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Characterization of Tank 51 Sludge Slurry Samples (HTF-51-17-67, -68, -69, -74, -75, and -76) in Support of Sludge Batch 10 Processing

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EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) was requested by Savannah River Remediation (SRR) Engineering (SRR-E) to provide sample characterization and analyses of Tank 51 sludge samples in support of Sludge Batch (SB) 10. The six Tank 51 sludge samples were sampled and delivered to SRNL in August of 2017. These six Tank 51 sludge samples, after undergoing physical characterizations which included rheology, weight percent total solid, dissolved solids and density measurements, were combined into one composite Tank 51 sample and analyzed for corrosion controls analytes, select radionuclides, chemical elements, density and weight percent total solids. A summary of the average analytical results are as follows:

- The composite Tank 51 sludge and supernatant densities are 1.22 and 1.18 g/mL, respectively, with a measurement variation (%RSD) between replicates of less than 2.0%.
- The total solids of this batch of the Tank 51 composite sample was 25.1 wt% total slurry, while the total dissolved solids was 20.9 wt% supernatant. This gives a calculated insoluble solids value of 5.2 wt%.
- The dominant elemental constituents in the sludge slurry were Na (28.1 wt%), Al (8.67 wt%), Fe (2.11 wt%), Hg (1.44 wt%), Mn (0.560 wt%) and S (0.390 wt%). U-238 and Th-232 were present at the highest radionuclide mass concentrations of ~0.16 and ~0.64 wt%, respectively.
- Sodium was the most dominant constituent in the Tank 51 supernatant with a concentration of 3.73 M (8.58E+04 mg/L). The second and third most dominant constituents in the supernatant were aluminum and sulfur, with concentrations of 1.75E-01 M (4.72E+03 mg/L) and 4.40E-02 M (1.41E+03 mg/L), respectively.
- The highest measured activity in the Tank 51 supernatant was associated with Cs-137 (7.55E-01 Ci/gal).
- The predominant anions in this Tank 51 supernatant were nitrite, hydroxide, nitrate, carbonate and sulfate, which were present at average concentrations of 0.870, 1.03, 0.931, 0.298 and 0.0347 M, respectively.

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LIST OF ABBREVIATIONS

AD	Analytical Development
AQR	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
MDL	Minimum detection limit
M	Mole/Liter
PF	Peroxide fusion
RSD	Relative standard deviation
SB10	Sludge Batch 10
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TIC	Total inorganic carbon
TOC	Total organic carbon

1.0 INTRODUCTION

In August of 2017, Savannah River Remediation (SRR) Engineering (SRR-E) delivered six Tank 51 slurry samples, identified as HTF-51-17-67, -68, -69, -74, -75, and -76 (combined total sample volume of about 1,200 mL) to the Savannah River National Laboratory (SRNL) for characterization in support of Sludge Batch (SB) 10 processing.

After the physical characterizations (rheology, wt% solids, dissolved solids, densities of the "as-received" slurry and filtrate) of each of the six samples, a material blend consisting of 80 grams of the slurry from each of the six samples was made to get a composite Tank 51 sample for further characterizations in the SRNL Shielded Cells Facility. Aliquots of the composite sludge were digested by Aqua Regia (AQR) or Peroxide Fusion (PF) methods in the SRNL Shielded Cells, diluted and transferred to Analytical Development (AD) for various analyses. Aliquots of filtrate (supernate) from the filtered slurry sample (composite) were also diluted and removed from the Shielded Cells for analysis by AD for corrosion chemistry analytes and others. With the exception of density and weight percent solids determinations, which were performed in triplicate, all other the analyses were performed in duplicate.

This report contains analyses results for the physical characterizations of the six Tank 51 sludge slurries and the physical characterizations of the composite Tank 51 sample. The composite Tank 51 sample was also analyzed for supernate (filtrate) corrosion control analytes, select radionuclides and elementals. This Tank 51 characterization effort is governed by a Technical Task Request (TTR)[1] and a Task Technical and Quality Assurance Plan (TTQAP)[2] as presented in Section 4.0, Task Activities for stable constituents, radionuclides of interest and other parameters.

2.0 Objectives

The specific objectives of this Tank 51 characterization were to quantify the following for the composite Tank 51 material:

- Densities of the "as-received" Tank 51 sludge slurry and the supernatant (filtrate)
- The solids distribution of the sludge slurry (total solids, dissolved solids, insoluble solids and soluble solids)
- Anions in the supernatant
- ICP-ES elemental suite including Na, K, Al, elemental sulfur and other elements
- Total mercury in the slurry and supernate
- Select radionuclides in the "as-received" sludge slurry including total gamma, total alpha and beta.

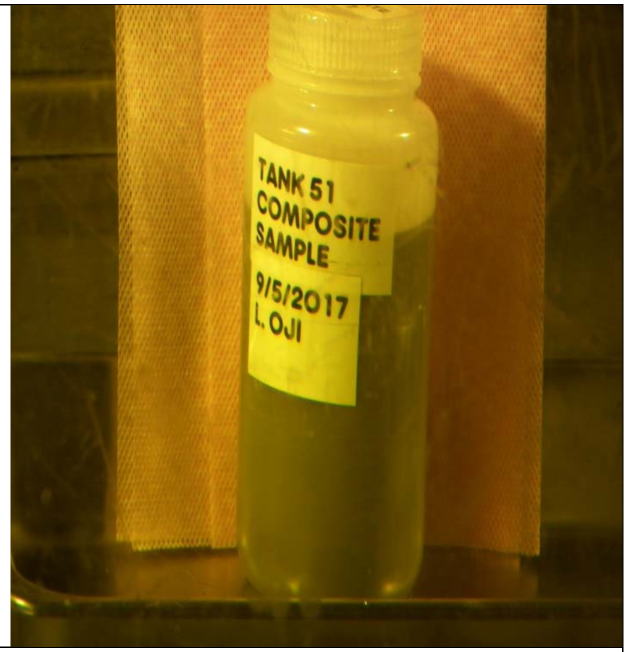
3.0 Sample Processing and Preparations

The six Tank 51 slurry samples sent to SRNL, identified as HTF-51-17-67, -68, -69, -74, -75, and -76, were taken out of the metal transport containers and transferred into 300-mL capacity poly-methyl pentane beakers as shown in Figure 3-1, inserts A and B. Physical characterizations, which included rheology, wt% solids, dissolved solids, densities of the "as-received" slurry and filtrate were performed on each sample.

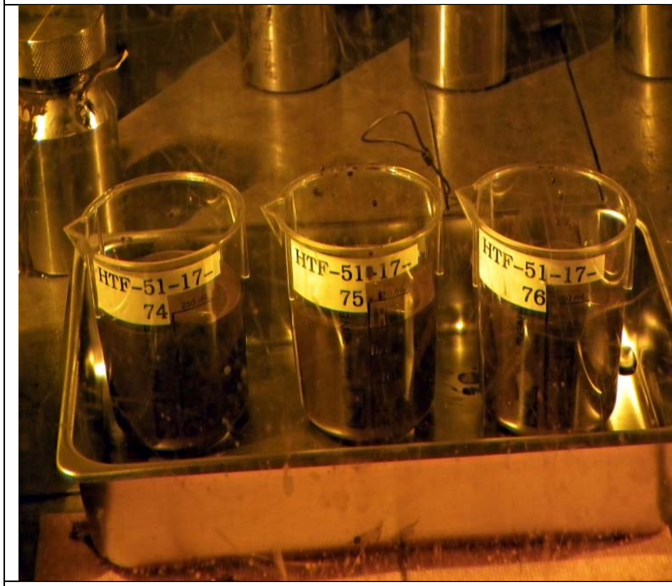
Rheology characterization was performed in duplicate while the other physical characterizations were performed in triplicate. After the physical characterizations, a composite Tank 51 sample was obtained by blending 80 grams of the slurry from each of the six samples into a common one liter capacity Poly bottle as shown in Figure 3-1 insert C. The physical characterizations performed on the composite Tank 51 sample included, density of the composite slurry, and weight percent total solids. The composite Tank 51 sludge slurry aliquots were also digested (AQR and PF digestions) and diluted in the shielded cell before submission to AD for analysis for specific analytes. Details of the laboratory methods and experimental approach employed to meet the Tank 51 characterization objectives are presented in Appendix A.

The filtrate or supernatant sample was obtained by filtering about 50 mL composite Tank 51 sample through a 0.45 µm Nalgene® membrane. The supernatant sample density and weight percent soluble or dissolved solids were determined using the resulting filtrate solution. Where appropriate, supernatant sample aliquots were diluted with Super-Q water (de-ionized water) or 2.0 M nitric acid to enable removal from the shielded cell and submitted for appropriate analysis to the SRNL AD.

Insert A: Picture of three Tank 51 samples (HTF-51-17-67, -68, and -69)



Insert C: Composite Tank 51 Sample (blend of samples HTF-51-17-67, -68, -69, -74, -75, and -76)



Insert B: Picture of three other Tank 51 samples (HTF-51-17-74-75,-and-76)

No picture inert here.

Figure 3-1: Photographs of individual Tank 51 samples and the tank 51 composite sample.

4.0 Data Presentation

4.1 Analytes and MDLs

Chemical processing of the composite Tank 51 samples, as earlier mentioned, included routine digestions (by peroxide fusion and/or aqua regia), filtering/dilutions, and constituent-specific dissolution methods. Concentrations for all stable elements and radionuclides analyzed, regardless of whether the concentrations are greater than the minimum detection limits (MDL) or less than the MDL are reported accordingly. All analyses were performed in duplicate, using laboratory methods developed to target the MDLs.

4.2 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). The %RSD provides an indication of the measurement variation between duplicate 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/TOC analyses; b) ~20% for CVA-Hg analyses; and c) ~5% for Cs-137 determined by gamma spectroscopy. As such, only one to two of the leading digits reported for the AD analysis results should be considered significant.

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) uranium and plutonium distributions; d) dominant constituents in the supernatant; and e) charge balance ions in the supernatant (filtrate).

5.0 RESULTS and DISCUSSION

5.1 Six Tank 51 "as-received" Sludge Slurry Samples

As indicated earlier, the SRR-E customer wanted the six Tank 51 samples which were sampled and delivered to SRNL in August 2017 (HTF-51-17-67, -68, -69, -74, -75, and -76) to be characterized individually first for slurry density, supernatant (filtrate) density, total solids concentration, dissolved solids concentrations, insoluble solids and soluble solids concentrations, yield stress and plastic viscosity results before preparing a composite Tank 51sample based on all six samples. These initial physical characterizations of the six Tank 51 samples are presented in the following order:

- Slurry density results given in Table 5-1
- Supernatant density results given in Table 5-2
- Total solids concentration results given in Table 5-3
- Dissolved solids concentration results given in Table 5-4
- Insoluble solids and soluble solids concentration results given in Table 5-5
- Yield stress results given in Table 5-6
- Plastic viscosity results given in Table 5-7

Since the results will be utilized to address sampling and analytical uncertainties, the information in the tables includes:

- Results for each replicate measurement, with the reported result containing all significant digits and at least one insignificant digit (to elucidate variations and to minimize round-off error when calculating averages)
- Results for each average value, with the reported result containing only the number of digits deemed significant (this is typically one digit less than what is reported for the individual measurements)
- Percent relative standard deviation (%RSD) associated with each average value
- Calculated values for insoluble solids and soluble solids concentrations, based on the average total solids and average dissolved solids results for each sample

Note that the density measurements were performed at an ambient shielded cell temperature of 27 degrees Celsius.

As shown in Tables 5-1 and 5-2, the average slurry densities ("as received" densities) of the six samples ranged from 1.21 to 1.23 g/mL, while the average supernatant density (filtrate density) was 1.18 g/mL for all six samples. The variation in the average slurry density was thought to be in the range of normal analytical fluctuations, and therefore, suggests that differences between the slurry densities were minor or insignificant. Similarly, the consistency of the average supernatant density value suggests that differences between the supernatant densities were insignificant. The RSD values for the density averages were all limited to a few percent, indicating good measurement precision.

As shown in Tables 5-3 and 5-4, the average total solids concentrations of the six samples ranged from 24.7 to 25.1 wt%, while the average dissolved solids concentrations ranged from 21.1 to 21.4 wt%. As with the density results, the variations in the average solids concentrations were thought to be in the range of normal fluctuations, suggesting that differences between the solids distribution were minor or insignificant. The RSD values for the average solids concentrations were all less than or equal to one percent, indicating good measurement precision.

As shown in Table 5-5, the calculated insoluble solids concentrations for the six samples ranged from 4.3 to 4.9 wt%, while the calculated soluble solids concentrations ranged from 20.1 to 20.5 wt%. In the case of the insoluble solids concentrations, uncertainties in the calculated values are expected to be relatively high, given that results are based on a relatively small difference between two relatively large values (the numerator of the insoluble solids relationship is the difference between the total solids concentration and the dissolved solids concentration). As such, the difference between 4.3 wt% and 4.9 wt% is expected to be in the normal range of uncertainties, suggesting statistical insignificance. In contrast, the relative differences between the soluble solids are expectedly smaller, given that the magnitudes of the soluble solids concentrations are significantly higher than those of the insoluble solids concentrations.

As shown in Tables 5-6 and 5-7, the average yield stresses of the six samples ranged from 3.8 to 4.4 Pa, while the average plastic viscosities ranged from 8.3 to 9.8 cP. Variations between the yield stresses were thought to be in the normal range of analytical uncertainties, especially when considering that yield stress measurements are impacted by settling and suspension of insoluble solids particles, which can limit measurement stability. In the case of the average plastic viscosities, results for the first four samples (8.3 to 8.8 cP) appear to all be in the same range of the expected analytical uncertainties - however, results for the fifth and sixth samples (9.8 and 9.5 cP) appear to be slightly higher. Given that the densities, solids distributions, and yield stresses for the fifth and six samples were similar to those of the first four samples, it is likely that the slightly higher apparent plastic viscosities for the fifth and sixth samples were due to analytical uncertainties, as opposed to true sample variations. Note that the RSDs for the average rheology results were limited to about 5%, again indicating good measurement precision.

A "gross" check of the calculated insoluble solids concentrations for the composite Tank 51 samples can be performed using the yield stresses measured for the Tank 51 slurry samples and the insoluble solids-yield stress relationship observed for the first three Tank 15 waste removal samples[1] To do so, the Tank 15 insoluble solids concentrations were plotted as function of the Tank 15 yield stresses (see plot below; Figure 5-1), utilizing the analytical results documented in Table 3 of SRNL-L3100-2017-00070. Based on this plot and the yield stresses measured for the Tank 51 samples (3.8 to 4.4 Pa), an estimate of the expected insoluble solids content of the Tank 51 slurry samples is determined to be on the order of 5 wt%, which is reasonably consistent with the calculated values (4.3 to 4.9 wt%).

The "gross" check value described above for the calculated insoluble solids for composite Tank 51 insoluble solids is relatively consistent with the experimentally determined insoluble solids for the Tank 51 composite sample. The estimate insoluble solids content of Tank 51 slurry samples based on Tank 15 slurry transfer to Tank 51 was determined to be on the order of 5 wt%, while the experimentally determined insoluble solids for composite Tank 51 samples is 5.2 wt% as presented in Table 5-8.

Table 5-1.Sludge Slurry Density for Samples HTF-51-17-67-69 through HTF-51-17-74-76

Sample Identification #	Slurry Density (g/mL)				
	Measurement #1	Measurement #2	Measurement #3	Average	%RSD
HTF-51-17-67	1.216	1.263	1.217	1.23	2.2
HTF-51-17-68	1.208	1.203	1.220	1.21	0.7
HTF-51-17-69	1.217	1.261	1.223	1.23	1.9
HTF-51-17-74	1.210	1.209	1.220	1.21	0.5
HTF-51-17-75	1.214	1.217	1.216	1.22	0.1
HTF-51-17-76	1.211	1.204	1.211	1.21	0.3

Table 5-2. Supernatant Density for samples HTF-51-17-67-69 through HTF-51-17-74-76

Sample Identification #	Supernatant Density (g/mL)				
	Measurement #1	Measurement #2	Measurement #3	Average	%RSD
HTF-51-17-67	1.196	1.176	1.177	1.18	1.0
HTF-51-17-68	1.185	1.192	1.177	1.18	0.6
HTF-51-17-69	1.180	1.181	1.176	1.18	0.2
HTF-51-17-74	1.178	1.176	1.176	1.18	0.1
HTF-51-17-75	1.191	1.181	1.178	1.18	0.6
HTF-51-17-76	1.176	1.181	1.176	1.18	0.2

[1] Note: The Tank 15 slurry data is expected to be at least somewhat applicable to the Tank 51 slurry data, since a portion of the sludge in Tank 51 originated from Tank 15.

Table 5-3. Total Solids Concentration for samples HTF-51-17-67-69 through HTF-51-17-74-76

Sample Identification #	Total Solids Concentration (wt% of slurry)				
	Measurement #1	Measurement #2	Measurement #3	Average	%RSD
HTF-51-17-67	24.68	24.77	24.88	24.8	0.4
HTF-51-17-68	24.76	24.75	24.65	24.7	0.2
HTF-51-17-69	25.02	24.92	24.83	24.9	0.4
HTF-51-17-74	24.94	25.13	25.15	25.1	0.5
HTF-51-17-75	25.12	25.11	25.01	25.1	0.2
HTF-51-17-76	24.89	24.88	24.95	24.9	0.2

Table 5-4. Dissolved Solids Concentration for samples HTF-51-17-67-69 through HTF-51-17-74-76

Sample Identification #	Dissolved Solids Concentration (wt% of supernatant)				
	Measurement #1	Measurement #2	Measurement #3	Average	%RSD
HTF-51-17-67	21.33	21.50	21.43	21.4	0.4
HTF-51-17-68	21.15	21.28	21.32	21.3	0.4
HTF-51-17-69	20.96	21.04	21.27	21.1	0.8
HTF-51-17-74	21.07	21.30	21.40	21.3	0.8
HTF-51-17-75	21.25	21.17	21.22	21.2	0.2
HTF-51-17-76	21.51	21.15	21.47	21.4	0.9

Table 5-5. Calculated Insoluble Solids and Soluble Solids

Sample ID #	Insoluble Solids Concentration (wt% of slurry)	Soluble Solids Concentration (wt% of slurry)
HTF-51-17-67	4.3	20.5
HTF-51-17-68	4.3	20.4
HTF-51-17-69	4.8	20.1
HTF-51-17-74	4.8	20.3
HTF-51-17-75	4.9	20.2
HTF-51-17-76	4.5	20.4

Table 5-6. Yield Stress of Individual Tank 51 Slurry Samples

Sample Identification #	Yield Stress (Pa)			
	Measurement #1	Measurement #2	Average	%RSD
HTF-51-17-67	4.26	4.54	4.4	4.5
HTF-51-17-68	3.95	3.73	3.8	4.1
HTF-51-17-69	3.92	3.83	3.9	1.6
HTF-51-17-74	4.16	4.20	4.2	0.7
HTF-51-17-75	4.07	4.09	4.1	0.3
HTF-51-17-76	4.24	4.39	4.3	2.5

Table 5-7. Plastic Viscosity of Individual Tank 51 Slurry Samples

Sample Identification #	Plastic Viscosity (cP)			
	Measurement #1	Measurement #2	Average	%RSD
HTF-51-17-67	8.64	8.99	8.8	2.8
HTF-51-17-68	8.52	8.62	8.6	0.8
HTF-51-17-69	8.23	8.38	8.3	1.3
HTF-51-17-74	8.46	8.59	8.5	1.1
HTF-51-17-75	9.70	9.88	9.8	1.3
HTF-51-17-76	9.41	9.64	9.5	1.7

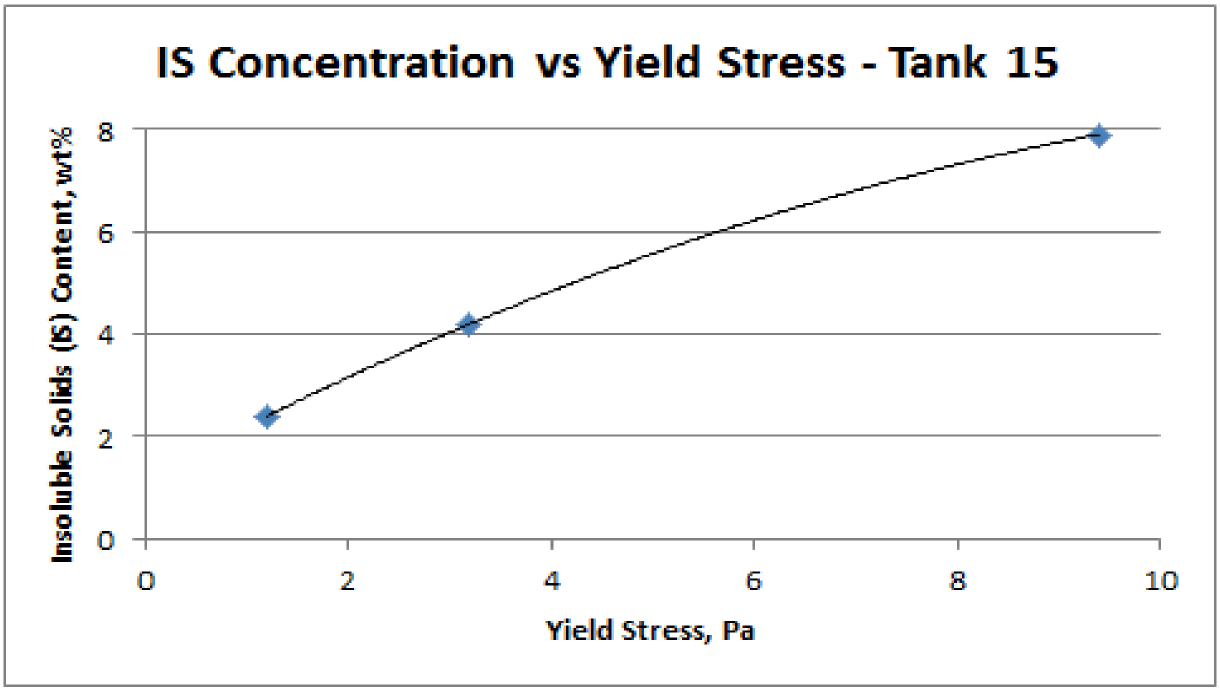


Figure 5-1. Insoluble Solids Content Versus Yield Stress for Tank 15 Slurry Samples

5.2 Composite Tank 51 "as-received" sludge Slurry and Supernatant (Filtrate)

The average densities and solids content for the Tank 51 composite "as-received" sludge and supernatant samples are presented in Table 8. The average sludge and supernatant densities are 1.22 and 1.18 g/mL, respectively, with a measurement variation (%RSD) between replicates of less than 2%. The measurement variations for the solids wt% determinations were all lower than 0.5 %RSD. These low %RSD values for these measurements in the shielded cells demonstrate high measurement precision and lack of any apparent shielded cells processing anomalies.

The weight percent solids in the slurry composite sample were measured in the SRNL Shielded Cell facility using a conventional drying oven at 110 ^{0}C. The sample was dried until repeated weights indicated no further loss of water. The weight percent dissolved solids content in a sample of the filtrate supernate was measured in the same manner. All weight percent measurements were made in triplicate. The weight percent total solids and the weight percent dissolved solids (supernate-based) were used to calculate the weight percent soluble and insoluble solids (slurry-based). The total solids content is 25.1 wt% of the slurry, while the total dissolved solids content is 20.9 wt% of the supernatant. This gives a calculated insoluble solids content of 5.2 wt% of the slurry.

Table 5-8. Tank 51 Composite Sample Densities and Solids Content

Analyte	Average	%RSD	Units
Composite Tank 51 sludge slurry density	1.22	*1.5*	g/mL
Composite Tank 51supernatant density (filtrate density)	1.18	*0.2*	g/mL
Total solids, wt % of sludge slurry	25.1	*0.2*	Wt %
Dissolved solids, wt % of supernatant	20.9	*0.2*	Wt %
Insoluble solids, wt % of sludge slurry	5.2*	-	Wt %
Soluble solids wt % of sludge slurry	19.9*	-	Wt %

*Calculated data.

Elemental analysis of the composite Tank 51 sludge slurry involved both AQR and PF digestion methods followed by ICP-ES analysis of the resulting solution for elemental concentrations. The results presented in Table 5-9 are, in general, an average of the concentrations (wt.% total solids basis and mol/L) from the AQR method. The supernate elemental data were all based on AQR digestions. Most of the radionuclide analysis for the composite sludge slurry are based on PF digestions because this method is more suited to quantify these radionuclides than AQR method.

Elemental sodium, potassium and zirconium concentrations are from analyses following AQR digestions only because this method is more suited to quantify these elements than the PF digestion method. Reported concentrations for silicon, beryllium and zinc are based on analyses following AQR digestions only because they were not reported as less than values with this method. Be, Si and Zn results for samples digested by PF were less than instrument detection limits but generally indicated the same scaler magnitudes of concentration as those obtained by AQR. The supernate elemental data were all based on AQR digestions and analysis.

The silver (Ag) concentration reported in Tables 5-9 and 5-12 are based on ICP-MS results for masses 107 and 109. These concentrations reported for Ag may be biased high because of Pd 107 interference, which is a fission product.

Table 5-9 contains the analytical results for the primary elemental constituents measured by ICP-AES, sulfur by ICP-AES-S, and mercury by CVAA. Most of the RSDs for the elemental analyses were limited to 7% or less, which demonstrates normal precision for sample replicates. As presented in Table 5-9, the dominant constituents in the sludge solids include sodium (28.1 wt%), Al (8.67 wt%), Fe (2.11 wt%), Hg (1.44 wt%), Th (0.644 wt%), Mn (0.560 wt%), S (0.390 wt%) and K (0.129 wt%).

Concentrations of select radioisotopes in the composite Tank 51 slurry solids are given in Table 5-10, both on a mass concentration basis (wt% solids) and a slurry activity basis (Ci/gallon slurry). As expected, U-238 and Th-232 were present at the highest radionuclide mass concentrations of ~0.16 and ~0.65 wt%, respectively. In contrast, the mass concentrations of the other radioisotopes were more than two orders of magnitude lower. Based on the isotopic results in Table 5-10, the calculated U-235 mass enrichment is about 2% and the calculated ratio of Pu-240 mass to Pu-239 plus Pu-240 mass is about 12.5%.

A comparison of the U-238 and Th-232 mass concentrations presented in Table 5-10 (0.162 and 0.652 wt%, respectively) with the elemental uranium and thorium concentrations presented in Table

5-9 (0.158 and 0.644 wt%, respectively) shows relatively good agreement between the ICP-MS and the ICP-AES measurements. Specifically, the uranium results from the two methods differed by about 2.5%, while the thorium results differed by about 1.2%. These differences are reasonable, given that 10% is the estimated one sigma analytical uncertainty of each of these methods and these values fall within one sigma analytical uncertainties for the two methods.

Table 5-9. Elemental Results for Tank 51 Composite Sludge Slurry Sample

Analyte	Wt% Total Solids (Average)	Concentration, M (Average)	Average %RSD
Ag#	1.94E-03	5.50E-05	3.2
Al	8.67E+00	9.84E-01	1.6
B	1.26E-02	3.56E-03	2.0
Ba	1.57E-02	3.51E-04	0.7
Be	2.12E-04	7.20E-05	0.1
Ca	9.53E-02	7.27E-03	0.6
Cd	<1.12E-03	<3.06E-05	-
Ce	4.07E-02	8.88E-04	0.0
Co	<1.58E-03	<8.22E-05	-
Cr	4.09E-02	2.41E-03	0.7
Cu	<7.24E-03	<3.48E-04	-
Fe	2.11E+00	1.15E-01	0.3
Gd	1.20E-02	2.33E-04	0.0
K	1.29E-01	1.01E-02	2.0
La	1.35E-02	2.97E-04	0.6
Li	3.06E-03	1.35E-03	6.6
Mg	3.45E-02	4.34E-03	1.1
Mn	5.60E-01	3.12E-02	0.5
Mo	1.12E-02	3.59E-04	5.0
Na	2.81E+01	3.73E+00	0.3
Ni	9.03E-02	4.71E-03	1.6
P	<3.15E-02	<3.11E-03	-
Pb	<1.45E-02	<2.14E-04	-
S*	3.90E-01	3.73E-02	0.4
Sb	<1.52E-02	<3.83E-04	-
Si	1.19E-01	1.30E-02	1.2
Sn	<9.17E-03	<2.36E-04	-
Sr	8.97E-03	3.13E-04	0.6
Th	6.44E-01	8.49E-03	0.4
Ti	<3.54E-03	2.26E-04	-
U	1.58E-01	2.04E-03	0.5
V	1.20E-03	7.22E-05	1.2
Zn	5.06E-03	2.37E-04	0.0
Zr	5.86E-02	1.97E-03	1.0
Hg**	1.44E+00	2.19E-02	3.7

- Rad-ICP-ES sulfur axial method. # ICP-MS data. ** Hg is analyzed by digested cold vapor mercury method (CVHg)

Table 5-10. Results of Analyses of Tank 51 composite sample Sludge Slurry -Radionuclides

Analyte	Mass Concentration Average Wt% total solids	Activity Concentration Average Ci/gallon Slurry	%RSD
Co-60	1.69E-09	2.25E-05	7.3
Sr-90	1.50E-03	2.36E+00	8.1
Tc-99	1.63E-03	3.19E-04	0.5
Cs-134	<7.62E-08	<1.14E-03	-
Cs-137	7.41E-04	7.47E-01	7.1
Ce-144	<8.02E-09	<2.96E-04	-
#Pm-147	<1.84E-06	<1.97E-03	-
Sm-147	<8.02E-05	<2.44E-02	-
Pr-144	<3.39E-13	<2.96E-04	-
Eu-154	7.99E-07	2.50E-03	13.0
Eu-155	<3.54E-08	<1.90E-04	-
Th-232	6.52E-01	8.29E-07	0.6
U-233	1.83E-04	2.05E-05	0.4
U-234	1.16E-04	8.38E-06	0.3
U-235	3.27E-03	8.19E-08	0.4
U-236	4.65E-04	3.49E-07	0.9
U-238	1.62E-01	6.31E-07	0.4
Np-237	4.33E-04	3.53E-06	1.8
Pu-238	1.17E-04	2.32E-02	8.2
Pu-239*	8.92E-04	6.42E-04	0.0
Pu-240*	1.27E-04	3.35E-04	0.2
Pu-239/240	1.08E-03	7.75E-04	14.6
Pu-241	3.48E-06	4.15E-03	8.9
Am-241	5.39E-05	2.14E-03	0.5
Am-243	7.03E-06	1.62E-05	11.4
Am-242m	3.06E-08	3.44E-06	19.2
Cm-242	7.42E-11	2.84E-06	19.2
Cm-243	<3.57E-08	<2.13E-05	-
Cm-244	5.00E-07	4.68E-04	3.1
Cm-245	<8.96E-06	<1.78E-05	-
Cm-247	<5.76E-02	<6.19E-05	-
Cf-249	<2.22E-07	<1.05E-05	-
Cf-251	<4.80E-07	<8.83E-06	-
#Total alpha	-	<3.45E-02	-
Total beta	-	6.76E+00	8.7

Upper limit values, * ICP-MS data

The anion concentrations in the composite Tank 51 supernatant medium are presented in Table 5-11. The dominant anions include nitrite, nitrate, and carbonate, at concentrations of 0.87 M, 0.93M and 0.30 M, respectively. The other anions, F^-, Cl^-, PO_4^{---} and HCO_2^-, were all present at concentrations less than instrument minimum detection limits. To check the results, a cation-anion molarity balance based on the supernate was performed. The normal concentrations of cations (Na^+ and K^+) were summed, as were the anions (NO_3^-, NO_2^-, SO_4^{--}, CO_3^{--}, PO_4^{---}, Cl^-, and free OH^-). The above data are based upon the analytical results obtained for the respective supernatant analyses (ICP-AES results for potassium, and sodium; IC results for nitrate, nitrite, oxalate, and sulfate; base titration for free hydroxide; and TIC for carbonate). In this comparison, molar concentrations of the respective ions were converted to equivalent concentrations, based on the applicable ionic charge (an ion charge of one for sodium, potassium, aluminate, free hydroxide, nitrate, and nitrite; an ion charge of two for carbonate, oxalate, and sulfate; and an ion charge of 3 for phosphate). The sums of the equivalent concentrations for the cations and anions were then calculated and compared to one another, to determine consistency. The cations summed to 3.74 M, while the anions summed to 3.52 M. The anions summed to 94 % of the cations, which is within 10% of the cation value. The pH of the supernate, as presented in Table 5-11, was calculated from the free OH concentration$^-$ using the following equation: $pH = 14 + \log_{10}\left(OH^-\right)$.

The concentrations of elemental constituents in the composite Tank 51 supernatant (filtrate) are given in Table 5-12. As shown in the table, sodium was the most dominant constituent with a concentration of 3.80E+00 M. The second, third and fourth most dominant constituents were aluminum, sulfur and potassium, with concentrations of 1.75E-01 M, 4.40E-02 M, and 1.08E-02 M, respectively.

The analytical results for select radionuclides in the supernate phase (filtrate) of the composite Tank 51 sample are presented in Table 5-13. As shown in the Table 5-13, the select radionuclide concentrations varied over several orders of magnitude. The activity concentrations of U-236 (4.16E-09 Ci/gal) and U-235 (9.83E-10 Ci/gal) were low. This is consistent with expectations, given the low solubility and low specific activity of the uranium isotope. The dominant radionuclide in the supernate phase was cesium-137, which was present at an activity concentration of 7.55E-01 Ci/gal, consistent with the high solubility and specific activity of this radionuclide.

Table 5-11. Corrosion Chemistry Analyses Results for Tank 51 Supernate (filtrate)

Analyte	**Average Concentration M**	**%RSD**
Free OH^-	1.03E+00	4.1
NO_3^-	9.31E-01	0..8
NO_2^-	8.70E-01	1.1
SO_4^{--}	3.47E-02	0.5
CO_3^{--}	2.98E-01	2.0
PO_4^{---}	<6.51E-04	-
$C_2O_4^{--}$	1.02E-02	*0.6*
F^-	<6.01E-03	-
HCO_2^-	<2.54E-03	-
Cl^-	6.35E-03	*0.1*
Na+	3.80E+00	1.0
TIC	2.98E-01	2.0
TOC	2.49E-02	2.3
Al	1.75E-01	1.1
pH	14E+00	-
Total gamma (dpm/mL)	4.43E+08	0.5

Table 5-12. Elemental Analyses of Tank 51 Supernate (Filtrate)

Analyte	Average Concentration M	%RSD
Ag[#]	< 4.50E-07	-
Al	1.75E-01	1.1
B	3.58E-03	1.0
Ba	<3.18E-06	-
Be	<1.01E-05	-
Ca	<3.92E-05	-
Cd	<1.66E-05	-
Ce	<3.47E-05	-
Co	<4.45E-05	-
Cr	1.46E-03	0.7
Cu	<1.89E-04	-
Fe	<5.34E-05	-
Gd	<2.59E-05	-
K	1.08E-02	1.4
La	<9.74E-06	-
Li	<2.60E-04	-
Mg	<1.13E-05	-
Mn	<1.61E-05	-
Mo	3.58E-04	0.4
Na	3.80E+00	1.0
Ni	<2.07E-04	-
P	<1.68E-03	-
Pb	<1.15E-04	-
S*	4.40E-02	0.3
Sb	<2.07E-04	-
Si	<4.12E-04	-
Sn	<1.28E-04	-
Sr	<1.40E-06	-
Th	<3.55E-05	-
Ti	<1.22E-04	-
U	<1.04E-04	-
V	<1.59E-05	-
Zn	<3.98E-05	-
Zr	<9.12E-06	-
Hg	7.24E-04	2.0

- Rad-ICP-ES sulfur axial method. # ICP-MS data.

Table 5-13. Results of Analyses of Tank 51 Composite Supernate (Filtrate)-Select Radionuclides

Analyte	Average Concentration dpm/mL	Activity Concentration Average, Ci/gallon Supernate	%RSD
Tc-99	1.85E+05	3.16E-04	5.2
Cs-134	<3.53E+04	<6.01E-05	-
Cs-137	4.43E+08	7.55E-01	0.5
Th-232	<4.87E-05	<8.30E-14	-
U-233	<4.75E+01	<8.10E-08	-
U-234	6.80E+01	1.16E-07	11.9
U-235	5.77E-01	9.83E-10	7.3
U-236	2.44E+00	4.16E-09	6.6
U-238	1.69E+00	2.87E-09	6.9
Np-237	1.28E+01	2.19E-08	2.0

6.0 CONCLUSION and RECOMMENDATIONS

A summary of the analytical results are as follows:

- The average composite Tank 51 sludge and supernatant densities are 1.22 and 1.18 g/mL, respectively, with a measurement variation (%RSD) between replicates of less than 2.0%.
- The total solids content of this batch of Tank 51 composite sample was 25.1 wt% of the sludge slurry, while the total dissolved solids content is 20.9 wt% of the supernate. This gives a calculated insoluble solids content of 5.2 wt% of the sludge slurry.
- The dominant elemental constituents in the sludge slurry were Na (28.1 wt%), Al (8.67 wt%), Fe (2.11 wt%), Hg (1.44 wt%), Mn (0.560 wt%) and S (0.390 wt%). U-238 and Th-232 were present at the highest radionuclide mass concentrations of ~0.16 and ~0.64 wt%, respectively.
- Sodium was the most dominant constituent in the Tank 51 supernatant with a concentration of 3.73 M (8.58E+04 mg/L). The second and third most dominant constituents in the supernatant were aluminum and sulfur, with concentrations of 1.75E-01 M (4.72E+03 mg/L) and 4.40E-02 M (1.41E+03 mg/L), respectively.
- The highest measured activity in the Tank 51 supernatant was associated with Cs-137 (7.55E-01 Ci/gal).
- The predominant anions in this Tank 51 supernatant were nitrite, hydroxide, nitrate, carbonate and sulfate, which were present at average concentrations of 0.870, 1.03, 0.931, 0.298 and 0.0347 M, respectively.

7.0 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.

The Task Technical and Quality Assurance Plan (TTQAP) details the planned activities and associated quality assurance implementing procedures for the characterization of Tank 51 slurry sludge sample (HTF-51-17-44/ HTF-51-17-48) in support of sludge batch 10 preparations[2]. The documents referenced in the TTQAP include the following: L5575-00080-09 SRNL Electronic Notebook (Production); SRNL, Aiken, SC 29808 (2014) and various AD notebooks containing the analytical/digestion data.

8.0 REFERENCES

1. "Sample Analysis for Sludge Batch 9B/10 Assembly," X-TTR-S-00050, Rev. 0, 2016.
2. "Task Technical and Quality Assurance Plan for Tank 51 Sample Characterizations in Support of Sludge Batch 10 Preparation," SRNL-RP-2017-00280, Rev. 0.

Appendix A: Analytical Methodologies

Densities:

Density measurements were conducted at a temperature of ~20 °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 "as-received" Tank 51 slurry aliquots and three individual supernatant aliquots (filtrate) were utilized in the measurements. The 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 and 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 analyses requested included weight fraction solids and density, as well as gross alpha, gross gamma, corrosion chemistry and elementals and select radionuclides. The density and weight percent solids of the "as-received" composite sample and filtrate were completed in the Shielded Cells Facility. Aliquots of the "as-received" composite samples were digested, diluted and removed from the Shielded Cells for analysis by ADS. With the exception of weight percent solids and density, all analyses were conducted in duplicate. Weight percent solids determinations were performed in the Shielded cell in triplicate with a reference sodium chloride solution.

The specific gravity of the "as-received" sample along with total solids in the slurry and the dissolved solids in the slurry, were measured directly on the "as-received" composite material. The insoluble solids and soluble solids were calculated from the total solids and dissolved solids (filtrate) using the following equations:

Wis = (Wts – Wds)/(1 – Wds) and
Wss = Wts - Wis
Where Wds = weight fraction dissolved solids in the supernate,
Wts = weight fraction total solids in the slurry,
Wis = weight fraction insoluble solids in the slurry and
Wss = weight fraction soluble solids in the slurry.

Digestions

In preparation for the elemental analyses (prior to submittal to AD), two slurry aliquots were digested by the aqua regia (AQR) method and four slurry aliquots were digested by the peroxide fusion (PF) method. Note that the AQR 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 AQR 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 AQR digest solutions for quantifying sulfur. Cold vapor atomic absorption (CVAA) spectroscopy was performed on the AQR digest solutions (along with the AQR blank) for the purpose of quantifying mercury.

The elemental results determined through ICP-AES analyses were based either solely on the AQR digest solutions, solely on the PF digest solutions, or on both the AQR 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.

Elemental Analysis of Supernatant:
In preparation for the elemental analyses (prior to AD submittal), two supernatant aliquots were each diluted by a factor of ~11 (on a volume basis), using ~3 M HNO3. The use of the ~3 M HNO3 diluent 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, ICP-AES-S, and CVAA were performed on the acidified/diluted supernatant aliquots, to quantify routine elemental constituents, sulfur, and mercury, respectively. 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.

Anions in the Supernatant:
In preparation for the anion analyses (prior to AD submittal), two supernatant aliquots were each diluted by a factor of ~11 (on a volume basis), using de-ionized water. 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, assuming 100% of the aluminum was present as aluminate. Dilution-correction of the results was performed prior to reporting.

Select Radioisotopes in the Slurry Solids:
The same AQR digestion method that was used for the slurry elemental analyses was utilized for preparing the slurry aliquots for the select radioisotope analyses (two slurry aliquots digested by AQR plus an AQR blank for quality assurance purposes). ICP-MS was performed on the AQR digest solutions to quantify Tc-99, 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.

Select Radioisotopes in the Supernatant:
The same acid dilution method that was used for the supernatant elemental analyses was utilized for preparing the supernatant aliquots for the select radioisotope analyses (two supernatant aliquots acidified and diluted using ~2.0 M nitric acid plus a ~3.0 M acid blank for quality assurance purposes). Gamma spectroscopy was performed on the acidified/diluted supernatant aliquots to quantify Cs-137, and ICP-MS was performed to quantify Tc-99, U-235, and U-238 (these were the only radioisotopes with concentrations exceeding the minimum detection limits).

Appendix B: Tank 51 AD Tracking Numbers for Slurry and Supernatant*

Analytes	Method (s)	SRNL AD Tracking Number (LIMS):
Anions	IC	LW8134-8136
Free-OH	Free-OH	LW8137-8139
TIC/TOC	TIC/TOC	LW8137-8139
Elemental	ICP-ES	LW8115-8117; LW8109-8111
Select Elements (Ag, Th)	ICP-MS	
Sulfur	Axial Sulfur ICP-ES	LW8146-8148; LW8109-8111
Hg	CVV-Hg	LW8109-8111; LW8146-8148
Total Alpha	Rad Screen (LSC)	LW8112-8114
Non-volatile Beta	Rad Screen (LSC)	LW8112-8114
Sr-90	Sr90	LW8112-8114
Pu-238	Pu-238/241	LW8112-8114
Pu-241	Pu-238/241	LW8112-8114
Pu-239/ Pu-240	Pu-TTA	LW8112-8114
Cs-134	GAMMA SPEC	LW8142-8143
Cs-137	GAMMA SPEC	LW8142-8143
U-233	ICP-MS	LW8109-8111; LW8144-8145
U-234	ICP-MS	LW8109-8111; LW8144-8145
U-235	ICP-MS	LW8109-8111; LW8144-8145
U-236	ICP-MS	LW8109-8111; LW8144-8145
U-238	ICP-MS	LW8109-8111; LW8144-8145
Np-237	ICP-MS	LW8109-8111; LW8144-8145
Co-60	GAMMA SPEC Cs REMOVED	LW8112-8114
Sb-126	GAMMA SPEC Cs REMOVED	LW8112-8114
Ce-144	GAMMA SPEC Cs REMOVED	LW8112-8114
Pr-144	GAMMA SPEC Cs REMOVED	LW8112-8114
Eu-154	GAMMA SPEC Cs REMOVED	LW8112-8114
Eu-155	GAMMA SPEC Cs REMOVED	LW8112-8114
Am-241	Gamma Spec.	LW8112-8114
Cm-244	Am/Cm	LW8112-8114
Pm-147/ Sm-151	Pm-147/Sm-151	LW8112-8114
Tc-99	Tc-99	LW8109-8111; LW8144-8145

*Project: IDs: LW-AD-PROJ-170905-1 to Project: ID: LW-AD-PROJ-170905-5