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TANK 7 CHARACTERIZATION AND WASHING STUDIES

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EXECUTIVE SUMMARY

A 3-L PUREX sludge sample from Tank 7 was characterized and then processed through a series of inhibited water washes to remove oxalate, sodium, and other soluble ions. Current plans use Tank 7 as one of the feed sources for Sludge Batch 7 (SB7). Tank 7 is high in oxalate due to the oxalic acid cleaning of the sludge heels from Tanks 5 and 6 and subsequent transfer to Tank 7.

Ten decant and nine wash cycles were performed over a 47 day period at ambient temperature. Initially, seven decants and seven washes were completed based on preliminary estimates of the number of wash cycles required to remove the oxalate in the sludge. After reviewing the composition data, SRNL recommended the completion of 2 or 3 more decant/wash cycles to ensure all of the sodium oxalate had redissolved. In the first 7 washes, the slurry oxalate concentration was 12,300 mg/kg (69.6% oxalate removal compared to 96.1% removal of the other soluble ions). After all ten decants were complete, the slurry oxalate concentration was 3,080 mg/kg (89.2% oxalate removal compared to 99.0% of the other soluble ions). The rate of dissolution of oxalate increased significantly with subsequent washes until all of the sodium oxalate had been redissolved after seven decant/wash cycles. The measured oxalate concentrations agreed very well with LWO predictions for washing of the Tank 7 sample.

Highlights of the analysis and washing of the Tank 7 sample include:

- Sodium oxalate was detected in the as-received filtered solids. 95% of the oxalate was insoluble (undissolved) in the as-received slurry.
- No sodium oxalate was detected in the post-wash filtered solids.
- Sodium oxalate is the last soluble species that redissolves during washing with inhibited water. In order to significantly reduce the sodium oxalate concentration, the sludge must be highly washed, leaving the other soluble anions and cations (including sodium) very low in concentration.
- The post-wash slurry had 1% of the soluble anions and cations remaining, with the exception of sodium and oxalate, for which the percentages were 2.8% and 10.8% respectively. The post-wash sodium concentration was 9.25 wt% slurry total solids basis and 0.15 M supernate.
- The settling rate of slurry was very fast allowing the completion of one decant/wash cycle each day.
- The measured yield stress of as-received (6.42 wt% undissolved solids) and post-wash (7.77 wt% undissolved solids) slurry was <1 Pa. For rapidly settling slurries, it can be hard to measure the yield stress of the slurry so this result may be closer to the supernate result than the slurry.

The recommended strategy for developing the oxalate target for sludge preparation for Sludge Batch 7 includes the following steps:

1. CPC simulant testing to determine the percent oxalate destruction and acid mix needed to produce a predicted redox of approximately 0.2 $Fe^{+2}/\Sigma Fe$ in a SME product while meeting all DWPF processing constraints.
2. Perform a DWPF melter flammability assessment to ensure that the additional carbon in the oxalate together with other carbon sources will not lead to a flammability issue.
3. Perform a DWPF glass paper assessment to ensure the glass produced will meet all DWPF glass limits due to the sodium concentration in the sludge batch.

The testing would need to be repeated if a significant CPC processing change, such as an alternative reductant to formic acid, is implemented.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AD	Analytical Development
ARG – 1	Analytical Reference Glass – 1
CV-AA	Cold Vapor – Atomic Absorption Spectroscopy
DWPF	Defense Waste Processing Facility
IC	Ion Chromatography
DI	Deionized
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
HM	H-Area Modified PUREX
L	Liter
M	Molar
NA	Not Available (Not Measured)
NIST	National Institute of Standards and Testing
PUREX	Plutonium Uranium Redox Extraction
RSD	Relative Standard Deviation
SB6	Sludge Batch 6
SB7	Sludge Batch 7
SRNL	Savannah River National Laboratory
St Dev.	Standard Deviation
TTQAP	Task Technical and Quality Assurance Plan
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TTR	Task Technical Request
WSE	Waste Solidification Engineering
Wt %	Weight Percent
XRD	X-ray Diffraction

1.0 Introduction and Background

A sample of Plutonium Uranium Redox Extraction (PUREX) sludge from Tank 7 was characterized and a washing study was performed to support Sludge Batch 7 (SB7) planning and preparation. The slurry in Tank 7 has a high oxalate concentration since it came from oxalic acid cleaning of Tanks 5 and 6. It was expected that the Tank 7 sample would contain both sodium oxalate and iron oxalate.

Savannah River National Laboratory (SRNL) analyses of Tank 7 were requested by Waste Solidification Engineering (WSE) via Technical Task Request (TTR) HLE-TTR-2009-00027[1]. The sample preparation and analysis work is governed by a Task Technical and Quality Assurance Plan (TTQAP)[2], and modifications received via customer communications[3,4]. Additional scope included a request for analysis of Cs-137/Ba-137m in the as-received slurry sample, completion of two additional wash cycles, and analysis of the post-wash solids using X-ray Diffraction (XRD).

One 3-L sample of Tank 7 was pulled on June 29, 2009 by F-Tank Farm Operations following slurry operations. The sample # is FTF-07-09-37. The sample was received in the SRNL Shielded Cells on June 30, 2009.

SB7 is not the first sludge batch that is high in oxalate. SB3 was primarily Tank 7 sludge and was also relatively high in oxalate[5]. Simulant testing completed in qualifying the sludge processing for SB3 was completed at oxalate concentrations as high as 40,000 mg/kg[6]. Although the simulant testing was completed at elevated oxalate concentrations, the measured oxalate concentration in Tank 51, after the Tank 7 transfer for SB3, was 1,590 mg/kg and the actual SB3 blend in Tank 40 was 919 mg/kg oxalate[7].

2.0 Experimental Procedure and Results

The methods for preparing and analyzing the samples, together with the analytical results are summarized in this section. For instances where results were both above and below the analytical detection limit, the mean value was calculated using all four results, assuming any analysis below the detection limit was at the detection limit to be conservatively high. No estimate is made of the uncertainty in these cases.

As-Received and Post-Wash Analytical Methods

At the SRNL Shielded Cells facility, the 3-L Tank 7 sample was transferred from the shipping container into a calibrated 4-L glass bottle. The insoluble solids were allowed to settle overnight. Supernate was then siphoned off and circulated through the shipping container to complete the transfer of the sample of 3,673 g. Following thorough mixing of the 3-L sample, three sub-samples, totaling 433 g, were removed. These sub-samples were then utilized for all subsequent as-received analytical samples. Once all of the washing was complete, 1,482 g of slurry remained. Following thorough mixing of the 3-L post-wash slurry, two sub-samples, totaling 153 g, were removed. In addition, 559 g of supernate was available for any required supernate analyses. These sub-samples were then utilized for all subsequent post-wash analytical samples.

Eight separate aliquots of the slurry were digested, four with HNO_3/HCl (aqua regia[8]) in sealed Teflon® vessels and four in Na_2O_2 (alkali or peroxide fusion[9]) using Zr crucibles. Due to the use of Zr crucibles and Na in the peroxide fusions, Na and Zr cannot be determined from this preparation. Additionally, other alkali metals, such as Li and K that may be contaminants in the Na_2O_2 are not determined from this preparation. Three Analytical Reference Glass – 1 (ARG-1) standards[10] were digested along with a blank for each preparation. The ARG-1 glass allows for an assessment of the completeness of each digestion. Each aqua regia digestion and blank was diluted 1:100 by volume with deionized (DI) water and submitted to Analytical Development (AD) for inductively coupled plasma – atomic emission spectroscopy (ICP-AES) analysis and cold vapor atomic absorption (CV-AA) analysis for Hg. Equivalent dilutions of the peroxide fusion digestions and blank were submitted to AD for ICP-AES analysis.

Four separate aliquots of the slurry were diluted 20:1 by mass with DI water and submitted to AD for Total Inorganic Carbon (TIC)/Total Organic Carbon (TOC) analysis. Four separate aliquots of the slurry were diluted 20:1 by mass with DI water and submitted to AD for analysis by titration to determine the free hydroxide and total base concentration.

Four separate aliquots of the slurry were digested with equal volumes of nitric and hydrochloric acid, a special preparation approach to ensure complete digestion of all oxalate. The samples were quickly transferred out of the cells and analyzed by Ion Chromatography (IC) for oxalate within 24 hours to minimize decomposition of the oxalate. As large quantities of nitrate and chloride were added with this preparation, only oxalate was reported from this analysis.

Tank 7 supernate was collected with a 0.45 µm filter cup from a mixed slurry sample in the SRNL Shielded Cells and submitted to AD for ICP-AES and IC. The IC and ICP-AES samples were diluted 50:1 by volume with DI water. The solids remaining on the filter were washed well with DI water, dried, and submitted to AD for XRD analysis.

Four separate aliquots of the slurry before and after washing were analyzed in the Shielded Cells for density. Four separate aliquots of the slurry were analyzed in the Shielded Cells for total slurry solids.

Four separate aliquots of the filtered supernate before and after washing were analyzed in the Shielded Cells for density. Four filtered separate aliquots of the supernate were analyzed in the Shielded Cells for total supernate solids.

As-Received Analytical Results

The as-received results were reported in a memo[11] on September 16, 2009 and the memo was reissued[12] on October 13, 2009 with added XRD and supernate ICP-AES data. These data are reported again in the following tables. The only change from the original memo is that the oxalate balance has been moved to Section 2.2. These data are reported in Tables 1-1 to 1-9 and Figure 1-1.

Table 2-1. - As-Received Tank 7 Slurry Oxalate Concentration, mg/kg

Anion	Result	Std. Dev.	%RSD
Oxalate	18,100	218	1.20

Table 2-2 - As-Received Tank 7 Solids and Density

Analysis	Result	Std. Dev.	%RSD
Wt % Total Solids	24.3	0.205	0.845
Wt % Dissolved Solids (uncorrected)	19.1	0.183	0.956
Wt % Insoluble Solids (Corrected)	6.32	0.425	6.72
Wt % Soluble Solids	17.9	0.608	3.39
Slurry Density, g/mL	1.24	0.011	0.888
Supernate Density, g/mL	1.17	0.009	0.767

Table 2-3 - As-Received Tank 7 Slurry Titration Results

	Free OH, M	Total Base, M	Other Base Excluding Carbonate, M
Average	1.68	2.25	0.296
Std. Dev.	0.133	0.055	0.012
%RSD	7.92	2.43	4.03

Table 2-4 - As-Received Tank 7 Slurry Carbon Results, mg/kg

Analysis	Total Carbon	Total Inorganic Carbon	Total Organic Carbon	TOC if Oxalate*	TIC if Carbonate, M[&]
Average	6,950	1,370	5,580	20,400	0.141
Std. Dev.	245	46.3	225	824	0.0048
%RSD	3.53	3.38	4.03	4.03	3.38

* If all the organic carbon is present as oxalate, the oxalate concentration would be 5580 mg C/kg * mol C/12.0107 g * mol oxalate/2 mol C *88.019 g oxalate/mol

& If all the inorganic carbon is present as carbonate, the carbonate concentration would be 1370 mg C/kg * 1.239 kg/L * g/1000 mg * mol C/12.0107 g

Table 2-5 - As-Received Tank 7 Slurry Mercury Concentration, wt % total solids basis

Metal	Concentration	Std. Dev.	%RSD
Mercury	0.0492	0.0018	3.62

Table 2-6 - As-Received Tank 7 Slurry ICP-AES Concentration, wt % total dried solids basis

Element	Prep	Wt%	Std. Dev.	%RSD
Ag	AR	<9.70E-03	NA	NA
Al	PF	2.58E+00	1.41E-02	5.5E-01
B	AR	2.09E-02	7.93E-04	3.8E+00
Ba	AR/PF	2.79E-02	4.71E-04	1.7E+00
Be	PF	<2.56E-03	NA	NA
Ca	AR	2.04E-01	5.35E-03	2.62E+00
Cd	AR/PF	1.76E-02	4.17E-04	2.37E+00
Ce	AR	3.47E-02	1.28E-03	3.68E+00
Cr	AR/PF	3.87E-02	4.58E-03	1.18E+01
Cu	AR/PF	1.21E-02	7.98E-04	6.62E+00
Fe	AR/PF	4.38E+00	4.31E-01	9.84E+00
Gd	AR	<8.81E-03	NA	NA
K	AR	4.59E-01	2.52E-02	5.48E+00
La	AR	1.41E-02	3.56E-04	2.52E+00
Li	AR	1.48E-02	4.69E-04	3.17E+00
Mg	AR/PF	1.15E-01	9.16E-03	7.94E+00
Mn	AR/PF	9.23E-01	1.43E-02	1.55E+00
Mo	AR	9.60E-03	3.30E-04	3.44E+00
Na	AR	3.18E+01	1.00E+00	3.15E+00
Ni	AR/PF	7.18E-01	1.47E-02	2.04E+00
P	AR	7.46E-02	2.40E-03	3.22E+00
Pb	AR	9.43E-03	5.77E-04	6.12E+00
S	AR	3.36E-01	2.72E-02	8.12E+00
Sb	AR	<1.03E-02	NA	NA
Si	PF	5.89E-01	1.22E-02	2.07E+00
Sn	AR	<5.19E-03	NA	NA
Sr	AR/PF	1.35E-02	8.43E-04	6.24E+00
Ti	AR/PF	7.35E-03	5.84E-04	7.94E+00
U	AR/PF	2.04E+00	1.27E-01	6.22E+00
V	AR	<4.81E-03	NA	NA
Zn	AR/PF	1.65E-02	2.04E-03	1.24E+01
Zr	AR	6.54E-02	1.40E-03	2.14E+00

Note:
AR = Aqua Regia Digestion
PF= Peroxide Fusion Digestion

Table 2-7 - As-Received Tank 7 Supernate Anion Concentration

Anion	Result, mg/kg	Std. Dev.	%RSD	Result, Molarity
Fluoride	<244	NA	NA	<0.0150
Formate	<244	NA	NA	<0.0064
Chloride	244	5.94	2.44	0.0081
Nitrite	19,500	60.5	0.31	0.497
Bromide	<1220	NA	NA	<0.0179
Nitrate	36,600	184	0.50	0.692
Phosphate	292	7.13	2.44	0.0036
Sulfate	2,000	10.7	0.53	0.0244
Oxalate	1,000	5.33	0.53	0.0133

Table 2-8 - As-Received Tank 7 Supernate* ICP-AES Concentration, mg/L

Element	Result	Std. Dev.	%RSD
Ag	<1.60	NA	NA
Al	5,320	72.5	1.36
B	56.4	0.243	0.431
Ba	<3.86	NA	NA
Be	<0.949	NA	NA
Ca	5.39	0.429	7.96
Cd[#]	0.886	0.150	16.9
Ce	<5.58	NA	NA
Cr	69.3	0.193	0.278
Cu	<1.29	NA	NA
Fe	<2.79	NA	NA
Gd	<2.64	NA	NA
K	1,060	9.00	0.849
La	<2.30	NA	NA
Li	<4.69	NA	NA
Mg	<1.15	NA	NA
Mn	<1.23	NA	NA
Mo	23.0	0.306	1.33
Na	88,000	460	0.523
Ni	<5.23	NA	NA
P	137	0.553	0.404
Pb	<7.89	NA	NA
S	903	32.3	3.58
Sb	<14.7	NA	NA
Si	<13.6	NA	NA
Sn	<3.73	NA	NA
Sr	<0.617	NA	NA
Ti	<2.37	NA	NA
U	<33.4	NA	NA
V	<2.77	NA	NA
Zn	2.27	0.308	13.6
Zr	<1.29	NA	NA

* The supernate was diluted ~50:1 with water
[#] The Cd concentration was calculated using the two analyses above the detection limit.

Table 2-9 As-Received Tank 7 Supernate Gamma Spec, dpm/mL

Analysis	Cs-134	Cs-137
Mean value, dpm/mL	5.70E+04	6.01E+08
Std. Dev.	5.16E+03	1.17E+07
%RSD	9.05E+00	1.94E+00

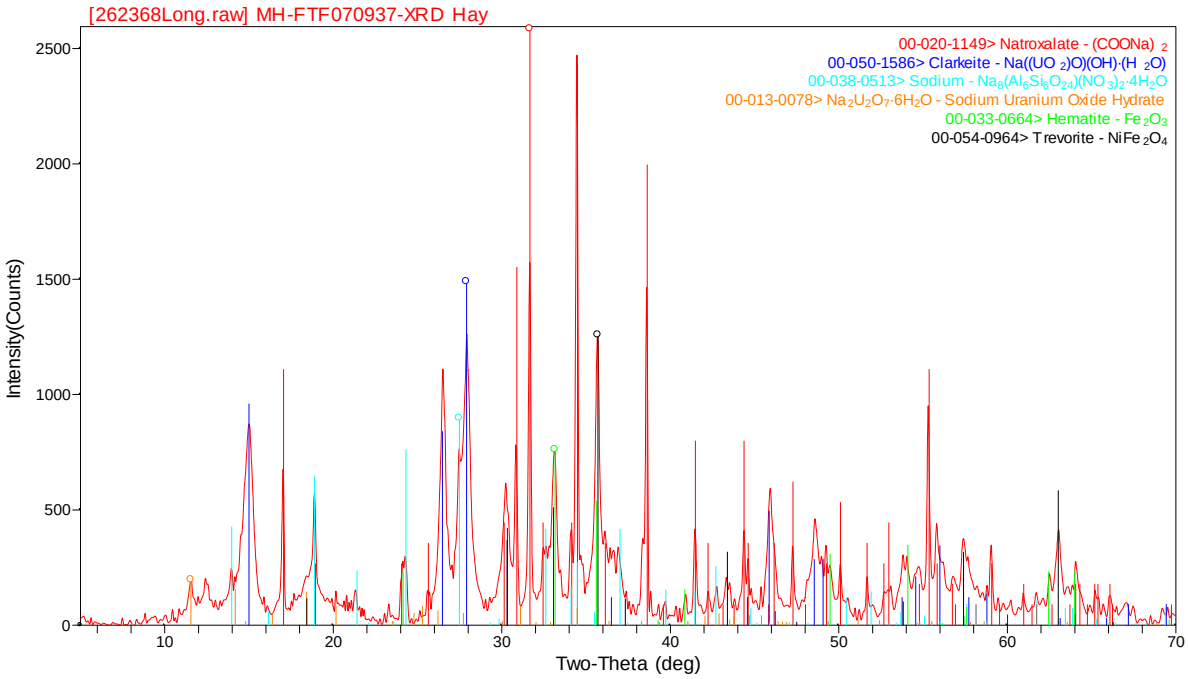

Figure 2-1- As-Received Tank 7 Washed[&] Sludge Solids XRD Analysis

[&] The Tank 7 slurry was filtered and the solids were washed with water to remove as much soluble radioactive isotopes as feasible (mainly Cs-137). The remaining solids were analyzed using XRD. Natroxalate $(COONa)_2$ is also referred to as sodium oxalate.

Post-Wash Analytical Results

After the ninth wash and tenth decant were completed, a supernate sample was submitted for analysis by AD. The data is reported in Tables 1-10 to 1-16 and Figure 1-2.

Table 2-10 - Post-Wash Tank 7 Slurry Oxalate Concentration, mg/kg

Anion	Result	Std. Dev.	%RSD
Oxalate	1,310	156	11.9

Table 2-11 - Post-Wash Tank 7 Solids and Density

Analysis	Result	Std. Dev.	%RSD
Wt % Total Dried Solids	8.73	0.02	0.259
Wt % Dissolved Solids (uncorrected)	1.04	0.04	3.83
Wt % Insoluble Solids (Corrected)	7.77	0.08	0.997
Wt % Soluble Solids	0.932	0.10	10.7
Slurry Density, g/mL*	1.07	0.00	0.396
Supernate Density, g/mL	1.01	0.00	0.423

* Average of 3 valid supernate density measurements, the fourth measurement had a density <1, likely due to inadequate filling of density tube.

Table 2-12 - Post-Wash Tank 7 Slurry Titration Results

	Free OH, M	Total Base, M	Other Base Excluding Carbonate, M
Average	0.0214	0.442	0.0214
StDev	0.000	0.029	0.000
%RSD	1.93	6.56	1.93

Table 2-13 - Post-Wash Tank 7 Slurry Mercury Concentration, wt % total solids basis

Metal	Concentration	Std. Dev.	%RSD
Mercury	0.178	0.0492	2.77

Table 2-14 - Post-Wash Tank 7 Slurry ICP-AES Concentration, wt % total solids basis

Element	Prep	Wt%	Std. Dev.	%RSD
Ag	AR	2.68E-02	1.29E-04	4.83E-01
Al	PF/AR	4.3E+00	1.80E-01	4.22E+00
B	AR	<3.83E-03	NA	NA
Ba	AR/PF	1.30E-01	3.66E-03	2.81E+00
Be	AR	<6.90E-05	NA	NA
Ca	AR	9.90E-01	5.07E-03	5.12E-01
Cd	AR/PF	8.35E-02	2.44E-03	2.92E+00
Ce	AR	3.86E-01	1.29E-03	3.35E-01
Cr	AR/PF	6.76E-02	7.51E-03	1.11E+01
Cu	AR/PF	5.95E-02	2.27E-03	3.82E+00
Fe	AR/PF	1.99E+01	8.38E-01	4.21E+00
Gd	AR	3.48E-02	2.87E-04	8.26E-01
K	AR	6.38E-02	2.20E-03	3.45E+00
La	AR	7.34E-02	5.06E-04	6.89E-01
Li	AR	7.15E-02	5.32E-04	7.45E-01
Mg	AR/PF	6.03E-01	2.34E-02	3.87E+00
Mn	AR/PF	4.3E+00	1.63E-01	3.77E+00
Mo	PF	<2.05E-02	NA	NA
Na	AR	9.25E+00	1.57E-01	1.70E+00
Ni	AR/PF	3.31E+00	1.25E-01	3.77E+00
P	PF	1.27E-01	3.29E-02	2.60E+01
Pb	AR	3.90E-02	6.22E-04	1.59E+00
S	AR	1.16E-01	NA	NA
Sb	AR	1.70E-02	3.16E-04	1.86E+00
Si	PF	3.23E+00	1.47E-01	4.57E+00
Sn	PF	3.38E-02	5.03E-03	1.49E+01
Sr	AR/PF	6.86E-02	5.00E-03	7.28E+00
Ti	AR/PF	2.96E-02	1.05E-03	3.54E+00
U	AR/PF	1.04E+01	5.83E-01	5.60E+00
V	AR	<5.04E-04	NA	NA
Zn	AR/PF	8.16E-02	3.00E-03	3.68E+00
Zr	AR	1.12E-01	6.58E-03	5.88E+00

Note:
AR = Aqua Regia Digestion
PF= Peroxide Fusion Digestion

Table 2-15 - Post-Wash Tank 7 Supernate Anion Concentration

Anion	Result, mg/kg	Std. Dev.	%RSD	Result, Molarity
Fluoride	<5	NA	NA	<0.0003
Formate	<5	NA	NA	<0.0001
Chloride	<5	NA	NA	<0.0001
Nitrite	359	3.24	0.90	0.0077
Bromide	<5	NA	NA	<0.0001
Nitrate	600	8.73	1.45	0.0096
Phosphate	<50	NA	NA	<0.0005
Sulfate	<50	NA	NA	<0.0005
Oxalate	3,340	10.0	0.30	0.0375

Table 2-16 Post-Wash Tank 7 Supernate* ICP-AES Concentration, mg/L

Element	Result, mg/L	Std. Dev.	%RSD
Ag	<0.0559	NA	NA
Al	110	1	0.74
B	1.03	0.01	0.93
Ba	0.046	NA	NA
Be	<0.0331	NA	NA
Ca	0.179	0.009	4.8
Cd	<0.0244	NA	NA
Ce	<0.195	NA	NA
Cr	1.42	0.05	3.50
Cu	0.0266	NA	NA
Fe	0.136	0.018	13.0
Gd	0.0567	NA	NA
K	17.6	0.7	3.91
La	<0.0535	NA	NA
Li	0.193	0.008	3.89
Mg	<0.0424	NA	NA
Mn	0.0571	NA	NA
Mo	0.389	0.014	3.5
Na	3510	29	0.83
Ni	<0.183	NA	NA
P	2.54	0.05	1.97
Pb	<0.275	NA	NA
S	16.9	0.6	3.50
Sb	<0.277	NA	NA
Si	1.78	0.05	2.81
Sn	<0.13000	NA	NA
Sr	<0.0276	NA	NA
Ti	<0.0242	NA	NA
U	<1.17	NA	NA
V	<0.0484	NA	NA
Zn	<0.0373	NA	NA
Zr	<0.0314	NA	NA

*** The supernate was not diluted**

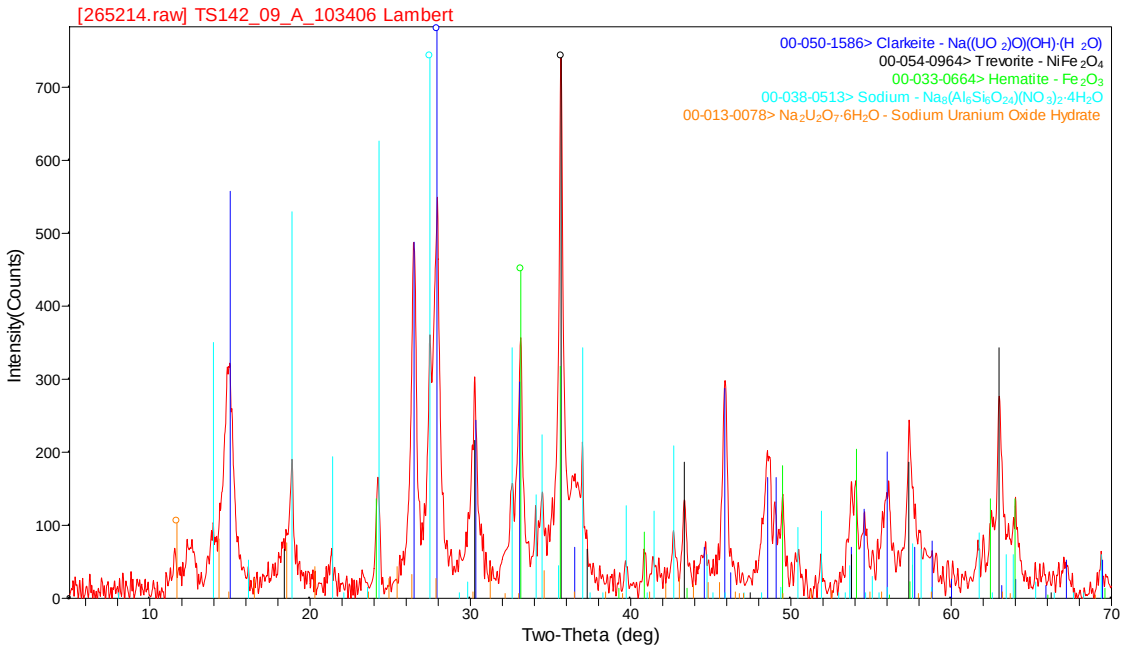

Figure 2-2 - Post Wash Tank 7 Sludge Solids XRD Analysis

The Tank 7 post-wash slurry was filtered and the dried solids were analyzed using XRD. No sodium oxalate or iron oxalate was detected.

Washing Study Methods

The Tank 7 sludge washing was completed in the SRNL Shielded Cells. The Tank 7 sample was subjected to a series of 10 decants and 9 wash cycles to decrease the concentration of soluble cations and anions. The washing followed the Gillam plan for SB7[13]. The Shielded Cells technicians work was controlled by a general wash/decant Work Instruction[14] along with an R&D instruction specific to each decant/wash cycle.

The following steps were completed for each decant/wash cycle:

1. Weigh Tank 7 slurry bottle, empty decant bottle, and empty slurry sample bottle.
2. Pump approximately 650 mL (597-724 mL) of decanted supernate to 1-liter bottle.
3. Weigh full supernate bottle.
4. Sample supernate for analysis (analyze for total supernate solids[15], density[16])
5. Weigh Tank 7 slurry bottle.
6. Add approximately 650 mL of inhibited water (0.001 M OH^-, 0.0015 M nitrite) to Tank 7 slurry bottle.
7. Mix slurry for 30 minutes.
8. Pull slurry sample (analyze for total slurry solids[15], insoluble solids, density[16]).
9. Weigh full slurry sample bottle.
10. Prepare diluted supernate samples for IC and ICP-AES analysis and submit samples.

The first decant was large and removed approximately 50% of the supernate volume and 50% of the soluble species. After each decant, inhibited water was added, the slurry was mixed 30 minutes, and the slurry was sampled. After settling overnight, the process is repeated for the next decant/wash cycle.

As washing continued, the concentration of the soluble anions and cations dropped exponentially and can be predicted knowing the supernate volume and the added inhibited water volume.

Equation 1: $X_n=X_{n-1}*V_{sup}/(V_{sup}+V_{IW})$

Xn is the concentration of cation or anion after wash n
V_{sup}= Volume of Supernate after decant n
V_{IW}=Volume of Added Inhibited Water for wash n

If the wash ratio (R) is defined as

Equation 2: $R_n= (V_{sup}+V_{IW})/V_{sup}$

$X_n = X_{n-1}/R_n$

Equation 3: $R_n = X_{n-1}/X_n$

Washing Analytical Methods

Tank 7 supernate was collected with a 0.45 μm filter cup from a supernate decant sample in the SRNL Shielded Cells and submitted to AD for ICP-AES and IC. Four separate approximately 1 mL samples were weighed then diluted to 50 mL with DI water in volumetric flasks. Two aliquots of diluted supernate were removed from each volumetric flask, one for IC and one for ICP-AES analysis.

Four separate aliquots of the slurry and four separate aliquots of the supernate were analyzed in the Shielded Cells for density[16] and for total supernate solids[15]. A pH measurement of the supernate was completed four times using the decant supernate from each decant/wash cycle.

Washing Study Results

The washing of the sludge has three steps. First the settled slurry is decanted to approximately the settled sludge level to maximize the removal of supernate and minimize the number of wash steps required. Second, approximately the same volume inhibited water is added to the slurry and mixed to redissolve the undissolved solids. Third, the slurry solids are allowed to settle in preparation for a subsequent decant. The slurry was sampled after 30 minutes of mixing was complete and the decanted supernate was used for all supernate analyses required. The anion analysis of the supernate is summarized in Table 2-17 and the ICP-AES analysis of the supernate is summarized in Table 2-18. The pH and solids data are summarized in Table 2-19.

Table 2-17 - Tank 7 Supernate Anion Concentration during Washing, mg/kg

	Wash B	Wash C	Wash D	Wash E	Wash F	Wash G	Wash H	Wash I
Fluoride	<241	<256	<265	<272	<259	<271	<266	<258
Formate	<241	<256	<265	<272	<259	<271	<266	<258
Chloride	<241	<256	<265	<272	<259	<271	<266	<258
Nitrite	12,200	7,770	5,030	3,060	2,230	1,380	929	594
Bromide	<241	<256	<265	<272	<259	<271	<266	<258
Nitrate	25,500	15,600	9,940	5,600	4,160	2,840	1,750	1,080
Phosphate	<241	<256	<265	<272	<259	<271	<266	<258
Sulfate	1,390	869	584	367	<259	<271	<266	<258
Oxalate	1,940	3,920	5,920	9,740	13,220	13,490	8,690	5,490

Table 2-18 -- Tank 7 Supernate ICP-AES during Washing, mg/L

Sample	Wash B	Wash C	Wash D	Wash E	Wash F	Wash G	Wash H	Wash I
Ag	<1.52	<1.58	<1.57	<1.60	<1.51	<1.36	<1.34	<1.34
Al	3,610	2,290	1,490	908	582	366	261	175
B	38.5	24.0	14.9	9.36	5.05	<5.14	<5.05	<5.05
Ba	<3.63	<0.381	<0.379	<0.385	<3.64	<0.377	<0.370	<0.370
Be	<0.867	<0.0526	<0.523	<0.532	<0.503	<0.521	<0.0910	<0.0910
Ca	<2.06	1.84	<1.56	1.77	1.76	<1.06	<1.04	1.52
Cd	<0.650	<0.689	<0.685	<0.696	<0.658	<0.682	<0.669	<0.669
Ce	<5.26	<5.48	<5.44	<5.53	<5.23	<8.55	<5.32	<5.32
Cr	47.2	29.7	19.6	12.0	7.70	5.17	3.68	2.40
Cu	<1.19	<0.638	<0.634	<0.64	<0.609	<0.632	<0.620	<0.620
Fe	<2.60	0.891	<2.24	0.584	<0.561	0.764	<0.570	0.778
Gd	<2.49	<1.30	<1.30	<1.32	<1.25	<1.29	<1.27	<1.27
K	670	431	276	168	104	<75.4	41.3	27.3
La	<2.17	<0.683	<0.679	<0.690	<0.652	<1.12	<0.664	<0.664
Li	<4.44	<1.16	<1.15	<1.17	<1.11	<1.15	<1.12	<1.12
Mg	<1.08	<0.286	<0.284	<0.286	<0.273	<0.283	<0.277	0.296
Mn	<1.14	<0.480	<0.477	<0.485	<0.458	<0.301	<0.295	0.297
Mo	15.7	9.96	6.23	<3.54	<2.49	<2.77	<2.35	<2.35
Na	59,500	38,500	27,400	20,300	16,800	13,500	8770	5730
Ni	<4.93	<5.16	<5.13	<5.21	<4.93	<5.11	<5.01	<5.01
P	92.8	52.3	34.7	<21.1	15.2	<15.4	<15.1	<15.1
Pb	<7.48	<7.79	<7.74	<7.87	<7.44	<7.71	<7.57	<7.57
S	613	<423	<219	<168	<145	<168	<148	<148
Sb	<14.0	<7.79	<7.74	<7.87	<13.9	<9.44	<7.57	<7.57
Si	<12.9	<6.72	<6.68	3.67	<6.42	<6.65	<6.53	<6.53
Sn	<3.52	<3.68	<3.66	<3.72	<3.52	<3.64	<3.58	<3.58
Sr	<0.542	<0.0610	<0.0606	<0.0616	<0.582	<0.060	<0.0592	<0.0592
Ti	<2.22	<0.234	<0.233	<0.690	<2.24	<0.676	<0.228	<0.228
U	<31.7	<33.0	<32.8	<33.4	<31.5	<32.7	<35.6	<35.6
V	<2.60	<0.683	<0.679	<0.690	<0.65	<0.68	<0.664	<0.664
Zn	<1.12	<0.431	<1.049	<0.410	<0.387	<0.401	<1.03	<1.03
Zr	<1.19	<0.444	<0.441	<0.448	<0.424	<0.439	<0.431	<0.431

Table 2-19 - Tank 7 pH, Solids and Density during Washing

Decant	Slurry Density, g/ml	Supernate Density, g/ml	Measured Total Solids, wt %	Calculated Insoluble Solids, wt %	Measured Dissolved Solids, wt %	pH
B	1.22	1.12	26.2	14.1	14.0	13.5
C	1.19	1.11	22.0	14.0	9.32	13.4
D	1.15	1.06	19.5	13.5	6.97	13.4
E	1.14	1.05	16.6	11.9	5.31	13.3
F	1.13	1.04	14.3	10.3	4.44	13.1
G	1.11	1.03	12.3	8.91	3.66	NA
H	1.09	1.02	10.8	8.42*	2.56	12.9
I	1.08	1.02	9.80	8.49	1.42	12.7

* Used three of four total solids results as the fourth result was approximately 20% low.

Particle size Results

The as-received and post-wash slurry was diluted with supernate simulant to dilute the solids as needed for particle size analysis. The simulant is designed to match the composition of the supernate to ensure that no dissolution of undissolved solids occurs as the result of the dilution. The particle size was measured using a Microtrac X-100 Laser Diffraction Analyzer. The composition of the supernate simulants is summarized in Table 2-20. The particles size results are summarized in Table 2-21.

Table 2-20 - Supernate Simulant for Particle Size Dilution

		As-Received		After Washing	
Recipe	MW	M	Add, g/L	M	Add, g/L
KOH	56.1056	0.027	1.521	0.00045	0.025
NaOH	39.9771	1.653	66.078	0.00007	0.003
$NaAlO_2$	81.97	0.197	16.162	0.00430	0.352
Na_2SO_4	322.18	0.028	9.073	0.00050	0.161
$NaNO_2$	68.9953	0.496	34.216	0.00860	0.593
$NaNO_3$	84.9947	0.691	58.699	0.01160	0.986
Na_3PO_4	380.11	0.004	1.367	0.00050	0.190
Na_2C_2O4	133.9991	0.013	1.781	0.04140	5.548
Na_2CO_3	105.9884	0.027	2.831	0.00052	0.055

Table 2-21 - Tank 7 Particle Size Results, microns

Sample	Particle size, number average	Particle size, volume average
As-received	To be added in Rev 1.	
Post-wash		

Rheology Methods and results

Rheological properties of radioactive samples are determined using a Haake M5/RV30 rotoviscometer. The M5/RV30 is a Searle sensor system, where the bob rotates and the cup is fixed. The torque and rotational speed of the bob are measured. Heating/cooling of the cup/sample/bob is through the holder that holds the cup. The shear stress is determined from the torque measurement and is independent of the rheological properties. Conditions that impact the measured torque are; slip (material does not properly adhere to the rotor or cup), phase separation (buildup of a liquid layer on the rotor), sedimentation (particles settling out of the shearing zone), homogeneous sample (void of air), lack of sample (gap not filled), excess sample (primarily impacts rheologically thin fluids), completely filling up the void below the bob (air buffer that is now filled with fluid) and Taylor vortices. The first five items yield lower stresses and the last three add additional stresses.

The shear rate is geometrically determined using the equations of change (continuity and motion) and is that for a Newtonian fluid. This assumption also presupposes that the flow field is fully developed and the flow is laminar. The shear rate can be calculated for a non-Newtonian fluid using the measured data and fitting these data to the rheological model or corrected as recommended by Darby[17]. In either case, for shear thinning non-Newtonian fluids typical of Savannah River Site (SRS) sludge wastes, the corrected shear rates are greater than their corresponding Newtonian shear rates, resulting in a thinner fluid. Correcting the flow curves was not performed in this task; therefore, the results are biased high.

The bob typically used for measuring tank sludge is the MV I rotor. The shape, dimensions, and geometric constants for the MV I rotor is provided in Table 2-22. Prior to performing the measurements, the rotors and cups were inspected for physical damage. The torque/speed sensors and temperature bath verified for functional operability using a bob/cup combination with a National Institute of Standards and Technology (NIST) traceable Newtonian oil standard, using the MV I rotor. The resulting flow curves were then fitted as a Newtonian fluid and this calculated viscosity must be within ± 10% of the reported NIST viscosity at a given temperature for the system to be considered functionally operable. A N10 oil standard was used to verify system operability prior to the sludge measurements. The flow curves for the sludge are fitted to the down curves using the Bingham Plastic rheological model, Equation (1), where τ is the measured stress (Pa), τ_o is the Bingham Plastic yield stress (Pa), μ_∞ is the plastic viscosity (Pa·sec), and γ_{is} the measured shear rate (sec^{-1}). During all these measurements, the sample remained in the cup for the 2nd measurement, due to the limited sample availability.

Equation 4: $\tau = \tau_o + \mu_\infty \gamma$

Table 2-22 - Rheology Specifications and Flow Curve Program

Dimensions and Flow Curve Program	
Rotor Type	MV I
Rotor radius - R_i (mm)	20.04
Cup Radius - R_a (mm)	21.0
Height of rotor -L (mm)	60
Sample Volume (cm^3) minimum	40
A factor (Pa/%torque)	3.22
M factor (s^{-1}/%RPM)	11.7
Shear rate range (s^{-1})	0 – 600
Ramp up time (min)	5
Hold time (min)	1
Ramp down time (min)	5

The rheology of the slurry is a very thin with virtually no yield stress. The slurry undissloved solids settle very quickly, allowing subsequent washing cycles to be completed each day. For rapidly settling slurries, it can be hard to measure the yield stress of the slurry so this result may be closer to the supernate result than the slurry. The results are summarized in Table 2-23.

Table 2-23 - Tank 7 Slurry Rheology

Sample	Plastic Viscosity (cP)	Yield Stress (Pa)
As-received	3.5	~0.0
Post-wash	3.3	~0.0

3.0 Discussion

The following section discusses the sludge washing, oxalate removal, elemental ratios, rheology, and optimum washing strategy for Tank 7.

Sludge Washing

The Tank 7 sludge was subjected to a series of 10 decants and 9 wash cycles to decrease the concentration of soluble cations and anions. The first decant was large and removed approximately 50% of the supernate volume and 50% of the soluble species. After each decant, inhibited water was added, the slurry was mixed for at least 30 minutes, and the slurry was sampled. After settling overnight, the process is repeated for the next decant/wash cycle.

A mass balance was used to track the volume and mass of the slurry during washing. Using the measured insoluble solids and density of supernate for each wash cycle, the volume of supernate can be calculated. The mass of wash water added in each wash cycle was measured and its volume was calculated. The volume of after washing divided by the volume before washing was calculated and these data are summarized in Table 3-1. The calculated concentration ratios for the soluble species are summarized in Table 3-2.

Table 3-1 Calculated Volume and Volume Ratio Data during Washing

Wash Cycle	Volume Supernate after decant, mL	Volume supernate after wash, mL	Volume Ratio
A	1,248	1,910	1.53
B	1,223	1,912	1.56
C	1,318	1,908	1.45
D	1,231	1,971	1.60
E	1,219	1,908	1.56
F	1,231	1,922	1.56
G	1,253	1,959	1.56
H	1,198	1,891	1.58
I	1,263	1,936	1.53

Table 3-2 Calculated Concentration Ratios Data during Washing

Wash Cycle	Nitrate Ratio	Nitrite Ratio	Sulfate Ratio	Oxalate Ratio	Na Ratio	Al Ratio	B Ratio	K Ratio	S Ratio	P Ratio
B	1.64	1.57	1.60	0.49	1.52	1.58	1.60	1.55	1.45	1.77
C	1.57	1.55	1.49	0.66	1.45	1.54	1.62	1.56	2.02	1.51
D	1.66	1.64	1.59	0.61	1.60	1.64	1.59	1.64	1.24	NA
E	1.44	1.37	1.41	0.74	1.52	1.57	NA	1.62	1.16	NA
F	1.47	1.62	NA	0.98	1.52	1.57	NA	NA	NA	NA
G	1.62	1.49	NA	1.55	NA	NA	NA	NA	NA	NA
H	1.62	1.56	NA	1.58	NA	NA	NA	NA	NA	NA
I	1.83	1.67	NA	1.50	NA	NA	NA	NA	NA	NA

A graph of the wash ratios (R_n) versus decant cycle should give the same ratio for each soluble species (Figure 3-1). This is true for all measured soluble species (until the species concentration approaches its analytical detection limit) except oxalate.

Overall, the concentration of the soluble species decreased by a factor of 51.3 as a result of the washing.

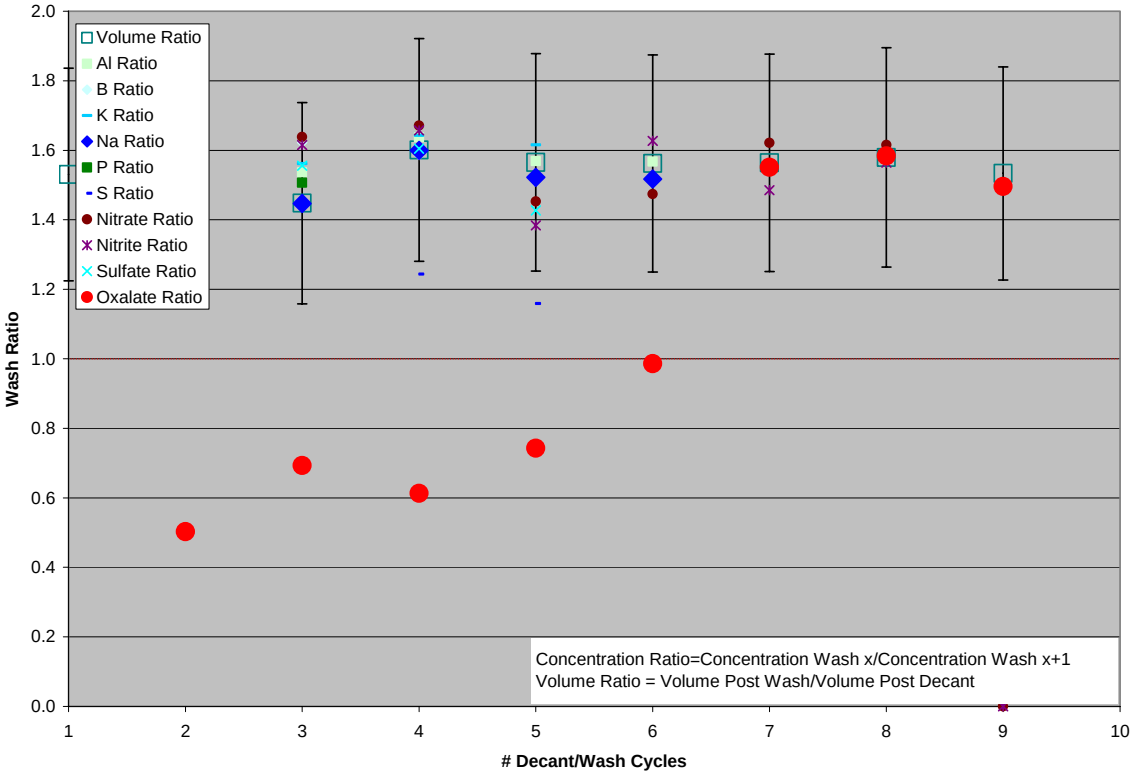

Figure 3-1 – Volume and Concentration Wash Ratios (R) throughout Washing

The overall wash ratio can also be calculated using the as-received and post-wash sample results. The results for soluble cations and anions are summarized in Table 3-3. As can be seen from these data, the wash ratio varies from 48.4 to 72.4. Using Al, B, Cr, K P and S to calculate an average wash ratio yields 51.8. This agrees well with the 51.3 ratio predicted by the wash and decant volumes.

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Table 3-3 - Determination of Overall Wash Ratio for Slurry

Anion or Element	As-Received mg/L^	Post Wash mg/L	Wash Ratio
Nitrite	22,800	355	65.2
Nitrate	42,900	592	72.4
Sulfate	2,340	<50	>46.8
Oxalate	1,170	3,295	0.355
Al	5,320	110	48.4
B	56.4	1.03	54.8
Cr	69.3	1.42	48.8
K	1060	17.6	60.2
Mo	23.0	0.389	59.1
Na	88,000	3510	25.0
P	136.7	2.54	53.8
S	903	16.9	53.4

^ Calculated by multiplying anion concentration (mg/kg) * 1.17 kg/L

Oxalate Removal

The Tank 7 as-received sample contained oxalate only as sodium oxalate. No iron oxalate was detected in the as-received or post-wash Tank 7 sample based on XRD analysis. It was expected that some iron oxalate would be present in the as-received sample as oxalic acid was added to dissolve sludge remaining in Tanks 5 and 6. Approximately 95% of the sodium oxalate was undissolved in the as-received sample since its concentration exceeded solubility (Table 3-4). The true insoluble solids concentration of the incoming sample was 3.704 wt % with 2.620 wt % undissolved sodium oxalate present in the filtered solids.

The TOC analysis is another potential measure of oxalate. The TOC concentration of sludge samples is generally low, so most of the TOC in the as-received sample was likely oxalate. If all of the TOC is oxalate, the as-received sample was 20,400 mg/kg oxalate, approximately 13% higher than the actual measurement. This is an independent measurement confirming that the oxalate concentration is likely approximately 18,100 mg/kg as measured.

Table 3-4 - As-Received Tank 7 Oxalate Balance

Analysis	Tank 7	Mass, g	% by mass
TOC if Oxalate	20,400 mg/kg	75.11	113
Total Oxalate	18,100 mg/kg	66.65	100
Supernate Oxalate	1,000 mg/kg	3.43	5
Undissolved Oxalate		63.22	95
Undissolved Sodium Oxalate	2.620 wt %	96.24	
Insoluble Solids (without oxalate)	3.704 wt %		

Because most of the sodium oxalate in the as-received sample is undissolved, the oxalate has a very different concentration profile than the soluble anions and cations which are all dropping in concentration from one wash to the next while the supernate oxalate concentration is rising (Figure 3-1). The sodium concentration decreases approximately exponentially as predicted by

the wash ratio while the oxalate concentration continues to climb until decant/wash cycle 7, after which it declines exponentially. Also graphed is the prediction by Gillam[13] based on measured oxalate solubility data developed by Kilpatrick.[18]

Note that oxalate is the only anion that did not follow the washing curve and the only potentially soluble anion that redissolved during washing. Sodium oxalate is the last soluble species to be dissolved during washing of sludge with inhibited water.

After washing was complete, the total oxalate concentration was 1,310 mg/kg and the supernate oxalate concentration was 3,340 mg/kg supernate basis (3,080 mg/kg slurry basis). The measured slurry oxalate number is 39.2% of the supernate oxalate (Table 3-5). The oxalate concentration in the slurry this is likely underreported. The slurry is undergoes an aggressive digestion step using HCl and HNO_3 to ensure any undissolved oxalate is dissolved. The digested sample is analyzed within 24 hours and protected from light to minimize decomposition of the oxalate. The oxalate likely decomposed before analysis leading to underreporting of oxalate in the slurry sample.

Table 3-5 - Post-Wash Tank 7 Oxalate Balance

Analysis	Tank 7 mg/kg	% by mass
Total Oxalate	1,310	100%
Supernate Oxalate	3,080	235%

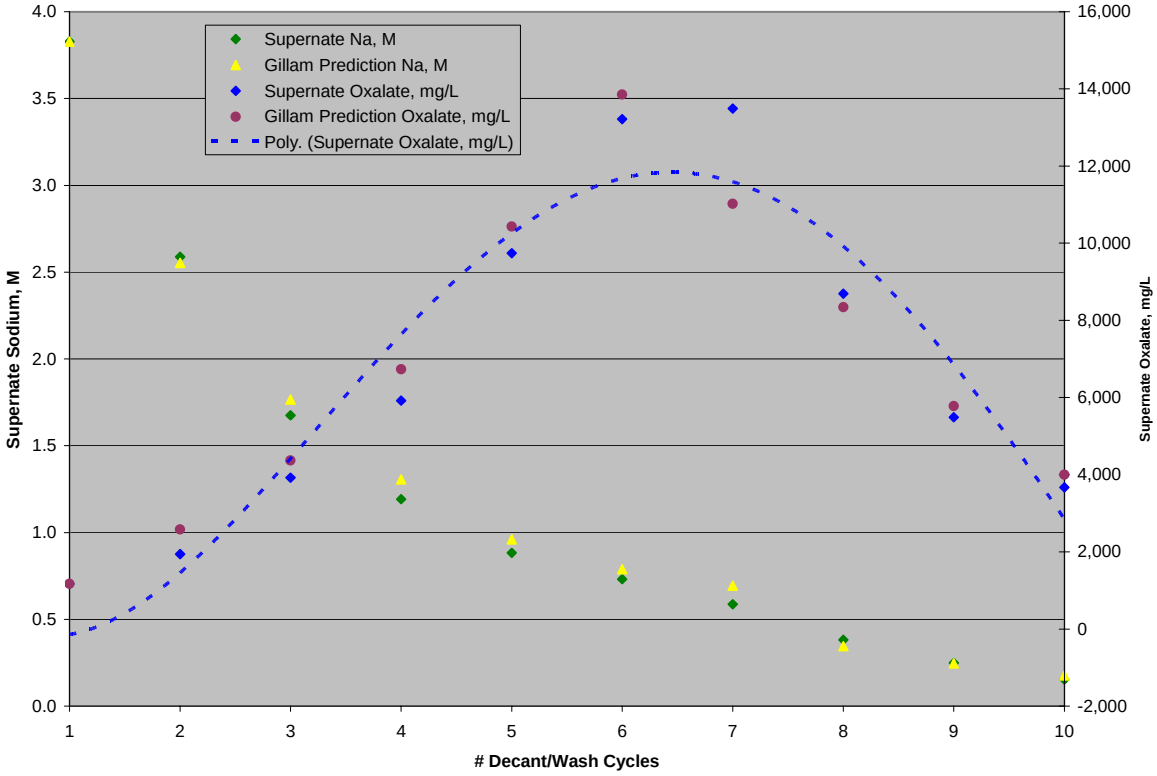

Figure 3-2 – Sodium, M and Oxalate, mg/L Profile throughout Washing

The % removal of the various anions can be calculated and compared to oxalate. Soluble oxalate is removed via washing at the same rate as the others anions. However, in each wash step, some of the undissolved sodium oxalate is redissolved and can be removed by decanting a portion of the supernate.

For example, as received there are 2650 mL of supernate. The first task in the decant/wash cycle is to decant 1394 mL of supernate from the slurry. The remaining supernate in the slurry is 1256 mL so 52.6% of the supernate has been removed. For any species that is totally soluble, 52.6% of that cation or anion has been removed. The volume ratio (Table 3-1) is used to calculate the original supernate volume remaining after each wash step. For example, the remaining supernate after wash A/decant B is 1256 mL/1.53 = 821 mL. The cumulative removal is (1-821/2650) *100% = 69.0%. Therefore column B of Table 3-6is the expected result for any anion or cation that is totally soluble.

For oxalate and sodium a mass balance was used to determine the % of sodium and oxalate that were removed. Only the soluble sodium oxalate is removed via washing at the same rate as the others anions. However, in each wash step, some of the undissolved sodium oxalate is redissolved and can be removed by decanting a portion of the supernate. Note that after 5 washes, 91.9% of the soluble species have been removed while only 40.3% of the oxalate has been removed. Column C and D of Table 3-6 are the calculated removal percentages for oxalate and sodium respectively.

Table 3-6 - Cumulative Percent Removal of Soluble Ions and Oxalate during Slurry Washing

Decant/Wash Cycle	% anions/cations removed	% oxalate removed	% sodium removed
B or 2	69.0%	10.0%	63.1%
C or 3	80.2%	16.5%	72.1%
D or 4	86.3%	28.1%	79.3%
E or 5	91.4%	40.3%	85.0%
F or 6	94.5%	54.9%	89.3%
G or 7	96.5%	69.6%	92.6%
H or 8	97.8%	80.2%	95.1%
I or 9	98.6%	85.8%	96.4%
J or 10	99.1%	89.2%	97.2%

Elemental Ratios

The as-received sample can be compared to the post-wash sample to determine whether any of the elements were removed during washing. If a cation is insoluble (such as nickel), the iron to nickel ratio will be the same in the as-received sample (6.10) as it is after the washing is complete (6.03). The iron to element ratios are summarized in column 3 for the as-received sample and column 7 for the post-wash sample in Table 3-7.

Also, the composition of these elements in the post-wash sample can be predicted by the following equation. The results are summarized in column 4 of Table 3-7

Predicted Composition = $Fe_{PW}*El_{AR}/Fe_{AR} = 1.99E+01/4.38E+00* El_{AR} = 4.54* El_{AR}$

where El_{AR} is the as-received composition of any element.

Knowing the predicted composition, a "% of predicted" can be calculated as a ratio of measured post-wash divided by predicted post-wash and are summarized in column 5 of Table 3-7. If the element is insoluble, the % prediction should be between 80-120%. Thus Ba, Ca, Cd, Cu, Fe, Hg, La, Li, Mg, Mn, Ni, Pb, Si, Sr, Ti, U and Zn were virtually insoluble throughout the washing. For elements such as Al, Cr, K, Na, P, and Zr, much of these elements were soluble. Had an element been completely soluble, then99.1% of that element would be removed during washing. For sodium and potassium, 97% of the K and 94% of the Na were removed during washing.

Table 3-7 – Iron to Elemental Ratios and Predicted Post-Wash Composition

	As-Received		Post-Wash			
Element	Measured Wt%	Fe:Element Ratio	Predicted, wt %	% prediction	Measured Wt%	Fe:Element Ratio
Al	2.58E+00	1.70	1.17E+01	37%	4.30E+00	4.63
Ba	2.79E-02	157	1.27E-01	103%	1.30E-01	153
Ca	2.04E-01	21.5	9.27E-01	107%	9.90E-01	20.1
Cd	1.76E-02	249	8.00E-02	104%	8.35E-02	238
Ce	3.47E-02	126	1.58E-01	245%	3.86E-01	51.6
Cr	3.87E-02	113	1.76E-01	39%	6.80E-02	293
Cu	1.21E-02	362	5.50E-02	107%	5.90E-02	337
Fe	4.38E+00	1.00	1.99E+01	100%	1.99E+01	1.00
Hg	4.92E-02	89.0	2.24E-01	80%	1.78E-01	110
K	4.59E-01	9.54	2.09E+00	3%	6.40E-02	311
La	1.41E-02	311	6.41E-02	115%	7.34E-02	271
Li	1.48E-02	296	6.72E-02	106%	7.15E-02	278
Mg	1.15E-01	38.1	5.22E-01	115%	6.03E-01	33.0
Mn	9.23E-01	4.75	4.19E+00	103%	4.30E+00	4.63
Na	3.18E+01	0.14	1.44E+02	6%	9.20E+00	2.16
Ni	7.18E-01	6.10	3.26E+00	101%	3.30E+00	6.03
P	7.46E-02	58.7	3.39E-01	38%	1.30E-01	153
Pb	9.43E-03	465	4.28E-02	91%	3.90E-02	510
Si	5.89E-01	7.44	2.68E+00	120%	3.20E+00	6.22
Sr	1.35E-02	324	6.13E-02	112%	6.90E-02	288
Ti	7.35E-03	596	3.34E-02	89%	2.96E-02	672
U	2.04E+00	2.15	9.27E+00	112%	1.04E+01	1.91
Zn	1.65E-02	265	7.50E-02	109%	8.20E-02	243
Zr	6.54E-02	67.0	2.97E-01	38%	1.12E-01	178

Rheology and Particle Size Results

The as-received and post-wash Tank 7 slurry is very thin rheologically, settles very quickly, and is nearly Newtonian (very small measured yield stress). The Tank 7 slurry could easily be washed everyday as the settling was virtually complete by the next morning after decanting, adding inhibited water, mixing, and sampling the day before.

The particle size data will be added when the analyses are complete.

Optimal washing strategy

If significant oxalate removal is needed for SB7, the oxalate would be best removed prior to transferring the sludge to Tank 51. In order to remove a significant portion of the oxalate, the sludge must be washed thoroughly and the other soluble species will be very low.

The appropriate oxalate wash endpoint depends on several factors. First, some oxalate can be handled in the DWPF Chemical Processing Cell (CPC). Testing in SB3 was completed with oxalate concentrations as high as 40,000 mg/kg. Also, approximately 10-50% of the oxalate is destroyed in DWPF processing. If oxalate removal is needed in preparing SB7 sludge, the oxalate may be removed most efficiently in Tank 7 (or Tank 4). The most flexible method for preparation of sludge for SB7 would be to wash out oxalate in Tank 7 and do minimal washing in Tank 51. This is because the oxalate is the last to be removed in any washing scenario. Several wash scenarios are discussed below:

- If Tank 7 is washed prior to transfer to Tank 51, the removal of oxalate will require extensive washing to lower the oxalate concentration. In this case, the sodium, potassium and anion concentrations will all be very low. If the oxalate is washed thoroughly in Tank 7, the washed sludge can be combined with other tanks that are high in sodium concentration in Tank 51.
- If Tank 7 is transferred to and washed in Tank 51, the removal of oxalate will require extensive washing to significantly lower the oxalate concentration. If the sodium is approximately 1 M (typical washing endpoint), less than half of the oxalate will be removed.

4.0 Conclusions

A 3-L PUREX sludge slurry sample from Tank 7 was characterized and then processed through a series of inhibited water washes to remove oxalate and other soluble ions. Current plans use Tank 7 as one of the feed sources for Sludge Batch 7 (SB7). Tank 7 is high in oxalate due to the oxalic acid cleaning of Tanks 5 and 6 and subsequent transfer to Tank 7.

Ten decant and nine wash cycles were performed over a 47 day period at ambient temperature. Initially, seven decants and seven washes were completed based on preliminary estimates of the number of wash cycles required to remove the oxalate in the sludge. After reviewing the composition data, SRNL recommended the completion of 2 or 3 more decant/wash cycles to ensure all of the sodium oxalate had redissolved. In the first 7 washes, the slurry oxalate concentration was 12,300 mg/kg (69.6% oxalate removal compared to 96.1% removal of the other soluble ions). After all ten decants were complete, the slurry oxalate concentration was 3,080 mg/kg (89.2% oxalate removal compared to 99.0% of the other soluble ions. The rate of dissolution of oxalate increased significantly with subsequent washes until all of the sodium oxalate had been redissolved after seven decant/wash cycles. The measured oxalate concentrations agreed very well with Jeff Gillam's predictions for washing of the Tank 7 sample.

Highlights of the analysis and washing of the Tank 7 sample include:

- Sodium oxalate was detected in the as-received filtered solids. 95% of the oxalate was insoluble (undissolved) in as-received slurry.
- No sodium oxalate was detected in the post-wash filtered solids.
- Sodium oxalate is the last soluble species that redissolves during washing with inhibited water. In order to significantly reduce the sodium oxalate concentration, the sludge must be highly washed, leaving the other soluble anions and cations (including sodium) very low in concentration.

- The post-wash slurry had <2% of the soluble anions and cations remaining, with the exception that for sodium and oxalate
- The yield stress of as-received and post-wash slurry was <1 Pa.

The settling rate of slurry was very fast allowing the completion of decant/wash cycles each day.

5.0 Recommendations

The recommended strategy for developing the oxalate target for sludge preparation includes the following steps:

1. CPC simulant testing to determine the percent oxalate destruction and acid mix needed to produce a predicted redox of approximately 0.2 $Fe^{+2}/\Sigma Fe$ in a SME product while meeting all DWPF processing constraints.
2. Perform a DWPF melter flammability assessment to ensure that the additional carbon in the oxalate together with other carbon sources will not lead to a flammability issue.
3. Perform a DWPF glass paper assessment to ensure the glass produced will meet all DWPF glass limits due to the sodium concentration in the sludge batch.

The testing would need to be repeated if a significant CPC processing change, such as an alternative reductant to formic acid, is implemented.

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The sample was handled capably by the SRNL shielded cells operators. The task was led by Mona Galloway but was supported by almost all of the shielded cells technicians, especially Monica Jenkins and Jane Howard. The Tank 7 sample was washed and decanted daily, a Herculean task in the shielded cells which included daily analyses of solids, density, pH and sample preparation for delivery to AD. Steve Beard and Babb Attaway managed the tasks capably.

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Holly Hall capably handled the disposition of residue generated during preparation and as a result of analyzing the samples.

Jeff Gillam predicted the composition of the SB7 batch, including the redissolution of oxalate. His spreadsheet was modified to simulate the actual cells washing and did an excellent job of predicting the redissolution of sodium oxalate during washing of the Tank 7 sample in the cells.

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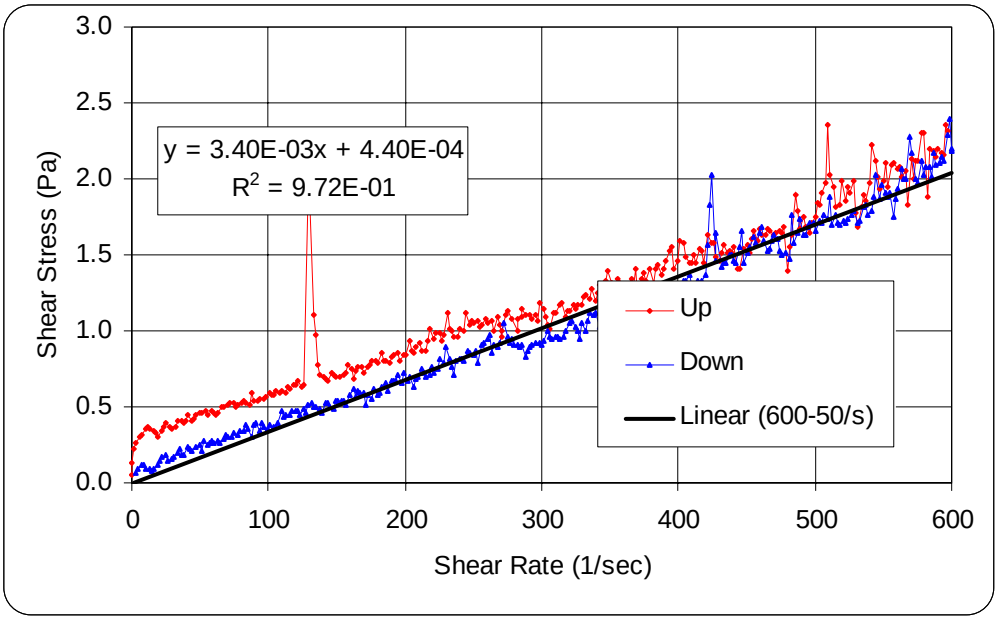
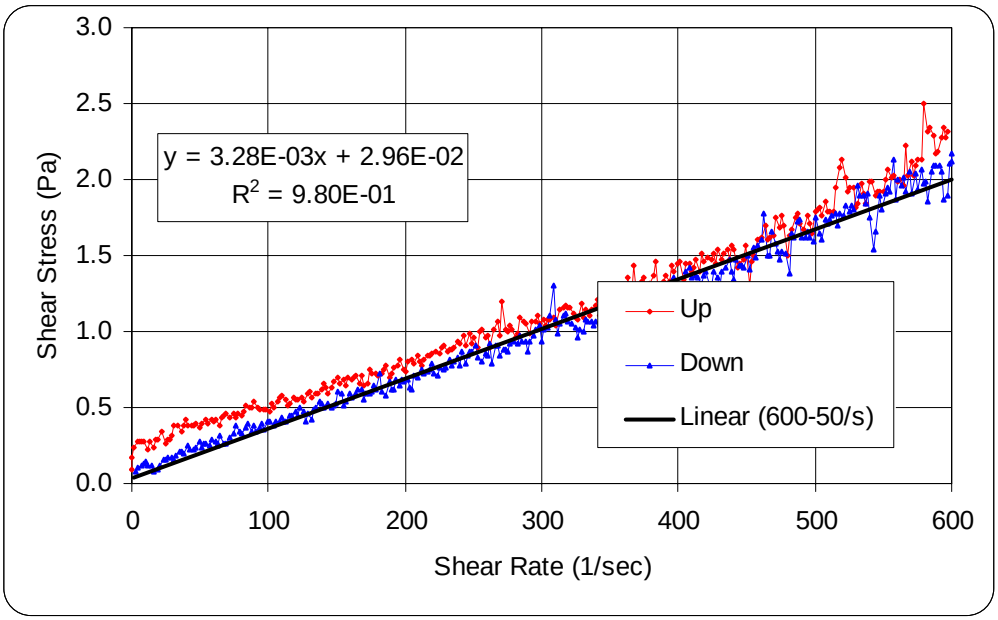
Appendix A – Tank 7 Post-wash Rheology Results





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