassium, with a concentration less than the minimum detection limit (MDL) of 2.0E-02 M. In contrast, the measurable anions include free hydroxide, nitrite, nitrate, carbonate, aluminate, sulfate, and oxalate, with concentrations of approximately 1.4, 0.9, 0.8, 0.3, 0.2, 0.04, and 0.02 M, respectively. Other anions, including bromide, fluoride, chloride, formate, and phosphate, were less than the MDLs, which ranged from approximately 3E-03 to 2E-02 M.

For the charge balance comparison, the molar ion concentrations were converted to equivalence concentrations based upon the applicable ionic charges – one for the measurable monovalent ions including sodium, free hydroxide, nitrite, nitrate, and aluminate – and two for the measurable divalent ions including carbonate, sulfate, and oxalate. Note that the ions with concentrations below the MDLs were not included in the charge balance assessment, as they were assumed to have an insignificant impact on the total charge balance.

As shown in Table 4-5, the sum of the pertinent cations was 3.65 eq/L, while the sum of the pertinent anions was 3.96 eq/L. The difference between these values is ~8%, a value which indicates good data consistency, as it is clearly below the total anticipated sampling and analysis uncertainty. (Neglecting

processing uncertainty, the estimated one sigma analytical uncertainty for an individual determination is approximately 10%).

**Table 4-5. Primary Supernatant Ions and Charge Balance**

| Ion | Mean Concentration, Molarity | %RSD, n=3 | Corresponding eq/L | | Difference |
|---|---|---|---|---|---|
| | | | Cationic | Anionic | |
| $Na^+$ | 3.65E+00 | 2.4 | 3.65 | N/A | |
| $K^+$ | <2.0E-02 | N/A | N/A | N/A | |
| Free $OH^-$ | 1.36E+00 | 9.6 | N/A | 1.36 | |
| $NO_2^-$ | 9.41E-01 | 1.9 | N/A | 0.941 | |
| $NO_3^-$ | 7.85E-01 | 1.0 | N/A | 0.785 | |
| $CO_3^{2-}$ | 2.90E-01 | 2.3 | N/A | 0.580 | |
| $Al(OH)_4^-$ | 1.95E-01 | 2.9 | N/A | 0.195 | |
| $SO_4^{2-}$ | 3.56E-02 | 0.8 | N/A | 0.0712 | |
| $C_2O_4^{2-}$ | 1.63E-02 | 0.6 | N/A | 0.0326 | |
| $Br^-$ | <1.6E-02 | N/A | N/A | N/A | |
| $F^-$ | <1.4E-02 | N/A | N/A | N/A | |
| $Cl^-$ | <7.4E-03 | N/A | N/A | N/A | |
| $CHO_2^-$ | <5.8E-03 | N/A | N/A | N/A | |
| $PO_4^{3-}$ | <2.7E-03 | N/A | N/A | N/A | |
| | | | Σ = 3.65 | Σ = 3.96 | 8% |

A separate assessment utilizing the measured ion concentrations was performed to gauge consistency between the primary constituent concentrations and the measured dissolved solids content. Projected wt% values were calculated based on the molar concentrations of the known sodium salts, the molecular weights (MWs) of the sodium salts, and the measured density of the supernatant phase (1.16 g/mL). The results of these calculations are presented in Table 4-6, which shows that the projected dissolved solids content based on the ion data is 21.3 wt%, which is about 11% higher than the dissolved solids content measured in the Shielded Cells. An eleven percent difference is considered good, as it the same order of magnitude as the expected one sigma analytical uncertainty for a single ion determination and is surely lower than the propagated analytical uncertainty associated with the seven constituents that were summed.

**Table 4-6. Projected Dissolved Solids Content Based on Primary Constituents**

| Constituent | Molarity | MW, g | Projected wt% | Measured wt% | Difference |
|---|---|---|---|---|---|
| NaOH | 1.36 | 40 | 4.69 | | |
| $NaNO_2$ | 0.941 | 69 | 5.60 | | |
| $NaNO_3$ | 0.785 | 85 | 5.75 | | |
| $Na_2CO_3$ | 0.290 | 106 | 2.65 | | |
| $NaAl(OH)_4$ | 0.195 | 118 | 1.98 | | |
| $Na_2SO_4$ | 0.0356 | 142 | 0.44 | | |
| $Na_2C_2O_4$ | 0.0163 | 134 | 0.19 | | |
| | | | Σ = 21.3 | 19.1 | 11% |

As shown in Table 4-7, the supernatant mercury concentration is ~57 mg/L. The RSD for this value is 12%, which is reasonable given that the expected one sigma analytical uncertainty for the CVAA method is ~20%.

**Table 4-7. Supernatant Mercury**

| Mean Concentration, mg/L | %RSD (n) |
|---|---|
| 5.73E+01 | 12 (3) |

Settled sludge volumes as a function of time are given in Table 4-8 and plotted in Figure 4-2. As shown in the table and figure, the bulk of the settling occurred over the first two days, when the settled sludge volume dropped from 100 mL to ~74 mL. After about two days, settling continued at a much slower rate, resulting in a settled sludge volume of ~65 mL at one week and ~59 mL at four weeks. As identified in Figure 4-2, the relationship between settled sludge volume in units of mL (y) and settling time in units of days (x) is approximated to be: $y = -6.488*\ln(x) + 78.09$.

Photographs of the initial suspended sludge slurry and the settled sludge slurry at times of 7 hours and 7 days are given in Figure 4-3. As shown in the photographs, the color of the sludge was brown and the supernatant layer above the settled sludge was free of obvious suspended particles. An exception was the top surface of the supernatant layer, where a thin layer of sludge particles remained throughout the settling period.

**Table 4-8. Settled Sludge Volumes as a Function of Settling Time**

| Settling Time, Days | Settled Sludge Volume, mL |
|---|---|
| 0.00E+00 | 100.0 |
| 8.54E-02 | 96.0 |
| 1.41E-01 | 91.0 |
| 1.86E-01 | 89.0 |
| 2.14E-01 | 88.0 |
| 2.83E-01 | 86.0 |
| 9.19E-01 | 78.0 |
| 1.06E+00 | 77.5 |
| 1.27E+00 | 76.5 |
| 1.88E+00 | 74.0 |
| 2.14E+00 | 73.0 |
| 2.96E+00 | 70.5 |
| 3.93E+00 | 68.5 |
| 4.93E+00 | 67.0 |
| 5.93E+00 | 66.0 |
| 6.93E+00 | 64.5 |
| 7.93E+00 | 63.5 |
| 1.19E+01 | 61.5 |
| 1.39E+01 | 61.0 |
| 1.89E+01 | 60.0 |
| 2.20E+01 | 59.5 |
| 2.60E+01 | 59.0 |
| 2.80E+01 | 58.5 |

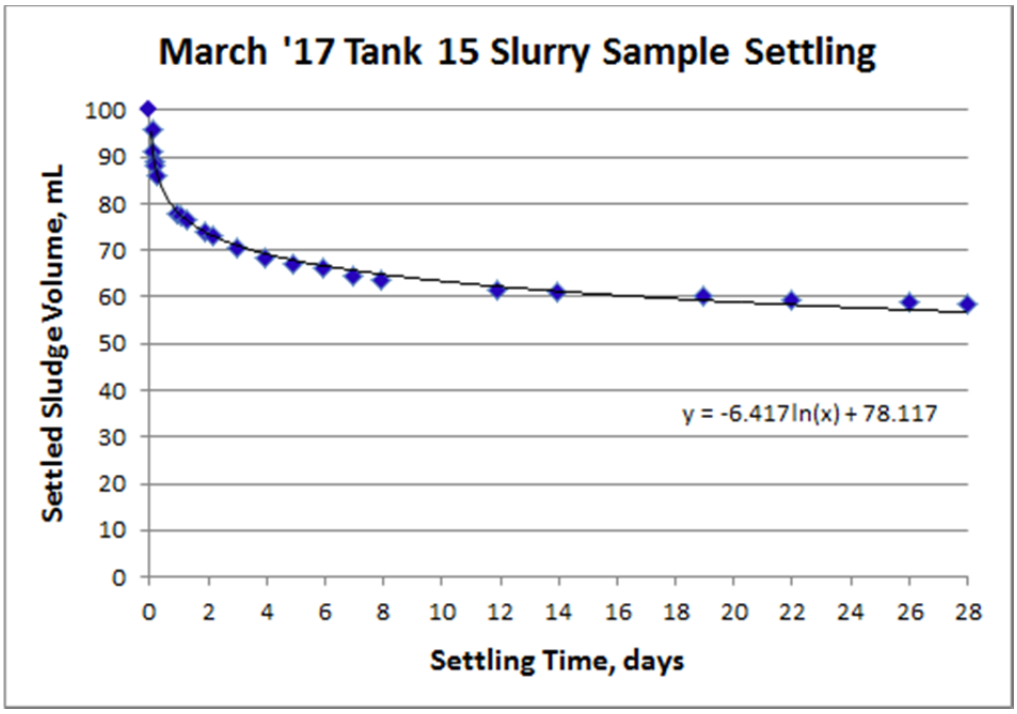



**Figure 4-2. Plot of Settled Sludge Volumes Versus Settling Time**

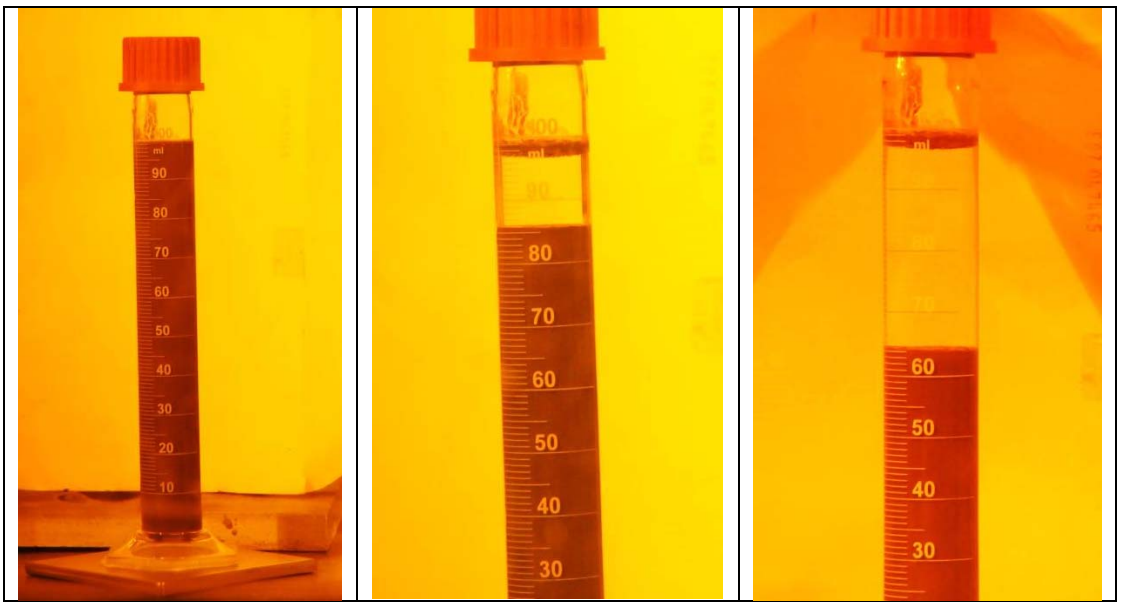



**Figure 4-3. Initial Suspended Slurry and Settled Sludge Slurry at t=7 hrs and t=7 days**

The moderate settling of the sludge slurry is consistent with expectations based on the high aluminum to iron ratio, which tends to hinder settling, and the relatively low insoluble solids content and yield stress, which tend to facilitate settling.

## 5.0 Conclusions

The characterization results for the March 2017 Tank 15 slurry sample are consistent with expectations based upon the waste type, process knowledge, comparisons between alternate analysis techniques, and comparisons with the characterization results obtained for the November 2016 Tank 15 slurry sample (the sample collected during the first bulk waste removal campaign).

The consistency of the March 2017 sample is visibly "thinner" than the November 2016 sample, which is borne out by the lower measured insoluble solids content and the lower measured yield stress. One of the impacts of the lower insoluble solids content is the lower concentrations of insoluble radionuclides (primarily actinides, Sr-90, and Y-90), which reduce the total alpha and total beta concentrations. As a result, the total alpha concentration is significantly less than the "low rem" limit (0.2247 Ci/L) of the inhalation dose potential determination.

The relatively low supernatant sodium concentration (~3.7 M) is reflective of the relatively low dissolved solids content (19.1 wt% of the supernatant). The relatively low plastic viscosity (7.3 cP) also reflects the magnitude of the dissolved solids content.

Settling of the March 2017 sludge slurry was found to be moderate, combining the typical slow settling of high aluminum content waste with the higher settling potential introduced by the low insoluble solids content.

## 6.0 References

[1] King, W. D., J. M. Pareizs, D. P. DiPrete, and S. H. Reboul, "*Characterization Results for SRS Tank 15H Sample HTF-15-16-100 to Support Waste Removal Operations*," Savannah River National Laboratory, SRNL-L3100-2016-00214, December 2, 2016.

[2] Fellinger, T. L., "*Technical Task Request: Shielded Cells Qualification Run – Nitric/Glycolic Flowsheet*," Savannah River Remediation, X-TTR-S-00002, Revision 1, October 2015.

[3] Pareizs, J. M. and D. P. Lambert, "*Task Technical and Quality Assurance Plan for Sludge Batch 9 Shielded Cells Qualification Run – Nitric/Glycolic Flowsheet*," Savannah River National Laboratory, SRNL-RP-2015-00838, December 2015.

[4] "*Sludge 1.5 Spreadsheets*," WG08 server, Savannah River Remediation, April 2017.

**Attachment A. Email Message from J. E. Occhipinti Dated March 9, 2017**

**TK 15 Sludge Slurry Sample Analysis**

John Occhipinti to: Frank Pennebaker, Boyd Wiedenman, Scott Reboul, David Diprete 03/09/2017 02:27 PM

Cc: Christie Sudduth, Jeffrey Gillam, John Tihey, Peter Hill, Victoria Kmiec, Vijay Jain, Hasmukh Shah, Thomas Huff, John Schwenker, Seth Campbell, Richard Edwards, Samuel Rollings,

History: This message has been forwarded.

With the intention to promote clear communication:

The following analyses are requested for the Tank 15 BWR Campaign 2 sample (2 x 200 mL vials, expected delivery of 3/13 or 3/14) as agreed in X-TTR-S-00050 Rev. 0: (This includes request made via email from Hasmukh yesterday)

**a - weight percent solids** (total, soluble, and **insoluble**)

**b - density (slurry and supernate)**

c - sludge slurry elements (as outlined in TTR)

e - sludge slurry specific element: Hg (CV-Hg)

f - supernate specific element: Hg (CV-Hg)

g - supernate anions (as outlined in TTR)

**j - inhalation dose potential**. **Total alpha** and **Cs-137** analysis should be pursued first. If total alpha ≥ 0.2247 Ci/L then pursue the balance (as outlined in TTR).

j - nuclear criticality (as outlined in TTR)

m - flow diagrams & rheology data (as outlined in TTR)

n - settling height vs. time (as outlined in TTR)

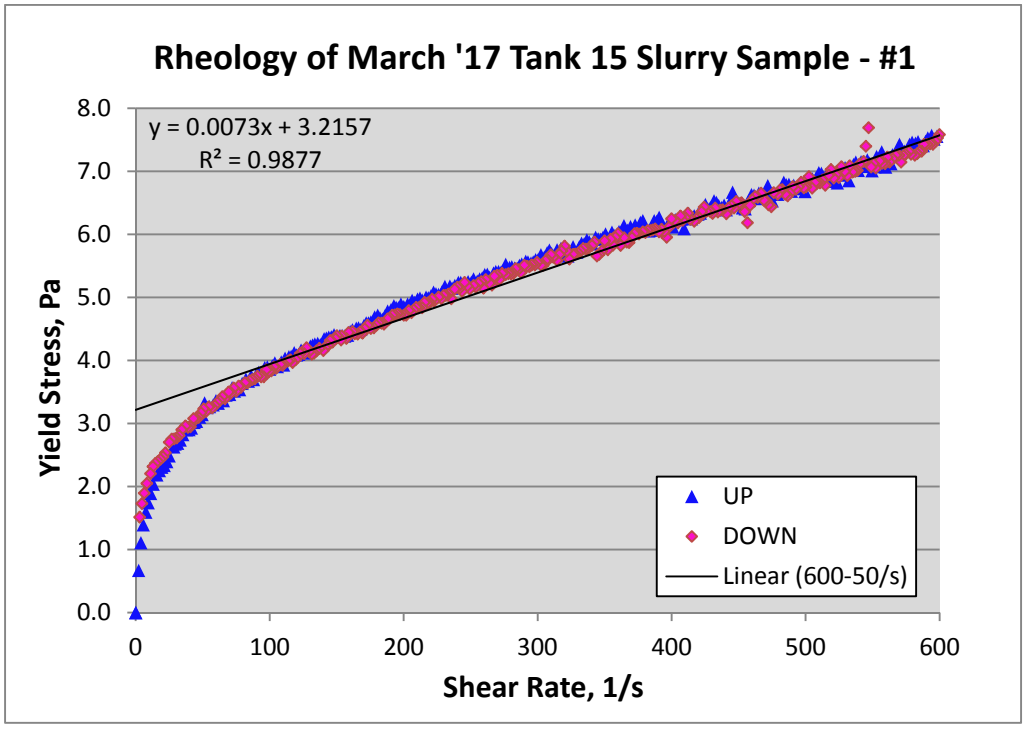
Analyses indicated in **bold underline** are needed as quickly as possible and should be given higher priority.

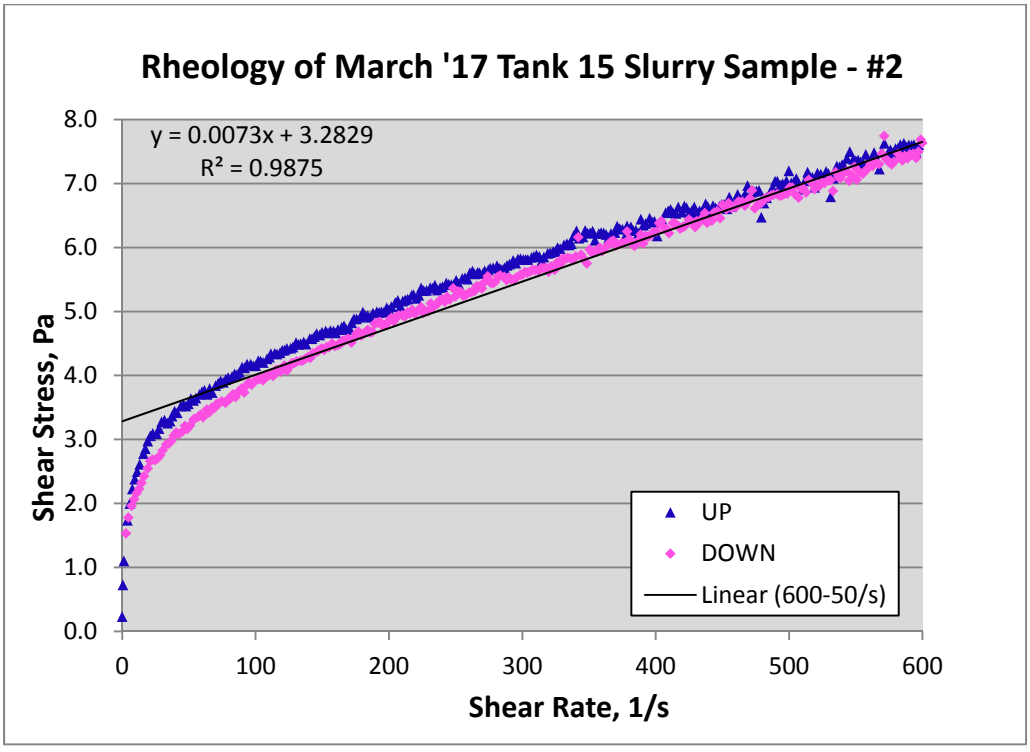
Please call /respond if there are any questions.

**X-TTR-S-00050 Rev 0.pdf**

John E. Occhipinti
Savannah River Remediation
Senior Manager
Ph (803) 208-8758 Cell: (706) 373- 9494

**Attachment B. Flow Curves for the March 2017 Tank 15 Slurry Sample**



**Distribution:**

I. P. Amidon, 704-56H
G. C. Arthur, 241-284H
H. P. Boyd, 704-27S
J. C. Black, 773-A
D. C. Bumgardner, 704-56H
J. M. Bricker, 704-S
L. W. Brown, 773-A
T. B. Brown, 773-A
H. Bui, 707-7E
P. U. Burkhalter, 773-A
S. G. Campbell, 241-162H
M. E. Cercy, 773-42A
C. J. Coleman, 773-A
T. E. Colleran, 773-67A
J. S. Contardi, 704-56H
A. D. Cozzi, 999-W
J. A. Crenshaw, 703-46A
D. A. Crowley, 773-43A
T. K. Deason, 773-A
R. D. Deese, 773-A
C. C. DiPrete, 773-A
D. P. DiPrete, 773-41A
D. E. Dooley, 773-A
R. E. Edwards, 766-H
A. A. Ekechukwu, 773-41A
P. A. Fairchild, 766-H
A. P. Fellinger. 773-42A
T. L. Fellinger, 766-H
S. D. Fink, 773-A
E. J. Freed, 704-S
J. M. Gillam, 766-H
C. M. Gregory, 773-A
D. R. Hallman, 707-62B
B. A. Hamm, 766-H
C. C. Herman, 773-A
P. J. Hill, 766-H
D. T. Hobbs, 773-A
E. N. Hoffman, 999-W
E. W. Holtzscheiter, 766-H
T. H. Huff, 704-56H
J. E. Hyatt, 773-A
J. F. Iaukea, 704-27S
S. T. Isom, 773-67A
V. Jain, 766-H
M. L. Jenkins, 773-A
M. A. Jones, 773-A
M. T. Keefer, 766-H
V. M. Kmiec, 704-27S
K. M. Kostelnik, 773-42A
P. R. Jackson, DOE-SR, 703-46A
V. Jain, 766-H
D. P. Lambert, 999-W
M. C. Lee, 773-A
B. B. Looney, 773-42A
M. A. Malek, 773-A
D. J. Martin, 766-H
K. B. Martin, 707-7E
C. J. Martino, 999-W
D. A. McGuire, 773-42A
R. T. McNew, 766-H
C. D. Nguyen, 773-A
J. E. Occhipinti, 704-56H
T. O. Oliver, 773-42A
J. M. Pareizs, 773-A
N. R. Pasala, 707-7E
F. M. Pennebaker, 773-42A
J. W. Ray, 704-27S
S. H. Reboul, 773-42A
L. T. Reid, 773-43A
C. Ridgeway, 707-4E
M. A. Rios-Armstrong, 766-H
S. P. Rollings, 241-156H
P. J. Ryan, 704-26S
A. M. Sadler, 773-A
J. P. Schwenker, 704-56H
H. B. Shah, 766-H
C. B. Sherburne, 707-17E
D. C. Sherburne, 249-8H
G. N. Smoland, 773-42A
C. B. Sudduth, 707-7E
R. C. Sullivan, 773-A
L. C. Terheggen, 707-3E
J. R. Tihey, 241-162H
D. J. Wheeler, 773-A
T. L. White, 773-A
B. J. Wiedenman, 773-42A
A. W. Wiggins, 241-168H
W. R. Wilmarth, 773-A
R. H. Young, 773-ARecords Administration (EDWS)