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Washing Study with SRS Tank 26 Samples FTF-26-19-12 and -13

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EXECUTIVE SUMMARY

A recent analysis of Tank 26, one of the feed tanks for the Defense Waste Processing Facility (DWPF) Sludge Batch 10 (SB10), determined a higher than anticipated sulfur concentration in the supernatant and a significant amount of insoluble sulfur, which could negatively impact the DWPF glass waste form. Savannah River Remediation Engineering (SRR-E) requested that the Savannah River National Laboratory (SRNL) perform a washing study with Tank 26 material to determine amount of sulfur removed during washing tests.

SRNL decanted supernate from a sample of Tank 26 until it was at 12 wt% insoluble solids. Subsequently, SRNL performed washing experiments from the 8 M sodium initial concentration to targeted endpoints of 4 M, 2 M and 1 M sodium concentration (assuming no sodium dissolution). Results show that over 80% of the sulfur was removed and nearly all the sulfur was in the aqueous phase at the end of washing, demonstrating effective removal of sulfur during washing. Additional washing is likely to decrease the sulfur concentration further since most of the sulfur was in the aqueous phase.

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LIST OF ABBREVIATIONS

AD	Analytical Development
AR	aqua regia
DMA	direct mercury analysis
HDPE	high density polyethylene
IC	ion chromatography
ICP-ES	inductively coupled plasma-emission spectroscopy
n	number of replicates
NA	not applicable
PF	peroxide fusion
RSD	relative standard deviation
SB	Sludge Batch
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TIC	total inorganic carbon
TOC	total organic carbon
TTQAP	task technical and quality assurance plan
TTR	technical task request
WD	water dilution

1.0 Introduction

A recent analysis of Tank 26, one of the feed tanks for the Defense Waste Processing Facility (DWPF) Sludge Batch 10 (SB10), determined a higher than anticipated sulfur concentration in the supernatant and a significant amount of insoluble sulfur, which has been speculated to be burkeite ($Na_6(CO_3)(SO_4)_2$)[1], High amounts of sulfur, if not significantly reduced, could negatively impact the DWPF glass waste form. Some sulfur will be removed during washing, but without knowing the form of sulfur, projecting sulfur removal has much uncertainty. In addition, a recent analysis of Tank 51 (the SB10 preparation tank) showed sulfate concentrations of concern.[2] Therefore, Savannah River Remediation Engineering (SRR-E) requested that the Savannah River National Laboratory (SRNL) perform a washing study with Tank 26 material.[3]

2.0 Experimental Procedure

A well-mixed sample of Tank 26 slurry was placed into a 100 mL graduated cylinder affixed with a cap to allow the cylinder to be inverted to mix the contents. The composition has previously been documented.[1] The slurry was allowed to settle overnight and supernatant was decanted to obtain a target slurry of 12 wt% insoluble solids (designated as Decant 1). Wash water was added, the contents of the cylinder were mixed by agitating/inverting the cylinder, and the slurry was again allowed to settle. Supernatant was again decanted to obtain a target of 12 wt% insoluble solids. This process was repeated two more times. Deionized water was used for all washes. Starting supernatant Na molarity was 8.00 M. The target was endpoint was 1 M. The intent in each wash was to double the supernatant volume (i.e., the target Na concentrations during each wash were 4 M, 2 M, and finally 1 M). Calculations used an assumption that the initial insoluble solids were inert to the washing process. Targeted decant and wash amounts along with actual amounts are presented in Table 3-1

Each decant was then submitted to Analytical Development (SRNL-AD) in duplicate for inductively coupled plasma-emission spectroscopy (ICP-ES) (elements) and ion chromatography for anions (IC-Anions) (anions). The density of each decant was also measured in duplicate. The final slurry was digested in triplicate by aqua regia and submitted to SRNL-AD for ICP-ES (elements) and IC-Anions (sulfate). The main purpose of the aqua regia digestions was to determine sulfur and sulfate remaining in the slurry and to determine fraction soluble. Weight percent solids (total and insoluble) were also determined on the final slurry.

2.1 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 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. This review meets the acceptable criteria to comply with the TTR classification for this work as Production Support.[3, 4] Data are recorded in the electronic laboratory notebook system as notebook/experiment number L3293-00022-35.

3.0 Results and Discussion

3.1 Washing

Target and measured wash and decant amounts are presented in Table 3-1. For Decant 1, sludge was allowed to settle overnight. During the decant, as the sludge level was approached, sludge solids were disturbed, and the decant was stopped before the target, with the intent of decanting more in Decant 2. For Decants 2 and 3, sludge was allowed to settle overnight. This was more than enough time to adequately allow separation between the sludge and decant level. For Decant 4, the slurry settled for four days due to the Labor Day holiday weekend. Deionized water was used for all washes. As can be seen, actual decant and addition amounts were close to targeted values

Table 3-1. Washing Study Target and Actual Decant and Addition Amounts

	Target (g)	Actual (g)
Initial Slurry Mass (As-received T26 slurry)	83.343	80.899
Decant 1	-23.614	-18.681
Addition 1	39.225	39.347
Decant 2	-39.225	-44.953
Addition 2	44.925	44.734
Decant 3	-44.925	-43.466
Addition 3	48.444	48.270
Decant 4	-48.444	-49.016
Final Slurry Mass	59.729	57.134

3.2 Characterization Results

Presented in Table 3-2 are key analytical results from the soluble wash decants. Data for Decant 1 (initial slurry supernatant) were taken from the Tank 26 characterization report.[1] Concentrations of anions such as nitrite, and nitrate dropped by factors of two after each wash showing that washes were approximately double slurry supernatant volumes. Aluminum concentrations also dropped by factors of two, suggesting no aluminum was precipitating from the slurry as hydroxide concentration (not measured) dropped during washing. Oxalate concentration increased as sodium concentration decreased. This is expected, since oxalate solubility is limited by sodium concentration.[5]

Sodium concentration decreased by factors slightly less than two, resulting in a final concentration of 1.24 M, 24% higher than the target of 1 M. This is likely due to dissolution of burkeite and sodium oxalate. These compounds were not explicitly measured in the slurry, but they have been documented in Tank Farm sludges.[5, 6] The ratio of sulfur and sulfate between decants 1 and 2 were barely over 1:1, suggesting dissolving of sulfur-bearing compounds from the insoluble solids. Ratios between subsequent washes were slightly less than 2.0:1 suggesting small amounts of sulfur-bearing compounds continued to dissolve during washing.

Table 3-2. Washing Study Decant (Supernatant) Results

	Decant 1	Decant 2	Decant 3	Decant 4
Density (g/mL)	1.34	1.19	1.10	1.06
Al (M)	3.03E-01	1.60E-01	8.01E-02	4.06E-02
K (M)	4.10E-02	2.03E-02	1.09E-02	5.24E-03
Na (M)	8.00E+00	4.44E+00	2.24E+00	1.24E+00
S (M)	3.04E-01	2.86E-01	1.50E-01	7.59E-02
Cl^- (M)	<2E-02	4.09E-03	2.04E-03	9.77E-04
NO_2^- (M)	8.09E-01	4.25E-01	2.09E-01	1.10E-01
NO_3^- (M)	1.99E+00	1.04E+00	5.33E-01	2.77E-01
SO_4^{2-} (M)	2.67E-01	2.32E-01	1.26E-01	7.20E-02
$C_2O_4^{2-}$ (M)	<7E-03	1.30E-02	2.92E-02	4.33E-02

Table 3-3 lists the washed slurry densities and weight percent solids along with the initial slurry data. Data for the initial slurry were taken from the Tank 26 characterization report.[1] The washed slurry targeted wt% insoluble solids was 12%, double the measured amount. Some of this difference may be related to analytical uncertainty in the initial and final total solids measurements. However, the difference is good indication that some insoluble solids in the initial slurry were sulfur bearing compounds as evidenced by comparing sulfur and sulfate results between Decants 1 and 2. If sulfur-bearing compounds had not dissolved from the initial slurry during the first wash, the sulfur and sulfate concentrations in the Decant 2 would have been roughly 50% of that in Decant 1, as was seen for most of the anions. The fact that sulfur in Decant 2 is 94% of the sulfur concentration in Decant 1 (87% for sulfate) shows that sulfur-bearing compounds have dissolved during the first wash.

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

Property	**Initial Slurry**	**Washed Slurry**
Slurry Density (g/mL)	1.39	1.10
Supernate Density (g/mL)	1.34	1.06
Wt% Total Solids (Slurry Basis)	40.8	12.9
Wt% Dissolved Solids (Supernate Basis)	35.2	7.5
Wt% Insoluble Solids (Slurry Basis)	8.6	5.9
Wt% Soluble Solids (Slurry Basis)	32.2	7.0

Elemental analysis of the initial and washed slurries is presented in Table 3-4. For the washed slurry, an aqua regia digestion was performed and digestate was submitted to ICP-ES and IC Anions (for sulfate). Therefore, Hg is not reported (not submitted for Hg analysis) and Si is not reported (aqua regia does not completely dissolve Si) consistent with the TTQAP. Data for the initial slurry were taken from the Tank 26 characterization report.[1]

As can be seen in the table, and as expected, concentration of partially soluble and soluble elements such as Al, K, Na, and S, decreased, while concentration of insoluble elements such as Fe, Mn, Mg, and U, increased.

In addition to submitting the digestates for ICP-ES analyses, they were submitted for sulfate by IC Anions. Sulfur by IC anions yielded a result that was approximately 20% higher than sulfur from ICP-ES. For all analyses of the decants, sulfate was reported to be less than sulfur. This difference in the digested slurry samples may have been caused by the high chloride and high nitrate concentrations in the acidic matrix. Per discussion with the IC Anion chemist, the method has never been used to analyze slurry digestions by IC anions. The chemist also noted that sulfate was detected in the blanks. Therefore, these results are provided for confirmation only.

Table 3-4. Elemental Composition of Total Dried Solids*

Element	Initial Slurry (wt% of Total Solids)	Washed Slurry (wt% of Total Solids
Ag	< 5E-03	<3E-04
Al	1.52E+00	1.26E+00
B	1.40E-02	<9E-03
Ba	5.74E-03	2.83E-02
Be	< 5E-03	<1E-05
Ca	3.43E-01	1.61E+00
Cd	< 8E-03	6.67E-03
Ce	4.72E-03	<2E-03
Co	< 5E-03	6.11E-03
Cr	2.80E-01	1.05E+00
Cu	< 5E-03	<9E-05
Fe	2.85E+00	1.36E+01
Gd	< 5E-03	<3E-02
K	2.36E-01	1.62E-01
La	< 5E-03	<2E-04
Li	< 5E-03	1.36E-02
Mg	1.21E-01	5.76E-01
Mn	1.60E-01	7.41E-01
Mo	< 1E-02	<7E-03
Na	3.35E+01	2.23E+01
Ni	4.75E-02	2.21E-01
P	5.20E-02	<5E-02
Pb	< 5E-03	<1E-02
S	2.84E+00	1.70E+00
S via IC Anions	NM	2.09E+00
Sb	< 5E-03	<2E-02
Sn	< 5E-03	<6E-03
Sr	< 5E-03	6.93E-03
Th	2.42E-04	<3E-02
Ti	< 5E-03	8.86E-03
U	2.11E+00	9.37E+00
V	< 5E-03	<8E-05
Zn	< 8E-03	2.08E-02
Zr	< 5E-03	5.78E-03

3.3 Evaluation of Sulfur Removal

Sulfur and sulfate concentrations in the supernate decants are plotted in Figure 3-1. The red and green circles represent measured sulfur and sulfate results, respectively. The solid blue dot is the concentration of sulfur in the supernatant if all the sulfur (based on the initial sample analysis) were soluble. The solid blue line represents the expected sulfur concentration for each decant if all the sulfur were soluble. The dashed blue line represents the expected sulfur concentration if no sulfur dissolved from the insoluble solids. The solid blue line closely follows the actual washing results demonstrating that virtually all the insoluble sulfur dissolved during the first wash.

As can be seen in Table 3-2, sulfate results are consistently lower than sulfur results. This is not unexpected and is often observed with SRS Tank Farm samples. For example, in SRNL washing of

Sludge Batch 6, the sulfate to sulfur ratio ranged from 0.78:1 to 1.0:1,[7] as compared to this study - 0.81:1 to 0.95:1. Both sulfur and sulfate results show sulfur is being removed from the slurry.

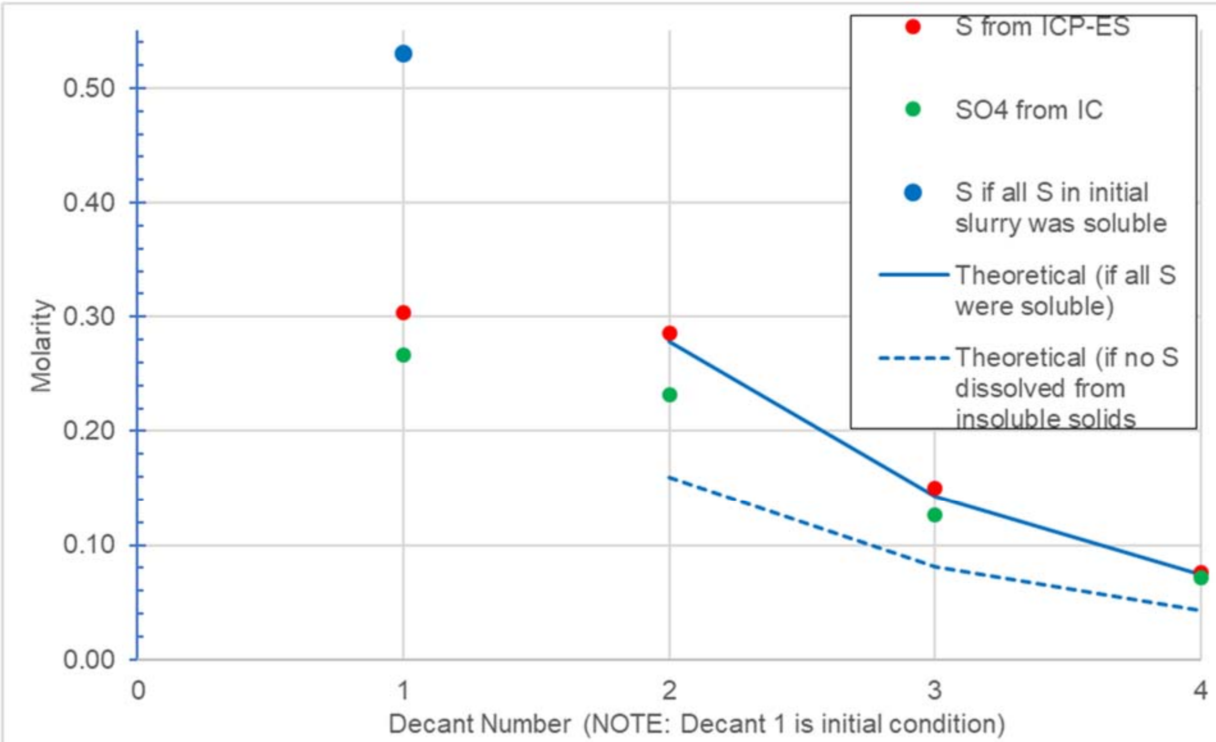

Figure 3-1. Graphical Presentation of Sulfur Removal

A sulfur mass balance is shown in Table 3-5. Because sulfur data on the initial slurry is available, and there is much uncertainty with the total sulfate in the final slurry (see last paragraph of Section 3.2), the mass balance is based solely on sulfur results. The initial sulfur amounts are based on the initial Tank 26 characterization.[1] The sulfur being removed is calculated from the mass of the decant, density of the decant, and the sulfur concentration. The sulfur in the Washed Slurry (Mass Balance) row is calculated by summing the initial total sulfur and the sulfur from Decants 1-4. The last row, Washed Slurry (Analysis), shows total sulfur calculated from the final washed slurry mass and analysis of the washed slurry provided in this report. Considering the small amount of washed material and the uncertainties of the analytical methods, there is good agreement between the calculated sulfur remaining after decants versus the sulfur from the analysis of the final slurry (0.152 g vs. 0.126 g). Overall, the washing process removed 84 to 87% of the initial slurry total sulfur based on the mass balance.

Table 3-5. Sulfur Mass Balance

	Total S (g)
Initial Slurry	0.937
Decant 1	-0.136
Decant 2	-0.346
Decant 3	-0.191
Decant 4	-0.113
Washed Slurry (Mass Balance)	0.152
Washed Slurry (Analysis)	0.126

Table 3-6 shows the total and soluble sulfur in the slurry before and after washing based on analyses. Total sulfur is taken from Table 3-5 - "Initial Slurry" and "Washed Slurry (Analysis)". Soluble sulfur was calculated from the slurry mass, wt% insoluble solids, and the measured sulfur concentration in the respective supernatant (Decant 4 in the washed slurry). Following is the methodology for calculating soluble sulfur and illustration using the final washed slurry data.

$$Soluble\ S(g) = slurry\ mass \times \frac{(100 - wt\%_{is})}{100} \times S(M) \times MW_s \times \frac{1}{density}$$

Using data from Tables 3-1, 3-2, and 3.3, the amount of soluble sulfur in the washed slurry is:

$$Soluble\ S(g) = 57.134\ g\ slurry \times \frac{(100 - 5.9)g\ sup}{100\ g\ slurry} \times \frac{0.0759\ mol\ S}{L\ sup} \times \frac{32.066\ g\ S}{mol\ S} \times \frac{mL}{1.06\ g\ sup} \times \frac{1\ L}{1000\ mL} = 0.123\ g\ soluble\ S$$

As can be seen in the table, based on analysis of the washed slurry, virtually all the sulfur is soluble following washing with water. Since the sulfur at the conclusion of this test appears to be soluble, additional washing would be expected to continue to remove sulfur.

Table 3-6. Soluble Sulfur Before and After Washing

	Total S (g)	Soluble S (g)	% Soluble
Initial Slurry	0.937	0.538	57%
Washed Slurry (Analysis)	0.126	0.123	98%

4.0 Conclusions

The following conclusions can be drawn from this study:

- Most of the insoluble sulfur compounds in Tank 26 dissolve and can be removed by traditional washing.
- At the end of washing, nearly all the sulfur was soluble. It is expected that additional washing would remove additional sulfur.

5.0 References

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