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Characterization of Tank 51 Sludge Slurry Samples (HTF-51-17-44/ HTF-51-17-48) in Support of Sludge Batch 10 Processing.

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LIST OF REVISIONS		
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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 two Tank 51 sludge samples were sampled and delivered to SRNL in May of 2017. These two tank 51 sludge samples were combined into one composite sample and analyzed for corrosion controls analytes, select radionuclides, chemical elements, density and weight percent total solids and aluminum hydroxides (gibbsite and boehmite) by x-ray diffraction. A summary of the analytical results are as follows:

- The sludge and supernatant densities are 1.15 and 1.10 g/mL, respectively, with a measurement variation (%RSD) between replicates of less than 0.5%.
- The total solids of this batch of Tank 51 composite sample was 24.50 wt% total slurry, while the total dissolved solids was 22.02 wt% supernatant. This gives a calculated insoluble solids value of 3.26 wt%'.
- The dominant elemental constituents in the sludge slurry were Na (26.80 wt%), Al (10.30 wt%), Fe (2.25 wt%), Hg (1.49 wt%), Mn (0.63 wt%) and S (0.38 wt%). U-238 and Th-232 were present at the highest radionuclide mass concentrations of ~0.2 and ~0.6 wt%, respectively.
- Sodium was the most dominant constituent in the Tank 51 supernatant with a concentration of 3.53 M (8.12E+04 mg/L). The second and third most dominant constituents in the supernatant were aluminum and sulfur, with concentrations of 1.72E-01 M (4.65E+03 mg/L) and 3.39E-02 M (1.09E+03 mg/L), respectively.
- The highest measured activities were associated with Cs-137 (8.94E-01 Ci/gal) and total beta (1.05E+0 Ci/gal.)
- The predominant anions in this Tank 51 supernatant were nitrite, hydroxide, nitrate and sulfate, which were present at average concentrations of 0.991, 0.938, 0.602, and 0.030 M, respectively.
- Tank 51 sludge solids contain both gibbsite and boehmite aluminum hydroxide/oxide minerals with less than 5 wt% of the mineral being gibbsite mineral. This finding is in line with previous Tank 51 sludge solid characterization for aluminum hydroxide/oxide compounds in the Tank 51 sludge.

The Tank 51 wt% solids data (total solids, insoluble solids and dissolved solids) did not meet customer's expectations and it is anticipated that the tank may be resampled.

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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
IC	Total inorganic carbon
TOC	Total organic carbon

1.0 INTRODUCTION

In May of 2017, Savannah River Remediation (SRR) Engineering (SRR-E) delivered two Tank 51 slurry samples, identified as HTF-51-17-44 and HTF-51-17-48 (combined total sample volume of about 400 mL) to the Savannah River National Laboratory (SRNL) for characterization in support of Sludge Batch (SB) 10 processing. This report contains analyses results for select Tank 51 supernate (filtrate) corrosion control analytes, sludge slurry analytes and other relevant Tank 51 sample characterization parameters. 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 Ag Al, elemental sulfur and total Hg in the supernatant
- Select radionuclides in the "as-received" sludge slurry including total gamma, total alpha and beta and
- Perform x-ray diffraction analysis of the sludge solids to confirm the presence of boehmite and gibbsite minerals and their relative ratio in the sludge, if possible.

3.0 Sample Processing and Preparations

The two Tank 51 slurry samples sent to SRNL, identified as HTF-51-17-44 and HTF-51-17-48, were taken out of the metal transport containers and composited into one "as-received" sample as shown in Figure 1 inserts A and B. The "as received" sample density and weight percent total solids were determined as soon as the two sludge slurry sample were transferred into the SRNL shielded cell and composited. Where appropriate, supernatant sample aliquots (supernate obtained by filtering 150 mL composited "as-received' sample through a 0.45 µm Nalgene® membrane) were diluted with Super-Q water (de-ionized water) or 3.0 M nitric acid to enable removal from the shielded cell and submitted for appropriate analysis to the SRNL AD. The supernantant sample density and weight percent soluble solids were determined using the resulting filtrate solution.

"As-received" 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.

4.0 Data Presentation

4.1 Analytes and MDLs

Chemical processing 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.

Insert A: **Picture of the two Tank 51 samples (HTF-51-17-44 and HTF-51-17-48)**

Insert B: **Composite Tank 51 Sample (blend of samples HTF-51-17-44 and HTF-51-17-48)**

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

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 duplicates 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 CVAA 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.

5.0 RESULTS and DISCUSSION

The densities and solids content for the Tank 51 composite "as-received" sludge and supernatant samples are presented in Table 1. The sludge and supernatant densities are 1.15 and 1.10 g/mL, respectively, with a measurement variation (%RSD) between replicates of less than 0.5%. The measurement variations for the solids wt% determination were all lower than 3%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 in a sample of the filtrate supernate were 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, wt % of sludge slurry, is 24.5 wt%, while the total dissolved solids, wt % of supernatant, is 22.02 wt%. This gives a calculated insoluble solids value of 3.26 wt%, a value which is lower than plant expectations for the contents of Tank 51 at this processing stage.

Elemental analysis of the Tank 51 sludge slurry involved both AQR and PF digestion methods followed by ICP-ES analysis of the resulting solution for elemental concentrations. The elemental analytical results are presented in Table 4. 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 4 and 5 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.

Concentrations of the elemental constituents in the Tank 51 sludge slurry solids are given in Table 4. This table contains 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 8% or less, which demonstrates normal precision for sample replicates. As presented in Table 4, the dominant constituents in the sludge solids include sodium (26.8 wt%), Al (10.30 wt%), Fe (2.25 wt%), Hg (1.49wt%), Mn (0.631wt%) and S (0.375 wt%).

Table **1: Tank 51 Sample Densities and Solids Content**

Analyte	Average	%RSD	Units
Sludge slurry density	1.15	*0.22*	g/mL
Supernatant density (filtrate density))	1.10	*0.40*	g/mL
Total solids, wt % of sludge slurry	24.56	*1.46*	Wt %
Dissolved solids, wt % of supernatant	22.02	*2.50*	Wt %
Insoluble solids, wt % of sludge slurry	3.26*	-	Wt %
Soluble solids wt % of sludge slurry	21.3*	-	Wt %

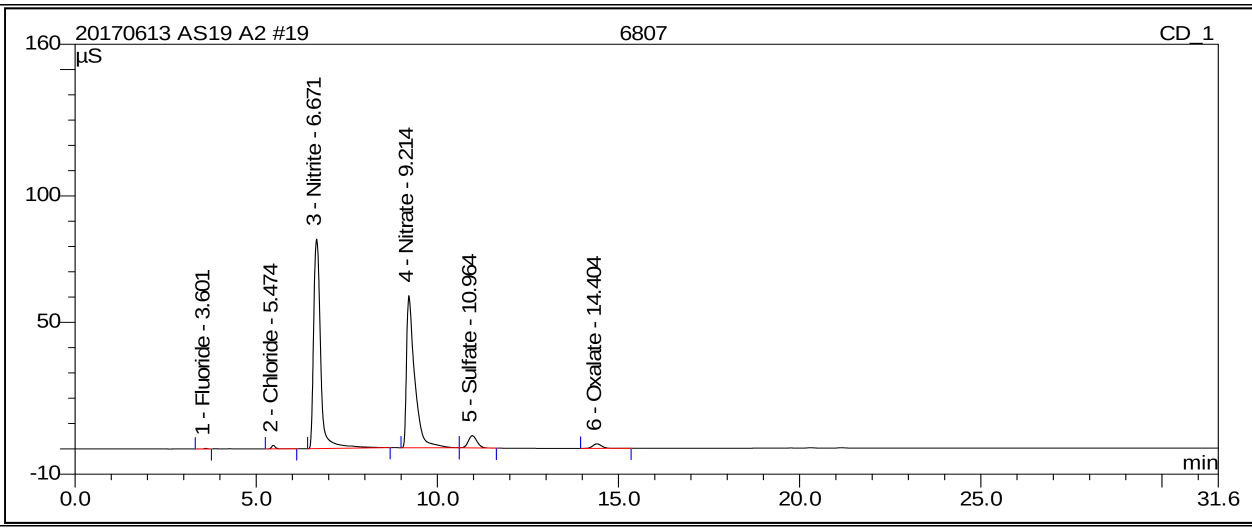
*Calculated data.

Concentrations of select radioisotopes in the slurry solids are given in Table 3, 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 ~0.2 and ~0.6 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 3, 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 9%.

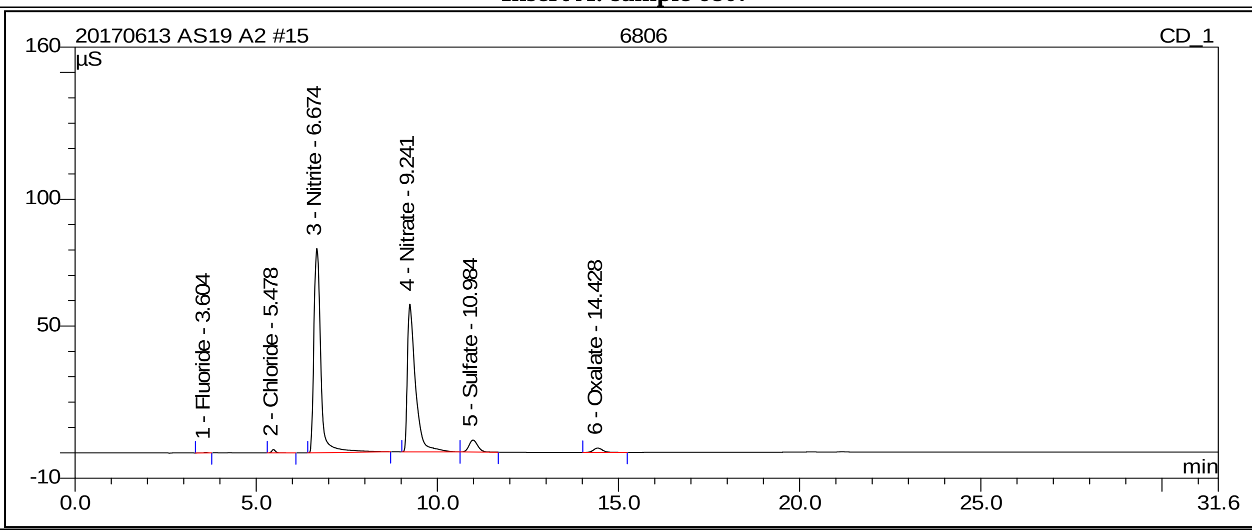
A comparison of the U-238 and Th-232 mass concentrations presented in Table 3 (0.174 and 0.583 wt%, respectively) with the elemental uranium and thorium concentrations presented in Table 4 (0.204 and 0.607 wt%, respectively) shows relatively good agreement between the ICP-MS and the ICP-AES measurements. Specifically, the uranium results from the two methods differed by about 16%, while the thorium results differed by about 4%. These differences are reasonable, given that 10% is the estimated one sigma analytical uncertainty of each of these methods and these values fall within two sigma analytical uncertainties for the two methods.

Table 2: Corrosion Chemistry Analyses Results for Tank 51 Supernate (filtrate)

Analyte	**Average Concentration M**	**%RSD**
Free OH^-	9.38E-01	11.11
NO_3^-	6.02E-01	1.96
NO_2^-	9.91E-01	1.55
SO_4^{--}	3.00E-02	2.00
CO_3^{--}	3.12E-01	1.13
PO_4^{---}	<1.12E-02	-
$C_2O_4^{--}$	<1.20E-02	-
F^-	<5.58E-02	-
Cl^-	<2.99E-02	-
Na^+	3.53E+00	0.88
TIC	3.12E-01	1.13
TOC	2.93E-02	1.16
Al	1.72E-01	1.05
pH	13.97	-
Total gamma (dpm/mL)	5.24E+08	0.06



Insert A: sample 6807



Insert B: sample 6806

Figure 2: Anion chromatograms

Table 3: 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	2.03E-09	2.45E-05	11.31
Sr-90	1.52E-03	2.22E+00	2.50
Tc-99	1.62E-03	2.94E-04	5.50
Cs-134	<2.38E-08	<3.29E-04	-
Cs-137	9.40E-04	8.74E-01	1.59
Ce-144	<5.26E-09	<1.79E-04	-
#Pm-147	<2.09E-06	<2.07E-02	-
Sm-147	9.03E-05	2.54E-02	0.55
Pr-144	<2.22E-13	<1.79E-04	-
Eu-154	9.51E-07	2.74E-03	1.01
Eu-155	<1.97E-08	<9.78E-05	-
Th-232	5.83E-01	6.84E-07	3.79
U-233	1.62E-04	1.67E-05	2.27
U-234	1.22E-04	8.17E-06	1.96
U-235	3.56E-03	8.23E-08	3.52
U-236	4.55E-04	3.15E-07	5.83
U-238	1.74E-01	6.27E-07	1.17
Np-237	4.18E-04	3.15E-06	1.68
Pu-238	1.28E-04	2.34E-02	1.78
Pu-239*	8.36E-04	5.56E-04	3.46
Pu-240*	1.17E-04	2.85E-04	1.54
Pu-239/240	1.27E-03	8.47E-04	6.22
Pu-241	3.80E-06	4.19E-03	2.98
Am-241	5.53E-05	2.03E-03	0.68
Am-243	7.21E-06	1.54E-05	3.25
Am-242m	3.32E-08	3.45E-06	4.82
Cm-242	8.07E-011	2.85E-06	4.37
Cm-243	<4.21E-08	<2.32E-05	
Cm-244	5.66E-07	4.89E-04	3.68
Cm-245	<1.06E-05	<1.94E-05	
Cm-247	<1.12E-02	<1.11E-05	
Cf-249	<2.61E-07	<1.14E-05	
Cf-251	<5.56E-07	<9.45E-06	
#Total alpha	-	<6.22E-02	-
Total beta	-	7.31	2.27

Upper limit values, * ICP-MS data

The concentrations and analytical IC spectrum of anions in the Tank 51 supernatant medium are presented in Table 2 and Figure 2, respectively. The dominant anions include nitrite, nitrate and sulfate, at concentrations of 0.991 M (4.14E+04 mg/kg), 0.602 M (3.42E+04 mg/kg) and 0.03 M (2.62E+03 mg/kg), respectively. The other anions, F^-, Cl^-, PO_4^{---} and $C_2O_4^{--}$, 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^-, AlO_2^- and free OH^-). The above data are based upon the analytical results obtained for the respective supernatant analyses (ICP-AES results for aluminum, 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 an ion charge of two for carbonate oxalate, and sulfate and charge of 3 for phosphate ion). 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 3.54 M, while the anions summed to 3.42 M. The anions summed to 96.6% of the cations, which is within 10% of the cation value.

The concentrations of elemental constituents in the Tank 51 supernatant (filtrate) are given in Table 5. As shown in the table, sodium was the most dominant constituent with a concentration of 3.53 M (8.12E+04 mg/L). The second and third most dominant constituents were aluminum and sulfur, with concentrations of 1.72E-01 M (4.65E+03 mg/L) and 3.39E-02 M (1.09E+03 mg/L), respectively.

The analytical results for select radionuclides in the supernate phase (filtrate) of the Tank 51 sample are presented in Table 6. As shown in the Table 6, the select radionuclide concentrations varied over several orders of magnitude. The concentrations of U-236 (1.42E-26 Ci/gal) and U-235 (2.91E-24 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 a concentration of 8.94E-01 Ci/gal, consistent with the high solubility and specific activity of this radionuclide. Note that the RSDs were less than three percent, indicating good measurement precision.

Table 4: Elemental Results for Tank 51 Composite Sludge Slurry Sample

Analyte	Wt% Total Solids (Average)	Concentration, M (Average)	Average %RSD
Ag#	1.87E-03	4.89E-05	4.30
Al	1.03E+01	1.08E+00	2.37
B	<9.98E-03	<2.61E-03	
Ba	1.55E-02	3.18E-04	1.78
Be	2.27E-04	7.12E-05	2.53
Ca	1.44E-01	1.01E-02	2.20
Cd	<5.42E-03	<1.36E-04	
Ce	<2.85E-02	<5.74E-04	
Co	<6.03E-03	<1.86E-04	
Cr	4.44E-02	2.40E-03	1.97
Cu	<2.11E-02	<9.34E-04	
Fe	2.25E+00	1.14E-01	2.10
Gd	<7.37E-03	<1.33E-04	
K	1.52E-01	1.10E-02	3.61
La	1.48E-02	3.01E-04	3.20
Li	<9.41E-03	<3.83E-03	
Mg	3.33E-02	2.28E-03	2.16
Mn	6.31E-01	3.25E-02	1.82
Mo	1.14E-02	3.34E-04	7.36
Na	2.68E+01	3.29E+00	2.15
Ni	1.04E-01	4.98E-03	2.36
P	<8.22E-02	<3.78E-03	
Pb	<7.45E-02	<6.30E-03	
S*	3.75E-01	3.30E-02	2.77
Sb	<8.39E-02	<3.75E-01	
Si	1.21E-01	1.21E-02	4.05
Sn	<4.68E-02	<9.71E-03	
Sr	9.45E-03	1.17E-03	1.68
Th	6.07E-01	3.85E-03	3.16
Ti	4.11E-03	2.44E-04	1.08
U	2.04E-01	2.42E-03	2.11
V	<2.47E-03	<1.37E-04	
Zn	5.29E-03	2.28E-04	3.82
Zr	2.04E-02	6.30E-04	2.83
Hg**	1.49E+00	2.10E-02	3.28

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

Table 5: Elemental Analyses of Tank 51 Supernate (Filtrate)

Analyte	Average Concentration M	%RSD
Ag#	<2.24E-05	-
Al	1.72E-01	0.75
B	1.93E-03	0.03
Ba	<9.45E-07	
Be	<9.60E-06	
Ca	<3.34E-05	
Cd	<1.44E-05	
Ce	<3.09E-05	
Co	<2.99E-05	
Cr	1.80E-03	0.92
Cu	<1.77E-04	
Fe	<3.95E-05	
Gd	<7.91E-06	
K	1.13E-02	2.08
La	<6.98E-06	
Li	<2.43E-04	
Mg	<9.78E-06	
Mn	<4.13E-06	
Mo	3.62E-04	0.90
Na	3.53E+00	0.62
Ni	<4.71E-05	
P	<1.57E-03	
Pb	<1.08E-04	
S*	3.39E-02	1.61
Sb	<1.94E-04	
Si	<6.62E-04	
Sn	<1.19E-04	
Sr	<4.93E-07	
Th	<2.33E-06	
Ti	<1.051E-4	
U	<9.72E-05	
V	<1.49E-05	
Zn	<9.76E-06	
Zr	<8.41E-06	
Hg	8.38E-04	1.24

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

Table 6: 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	1.77E+05	3.01E-04	0.74
Cs-134	<7.08E+04	<1.21E-04	
Cs-137	5.24E+08	8.94E-01	0.09
Th-232	<2.64E+09	<4.51E+00	
U-233	<4.66E+01	<7.95E-08	
U-234	5.79E+01	9.88E-08	0.41
U-235	4.18E-01	7.13E-10	0.56
U-236	1.86E+00	3.17E-09	2.57
U-238	1.89E+00	3.22E-09	1.52
Np-237	7.20E+00	1.23E-08	1.87
Pu-239	<2.99E+02	<5.11E-07	
Pu-240	<1.10E+03	<1.87E-06	
#Total alpha	<1.04E+06	<1.78E-03	
Total beta	6.15E+08	1.05E+00	0.40

Upper limit values

The X-ray analysis spectra for deionized water washed[1] and unwashed Tank 51 sludge slurry solid aliquots of about 0.2 grams are presented in Figure 3. The X-ray analysis data was used to identify the existence of minerals of aluminum hydroxide [boehmite (γ-Al(OH)) and gibbsite (α-$Al(OH)_3$)] in the Tank 51 sludge solids by matching the X-ray spectra with reference spectra. X-ray spectra of washed and unwashed Tank 51 solids show the presence of both of these mineral phases. The best estimate for the relative amounts of boehmite and gibbsite in the sludge solids indicates that the samples contains less than 5 wt% gibbsite with the balance being boehmite.

1 About 3 grams of Tank 51 slurry was washed six times with 100 mL portions of deionized water and the resulting solid fraction was air dried overnight in the shielded cell before submitting about 0.2 grams of the washed and air dried portion for x-ray analysis. The wet cake from filtered Tank 51 slurry was submitted for x-ray analysis as unwashed solid.

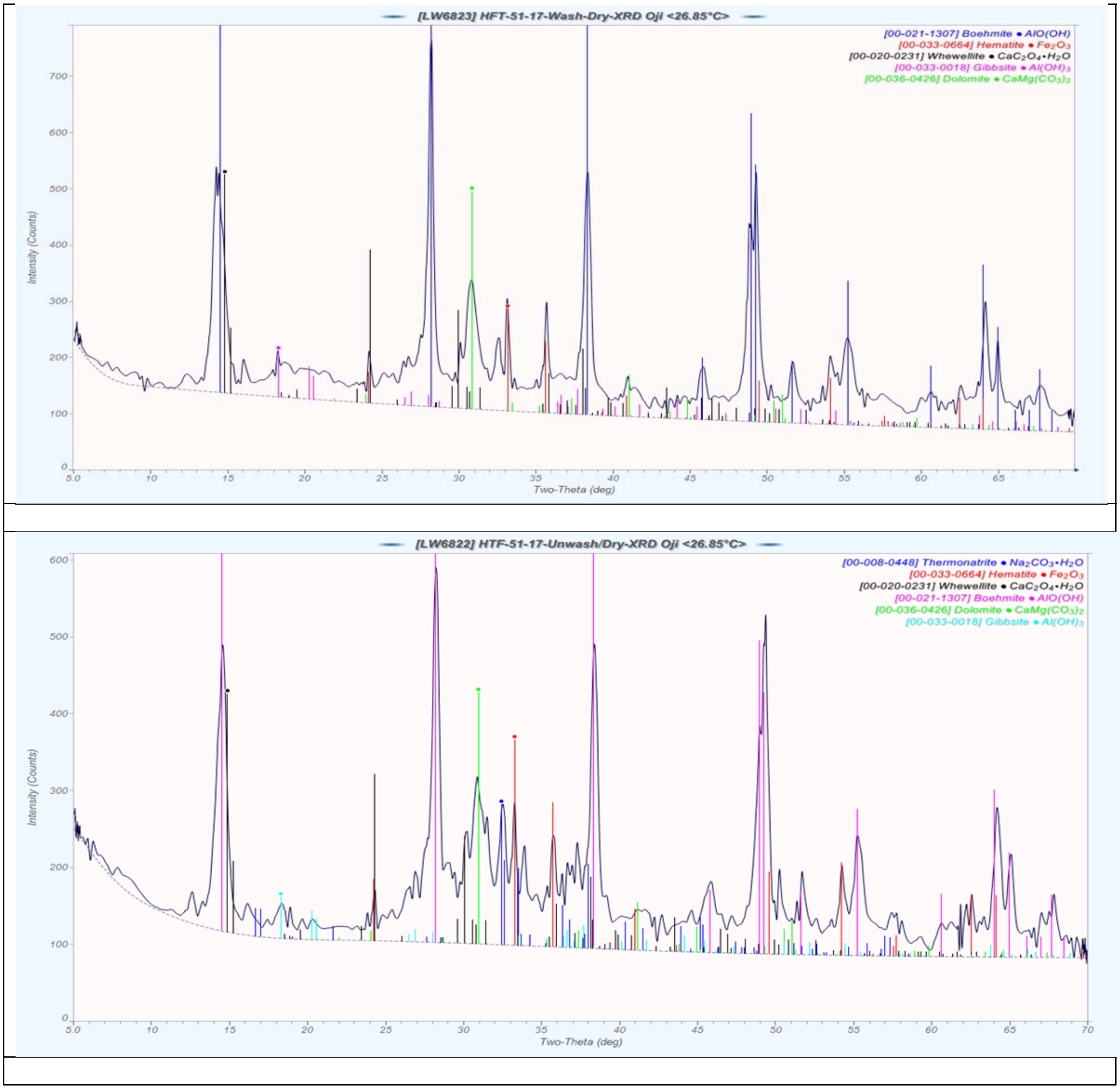


Figure 3: X-ray spectra for washed and unwashed Tank 51 composite solids

6.0 CONCLUSION and RECOMMENDATIONS

A summary of the analytical results are as follows:

- The sludge and supernatant densities are 1.15 and 1.10 g/mL, respectively, with a measurement variation (%RSD) between replicates of less than 0.5%.
- The total solids of this batch of Tank 51 composite sample was 24.50 wt% sludge slurry, while the total dissolved solids is 22.02 wt% supernate. This gives a calculated insoluble solids value of 3.26 wt%' sludge slurry.
- The dominant elemental constituents in the sludge solids include Na (26.80 wt%), Al (10.30 wt%), Fe (2.25 wt%), Hg (1.49 wt%), Mn (0.63 wt%) and S (0.38 wt%). U-238 and Th-232 were present in the sludge solids at the highest radionuclide mass concentrations of ~0.2 wt% and ~0.6 wt%, respectively.
- Sodium was the most dominant metal with a concentration of 3.53 M (8.12E+04 mg/L) in the Tank 51 supernatant. The second and third most dominant metals in the supernatant were aluminum and sulfur, with concentrations of 1.72E-01 M (4.65E+03 mg/L) and 3.39E-02 M (1.09E+03 mg/L), respectively.
- Select radionuclides analyzed in the supernatant varied over several orders of magnitude, ranging from a low of 1.42E-26 Ci/gal for U-236 and 2.91E-24 Ci/gal for U-235 to a high of 8.94E-01 Ci/gal for Cs-137.
- The predominant anions in this Tank 51 supernatant were nitrite, hydroxide, nitrate and sulfate, at average concentrations of 0.991, 0.938, 0.602 and 0.030 M, respectively.

- Tank 51 sludge solids contain both gibbsite and boehmite aluminum hydroxide/oxide minerals with less than 5 wt% of the mineral being gibbsite mineral. This finding is in line with previous Tank 51 sludge solid characterization for aluminum hydroxide/oxide compounds in the Tank 51 sludge.[3.]

The wt% data for the Tank 51 composite sample did not meet the customer's expectation for total insoluble solids and it is expected that the tank may be resampled for further analyses.

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 51slurry 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: Laboratory Notebook SRNL-NB-2013-00031, L5575-00080-09 SRNL Electronic Notebook (Production); SRNL, Aiken, SC 29808 (2014) and various AD notebooks contain the analytical/experimental 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.
3. M. S. Hay, K. Adu-Wusu, and D. J. McCabe, "Determination of the fraction of gibbsite and boehmite forms of aluminum in Tank 51H sludge," WSRC-STI-2008-00697, August 2008.

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	LW6806-6808
Free-OH	Free-OH	LW6809-6811
TIC/TOC	TIC/TOC	LW6809-6811
Elemental	ICP-ES	LW6825-6827 LW6813-6814
Select Elements (Ag, Th)	ICP-MS	
Sulfur	Axial Sulfur ICP-ES	LW6825-6827 LW6819,6820
Hg	CVV-Hg	LW6825-6827 LW6819,6821
Total Alpha	Rad Screen (LSC)	LW6815
Non-volatile Beta	Rad Screen (LSC)	LW6815
Sr-90	Sr90	LW6786, 6787
Pu-238	Pu-238/241	LW6786, 6787
Pu-241	Pu-238/241	LW6786, 6787
Pu-239	ICP-MS	LW825-656 LW6817-6818
Pu-240	ICP-MS	LW825-656 LW6817-6818
Pu-239/ Pu-240	Pu-TTA	LW6786-6788
Cs-134	GAMMA SPEC	LW6786, 6787 and 6815
Cs-137	GAMMA SPEC	LW6786, 6787 and 6815
U-233	ICP-MS	LW6825- 6827 LW6817, 6818
U-234	ICP-MS	LW6825- 6827 LW6817, 6818
U-235	ICP-MS	LW6825- 6827 LW6817, 6818
U-236	ICP-MS	LW6825- 6827 LW6817, 6818
U-238	ICP-MS	LW6825- 6827 LW6817, 6818
Np-237	ICP-MS	LW6825- 6827 LW6817, 6818
Co-60	GAMMA SPEC Cs REMOVED	LW6786, 6787
Sb-126	GAMMA SPEC Cs REMOVED	LW6786, 6787
Ce-144	GAMMA SPEC Cs REMOVED	LW6786, 6787
Pr-144	GAMMA SPEC Cs REMOVED	LW6786, 6787
Eu-154	GAMMA SPEC Cs REMOVED	LW6786, 6787
Eu-155	GAMMA SPEC Cs REMOVED	LW6786, 6787
Am-241	Gamma Spec.	LW6786- 6788
Cm-244	Am/Cm	LW6786- 6788
Pm-147/ Sm-151	Pm-147/Sm-151	LW6786- 6788
Tc-99	Tc-99	LW6817, LW6818

*Project: IDs: LW-AD-PROJ-170525-1 to Project: ID: LW-AD-PROJ-170525-8