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Sludge Batch 11 Assembly: Tank 26

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EXECUTIVE SUMMARY

Savannah River Mission Completion Nuclear Safety and Engineering Integration (SRMC-E) has requested that Savannah River National Laboratory (SRNL) perform Tank 26 characterization analyses in support of Sludge Batch 11 (SB11) assembly. This report provides important characterization of the slurry in Tank 26 prior to transfer from Tank 26 to Tank 51 that confirms the transfer is "Low Rem" and ensures the sludge concurs with the estimated transfer mass for the SB11 recipe. Two Tank 26 samples were delivered to SRNL and composited into a single sample in September 2023. The composite sample was analyzed for the following: density, weight percent solids, chemical composition, radionuclides, supernate corrosion control tests, and x-ray diffraction for burkeite, gibbsite, and boehmite. The slurry was also evaluated for sulfate washing behavior in order to provide knowledge on insoluble sulfate dissolution during Tank 51 sludge washing similar to a previous washing study performed in 2019. The Tank 26 sample results are consistent with and representative of PUREX sludge and the prior usage of Tank 26 as a feed tank for the 1F and 2F Evaporators.

- The slurry and supernate densities were observed to be 1.503 and 1.410 g/mL respectively.
- The weight percent solids analyses of the unwashed slurry yielded a total solids (slurry basis) weight percent of 51.8%, soluble solids (slurry basis) weight percent of 41.3%, soluble solids (filtrate basis) weight percent of 46.1%, insoluble solids (slurry basis) weight percent of 10.5%, and a calcined solids (slurry basis) weight percent of 31.4%.
- The most prevalent radiochemical species, by weight percent of the total solids, were found to be U-238 followed by U-235 and Pu-239 along with Tc-99, Cs-137, U-236, Np-237, Pu-240, and Am-241. The highest contributors of radioactivity, by Ci/gal, were Cs-137 and Ba-137m followed by Sr-90, Y-90, Am-241, Pu-238, and Pu-241.
- The most prevalent elements observed, by mg/kg slurry, were Al, Ca, Cr, Fe, Mn, Na, K, S, and U which is typical of slurry. Additionally, the highest concentration elements seen in the supernate were Na, Al, S, K, P, Cr, B, Hg, and Mo. The highest level of anions found in the slurry and supernate were nitrate, nitrite, sulfate, carbonate, and free hydroxide. Fluoride was found in the slurry but not in the supernate.
- The washing study of the Tank 26 slurry sample demonstrated that insoluble sulfur and fluoride salts dissolved and were removed over multiple washes with water. All insoluble sulfur and fluoride had dissolved by the fifth decant and wash step. The study simulated the future washing effort in the Tank Farm prior to the Tank 26 to Tank 51 slurry transfer.
- Through XRD, the phase composition of the unwashed slurry was determined to be hematite, kogarkoite, and darapskite with the possibility of clarkeite, jezekite, and calcium aluminum oxide nitrate hydrate. No boehmite, gibbsite, nor burkeite was observed in the sample.

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LIST OF ABBREVIATIONS

CSMPs	Commercial Submersible Mixing Pumps
CST	Crystalline Silicotitanate
DMA	Direct Mercury Analyzer
HM	H-Modified
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
LIMS	Laboratory Information Management System
MDA	Minimum Detectable Activity
MST	Monosodium Titanate
PUREX	Plutonium Uranium Reduction Extraction
RSD	Relative Standard Deviation
SB11	Sludge Batch 11
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
XRD	X-ray Diffraction

1.0 Introduction

Savannah River Mission Completion Nuclear Safety and Engineering Integration (SRMC-E) has requested through a Technical Task Request (TTR) that Savannah River National Laboratory (SRNL) perform Tank 26 characterization analyses in support of Sludge Batch 11 (SB11) assembly.[1] Tank 26 is a Type IIIA waste tank located in F-Tank Farm that contains Plutonium Uranium Reduction Extraction (PUREX) sludge which is higher in iron but lower in mercury, aluminum, and noble metals compared to H-Modified (HM) sludge from the H-Tank Farm. [2] Tank 26 has served several functions in the tank farm including being a receipt tank of F-Canyon waste and being a feed tank for the 242-1F (1F) and 242-16F (2F) evaporators.[3] After Tank 26 is characterized by SRNL, bulk waste removal will be performed by transfer to Tank 51. Two Tank 26 samples were delivered to SRNL and composited into a single sample in September 2023. The composite sample was analyzed for the following as defined in the Task Technical and Quality Assurance Plan (TTQAP): density, weight percent solids, slurry elementals, chemical composition, radionuclides, supernate corrosion control, silicon, volatile and semi-volatile organic analyses, a washing study, and x-ray diffraction for burkeite, gibbsite, and boehmite.[4]

2.0 Experimental Procedure

Two Tank 26 samples (FTF-26-23-17 and FTF-26-23-18) each containing approximately 200mL of slurry were delivered on September 01, 2023 to SRNL in metal dip bottle containers. Prior to pulling the samples, Tank 26 was mixed using 4 commercial submersible mixing pumps (CSMPs) for 17 days. The samples were pulled without foil within 30 minutes of pump shutdown at 24 inches below the liquid surface. Upon receipt, the samples were composited into a single sample (FTF-26-23-17/18). Each metal dip bottle was washed with decanted supernate and returned to the composite bottle in order to transfer all sludge into the composite bottle. Figure 2-1 shows the FTF-26-23-17/18 final composited sample bottle. All future aliquots taken from this sample were taken after vigorously mixing the sample.

Figure 2-1. FTF-26-23-17/18 composite sample.

After compositing the samples, the slurry density was measured gravimetrically by observing the weight of slurry at a known volume. Additionally, peroxide fusion digestion preparations utilizing sodium peroxide and nitric acid,[5] aqua regia digestions (utilizing a sealed vessel) preparations,[6] and slurry water dilutions (filtered and unfiltered) were performed for subsequent radiochemical and chemical slurry analyses. Supernate preparations were each diluted at a dilution factor of ~10 with deionized water and also submitted for radiochemical and chemical testing. Additionally, aliquots of supernate to be analyzed for silicon were digested with nitric acid, heated at 90 °C, and diluted to a final dilution factor of ~55 with deionized water.[7]

The I-129 analysis required a separate preparation due to the I-129 being removed through volatilization by peroxide fusion or aqua regia. These preparations required the use of monosodium titanate (MST), crystalline silicotitanate (CST), potassium iodide, nitric acid, and sodium hydroxide. The methods, analytes, and digestions/dilutions for the slurry radionuclides are displayed in Table 2-1.

Table 2-1. Slurry radionuclides methods, analytes, and digestions/dilutions

Methods and Digestions for Determination of Slurry Radionuclides		
Method:	Digestion:	Analyte:
Liquid Scintillation Counting	Peroxide Fusion	Total Alpha, Total Beta
Gamma Scan Cs-removed	Peroxide Fusion	Co-60, Ru-106, Rh-106 (calculated, secular equilibrium with Ru-106), Ag-110m, Sb-125, Te-125m (calculated, secular equilibrium with Sb-125), Ce-144, Pr-144 (calculated, secular equilibrium with Ce-144), Pr-144m (calculated, secular equilibrium with Ce-144), Eu-152, Eu-154, Eu-155, Am-241
Gamma Scan	Peroxide Fusion	Cs-134, Cs-137, Ba-137m (calculated, secular equilibrium with Cs-137)
Pm-147/Sm-151	Peroxide Fusion	Pm-147, Sm-151
U_233_234_235_236	Peroxide Fusion	U-233, U-234, U-235, U-236, U-238
ICP-MS	Aqua Regia	Np-237
Pu238_Pu241	Peroxide Fusion	Pu-238, Pu-241
Pu_242_244	Peroxide Fusion	Pu-239, Pu-240, Pu-242
Tc_99	Aqua Regia	Tc-99
Am_Cm	Peroxide Fusion	Am-242m, Cm-244, Cm-245
Sr_90	Peroxide Fusion	Sr-90, Y-90 (calculated, secular equilibrium with Sr-90)
I_129_With_Separation	Special Preparation	I-129
Tritium	Water Dilution, Filtered	H-3

Aliquots of slurry were filtered and dried under vacuum on the filtration apparatus for three hours at ambient temperature. Approximately 100 mg of unwashed solids were transferred into a shielded bottle. The filtered solid was washed with 15mL of deionized water three times, and 100 mg of washed solids were transferred into a shielded bottle. These shielded bottles were submitted for x-ray diffraction (XRD) analysis for gibbsite, boehmite, and burkeite.

The weight percent solids were measured and determined for total solids (slurry basis), soluble solids (slurry and filtrate bases), insoluble solids (slurry basis), and calcined solids (slurry basis). The total solids were obtained through evaporation of liquid by heating quadruplicate sample preparations in an oven at 115 °C until there was no or minimal further loss of mass. To measure calcined solids, the sample preparations used for total solids were further placed into a furnace and heated at 1100 °C for 2 hours. The soluble solids (filtrate basis) were determined by filtering slurry through a 0.45 µm nylon filter membrane and analyzing four aliquots of the filtrate. The filtrate was heated at 115 °C until all liquid had evaporated and no further or minimal loss of mass. The insoluble solids (slurry basis) and soluble solids (slurry basis) were calculated from total solids (slurry basis) and soluble solids (filtrate basis).

For the washing study, approximately 120 grams of slurry was transferred to a graduated cylinder, and the solids in the slurry were allowed to settle. Subsequently, a volume of the supernate was decanted (and collected), followed by washing the remaining slurry with deionized water (see Table 2-2). This cycle of decanting supernate and washing with water was repeated until 5 decants were collected with the following expected concentrations (molar) of sodium: 9.5, 6.0, 4.0, 2.1, and 1.1. These sodium concentrations were selected to match SRMC's planned wash of Tank 26 slurry prior to the Tank 26 to Tank 51 transfer (target decant sodium concentration from 9.5M to approximately 6M) and to replicate the Tank 26 washing study performed in 2019.[8] The decants were measured, by single replicate, for elementals and anions by inductively coupled plasma emission spectroscopy (ICP-ES) and ion chromatography (IC). The densities of decants 2, 3, 4, and 5 were measured, in duplicate, gravimetrically by implementing a known volume container. The density can be corrected to the tank temperature. The results from decant 1 (FTF-26-23-17/18 supernate) were obtained from the corrosion control preparation (Laboratory Information Management System (LIMS) Project ID: AL-230831-2).

Table 2-2. Washing and Decant Steps for Tank 26 (FTF-26-23-17/18) Washing Study

Washing and Decant Steps				
Initial Slurry (g):	119.957			
Step	Decant Subtraction (g)	Water Addition (g)	Decant Density (g/mL)	Target Decant Na Conc. (M)
1	26.529	33.202	1.410	9.5
2	53.075	24.489	1.304	6.0
3	37.706	41.094	1.213	4.0
4	36.193	48.810	1.125	2.1
5	31.714	N/A	1.077	1.1
Note: Temperature at Density Measurement: 15 °C				

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 2.60.[9] SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.[10] SRMC requested that a Functional Classification of Safety Class apply to this work. Additionally, the gibbsite, boehmite, and burkeite analyses are considered Production Support Functional Classification.[4]

3.0 Results and Discussion

Four memoranda were issued previously that reported weight percent solids and density (SRNL-L3130-2023-00005)[11], elemental analysis (SRNL-L3130-2023-00006)[12], radiochemical analyses (SRNL-L3130-2023-00010)[13], and the washing study (SRNL-L3130-2023-00013).[14] These results are again stated in this report. The weight percent solids and slurry density results in SRNL-L3130-2023-00005 Revision 0 are reported here as Table 3-1 and Table 3-2 respectively.

Table 3-1. Summary of Weight Percent Analyses of FTF-26-23-17/18

Summary of Weight Percent Analyses of FTF-26-23-17/18		
Test	**Average**	**%RSD (n)**
Total Solids (slurry basis) (%)	51.8	0.4 (4)
Calculated Soluble Solids (slurry basis) (%)	41.3	N/A
Soluble Solids (filtrate basis) (%)	46.1	0.2 (4)
Calculated Insoluble Solids (slurry basis) (%)	10.5 ± 0.7	N/A
Calcined Solids (slurry basis) (%)	31.4	6.8 (4)

Error propagation of the total solids (slurry basis) and soluble solids (filtrate basis) yielded a 95% confidence interval for the insoluble solids of approximately ±0.7 weight %. The confidence interval is derived using the inverse Student's t-distribution which requires probability and degrees of freedom, partial derivative of the weight percent of insoluble solids with respect to total solids, partial derivative of the weight percent of insoluble solids with respect to soluble solids, standard error of the weight percent total solids, and standard error of the weight percent soluble solids. Contributing factors to larger 95% confidence interval values include standard deviation of results (incorporated in standard error), number of replicates (incorporated in degrees of freedom), and average weight percent of soluble solids (incorporated in partial derivative of weight percent insoluble solids with respect to total solids and soluble solids). A higher standard deviation of results, larger amount of weight percent soluble solids, and fewer number of replicates can lead to a larger 95% confidence interval value. The high soluble solids weight percent, sodium content, and density is not unexpected with Tank 26's involvement as an evaporator feed tank.

Table 3-2. Summary of Slurry Density Analyses of FTF-26-23-17/18

Summary of Slurry Density Analyses of FTF-26-23-17/18			
Replicate 1 (g/mL)	**Replicate 2 (g/mL)**	**Average (g/mL)**	**%RSD**
1.503	1.504	1.503	0.08

The supernate density which was reported in the corrosion control LIMS sample results report was observed to be 1.410 g/mL. The supernate density being lower than the slurry density is due to the insoluble solids not being present in the supernate density replicates. The high densities correspond with the larger total solids observed in the sample.

The slurry radionuclides results reported in SRNL-L3130-2023-00010 Revision 0 with additional radionuclides are displayed in Table 3-3. The total beta/gamma was calculated by summing the total beta results with the gamma emitting radionuclides.

Table 3-3. Slurry Radionuclides

Radiochemical Analyses					
Slurry Analyses	Average (wt% of total solids)	Average (Ci/g of total solids)	Average (Ci/gal of sludge slurry)	%RSD, n=3	Uncertainty (1 sigma) (%)
Total Alpha	N/A	<3.22E-05	<9.48E-02	N/A	Upper Limit
Total Beta-Gamma	N/A	9.78E-04	2.88E+00	N/A	N/A
Ag-110m	<6.13E-11	<2.91E-09	<8.59E-06	N/A	MDA
Am-241	1.17E-04	4.01E-06	1.18E-02	0.57	5.0
Am-242m	4.98E-09	4.84E-10	1.43E-06	28.2 (2)	*42
Ba-137m	6.73E-11	3.62E-04	1.07E+00	1.64	5.00
Ce-144	<9.08E-10	<2.90E-08	<8.54E-05	N/A	MDA
Cm-244	1.14E-06	9.24E-07	2.72E-03	9.47	*5.9
Cm-245	<2.69E-06	<4.62E-09	<1.36E-05	N/A	MDA
Co-60	6.99E-10	7.90E-09	2.33E-05	6.16	*2.91
Cs-134	<3.06E-08	<3.97E-07	<1.17E-03	N/A	MDA
Cs-137	4.40E-04	3.83E-04	1.13E+00	1.64	5.00
Eu-152	<3.23E-09	<5.59E-09	<1.65E-05	N/A	MDA
Eu-154	7.06E-08	1.90E-07	5.61E-04	0.91	5.00
Eu-155	<3.01E-09	<1.40E-08	<4.13E-05	N/A	MDA
H-3	N/A	N/A	1.29E-05	44.0	*8.0
I-129	5.19E-05	9.16E-11	2.70E-07	1.45	*4.63
Np-237	1.25E-04	8.80E-10	2.59E-06	2.43	10
Pm-147	<1.76E-07	<1.63E-06	<4.82E-03	N/A	Upper Limit
Pr-144	<3.83E-14	<2.90E-08	<8.54E-05	N/A	MDA
Pr-144m	<1.60E-14	<2.90E-08	<8.54E-05	N/A	MDA
Pu-238	4.32E-05	7.40E-06	2.18E-02	6.52	*2.7
Pu-239	4.15E-03	2.58E-06	7.61E-03	6.91	19.8
Pu-240	2.83E-04	6.44E-07	1.90E-03	6.62	19.8
Pu-241	6.62E-06	6.82E-06	2.01E-02	6.64	*8.4
Pu-242	9.03E-06	3.45E-10	1.02E-06	7.45	19.8
Rh-106	<3.10E-16	<1.10E-08	<3.26E-05	N/A	MDA
Ru-106	<3.30E-10	<1.10E-08	<3.26E-05	N/A	MDA
Sb-125	<6.88E-10	<7.10E-09	<2.09E-05	N/A	MDA
Sm-151	<3.02E-06	<7.94E-07	<2.34E-03	N/A	Upper Limit
Sr-90	6.32E-05	8.61E-05	2.54E-01	3.99	*5.56
Tc-99	1.55E-03	2.62E-07	7.72E-04	15.6	*6.5
Te-125m	<3.94E-11	<7.10E-09	<2.09E-05	N/A	MDA
U-233	<3.88E-06	<3.76E-10	<1.11E-06	N/A	N/A
U-234	8.37E-05	5.23E-09	1.54E-05	7.36	10
U-235	4.56E-03	9.86E-11	2.91E-07	6.26	10
U-236	3.69E-04	2.39E-10	7.04E-07	6.12	10
U-238	1.85E+00	6.20E-09	1.83E-05	0.45	10
Y-90	1.58E-08	8.61E-05	2.54E-01	3.99	*5.56
Note: "<" results are not the average. They are the minimum of three replicate results. MDA= minimum detectable activity, * notes a pooled average of one sigma uncertainty.					

Due to beta spillover during liquid scintillation counting from beta emitting radionuclides, the measured value was biased high and was reported as the upper limit. Specific Activity values were obtained from DOE/RW-0006, Rev. 13. Tritium is not present in the dried solids; therefore, the tritium results for weight percent of total solids and Ci/g of total solids is reported as not applicable. The average one sigma uncertainty for each radionuclide for Am-242m, Co-60, Cm-244, H-3, I-129, Pu-238, Pu-241, Sr-90, Tc-99, and Y-90 were calculated (due to having a range of uncertainties for the results of each radionuclide) by taking the square root of the sum of the squares of each uncertainty divided by the number of measurements followed by dividing by the square root of the number of measurements. The most prevalent radiochemical species, by weight percent of the total solids, were found to be predominantly U-238 followed by U-235, Pu-239, Tc-99, Cs-137, U-236, Np-237, Pu-240, and Am-241. The highest contributors of radioactivity, by Ci/gal, were largely Cs-137 and Ba-137m followed by Sr-90, Y-90, Am-241, Pu-238, and Pu-241. These results agree with the total beta-gamma and total alpha observed.

$$\boldsymbol{Average\ Pooled\ One\ Sigma\ Uncertainty} = \frac{\sqrt{\frac{\boldsymbol{s1^2 + s2^2 + s3^2}}{\boldsymbol{3}}}}{\boldsymbol{\sqrt{3}}}$$

The methods, analytes, and digestions for the slurry elementals reported in SRNL-L3130-2023-00006 Revision 0 are displayed in Table 3-4. The most prevalent elements observed, by mg/kg slurry, were Al, Ca, Cr, Fe, Mn, Na, K, S, and U which is typical of slurry. As expected, Tank 26 (PUREX sludge) was lower in Al and Hg (while slightly higher in Fe) compared to typical HM sludge.

Table 3-4. Slurry elemental analyses results

Slurry Elemental Analysis								
Slurry	Average mg/kg Slurry	RSD	Uncertainty (1 sigma) (%)	Number of Replicates	Digestion Method (s)	Analytical Method	Average mg/kg total solids	Average mg/kg calcined solids
Ag	8.99E+00	N/A	10	3	Aqua Regia	ICP-MS	1.74E+01	2.86E+01
Al	8.21E+03	2.00	5	3	Peroxide Fusion	ICP-ES	1.59E+04	2.62E+04
B	5.96E+01	1.37	5	3	Aqua Regia	ICP-ES	1.15E+02	1.90E+02
Ba	3.65E+01	2.44	5	6	Peroxide Fusion, Aqua Regia	ICP-ES	7.05E+01	1.16E+02
Be	<1.1E-01	N/A	N/A	3	Aqua Regia	ICP-ES	<2.0E-01	<3.3E-01
Ca	2.19E+03	5.00	5	3	Aqua Regia	ICP-ES	4.23E+03	6.99E+03
Cd	8.19E+00	1.97	5	3	Aqua Regia	ICP-ES	1.58E+01	2.61E+01
Ce	<2.31E+01	N/A	N/A	3	Aqua Regia	ICP-ES	<4.46E+01	<7.36E+01
Co	4.75E+00	N/A	10	3	Aqua Regia	ICP-MS	9.18E+00	1.51E+01
Cr	1.27E+03	4.09	5	6	Peroxide Fusion, Aqua Regia	ICP-ES	2.45E+03	4.04E+03
Cu	<3.66E+01	N/A	N/A	3	Peroxide Fusion	ICP-ES	<7.07E+01	<1.17E+02
Fe	1.71E+04	2.21	5	6	Peroxide Fusion, Aqua Regia	ICP-ES	3.29E+04	5.44E+04
Gd	5.58E+01	1.71	5	3	Aqua Regia	ICP-ES	1.08E+02	1.78E+02
Hg	5.83E+02	4.57	10	3	Aqua Regia	DMA	1.13E+03	N/A
K	1.07E+03	1.94	5	3	Aqua Regia	ICP-ES	2.07E+03	3.42E+03
La	<1.49E+01	N/A	N/A	3	Aqua Regia	ICP-ES	<2.88E+01	<4.75E+01
Li	<3.41E+01	N/A	N/A	3	Aqua Regia	ICP-ES	<6.58E+01	<1.1E+02
Mg	7.68E+02	1.61	5	6	Peroxide Fusion, Aqua Regia	ICP-ES	1.48E+03	2.44E+03
Mn	1.19E+03	3.65	5	6	Peroxide Fusion, Aqua Regia	ICP-ES	2.29E+03	3.77E+03
Mo	2.05E+01	2.99	5	3	Aqua Regia	ICP-ES	3.95E+01	6.52E+01
Na	1.62E+05	0.62	2.5	3	Aqua Regia	ICP-ES	3.13E+05	5.16E+05
Ni	2.57E+02	4.23	5	6	Peroxide Fusion, Aqua Regia	ICP-ES	4.97E+02	8.20E+02
P	2.35E+02	2.10	5	3	Aqua Regia	ICP-ES	4.53E+02	7.47E+02
Pb	2.01E+01	N/A	10	3	Aqua Regia	ICP-MS	3.87E+01	6.39E+01
S	1.18E+04	4.40	5	6	Peroxide Fusion, Aqua Regia	ICP-ES	2.27E+04	3.74E+04
Sb	5.81E-01	N/A	10	3	Aqua Regia	ICP-MS	1.12E+00	1.85E+00
Si	5.79E+02	3.04	5	3	Peroxide Fusion	ICP-ES	1.12E+03	1.84E+03
Sn	3.12E+00	N/A	10	3	Aqua Regia	ICP-MS	6.03E+00	9.95E+00
Sr	9.52E+00	9.85	5	6	Peroxide Fusion, Aqua Regia	ICP-ES	1.84E+01	3.03E+01
Th	1.17E+00	N/A	10	3	Aqua Regia	ICP-MS	2.27E+00	3.74E+00
Ti	<2.47E+01	N/A	N/A	3	Aqua Regia	ICP-ES	<4.77E+01	<7.87E+01
U	9.93E+03	3.48	5	6	Peroxide Fusion, Aqua Regia	ICP-ES	1.92E+04	3.16E+04
V	<1.38E+01	N/A	N/A	3	Peroxide Fusion	ICP-ES	<2.66E+01	<4.39E+01
Zn	3.14E+01	6.87	5	3	Peroxide Fusion	ICP-ES	6.06E+01	1.00E+02
Zr	<1.09E+01	N/A	N/A	3	Aqua Regia	ICP-ES	<2.10E+01	<3.47E+01
Note: "<" results are not the average. They are the minimum of the replicates analyzed.								

A select number of supernate elementals and anions were analyzed as part of the corrosion control analyses. Therefore, the full elemental and anion suites were screened and are reported here in Table 3-5 and Table 3-7, respectively. Supernate total Hg was analyzed by DMA. The most prevalent elements seen in the supernate were Na, Al, S, K, P, Cr, B, Hg, and Mo which is typical of tank farm salt solution. The highest level of anions found in the slurry and supernate were nitrate, nitrite, sulfate, carbonate, and free hydroxide. Each of the anions (except fluoride) were found to be in good agreeance between the slurry and supernate with the differences being within method uncertainty. Fluoride was observed in the slurry, but it was not found in the supernate. The logical conclusion would be that some of the solids are made up of insoluble fluoride salts, which would be solubilized during the washing process. This will be further discussed with the washing study results. The ratio of the sum of the cations and sum of the anions for the slurry and supernate matched to 105% and 97%, respectively.

Table 3-5. Supernate elemental analyses results

Supernate Elemental Analysis by ICP-ES and DMA			
Element	Average (mg/L)	%RSD n = 2	Uncertainty (1 sigma) (%)
Ag	<1.97E-01	N/A	N/A
Al	1.04E+04	0.00	5
B	9.30E+01	1.90	5
Ba	<1.36E-01	N/A	N/A
Be	<1.29E-01	N/A	N/A
Ca	<3.31E+00	N/A	N/A
Cd	<3.22E-01	N/A	N/A
Ce	<3.86E+00	N/A	N/A
Co	<8.79E-01	N/A	N/A
Cr	4.58E+02	1.70	5
Cu	<6.04E+00	N/A	N/A
Fe	2.26E+00	2.50	5
Gd	<4.24E-01	N/A	N/A
K	1.48E+03	0.96	5
La	<3.47E-01	N/A	N/A
Li	<4.16E+01	N/A	N/A
Mg	<2.21E+00	N/A	N/A
Mn	3.88E+00	2.55	5
Mo	3.22E+01	0.88	5
Na	2.18E+05	0.00	2.5
Ni	<1.88E+00	N/A	N/A
P	2.56E+02	2.76	5
Pb	<1.66E+01	N/A	N/A
S	3.64E+03	1.55	5
Sb	<9.48E+00	N/A	N/A
Si	<1.79E+01	N/A	N/A
Sn	<4.33E+01	N/A	N/A
Sr	<9.8E-02	N/A	N/A
Th	<1.13E+01	N/A	N/A
Ti	<7.07E-01	N/A	N/A
U	<1.09E+01	N/A	N/A
V	<1.66E+00	N/A	N/A
Zn	8.80E+00	0.96	5
Zr	<1.36E-01	N/A	N/A
Hg	3.90E+01	78.7	10
Note: "<" results are not the average. They are the minimum of the replicates analyzed.			

Table 3-6. Supernate anions analyses results

Supernate Anions			
Anion	Average (M)	%RSD, n = 2	Uncertainty (1 sigma) (%)
Free Hydroxide	2.78	0.76	5
Carbonate	6.59E-01	0.64	7
Formate	<2.17E-03	N/A	N/A
Nitrite	6.60E-01	0.21	10
Nitrate	4.42E+00	2.08	10
Sulfate	1.04E-01	0.68	10
Oxalate	<1.14E-03	N/A	N/A
Phosphate	3.54E-03	10.1	10
Chloride	6.00E-03	8.37	10
Aluminate	3.85E-01	0.00	5
Fluoride	<5.26E-03	N/A	N/A
Glycolate	<6.66E-03	N/A	N/A
Note: For the "<" average, the smallest "<" result is reported.			

Table 3-7. Additional Supernate Analyses

Additional Supernate Analyses			
Analysis	Minimum (mg/L)	%RSD	Uncertainty
Si by Warm Acid Strike	<1.95E+01	N/A	N/A
All SVOA Compounds	<1.02E+00	N/A	N/A
All VOA Compounds	<2.03E+00	N/A	N/A

Table 3-8. Sludge slurry anions and carbon analyses results

Sludge Slurry Anions			
Anion	Average (mg/L)	%RSD, n = 3	Uncertainty (1 sigma) (%)
Free Hydroxide	2.42 (M)	3.00	5
Formate	<3.06E+03	N/A	N/A
Nitrite	2.90E+04	0.13	10
Nitrate	2.48E+05	0.21	10
Sulfate	4.71E+04	1.00	10
Oxalate	<1.67E+04	0.36	N/A
Phosphate	<3.06E+03	N/A	N/A
Chloride	<3.06E+03	N/A	N/A
Fluoride	6.82E+03	1.72	10
Carbonate	3.93E+04	18.1	7
Total Inorganic Carbon	7.86E+03	18.1	7
Total Organic Carbon	4.53E+03	18.4	N/A
Note: For the "<" average, the smallest "<" result is reported.			

The washing study results reported in SRNL-L3130-2023-00013 Revision 0 are displayed in Table 3-9, Table 3-10, Table 3-11, Figure 3-1, and Figure 3-2. Washing the sludge resulted in declining concentrations of Na, Al, Cr, chloride, nitrite, and nitrate. In contrast, oxalate, sulfate, and fluoride concentrations increased through washing. Observed sodium slightly differed from the expected sodium concentrations due to the dissolution of sodium salt solids that include sulfur/sulfate, fluoride, and oxalate. As the solids dissolved, the difference between expected and observed sodium concentration increased culminating at a % difference of 34%.

Table 3-9. Summary of Elementals and Anions Results for Washing of FTF-26-23-17/18

Summary of Elementals and Anions Results for Washing of FTF-26-23-17/18					
Analyte (M)	Decant 1	Decant 2	Decant 3	Decant 4	Decant 5
Al	3.85E-01	2.58E-01	1.68E-01	8.71E-02	4.82E-02
Cr	8.80E-03	6.46E-03	4.60E-03	2.65E-03	1.96E-03
Na	9.48E+00	6.39E+00	4.61E+00	2.84E+00	1.50E+00
S	1.14E-01	1.72E-01	2.29E-01	2.62E-01	1.33E-01
Sulfate	1.04E-01	1.62E-01	2.11E-01	2.48E-01	1.23E-01
Fluoride	< 5.26E-03	3.41E-02	1.34E-01	1.93E-01	8.55E-02
Chloride	6.00E-03	4.06E-03	< 2.82E-03	< 2.82E-03	< 2.82E-03
Nitrite	6.60E-01	4.26E-01	2.85E-01	1.40E-01	6.96E-02
Nitrate	4.42E+00	2.44E+00	1.61E+00	7.64E-01	3.76E-01
Oxalate	< 1.04E-03	3.50E-03	1.02E-02	2.76E-02	5.54E-02

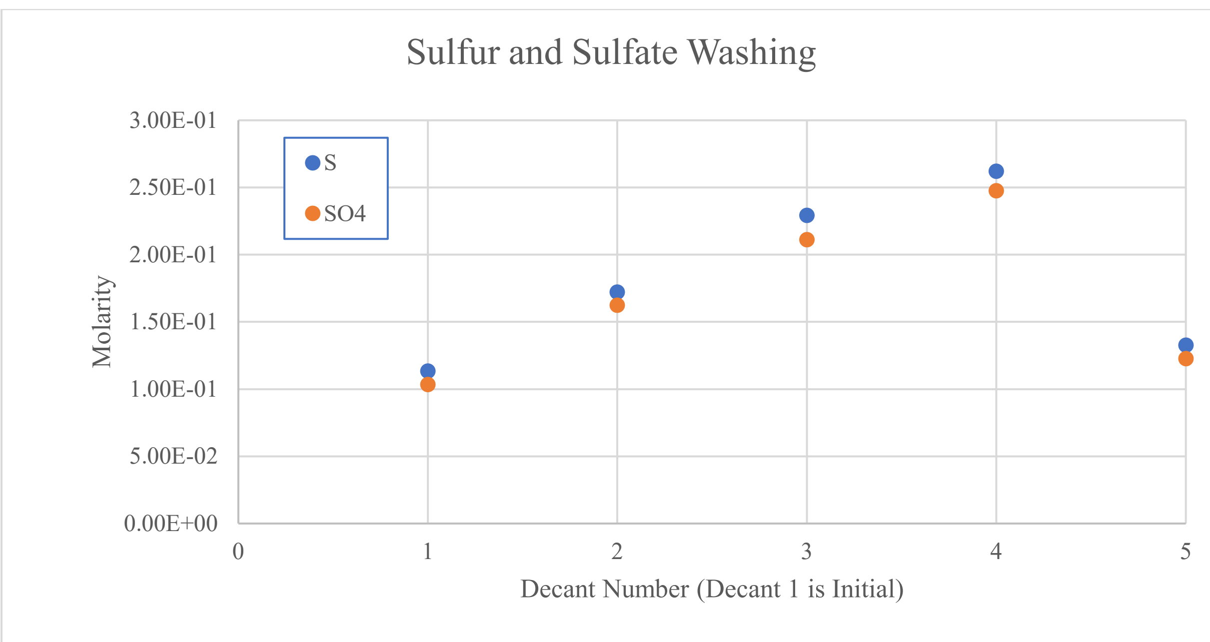

Figure 3-1. Sulfur and Sulfate Washing in FTF-26-23-17/18

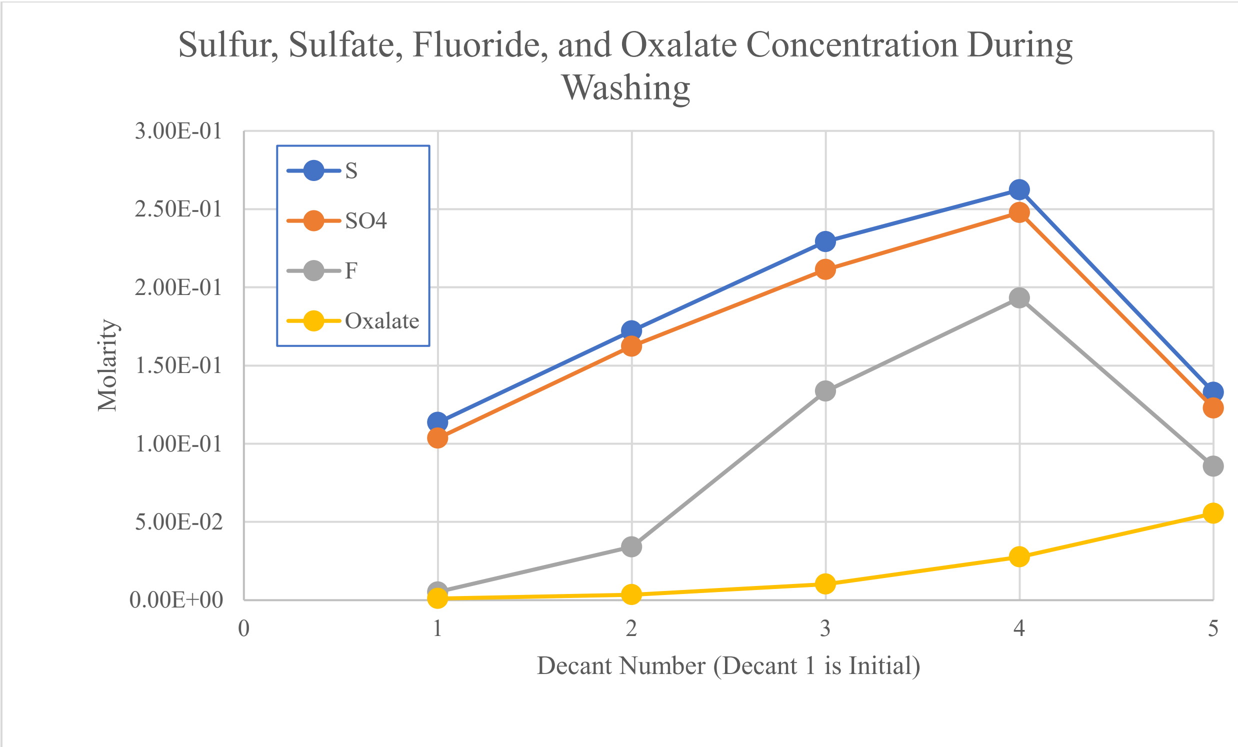

Figure 3-2. Sulfur, Sulfate, Fluoride, and Oxalate Concentration During Washing in FTF-26-23-17/18

Nitrite followed the expected concentration agreeably with the largest % difference occurring at the last decant as seen in Table 3-10. In Table 3-12, the slurry elemental results (in weight percent of total solids) before and after washing are provided. As expected, the weight percent of total solids of insoluble elementals such as iron increased after washing. By normalizing an element to iron (for example every 1 gram of iron in the washed slurry, 83 mg Al is also present in the washed slurry), it is possible to identify the rough amount of an element was removed. For aluminum, ~80% of the total aluminum was removed through washing. Additionally, prior to washing, the soluble aluminum present in the sample was approximately 80% of the total aluminum. After washing, approximately 50% of the total aluminum was dissolved aluminum.

Table 3-10. Nitrite Washing Behavior in FTF-26-23-17/18

Nitrite Washing Behavior			
Decant	**Expected Nitrite (M)**	**Observed Nitrite (M)**	**% Diff**
2	4.18E-01	4.26E-01	2.0
3	2.80E-01	2.85E-01	1.7
4	1.44E-01	1.40E-01	2.6
5	7.43E-02	6.96E-02	6.5

Table 3-11. Sodium Washing Behavior in FTF-26-23-17/18

Sodium Washing Behavior			
Decant	Expected Sodium (M)	Observed Sodium (M)	% Diff
2	6.00E+00	6.39E+00	6.3
3	4.02E+00	4.61E+00	13.6
4	2.06E+00	2.84E+00	31.6
5	1.07E+00	1.50E+00	33.8

Table 3-12. Slurry Elementals (Wt% Total Solids) Before and After Washing

Element	Initial Slurry (wt% total solids)	Washed Slurry (wt% total solids)
Ag	1.74E-03	<1.98E-02
Al	1.59E+00	1.22E+00
B	1.15E-02	<1.40E-02
Ba	7.05E-03	<4.07E-02
Be	<2.03E-05	<1.22E-03
Ca	4.23E-01	1.57E+00
Cd	1.58E-03	<1.08E-02
Ce	<4.46E-03	<4.60E-02
Co	9.18E-04	<8.44E-03
Cr	2.45E-01	7.45E-01
Cu	<7.07E-03	<1.79E-02
Fe	3.29E+00	1.46E+01
Gd	1.08E-02	<6.20E-02
K	2.07E-01	<1.61E+00
La	<2.88E-03	<7.21E-03
Li	<6.58E-03	<2.06E-01
Mg	1.48E-01	5.87E-01
Mn	2.29E-01	1.01E+00
Mo	3.95E-03	<1.03E-02
Na	3.13E+01	2.05E+01
Ni	4.97E-02	2.15E-01
P	4.53E-02	<1.60E-01
Pb	3.87E-03	<7.60E-02
S	2.27E+00	1.91E+00
Sb	1.12E-04	<4.59E-02
Si	1.12E-01	<4.33E-01
Sn	6.03E-04	<5.26E-02
Sr	1.84E-03	<6.20E-03
Th	2.27E-04	<1.12E-01
Ti	<4.77E-03	<2.78E-02
U	1.92E+00	8.36E+00
V	<2.66E-03	<4.99E-02
Zn	6.06E-03	<1.12E-01
Zr	<2.10E-03	<6.54E-03
Note: "<" results are not the average. They are the minimum of the replicates analyzed.		

From decant 2 through decant 4, insoluble sulfur/sulfate was observed (see Table 3-13) to dissolve into the added water until decant 5 where the sulfur concentration decreased. Fluoride in the sample also acted in a similar manner (see Figure 3-2). This insoluble fluoride salt solid is most likely $NaF \cdot Na_2SO_4$. As detailed in Figure 4 of CBU-PIT-2005-00232 Rev. 0, this salt, in addition to sodium oxalate, was predicted in OLI modeling to form at temperatures less than 30 °C in Tank 4 which also contained burkeite, the requested analyte of the washing study.[15]

Table 3-13. Sulfur/Sulfate Washing Behavior in FTF-26-23-17/18

Sulfur/Sulfate Washing Behavior			
Decant	**Expected Sulfur (M)**	**Observed Sulfur (M)**	**% Diff**
2	7.22E-02	1.72E-01	81.8
3	4.84E-02	2.29E-01	130.2
4	2.48E-02	2.62E-01	165.4
5	1.28E-02	1.33E-01	164.8
Decant	**Expected Sulfate (M)**	**Observed Sulfate (M)**	**% Diff**
2	6.58E-02	1.62E-01	84.4
3	4.41E-02	2.11E-01	130.8
4	2.26E-02	2.48E-01	166.5
5	1.17E-02	1.23E-01	165.2

Similar to SRNL-STI-2019-00580 Revision 0, the previous washing study in support of Sludge Batch 10 that observed sulfur also dissolving, the sulfur mass balance was calculated (see Table 3-14) which showed good agreeance between the calculated and analyzed washed slurry total S. Through washing, approximately 67-80% of the sulfur was removed. The washed slurry weight percent solids results (Table 3-15) demonstrated that the weight percent total solids, dissolved solids, and soluble solids significantly decreased post washing. Table 3-16 data is consistent with the sulfur, prior to washing, was mostly insoluble, while, after washing which required a significant amount of water, the sulfur was completely soluble. This observation is confirmed in decant 5 as all of the insoluble sulfur had been dissolved.

Table 3-14. Sulfur Mass Balance

	Total S (g)
Initial Slurry	1.409
Decant 1	0.068
Decant 2	0.225
Decant 3	0.228
Decant 4	0.271
Decant 5	0.125
Washed Slurry (Mass Balance)	0.492
Washed Slurry (Analysis)	0.281

Table 3-15. Weight Percent Solids of the Initial Slurry and Washed Slurry

Analysis	Initial Slurry	Washed Slurry
Wt% Total Solids (Slurry Basis)	51.8	17.9
Wt% Dissolved Solids (Supernate Basis)	46.1	8.7
Wt% Insoluble Solids (Slurry Basis)	10.5 ± 0.7	10.1 ± 0.1
Wt% Soluble Solids (Slurry Basis)	41.3	7.9

Table 3-16. Soluble Sulfur Before and After Washing

	Total S (g)	Soluble S (g)	% Soluble
Initial Slurry	1.41E+00	2.77E-01	20
Washed Slurry (Analysis)	2.81E-01	2.93E-01	104

Gibbsite, boehmite, and burkeite were not detected in the unwashed nor washed Tank 26 solids analyzed by XRD. The XRD patterns are shown here as Figures 3-3 and 3-4. By washing with water in order to remove residual supernate or soluble solid salts, the Tank 26 insoluble solids are shown to be hematite, kogarkoite, and darapskite. The solids and salt residues washed away by water were nitratine and calcite. Other possible phases found in the unwashed and washed patterns were clarkeite which has been found in other tank farm evaporator samples and jezekite which is unlikely as it has not been observed at the Tank Farm. One possible phase found in only the unwashed sample was calcium aluminum oxide nitrate hydrate. The insoluble fluoride compound that dissolved during the washing study was confirmed by XRD to be kogarkoite. The other insoluble sulfate complex seen in the washing study could be darapskite. These compounds are observed in the washed XRD sample because less water was used during the XRD washed sample preparation in relation to the washing study.

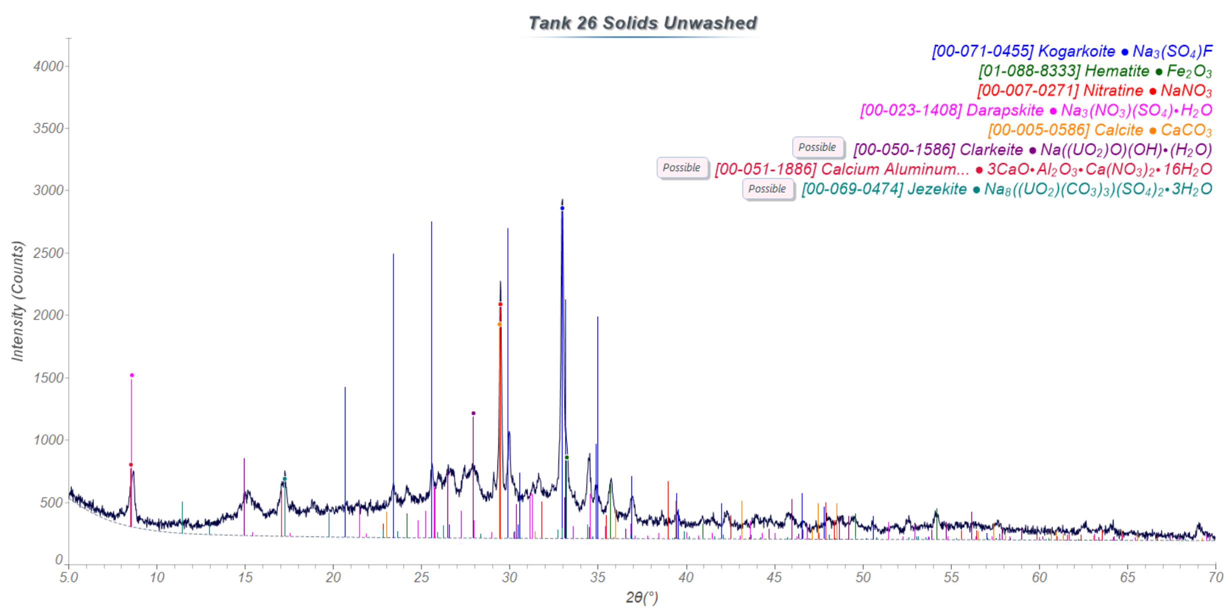

Figure 3-3. XRD of unwashed Tank 26 solids

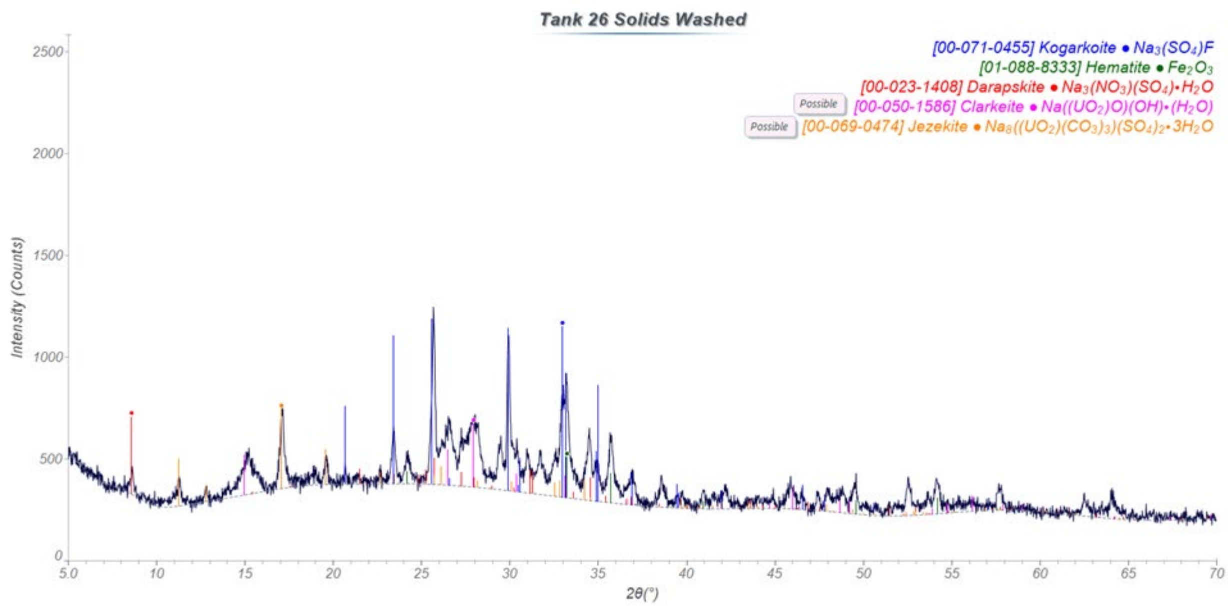

Figure 3-4. XRD of washed Tank 26 solids

4.0 Conclusions

SRNL performed Tank 26 characterization analyses in support of SB11 assembly. Two Tank 26 samples were delivered to SRNL and composited into a single sample in September 2023. The composite sample was analyzed for density, weight percent solids, chemical composition, radionuclides, supernate corrosion control tests, a washing study, and x-ray diffraction for burkeite, gibbsite, and boehmite.

- The slurry and supernate densities were observed to be 1.503 and 1.410 g/mL respectively.
- The weight percent solids analyses of the unwashed slurry yielded a total solids (slurry basis) weight percent of 51.8%, soluble solids (slurry basis) weight percent of 41.3%, soluble solids (filtrate basis) weight percent of 46.1%, insoluble solids (slurry basis) weight percent of 10.5%, and a calcined solids (slurry basis) weight percent of 31.4%.
- The most prevalent radiochemical species, by weight percent of the total solids, were found to be U-238 followed by U-235 and Pu-239 along with Tc-99, Cs-137, U-236, Np-237, Pu-240, and Am-241. The highest contributors of radioactivity, by Ci/gal, were Cs-137 and Ba-137m followed by Sr-90, Y-90, Am-241, Pu-238, and Pu-241.
- The most prevalent elements observed, by mg/kg slurry, were Al, Ca, Cr, Fe, Mn, Na, K, S, and U which is typical of slurry. Additionally, the highest concentration elements seen in the supernate were Na, Al, S, K, P, Cr, B, Hg, and Mo. The highest level of anions found in the slurry and supernate were nitrate, nitrite, sulfate, carbonate, and free hydroxide. Fluoride was found in the slurry but not in the supernate.
- The washing study of the Tank 26 slurry sample demonstrated that insoluble sulfur and fluoride salts dissolved and was removed over multiple washes with water. All insoluble sulfur and fluoride had dissolved by the fifth decant and wash step. The study simulated the future washing effort in the Tank Farm prior to the Tank 26 to Tank 51 slurry transfer.
- Through XRD, the phase composition of the unwashed slurry was determined to be hematite, kogarkoite, and darapskite with the possibility of clarkeite, jezekite, and calcium aluminum oxide nitrate hydrate. No boehmite, gibbsite, nor burkeite was observed in the sample.

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