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WASHING DEMONSTRATION USING NONRADIOACTIVE SIMULATED TANK 7 SLUDGE-SLURRY

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SUMMARY

Tank 7 will be processed as part of the next sludge batch (Sludge Batch 3*) in the Defense Waste Processing Facility (DWPF). Prior to processing in DWPF, a sludge-slurry must be washed to adjust the sodium content and weight percent total solids†. In typical sludge slurries, sodium is primarily soluble and easily adjusted by diluting and decanting the supernate (i.e., washing). For Tank 7, sodium adjustment is complicated by the presence of sodium oxalate which is partially soluble in aqueous solutions. To better understand how sodium oxalate would affect sludge washing, nonradioactive simulated Tank 7 sludge-slurry was prepared and washed. Soluble species (e.g., nitrate) were easily removed as expected. Sodium oxalate behaved like a partially soluble compound. As sodium concentration in wash water decreased, oxalate concentration increased until the equilibrium concentrations for sodium and oxalate were reached. Thus, sludge-slurry washing, even in the presence of sodium oxalate, is predictable.

INTRODUCTION

Tank 7 will be processed as part of Sludge Batch 3*) in the DWPF. Prior to processing in DWPF, a sludge-slurry must be washed to adjust the sodium content and weight percent total solids†. In typical sludge-slurries, sodium is primarily soluble and easily adjusted by diluting and decanting the supernate (i.e., washing). For Tank 7, sodium adjustment is complicated by the presence of sodium oxalate which is partially soluble in aqueous solutions. The presence of oxalate may also complicate glass processing (melter offgas, glass redox, etc.).

At the time of this work, the sodium and oxalate content in Sludge Batch 3 for DWPF processing were not defined. Therefore, the purpose of this work was to better understand how sodium, in the presence of oxalate, is washed from sludge slurry, and to provide input for washing the waste qualification sample in the Savannah River Technology Center (SRTC) Shielded Cells. To accomplish this purpose, two tests were conducted. The first was a small scale centrifuge tube test. Sludge slurry was washed, allowed to sit overnight, and then centrifuged to facilitate decanting. The second test was on a slightly larger scale. Also, instead of centrifuging, sludge was allowed to gravity settle prior to each decant. The purpose of this larger scale test was to identify any settling issues, especially as sodium supernate concentrations dropped below 0.5 M.

* Sludge Batch 3 for the Defense Waste Processing Facility will consist of the Sludge Batch 1B heel in Tank 51, Am/Cm and Pu/Gd slurries transferred from F and H-Areas into Tank 51, and the sludge slurry in Tank 7. However, the focus of this work is Tank 7 only; the other components of Sludge Batch 3 were not evaluated or considered.

† Although weight percent total solids adjustment is an important aspect of washing, the scope of this work was sodium and oxalate adjustment/removal.

EXPERIMENTAL

Sludge-Slurry Preparation

Nonradioactive simulated Tank 7 sludge-slurry was prepared from washed Tank 8 nonradioactive simulant used for Sludge Receipt and Adjustment Tank (SRAT) experiments[1]. The washed Tank 8 simulant was dewashed, and sodium oxalate, sand, and coal were added. See Appendix A for Tank 8 simulant composition and chemicals added to dewash the simulant.

Washing the Tank 7 Dewashed Simulant

Two separate sludge washing experiments were completed: a small scale (5 g of sludge-slurry) experiment utilizing a centrifuge prior to each decant, and a larger scale (100 mL of sludge-slurry) experiment where the sludge was allowed to gravity settle. All tests were conducted at room temperature.

For the centrifuge tube washes, 5 g of sludge slurry were placed into a 10 mL glass centrifuge tube. The sludge-slurry was washed ten times. Each wash consisted of:

- an addition of 5 g of inhibited water[‡]
- mixing well
- allowing the mixture to settle overnight
- centrifuging to make decanting easier
- decanting approximately 5 g of supernate with a slurry pipette.

The decanted supernates were submitted to SRTC Analytical Development Section (ADS) and to the SRTC Mobile Lab for cation analysis by Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES) and anion analysis by Ion Chromatography (IC).

For the larger scale washes, 100 mL of sludge slurry were placed into a 250 mL polycarbonate bottle. The sludge-slurry was washed ten times. Each wash consisted of

- an addition of 100 mL of inhibited water‡
- mixing well
- allowing the sludge to settle for at least two days to allow decanting of 100 mL supernate
- decanting approximately 100 mL of supernate with a slurry pipette.

The densities of the decanted supernates were measured using a 2 mL (nominal) Gay-Lussac bottle. The supernates were then submitted to SRTC-ADS for cation analysis by ICP-ES and anion analysis by IC.

‡ The inhibited water had a sodium concentration of 0.03 M, nitrite concentration of 0.015 M, and hydroxide concentration of 0.015 M.

RESULTS

Table 1 and Table 2 summarize the sludge-slurry washing results. Each table shows the concentrations of the major components of each wash water (decant). A more detailed table showing additional components and quantities of inhibited water added and supernate decanted for the gravity settling tests is given in Appendix B.

Table 1. Centrifuge Tube Wash Results

	Tube 12				Tube 14			
Wash No.	Sodium (M)	Nitrite (M)	Nitrate (M)	Oxalate (M)	Sodium (M)	Nitrite (M)	Nitrate (M)	Oxalate (M)
1	1.85	0.77	0.086	0.043	1.90	0.79	0.086	0.037
2	0.98	0.28	0.030	0.101	0.83	0.26	0.030	0.095
3	0.68	0.13	0.011	0.16	0.61	0.13	0.013	0.17
4	0.58	0.06	0.0044	0.21	0.51	0.06	0.0054	0.21
5	0.56	0.033	0.0019	0.22	0.48	0.036	0.0023	0.22
6	0.58	0.022	<0.0016	0.20	0.55	0.025	<0.0016	0.20
7	0.54	0.022	<0.0016	0.20	0.52	0.022	<0.0016	0.20
8	0.52	0.018	<0.0016	0.21	0.53	0.019	<0.0016	0.21
9	0.28	0.017	<0.0016	0.12	0.40	0.019	<0.0016	0.14
10	0.13	0.018	<0.0016	0.06	0.15	0.017	<0.0016	0.06

Table 2. Gravity Settling Wash Results

	Vessel A				Vessel B			
Wash No.	Sodium (M)	Nitrite (M)	Nitrate (M)	Oxalate (M)	Sodium (M)	Nitrite (M)	Nitrate (M)	Oxalate (M)
0 [a]	4.21	1.75	0.19	0.0064	4.21	1.75	0.19	0.0064
1	1.94	0.79	0.083	0.035	1.89	0.79	0.084	0.037
2	1.12	0.38	0.043	0.074	1.09	0.37	0.041	0.072
3	0.72	0.18	0.021	0.13	0.73	0.18	0.021	0.13
4	0.62	0.10	0.0091	0.18	0.61	0.10	0.0096	0.18
5	0.54	0.054	0.0042	0.21	0.58	0.056	0.0044	0.20
6	0.53	0.033	0.0018	0.23	0.55	0.037	0.0021	0.24
7	0.51	0.023	<0.0016	0.17	0.52	0.024	<0.0016	0.25
8	0.50	0.018	<0.0016	0.25	0.53	0.019	<0.0016	0.25
9	0.39	0.016	<0.0016	0.19	0.43	0.011	<0.0016	0.19
10	0.24	0.015	<0.0016	0.12	0.26	0.015	<0.0016	0.12

[a] Supernate composition prior to washing

DISCUSSION

Sludge-slurry washing is basically a diluting and dissolving process. Species soluble in the sludge-slurry supernate, such as nitrate, are diluted with wash water and removed by decanting the supernate. Partially soluble compounds, such as sodium oxalate, must dissolve into the wash water before removal. Dissolving of these compounds is limited by compound solubility. This is shown graphically in Figure 1 and Figure 2 as semi-log plots. For nitrate, the concentrations decrease linearly with each successive wash indicating that they follow the general serial dilution formula:

$$C_x = \frac{\mathrm{C_i}}{\mathrm{D}^x}$$

or, in log form,

$$\log C_x = -x \cdot \log \mathrm{D} + \log \mathrm{C_i}$$

where

x = number of serial dilutions
D = dilution factor
C_i = initial concentration of soluble component
C_x = concentration of soluble component after x serial dilutions.

A curve fit of the nitrate results from the gravity settled tests yields:

$$C_x = \frac{0.19}{2.1^x}, \ \mathrm{R}^2 = 0.999$$

where 0.19 is the nitrate molarity prior to washing.

Nitrite initially follows the serial dilution formula. However, its concentration eventually approaches 0.015 M, as this is the nitrite concentration in the wash water. This is shown in Table 3. The serial dilution formula predicts fairly well the nitrite concentration for the first 4 washes.

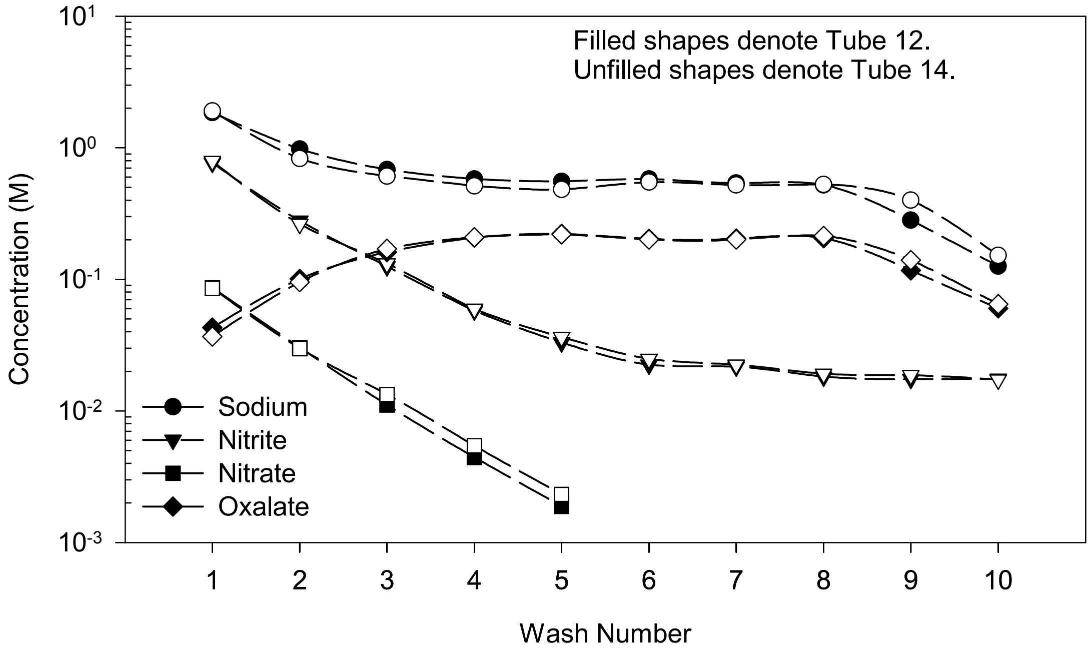

Figure 1. Supernate Concentration as a Function of Wash Number for Washing of Simulated Tank 7 Sludge-Slurry Utilizing a Centrifuge to Separate Sludge From Supernate

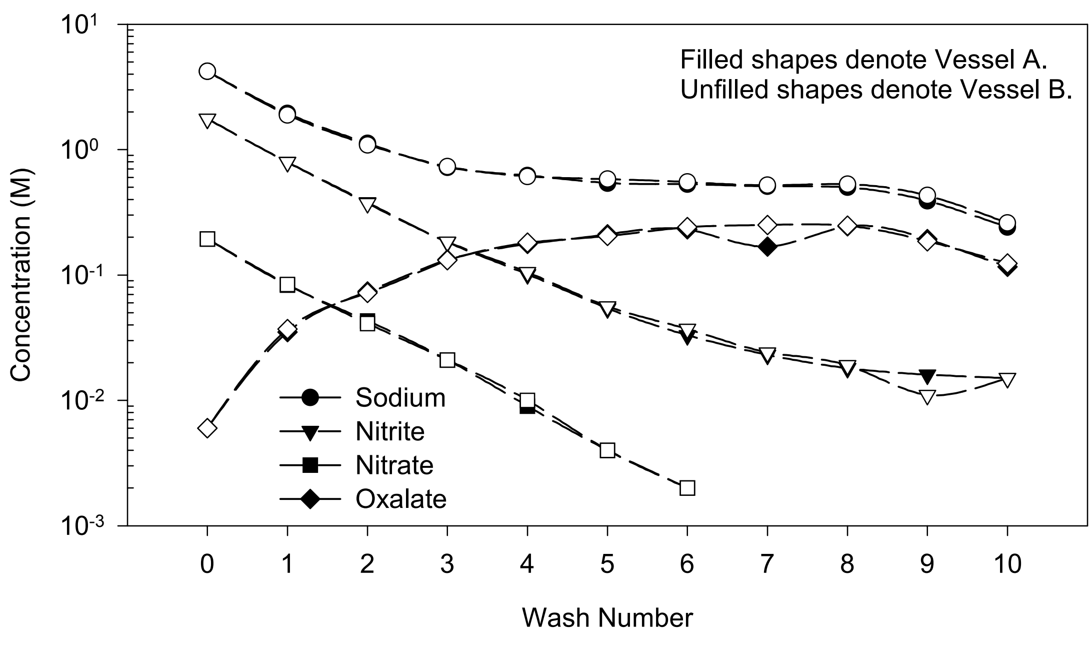

Figure 2. Supernate Concentration as a Function of Wash Number for Washing of Simulated Tank 7 Sludge-Slurry Allowing the Sludge to Gravity Settle

Table 3. Comaparison of Measured and Predicted Nitrite concentraiton in the Gravity Settling Tests Using the Serial Dilution Equation

Wash No.	Predicted Nitrite Concentration (M)	Vessel A Measured Nitrite Concentration (M)	Vessel B Measured Nitrite Concentration (M)
0	1.75	1.75	1.75
1	0.83	0.79	0.79
2	0.40	0.38	0.37
3	0.19	0.18	0.18
4	0.09	0.10	0.10
5	0.043	0.054	0.056
6	0.020	0.033	0.037
7	0.010	0.023	0.024
8	0.0046	0.018	0.019
9	0.0022	0.016	0.011
10	0.0010	0.015	0.015

The sodium concentration initially decreases, while oxalate concentration initially increases during washing. The concentrations then stabilize at approximately 0.5 M sodium and 0.25 M oxalate for several washes. These values are the published equilibrium concentrations for sodium oxalate in water at 20°C[2]. During these washes, sodium oxalate is dissolving up to its solubility limit. This shows that, in terms of equilibrium, sodium oxalate behaves as one would expect - increased sodium solution concentration decreases sodium oxalate solubility. An estimate of oxalate concentration can be made, given the sodium concentration using a calculated solubility product. The chemical equilibrium equation is:

$$\mathrm{Na_2C_2O_4(s) \leftrightarrow 2Na^+ + C_2O_4{}^{2-}},$$

with

$$K_{sp} = [Na^+]^2 \cdot [C_2O_4{}^{2-}].$$

Using the published equilibrium concentrations of 0.5 M sodium and 0.25 M oxalate, the calculated solubility product is 0.0625. Given the measured sodium content and the calculated solubility product, the oxalate concentration was measured and compared to the analytical results. This comparison is shown in Table 4.

An examination of Table 4 shows that the oxalate prediction method underestimates oxalate concentration in the first few washes, and overestimates oxalate concentration in the last few washes. The primary reason for the underestimation is the solubility product used for these predictions was assumed to be constant regardless of solution ionic strength. Predictions would be improved if one used a more rigorous model that took into consideration the variation in solubility product as ionic strength changed. The oxalate concentration is over predicted in the last few washes due to the implicit assumption in the prediction that oxalate concentration is only dependant on sodium concentration.

Table 4. Comparison of Measured and Predicted Oxalate Concentrations from the Gravity Settling Tests

	Vessel A			Vessel B		
Wash No.	Measured Sodium (M)	Measured Oxalate (M)	Predicted Oxalate (M)	Measured Sodium (M)	Measured Oxalate (M)	Predicted Oxalate (M)
0 [a]	4.21	0.0064	0.004	4.21	0.0064	0.004
1	1.94	0.035	0.017	1.89	0.037	0.018
2	1.12	0.074	0.050	1.09	0.072	0.053
3	0.72	0.13	0.12	0.73	0.13	0.12
4	0.62	0.18	0.16	0.61	0.18	0.17
5	0.54	0.21	0.21	0.58	0.20	0.19
6	0.53	0.23	0.22	0.55	0.24	0.21
7	0.51	0.17	0.24	0.52	0.25	0.23
8	0.50	0.25	0.25	0.53	0.25	0.23
9	0.39	0.19	0.41	0.43	0.19	0.33
10	0.24	0.12	1.12	0.26	0.12	0.96

[a] Supernate composition prior to washing

Knowing that sodium oxalate behaves as it should in sludge-slurry enables one to predict sodium oxalate removal during washing. Once sodium concentration is lowered to 0.5 M (after 4 washes in these experiments), the amount of oxalate removed per wash is simply equal to the oxalate solubility concentration multiplied by the decant volume.

A plot of fraction of oxalate removed as a function of number of washes is illustrative. For these experiments, inhibited water additions and decants were nearly equal. Therefore, once sodium concentration drops to 0.5 M, the rate of oxalate removal should be constant. This is indeed the case, as shown in Figure 3 by a nearly straight line.

In comparing the centrifuge tube tests to the gravity settling tests, there were no significant differences. Also, there were no issues with sludge settling in these tests. Two days of settling were sufficient to allow for easy decants.

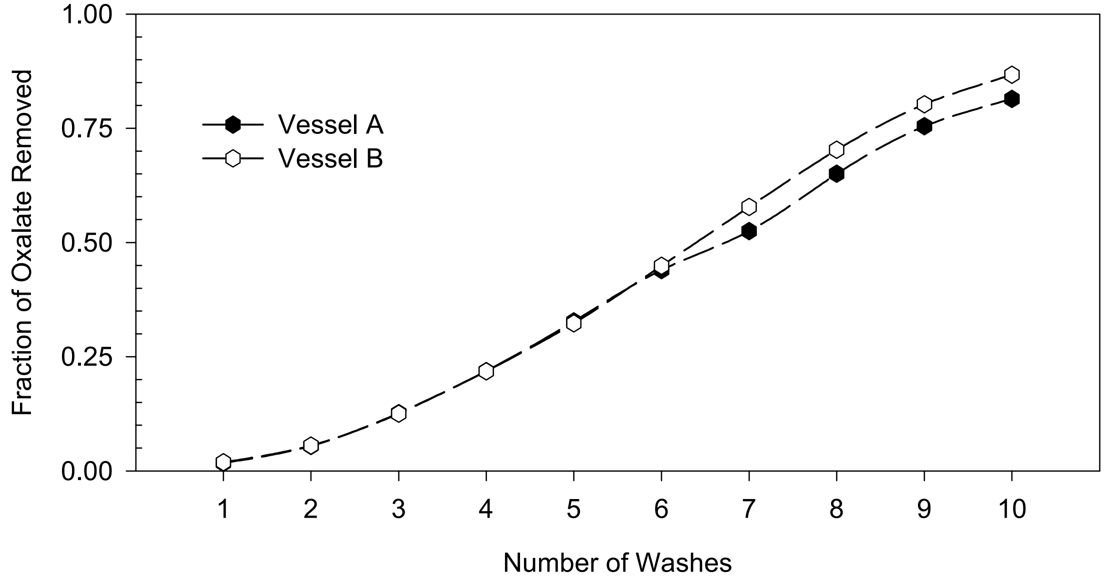

Figure 3. Fraction of Oxalate Removed as a Function of Number of Washes for Washing of Simulated Tank 7 Sludge-Slurry Allowing the Sludge to Gravity Settle

CONCLUSIONS

Washing of soluble species and sodium oxalate from simulated Tank 7 sludge-slurry is predictable. For example, soluble species such as nitrate and nitrite are washed from the sludge-slurry following a serial dilution equation, while sodium oxalate removal can be predicted based on published sodium oxalate solubility in aqueous solutions. Although the composition of Sludge Batch 3 will inevitably be different than the nonradioactive simulated Tank 7 sludge-slurry, this work gives confidence that a washing strategy for the next sludge batch can be developed.

APPENDIX A - SIMULATED TANK 7 SLUDGE-SLURRY PREPARATION

The starting material for simulated Tank 7 sludge-slurry was washed simulated Tank 8 sludge-slurry. The elemental composition of this Tank 8 simulant is given in Table A-1[3].

Table A-1. Elemental Composition of Washed Simulated Tank 8 Sludge-Slurry

Element	Wt. % Total Solids
Al	9.30
Ba	0.20
Ca	2.22
Cr	0.22
Cu	0.13
Fe	26.2
K	0.01
Mg	0.12
Mn	2.55
Na	6.0
Ni	2.81
Pb	0.10
Si	0.89
Sr	0.08
Zn	0.22
Zr	0.37

The Tank 8 simulant was dewashed by adding Na_2CO_3, NaCl, NaOH, $NaNO_2$, $NaNO_3$, and Na_2SO_4. Finally, sodium oxalate, coal, and sand were added to simulate Tank 7 sludge-slurry. The amount of sodium oxalate to add was based on the proposed ratio of 300,000 kg sodium oxalate to 413,000 kg total solids (excluding sodium oxalate) in Tank 7. This translates to 0.24 g of sodium oxalate per g of dewashed simulated Tank 8 sludge-slurry (wt% total solids = 33).

APPENDIX B - DETAILED SLUDGE-SLURRY WASHING RESULTS FOR THE GRAVITY SETTLING EXPERIMENTS

Vessel A Sludge-Slurry Mass 132.423 g
Vessel B Sludge-Slurry Mass 131.482 g

Wash No	Inhibited Water Added (g)	Supernate Decanted (g)	Decant Density (mg/L)	Concentration in Decanted Supernate: Na (mg/L)	Al (mg/L)	Ca (mg/L)	NO_2^- (mg/L)	NO_3^- (mg/L)	$C_2O_4^{2-}$ (mg/L)
Vessel A									
0	0	0	1.19[a]	96900	NM	NM	80700	12000	567
1	109.61	107.374	1.10	44600	3070	2.69	36500	5130	3050
2	100.013	102.551	1.04	25700	1760	2.35	17400	2640	6500
3	101.393	108.508	1.03	16600	938	0.99	8360	1290	11700
4	97.756	102.422	1.01	14300	517	1.77	4630	566	15600
5	100.114	102.353	1.02	12500	299	1.02	2470	259	18600
6	100.116	96.843	1.02	12300	211	0.80	1520	114	20300
7	99.005	101.701	1.03	11700	148	0.75	1080	<100	14800
8	100.066	101.646	1.02	11600	114	0.74	848	<100	21600
9	100.212	106.33	1.01	9050	96.8	0.47	754	<100	17000
10	98.933	102.223	1.02	5440	87.2	0.26	708	<100	10200
Vessel B									
0	0	0	1.19[a]	96900	NM	NM	80700	12000	567
1	105.727	108.282	1.081	43400	2980	2.67	36400	5180	3240
2	100.013	102.073	1.047	25000	1740	2.52	17100	2550	6360
3	100.242	107.512	1.040	16700	954	0.99	8440	1300	11500
4	98.391	101.769	1.026	14000	538	1.08	4810	594	15900
5	100.039	102.236	1.032	13400	313	1.10	2560	272	18000
6	100.219	102.871	1.019	12600	217	0.75	1690	132	21200
7	99.108	101.416	1.022	12000	153	0.78	1120	<100	22100
8	100.065	100.936	1.030	12100	118	0.75	881	<100	21700
9	100.499	105.307	1.018	10000	99.2	0.51	517	<100	16400
10	98.263	101.267	1.005	5890	87.7	0.26	696	<100	10900

NM - not measured
[a] Supernate density

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