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Composition and Flow Behavior of F-Canyon Tank 804 Sludge following Manganese Addition and pH Adjustment

M. R. Poirier
M. E. Stallings
P. R. Burket
S. D. Fink

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Washington Savannah River Company
Savannah River Site
Aiken, SC 29808

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LIST OF ACRONYMS

ADS	Analytical Development Section
BAB	Branched Alkyl Benzenes
DIN	Diisopropylnaphthalenes
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
Mn	Manganese
Pu	Plutonium
PuTTA	Plutonium Triphenyltrifluoroacetone Scintillation Analysis
SDD	Site Deactivation and Decommissioning
SEM	Scanning Electron Microscopy
SRNL	Savannah River National Laboratory
SVOA	Semi-volatile Organic Analysis
TBP	Tributyl phosphate
VOA	Volatile Organic Analysis

ABSTRACT

The Site Deactivation and Decommissioning (SDD) Organization is evaluating options to disposition the 800 underground tanks (including removal of the sludge heels from these tanks). To support this effort, SDD requested assistance from Savannah River National Laboratory (SRNL) personnel to examine the composition and flow characteristics of the Tank 804 sludge slurry after diluting it 10:1 with water, adding manganese nitrate to produce a slurry containing 5.5 wt % manganese (40:1 ratio of Mn:Pu), and adding sufficient 8 M caustic to raise the pH to 7, 10, and 14.

Researchers prepared slurries containing one part Tank 804 sludge and 10 parts water. The water contained 5.5 wt % manganese (which SDD will add to poison the plutonium in Tank 804) and was pH adjusted to 3, 7, 10, or 14. They hand mixed (i.e., shook) these slurries and allowed them to sit overnight. With the pH 3, 7, and 10 slurries, much of the sludge remained stuck to the container wall. With the pH 14 slurry, most of the sludge appeared to be suspended in the slurry. They collected samples from the top and bottom of each container, which were analyzed for plutonium, manganese, and organic constituents. Following sampling, they placed the remaining material into a viscometer and measured the relationship between applied shear stress and shear rate. The pH 14 slurry was placed in a spiral “race track” apparatus and allowed to gravity drain.

The conclusions from this work follow.

- Plutonium separation results from the process performed.
  - Gamma and PuTTA analyses show that plutonium separation occurs due to settling. The plutonium concentration in sludge samples collected from the container bottoms were higher than the plutonium concentration in the sludge/supernate samples collected from the container tops. The difference was 0 – 99%.
  - We saw no indication of the plutonium preferentially separating from the sludge.
- Manganese and plutonium remain together in the slurry solution under anticipated operating conditions (pH ranges 3-14).
  - ICP-MS analyses show manganese is present in samples collected from the top and bottom of the containers. The manganese concentration was higher in the samples collected from the container bottoms, which follows the same trend observed with the plutonium.
  - The SEM results show that all particles observed to contain plutonium, also contained manganese.
- The study identified the organic species that are present in the top and bottom layers of the container.
  - The following species were measured by SVOA at concentrations greater than 100 mg/L: tributyl phosphate (TBP), tetradecane, tridecane, diisopropylnaphthalenes (DIN), and dioctyl phthalates.
- The pH 3 slurry showed Newtonian flow behavior. The pH 14 slurry possessed a low yield stress (< 1 Pa), so it should not be difficult to mix or transport. The pH 7 and pH 10

slurries showed Bingham plastic behavior with a yield stress of approximately 7 Pa. The pH 14 slurry gravity drained rapidly.

- The study determined conditions required for suspending the sludge and manganese particles in a 5 ft diameter, 5 ft high process tank with either an agitator or a recirculation pump.

INTRODUCTION

The SRS Deactivation and Decommissioning Organization is evaluating options to disposition the 800 underground tanks (including removal of the sludge heels from these tanks) and requested assistance from SRNL personnel to develop methods to effectively mobilize the sludge from these tanks (Tanks 804, 808, and 809).

Previous work performed at SRNL provided measurements of fluid properties for sludge samples from F Area underground Tanks 804, 808, and 809. Personnel reported values for particle size measurements, solids concentration, density, and settling rate for the sludge. They also provided shear strength measurements and rheological properties from the flow curve measurements.[1] Because of the high plutonium content in Tank 804 (~ 1500 g), SDD is proposing to add manganese to the sludge as a poison. They asked SRNL to perform the following work to evaluate the addition of Mn $(NO_3)_2$ and water for removal of plutonium-containing sludge from Tank 804. This report describes the experimental work performed to examine the composition and flow characteristics of the sludge slurry after being mixed with 5.5 wt % manganese (40:1 ratio of Mn : Pu) and sufficient 8 M caustic to raise the pH to 7, 10, and 14. The objectives of this work follow.

- Determine if plutonium separation from the sludge results from the proposed processing, causing an increase in the plutonium concentration in any of the phases.
- Investigate whether the manganese and plutonium remain together in the slurry solution under anticipated operating conditions (pH ranges 3-14).
- Determine the organic species that are present in the top and bottom layers of the tank.
- Determine the flow characteristics of the solutions after manganese nitrate addition and pH adjustment to 7, 10, and 14.
- Determine the conditions required for suspending the sludge particles in the process tanks.

EXPERIMENTAL

SRS D&D provided SRNL with a sample of the sludge from Tank 804.

The samples used for this test were made by adding 8 grams of the 804 sludge sample to four labeled 200 mL polybottles. They added 80 mL of 0.001 M nitric acid to the container to provide a 10:1 dilution and reduce the pH to 3. After mixing the nitric acid and sludge, they added 14.3 g of $Mn(NO_3)_2$ and mixed the resulting slurry. Personnel then adjusted the pH to 7, 10 and 14 by adding 8 M sodium hydroxide to each sample. The final slurry volume was 80 – 120 mL. The measured pH of the slurry samples was 3, 7, 9, and 14.

We then shook each sample for 15 minutes and let it settle undisturbed overnight. Duplicate samples were taken from the top and bottom of each bottle (pH 3, pH 7, pH 10, and pH 14) and submitted to the Analytical Development Section (ADS) for analyses. The collected samples contained sludge and supernate. In the case of samples that showed settling (i.e., pH 14), the top sample contained mostly supernate. These sample layers were analyzed by scanning electron microscope (SEM) for identification of plutonium and manganese, by gamma ray spectroscopy for plutonium, by peroxide fusion/ICP-MS for manganese, by peroxide fusion/plutonium triphenyltrifluoroacetone scintillation analysis (PuTTA) for plutonium, and by volatile organic analysis (VOA)/semivolatile organic analysis (SVOA) for organic species.

SRNL Lab Operations personnel performed digestions of the samples to create solutions for PuTTA and ICP-MS measurements. They performed the digestions under directions of Analytical Development personnel. A sodium peroxide/sodium hydroxide fusion method carried out in zirconium crucibles at 675 degrees C was used to digest the samples and create clear solutions for analysis. The sample was diluted with water and nitric acid to a total volume of 1000 mL and a 10 mL aliquot of this solution removed from the cells for analysis.

During the addition of acid, they observed some foaming of the samples from the pH 3 top layer, the pH 7 bottom layer, and the pH 14 bottom layer resulting in a loss of sample. In the case of one of the pH 7 bottom layer samples, the entire sample was lost. After consulting with the Analytical Chemist on possible causes of the foaming, they decided to slow the addition of acid to the sample once in the crucible and to ensure the reaction is complete in subsequent dissolutions.

The authors believe this foaming is a result of the analytical technique rather than the manganese addition and pH adjustment, but SDD personnel should exercise caution when mixing the Tank 804 sludge with acid or caustic to avoid any foaming in their process.

Following sampling, personnel stirred the remaining material from each sample, placed it into a viscometer, and measured the relationship between applied shear stress and shear rate. Standard flow curves were performed on these solutions using the MV-1 rotor and cup arrangement on the RV-30 RotoVisco shielded cells rheometer. The rheometer program increased the shear rate linearly from 0 to 600 /sec in 5 minutes, held the shear rate at 600 /sec for 1 minute, then reduced the shear rate linearly from 600 to 0 /sec in 5 minutes. The data were fit either to a Newtonian model or a Bingham plastic model as appropriate.

After performing the rheology measurements, personnel collected a 20 mL sample of the slurry that was pH adjusted to 14 and placed it in a spiral "race track" apparatus.[2] They measured the time required for the slurry to gravity drain. They also diluted the slurry with NaOH and measured the drainage time for those slurries. The race track contains a spiral tube and is similar to an Ostwald viscometer. Because its tube has a larger diameter than the tube of an Ostwald viscometer, it provides an indication of the ability slurries to gravity drain.

Personnel employed cavern and cleaning radius models in the literature to determine the requirements for suspending sludge particles with mechanical agitators and recirculation pumps.

RESULTS

Distribution of Plutonium and Manganese

Figure 1 shows pictures of the various samples from Tank 804 after mixing and settling for several hours. The pH 14 sample shows settling and a supernate layer at the top. The pH 3, 7, and 10 samples did not show settling. The pH 14 sample appeared to be well mixed with few solids stuck to the container wall. The pH 3, 7, and 10 samples showed many solids attached to the container wall.

Figure 1. Tank 804 Sludge

Table 1 shows the plutonium concentration in the collected samples as measured by PuTTA analysis. The original Tank 804 sludge sample contained ~ 3.0 x 10^9 dpm Pu-238/g sludge and 1.6 x 10^8 dpm Pu-239/g sludge (as measured by gamma ray spectroscopy).[8] After considering the ~15:1 dilution with water, manganese nitrate, and sodium hydroxide and the settling, the pH 14 bottom plutonium measurements are consistent with previous plutonium analyses of this material. The Table 1 data shows a large difference in the plutonium concentration (both Pu-238 and Pu-239) measured in the duplicate pH 14 top samples. The likely cause of this difference is one sample contained more entrained sludge than the other. The plutonium concentration in the pH 3, 7, and 10 samples are less than expected based on these previous measurements. The likely cause of the lower plutonium concentrations is the sludge that remained stuck to the container walls and was not incorporated into the slurry.

The plutonium concentration in the samples collected from the container bottom is higher than in the samples collected from the top, indicating settling of the plutonium containing particles. The difference ranges from 10 – 93%.

Table 1. Plutonium Analysis by PuTTA

	Units	**Set 1 Pu-238 (dpm/g)**	**Set 2 Pu-238 (dpm/g)**	**Avg**	**Std Dev**	**Set 1 Pu-239/240 (dpm/g)**	**Set 2 Pu-239/240 (dpm/g)**	**Avg**	**Std Dev**
pH 3 top	dpm/g	4.33E+05	1.49E+05	2.91E+05	2.01E+05	< 2.09E+05	3.61E+04	3.61E+04	
pH 3 bottom	dpm/g	7.51E+05	6.84E+05	7.18E+05	4.74E+04	< 2.00E+05	7.11E+04	7.11E+04	
pH 7 top	dpm/g	6.07E+06	1.18E+07	8.94E+06	4.05E+06	< 5.12E+05	6.51E+05	6.51E+05	
pH 7 bottom	dpm/g		1.21E+08	1.21E+08			7.72E+06	7.72E+06	
pH 10 top	dpm/g	1.14E+07	7.75E+06	9.58E+06	2.58E+06	8.74E+05	5.41E+05	7.08E+05	2.35E+05
pH 10 bottom	dpm/g	1.55E+07	1.59E+07	1.57E+07	2.83E+05	1.43E+06	1.27E+06	1.35E+06	1.13E+05
pH 14 top	dpm/g	7.05E+07	5.15E+05	3.55E+07	4.95E+07	6.76E+06	4.63E+04	3.40E+06	4.75E+06
pH 14 bottom	dpm/g	1.18E+08	2.07E+08	1.63E+08	6.29E+07	1.14E+07	1.61E+07	1.38E+07	3.32E+06

Table 2 shows the plutonium concentration in the collected samples as measured by gamma ray spectroscopy. The original Tank 804 sludge sample contained ~ 3.0 x 10^9 dpm Pu-238/g sludge and 1.6 x 10^8 dpm Pu-239/g sludge.[8] After considering the ~15:1 dilution with water, manganese nitrate, and sodium hydroxide and the settling, the pH 14 bottom plutonium measurements are consistent with previous plutonium analyses of this material. The plutonium concentration in the pH 3, 7, and 10 samples are less than expected based on these previous measurements. The likely cause of the lower plutonium concentrations is the sludge that remained stuck to the container walls.

The plutonium concentration in the samples collected from the container bottom is higher than in the samples collected from the top, indicating settling of the plutonium containing particles. The difference ranges from 0 – 99%.

Table 2. Plutonium Analysis by Gamma Ray Spectroscopy

Sample	Units	Set 1 **Pu-238**	Set 2 **Pu-238**	Average **Pu-238**	Std Dev **Pu-238**	Set 1 **Pu-239**	Set 2 **Pu-239**	Average **Pu-239**	Std Dev **Pu-239**
pH3 top	dpm/mL	5.72E+05	3.13E+05	4.43E+05	1.83E+05	< 2.43e5	< 2.82e5	< 2.63E+05	2.76E+04
pH3 bottom	dpm/mL	3.11E+05	1.06E+06	6.86E+05	5.30E+05	< 2.36e5	< 2.20e5	< 2.28E+05	1.13E+04
pH7 top	dpm/mL	1.77E+07	1.52E+07	1.65E+07	1.77E+06	1.13E+06	7.81E+05	9.56E+05	2.47E+05
pH7 bottom	dpm/mL	1.89E+07	3.73E+07	2.81E+07	1.30E+07	9.32E+05	2.60E+06	1.77E+06	1.18E+06
pH10 top	dpm/mL	1.06E+07	9.38E+06	9.99E+06	8.63E+05	5.46E+05	5.28E+05	5.37E+05	1.27E+04
pH10 bottom	dpm/mL	1.67E+07	1.90E+07	1.79E+07	1.63E+06	1.11E+06	1.11E+06	1.11E+06	0.00E+00
pH14 top	dpm/mL	< 6.09e5	< 6.06e5	< 6.08E+0	2.12E+03	< 5.56e5	< 5.67e5	< 5.62E+05	7.78E+03
pH14 bottom	dpm/mL	2.44E+08	2.28E+08	2.36E+08	1.13E+07	1.34E+07	1.32E+07	1.33E+07	1.41E+05

Table 3 shows the manganese concentration in the collected samples as measured by ICP-MS. From the amount of sludge, manganese, water, and sodium hydroxide mixed to prepare the slurries, the authors calculated a theoretical amount of manganese in each sample. The calculated concentrations for the pH 3, pH 7, pH 10, and pH 14 samples were 3.4 x 10^4, 3.1 x 10^4, 3.1 x 10^4, and 3.0 x 10^4 mg/kg, respectively. These values approximate the measured manganese in the samples. The manganese concentration in the samples collected from the container bottom is higher than in the samples collected from the top, indicating settling of the manganese containing particles. The difference ranges from 0 – 80%. These results show the same trend as the plutonium results and suggest the manganese is staying with the plutonium.

Table 3. Manganese Analysis by ICPMS

	Units	Sample 1 Mn	Sample 2 Mn	Average	Std Dev
pH3 top	mg/Kg	4.03E+04	2.91E+04	3.47E+04	7.92E+03
pH3 bottom	mg/Kg	4.35E+04	2.42E+04	3.39E+04	1.36E+04
pH7 top	mg/Kg	7.83E+03	1.13E+04	9.57E+03	2.45E+03
pH7 bottom	mg/Kg	2.77E+04		2.77E+04	
pH10 top	mg/Kg	1.16E+04	1.04E+04	1.10E+04	8.49E+02
pH10 bottom	mg/Kg	1.50E+04	1.71E+04	1.61E+04	1.48E+03
pH14 top	mg/Kg	1.25E+04	1.66E+02	6.33E+03	8.72E+03
pH14 bottom	mg/Kg	2.17E+04	4.19E+04	3.18E+04	1.43E+04

Appendix B shows sample SEM results. We analyzed 97 particles from the eight samples. In 83 of the particles, we observed manganese. In 26 of the particles, we observed plutonium. In all instances where plutonium was observed, manganese was present. In addition, several samples show the presence of uranium. In all instances where uranium is observed, manganese is present. These results suggest the plutonium and manganese stay together.

However, the SEM may not detect all of the plutonium particles present in the samples, because of their small size or because they are not at the surface. The small sized undetected particles would not preferentially separate from the remaining particles in the slurry. Assuming a representative sample, we would expect the particles detected to be representative of the undetected particles.

Analysis of Organic Constituents

Table 4 shows the organic species measured in the samples by VOA. The only organic species detected by VOA were nonanenitrile, octanenitrile, and Flon (a Freon substitute used for oil and grease extractions in C-Lab). These species were only measured in a few of the samples and the concentrations were < 2 mg/kg.

Table 4. Results from Volatile Organics Analysis (VOA)

Sample	Nonanenitrile (mg/kg)	Octanenitrile (mg/kg)	Flon (mg/kg)
pH3 top	0.72	0.50	nd
	nd	nd	nd
pH3 bottom	nd	nd	nd
	nd	nd	nd
pH7 top	nd	nd	nd
	nd	nd	nd
pH7 bottom	nd	nd	nd
	nd	nd	1.9
pH10 top	nd	nd	nd
	nd	nd	nd
pH10 bottom	nd	nd	nd
	nd	nd	nd
pH14 top	nd	nd	0.58
	nd	nd	nd
pH14 bottom	1.0	0.60	3.4
	0.56	nd	5.5

nd: no detection

Table 5 shows the semi-volatile organic species detected in the samples. The following species were measured at concentrations greater than 100 mg/kg: tributyl phosphate (TBP), tetradecane, tridecane, diisopropylnaphthalenes (DIN), and dioctyl phthalates. In addition to these species, we detected branched alkyl benzenes (BAB), pentadecane, dodecane, 1-nonene, 5-butyl-4-nonene, 6-methyl-4-undecane, 2-[4-(1,1-dimethyl)phenoxy]-ethanol, 2,3-dihydro-2-methyl-4(or 6)-phenyl-benzofuran, bis(2-ethylhexyl) phthalate, 4-(1-methyl-1-phenylethyl) phenol, and bibutyl 3-hydroxybutyl phosphate.

Table 5a. Results from Semivolatile Organics Analysis (SVOA) of Container Top Sample

Analyte, mg/kg	pH 3	pH 3	pH 7	pH 7	pH 10	pH 10	pH 14	pH 14
TBP	nd	nd	70	24	63	16	110	2300
Tetradecane	nd	nd	20	nd	14	nd	nd	370
Tridecane	nd	nd	12	nd	nd	nd	nd	270
DIN	nd	nd	nd	nd	nd	nd	nd	370
Pyridine, 3,5-dichloro-	nd	nd	nd	nd	30	nd	nd	nd
Branched Alkyl Benzenes	nd	nd	nd	nd	nd	nd	nd	86
Pentadecane	nd	nd	nd	nd	nd	nd	nd	31
Dodecane	nd	nd	nd	nd	nd	nd	nd	12
1-Tetradecene	nd	nd	nd	nd	nd	nd	nd	20
Unidentified	nd	nd	nd	nd	nd	nd	nd	36
Ethanol, 2-[4-(1,1-dimethylethyl)phenoxyl-	nd	nd	nd	nd	nd	nd	nd	25
Benzofuran, 2,3-dihydro-2-methyl-4 (or 6)-phenyl-	nd	nd	nd	nd	nd	nd	nd	20
Bis(2-ethylhexyl) phthalate	nd	nd	nd	nd	nd	nd	nd	16

Table 5b. Results from Semivolatile Organics Analysis (SVOA) of Container Bottom Sample

Analyte, mg/kg	pH 3	pH 3	pH 7	pH 7	pH 10	pH 10	pH 14	pH 14
TBP	nd	nd	460	230	70	170	3200	2700
Tetradecane	nd	nd	120	45	21	30	900	84
Tridecane	nd	nd	72	27	13	21	400	nd
DIN	nd	nd	48	10	Nd	nd	423	330
Branched Alkyl Benzenes	nd	nd	nd	nd	nd	nd	85	14
Pentadecane	nd	nd	nd	nd	nd	nd	73	18
Dodecane	nd	nd	nd	nd	nd	nd	28	nd
1-Nonene	nd	nd	nd	nd	nd	nd	19	nd
4-Nonene, 5-butyl-	nd	nd	nd	nd	nd	nd	16	nd
4-Undecene, 6-methyl-	nd	nd	nd	nd	nd	nd	16	nd
Dioctyl phthalates	nd	nd	nd	nd	nd	nd	nd	470
Phenol, 4-1(1-methyl-1-phenylethyl)	nd	nd	nd	nd	nd	nd	nd	67
Unidentified	nd	nd	nd	nd	nd	nd	nd	28
Ethanol, 2-[4-(1,1-dimethylethyl)phenoxyl-	nd	nd	nd	nd	nd	nd	nd	25
Dibutyl 3 hydroxybutyl phosphate	---	---	---	---	---	---	ND	23

nd: no detection

DIN and BAB are characteristically found in organic residues of scintillation cocktails. The method detection limit (mdl) for each sample in this study is 10 mg/kg. The one sigma error associated with each value in Tables 5a and 5b is +/- 20%.

The original Tank 804 sludge sample contained ~ 38,000 mg/kg of TBP.[8] After considering the ~15:1 dilution with water, manganese nitrate, and sodium hydroxide and the settling, the pH 14 bottom TBP measurements are consistent with previous TBP analyses of this material. The Table 5 data shows a large difference in the TBP concentration measured in the duplicate pH 14 top samples. The likely cause of this difference is one sample contained more entrained sludge than the other. The data suggest that the organic material, sludge, and plutonium remain together. The organic composition in the pH 3, 7, and 10 samples is less than expected based on these previous measurements. The likely cause of the lower organic concentrations is the sludge that remained stuck to the container walls and was not incorporated into the slurry.

Flow Characteristics of Resulting Slurries

Table 6 shows the results from the measured flow curves of the samples. The pH 3 slurry did not possess a yield stress and behaved like salt solution with a viscosity of approximately 2 cp. The pH 7 and 10 slurries possessed yield stresses of approximately 7 Pa. These slurries will require properly sized agitators and pumps to mix and transport them. The pH 14 slurry possessed a yield stress of less than 1 Pa, so it should not present problems in mixing or transport. Details of the flow curve measurements are shown in Appendix A.

Table 6. Flow Curve Results

Sample	Description	Initial Yield Stress (Pa)	Yield Stress (Pa)	Viscosity (cP)	R^2 curve fitness
S-20 Oil Stnd	27.69 cP @ 25 ^{o}C Oil Standard			26.4	.9995
pH3-A	Clear liquid, all solids stuck to bottle.			1.8	.9128
pH3-B				2.1	.8845
pH7-A	Lumpy slurry, many solids stuck to bottle.	**16**	7.8	9.8	.9956
pH7-B			7.2	8.8	.9926
pH10-A	Lumpy slurry, many solids stuck to bottle.	**53**	6.8	10.5	.9906
pH10-B			6.2	7.3	.9758
pH14-A	Smooth slurry, few solids stuck to bottle.		0.55	3.4	.9763
pH14-B			0.33	3.5	.9877
S-20 Oil Stnd	27.69 cP @ 25 ^{o}C Oil Standard			28.93	

Based upon the flow curve measurements, one can calculate the requirements for mixing these slurries. The authors employed the cavern model to calculate the mixing requirements for these slurries with a mechanical agitator.

The basis of this model is that for a given impeller speed, the shear stresses generated by the impeller are greater than the yield stress of the slurry, and a cavern in the shape of a right circular cylinder forms, in which the slurry is well mixed. In areas outside of this cavern, where the slurry yield stress is larger than the shear stress generated by the impeller, the slurry remains motionless. This model assumes the fluid has constant rheological properties throughout the vessel. Equations [1] – [3] describe the cavern model to the point where the cavern reaches the cylindrical walls of the vessel.[3,4,5,6]

$$N_c = \frac{\pi}{D_I}\sqrt{\frac{\left(\frac{H_c}{D_c}+\frac{1}{3}\right)\left(\frac{T}{D_I}\right)^3 \tau_y}{\rho N_p}} \qquad [1]$$

$$N_c = \sqrt{\frac{4V_c\pi\left(\frac{H_c}{D_c}+\frac{1}{3}\right)\tau_y}{\left(\frac{H_c}{D_c}\right)\rho N_p D_I^{\,5}}} \qquad [2]$$

$$N_c = \sqrt{\frac{\left(\frac{T}{D_I}\right)^3 \pi^2 \tau_y}{1.32 N_p D_I^{\,2}}} \qquad [3]$$

In equations [1] – [3], N_c is the impeller speed required for the cavern to reach the cylindrical walls of the vessel, V_c is the cavern volume, H_c is the cavern height, D_c is the cavern diameter, T is the tank diameter, D_I is the impeller diameter, τ_y is the slurry yield stress, ρ is the slurry density, and N_p is the impeller power number (1.27 for pitched blade impeller).[4,5] The height to diameter ratio of the cavern is based on the type of impeller, and is 0.55 for a pitched blade turbine.[5] Once the cavern reaches the cylindrical walls of the tank, the cavern height increases linearly with impeller speed until it reaches the top of the vessel.

Using an 800 gallon cylindrical tank (5.1 ft diameter, 5.1 ft height), the authors calculated the required mixing speed as a function of impeller diameter. Table 7 shows the results. The yield stress is for a pH 7 or pH 10 slurry.

Table 7. Cavern Calculations

Tank Diameter (ft)	5.1	5.1	5.1
Tank Height (ft)	5.1	5.1	5.1
Impeller Diameter (ft)	1.3	1.7	2.55
Power number	1.27	1.27	1.27
Yield Stress (Pa)	7	7	7
Required speed equation [1] (rpm)	317	162	59
Required speed equation [2] (rpm)	317	162	59
Required speed equation [3] (rpm)	239	122	44
Required speed average (rpm)	291	149	54

The authors employed the Churnetski equation[7] to calculate the requirements for mixing the slurry with a rotating jet (see equation [4])

$$ECR = 0.97\ D_j\ V_j\ (\rho/\tau_y)^{1/2} \qquad [4]$$

.

where Dj is the jet diameter, Vj is the jet discharge velocity, ρ is density, and τ_y is yield stress. Table 8 shows the results for a pH 7 or pH 10 slurry.

Table 8. Jet Mixing Calculations

Tank Diameter (ft)	5.1	5.1	5.1
Nozzle diameter (in)	1.0	1.0	1.0
Fluid density (g/ml)	1.0	1.0	1.0
Yield Stress (Pa)	7	7	7
Flow rate (gpm)	42	32	24
Cleaning radius (ft)	5.0	3.9	3.0

SDD may use a stationary recirculation pump rather than a rotating pump. The recirculation pump would need to generate the same mixing energy (horsepower) as the rotating jet. Therefore, the nozzle diameter and jet discharge velocity would be the same. The discharge from the recirculation pump should be placed near the tank bottom and angled 10 – 30 degrees off center. Since the recirculation pump does not rotate, SDD should add some conservatism in sizing the equipment.

Tables 7 and 8 provide examples of mixing requirements for the slurries produced by SDD's proposed process. Once SDD selects the tank and mixing apparatus (agitator, rotating jet, or recirculation pump), the authors can calculate the required mixer size and operating parameters.

Table 9 shows the results from the race track tests for the pH 14 slurry with varying amounts of manganese nitrate. In all cases the slurry samples drained very quickly (within 12 seconds). We observed that the drain rate increased with decreasing manganese nitrate concentrations. Given these results we conclude that the slurry produced upon dilution of the Tank 800 material with water, addition of manganese nitrate, and adjustment to pH 14 with 8 M sodium hydroxide should gravity drain.

Table 9. Race Track Test Results

Sample	Drain Time (sec)	Drain Time (sec)
5.5 wt % Mn	11.09	9.99
2.75 wt % Mn	7.90	7.53
1.38 wt % Mn	7.36	7.06
1.0 wt % Mn	7.19	6.99
0.5 wt % Mn	6.87	6.79

CONCLUSIONS

The conclusions from this work follow.

- Plutonium separation results from the process performed.
    - Gamma and PuTTA analyses show that plutonium separation occurs due to settling. The plutonium concentration in sludge samples collected from the container bottoms were higher than the plutonium concentration in the

  - sludge/supernate samples collected from the container tops. The difference was 0 – 99%.
  - We saw no indication of the plutonium preferentially separating from the sludge.
- Manganese and plutonium remain together in the slurry solution under anticipated operating conditions (pH ranges 3-14).
  - ICP-MS analyses show manganese is present in samples collected from the top and bottom of the containers. The manganese concentration was higher in the samples collected from the container bottoms, which follows the same trend observed with the plutonium.
  - The SEM results show that all particles observed to contain plutonium, also contained manganese.
- The study identified the organic species that are present in the top and bottom layers of the container.
  - The following species were measured by SVOA at concentrations greater than 100 mg/L: tributyl phosphate (TBP), tetradecane, tridecane, diisopropylnaphthalenes (DIN), and dioctyl phthalates.
- The pH 3 slurry showed Newtonian flow behavior. The pH 14 slurry possessed a low yield stress (< 1 Pa), so it should not be difficult to mix or transport. The pH 7 and pH 10 slurries showed Bingham plastic behavior with a yield stress of approximately 7 Pa. The pH 14 slurry gravity drained rapidly.
- The study determined conditions required for suspending the sludge and manganese particles in a 5 ft diameter, 5 ft high process tank with either an agitator or a recirculation pump.

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Appendix A
Flow Curve Results

TO:	Michael Poirier
FROM:	Paul Burket
REVIEWER:	Erich Hansen

November 16, 2005

Rheology of Tank 804 Diluted Slurries

Sludge from tank 804 was diluted into four solutions of varying pH. The four solutions had a pH of 3, 7, 10, and 14. Standard flow curves were performed on these solutions using the MV-1 rotor and cup arrangement on the RV-30 RotoVisco shielded cells rheometer.

The rheometer program increased the shear rate linearly from 0 to 600 /sec in 5 minutes, held the shear rate at 600 /sec for 1 minute, then reduced the shear rate linearly from 600 to 0 /sec in 5 minutes.

The data were fitted either to a Newtonian model or a Bingham plastic model as appropriate. The models are explained below.

Rheological Model (Newtonian):

$$\tau = \frac{\mu \cdot \dot{\gamma}}{1000}$$

where:
τ = shear stress (Pa)
μ = Newtonian viscosity (cP - centipoise)
$\dot{\gamma}$ = shear rate (sec^{-1})

Rheological Model (Bingham Plastic):

$$\tau = \tau_o + \frac{\eta \cdot \dot{\gamma}}{1000}$$

where:
τ = shear stress (Pa)
τ_o = Bingham Plastic yield stress (Pa)
η = plastic viscosity (cP - centipoise)
$\dot{\gamma}$ = shear rate (sec^{-1})

Note that the plastic viscosity and viscosity have the same units. If the Bingham Plastic yield stress is zero, then the plastic viscosity and viscosity are the same.

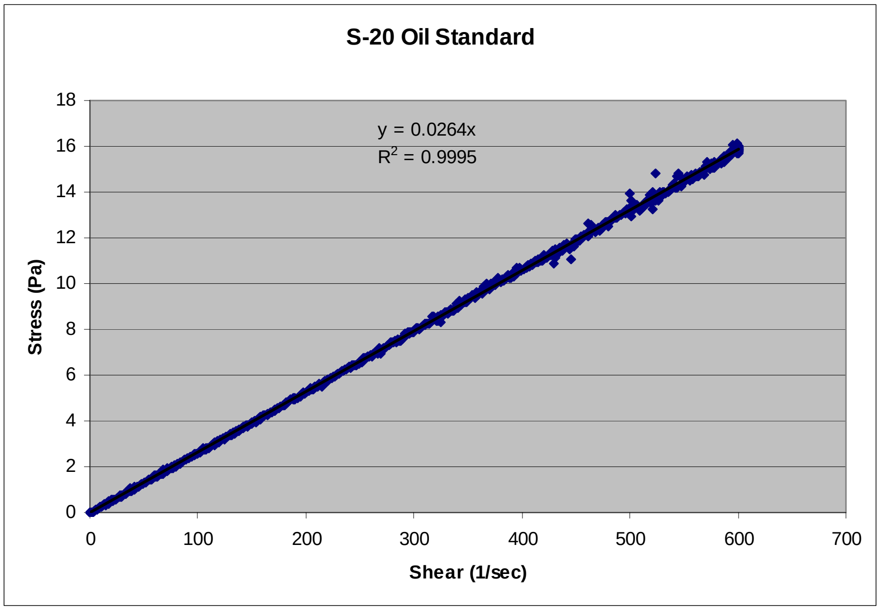
A NIST traceable viscosity calibration oil standard was used to verify the operation of the rheometer both before and after the slurry flow measurements. The oil used was S-20 oil from lot # 130509 with an expiration date of 2/19/07. The viscosity of the oil is 27.69 cP (centipoise) at 25 ^{o}C. The rheometer is considered to be functioning properly if the measured value of the oil is within 10% of the stated value.

The table below is a summary of the measured values with comments for all solutions measured. Important explanations of the values reported in the table follow after the table.

S-20 Oil Stnd Start

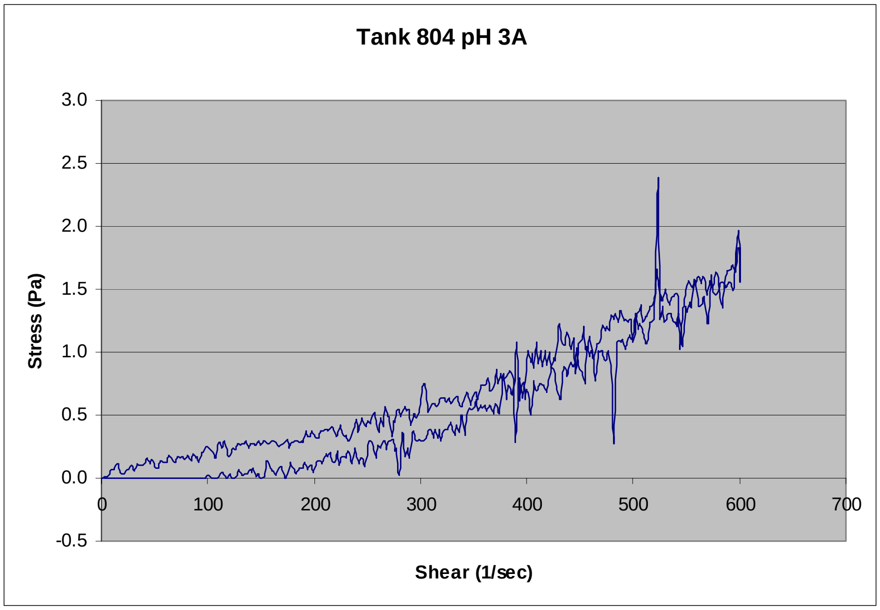
Sample Run	Description	Initial Yield Stress (Pa)	Yield Stress (Pa)	Viscosity (cP)	R^2 curve fitness
S-20 Oil Stnd	27.69 cP @ 25 ^oC Oil Standard			26.4	.9995
pH3-A	Clear liquid, all solids stuck to bottle.			1.8	.9128
pH3-B				2.1	.8845
pH7-A	Lumpy slurry, many solids stuck to bottle.	**16**	7.758	9.8	.9956
pH7-B			7.178	8.8	.9926
pH10-A	Lumpy slurry, many solids stuck to bottle.	**53**	6.83	10.5	.9906
pH10-B			6.2	7.3	.9758
pH14-A	Smooth slurry, few solids stuck to bottle.		0.55	3.4	.9763
pH14-B			0.33	3.5	.9877
S-20 Oil Stnd	27.69 cP @ 25 ^oC Oil Standard			28.93	

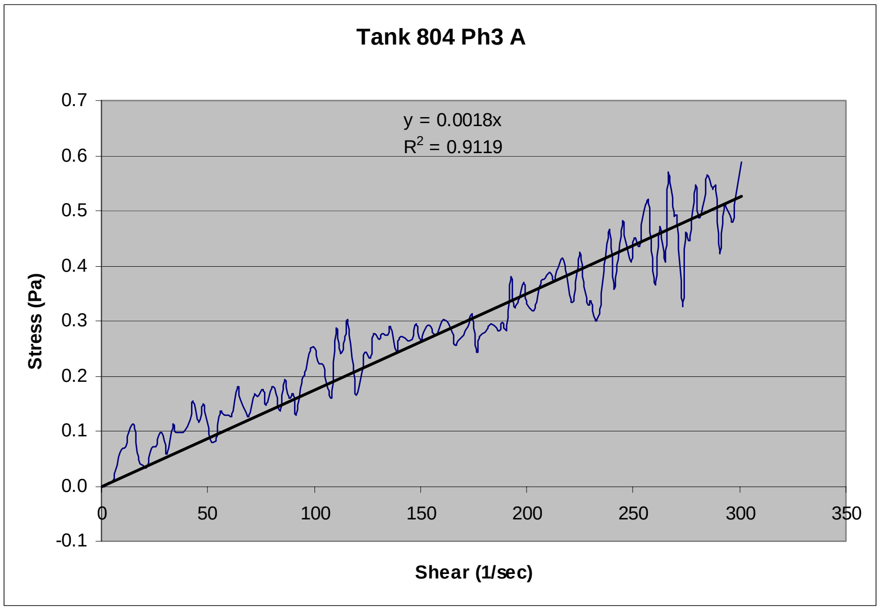
The measured value of 26.4 cP is 5% below the actual value of 27.69 cP which is within the required 10% acceptable error range.



pH3-A and pH3-B

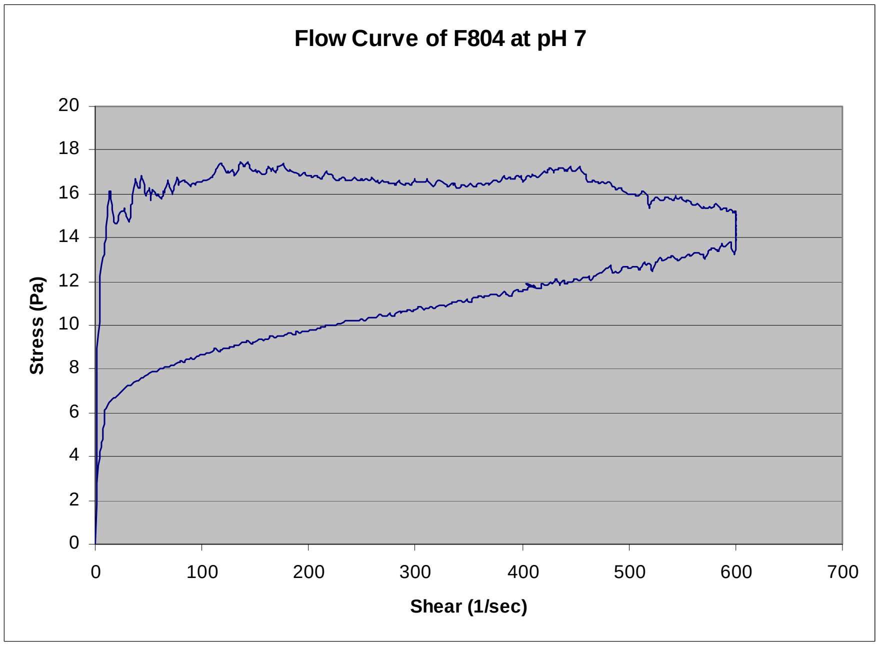
The acidic pH solution was clear since it did not slurry the solids into solution. The solids simply stuck to the sides of the sample bottle. The rheology curve simple gave the Newtonian model curve one would expect from a clear acid solution. Values were taken only from the upcurve (see second graph).

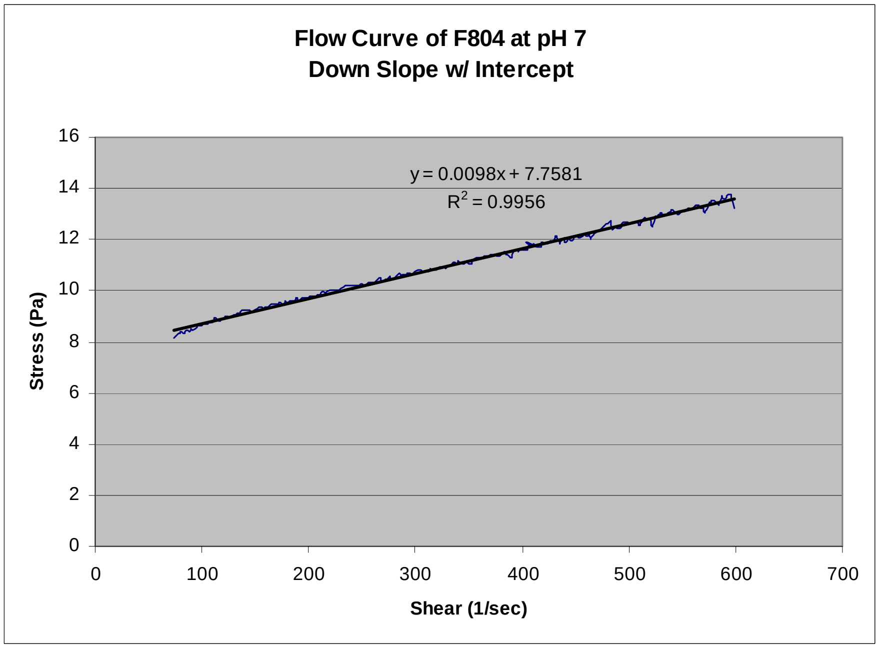




pH7-A and pH7-B

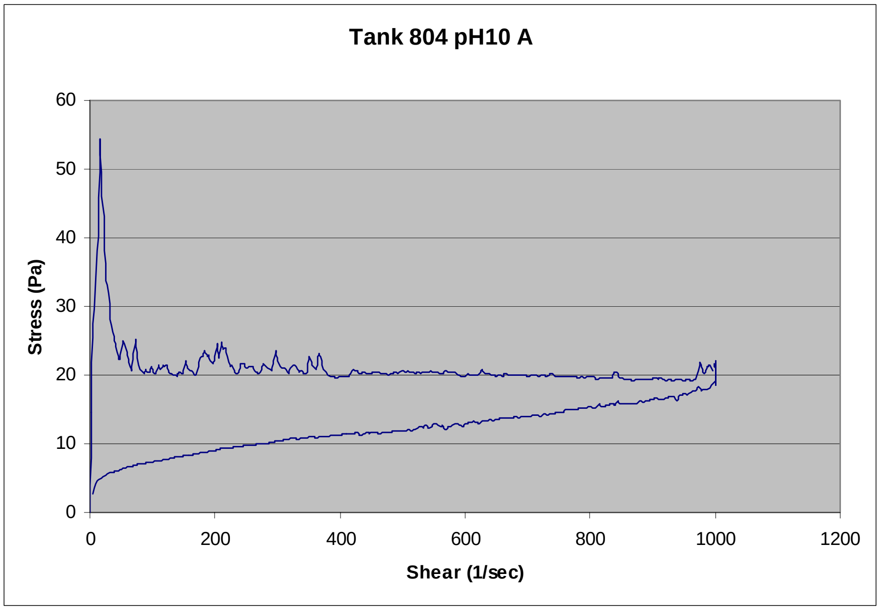
This neutral solution only partially slurried the solids. A large portion of the solids remained stuck to the sides of the sample bottle. The slurry formed clumps that were not easily broken up by shaking the sample bottle. The lumps caused the initial yield stress of 16 Pa (Pascals). The calculated values shown in the table are from the down curve portion of the measurement which gave an indication of the fluid properties after the slurry had been thoroughly broken down by the rheometer. This slurry acted like a Bingham plastic as expected.

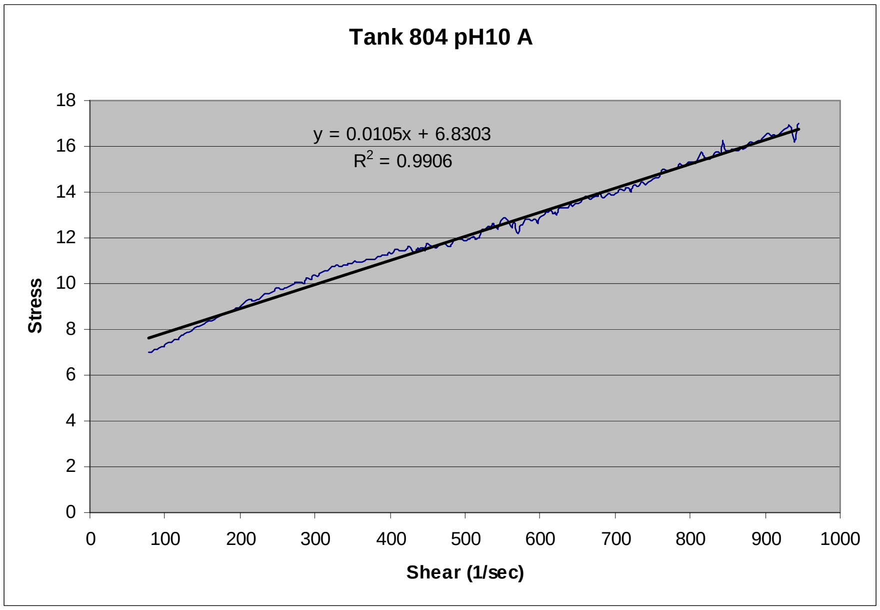




pH10-A and pH10-B

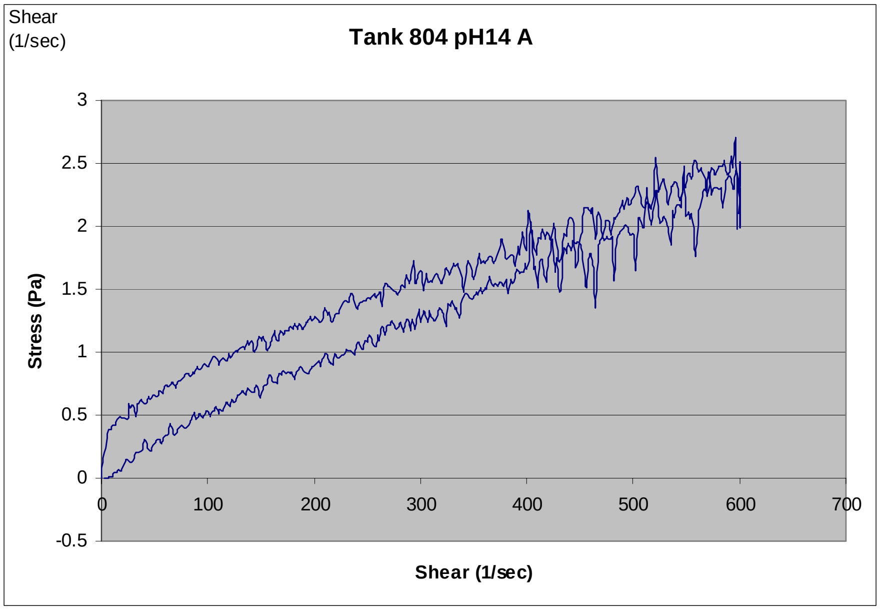
This mildly caustic solution only partially slurried the solids. A large portion of the solids remained stuck to the sides of the sample bottle. The slurry formed clumps that were not easily broken up by shaking the sample bottle. The lumps caused the initial yield stress of 53 Pa. The calculated values shown in the table come from the down curve portion of the measurement which gave an indication of the fluid properties after the slurry had been thoroughly broken down by the rheometer. This slurry acted like a Bingham plastic as expected.

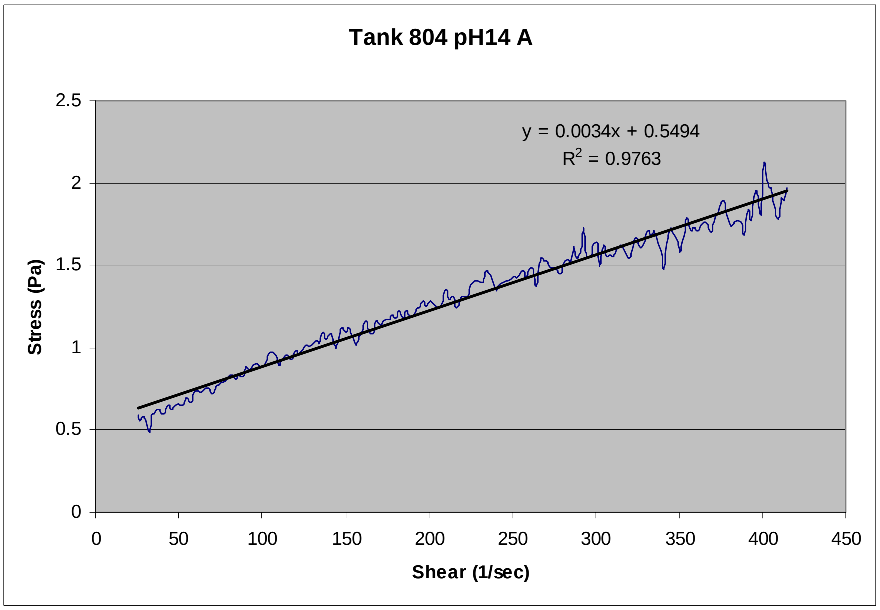




pH14-A and pH14-B

This caustic solution slurried the solids into a smooth pumpable slurry. Few solids stuck to the sides of the bottle. The flow curve exhibited Bingham plastic properties right from the start since there were no visible clumps in the slurry. With a yield stress of about 0.5 Pa and a consistency of about 3.5 cP, this slurry is easily pumpable. The upcurve was used for the calculation of the flow characteristics.

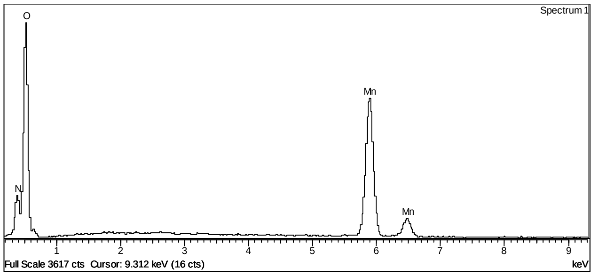




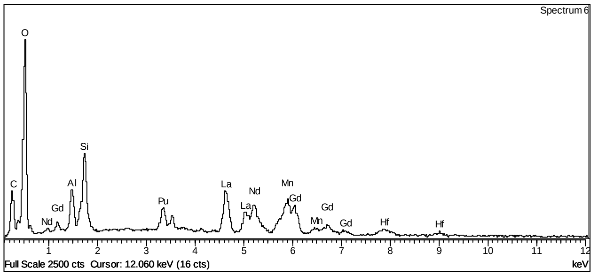
S-20 Oil Stnd End

The measured value of 28.93 cP is 5% above the actual value of 27.69 cP which is within the required 10% acceptable error range.

Appendix B
SEM



Tank 804 PH-3 Top ADS#3-224684 Poirier 11-15-05 Spot-1



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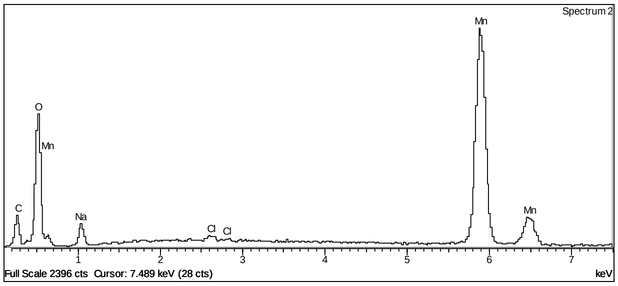

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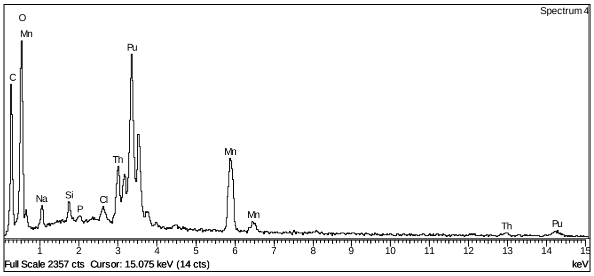

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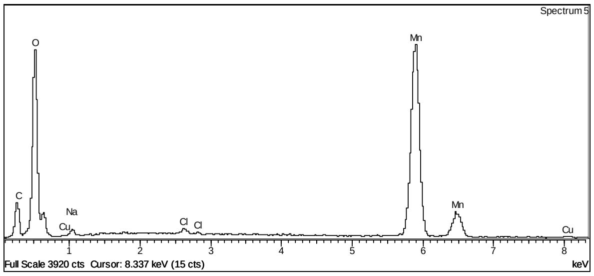

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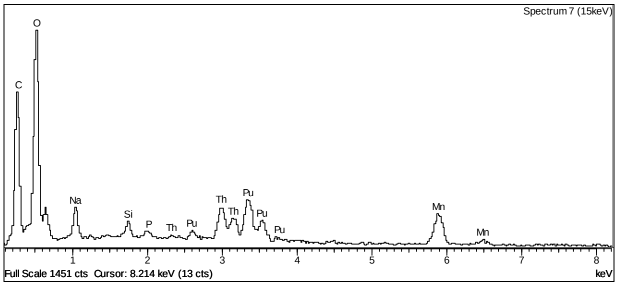
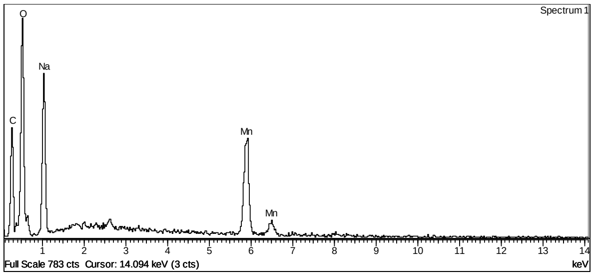
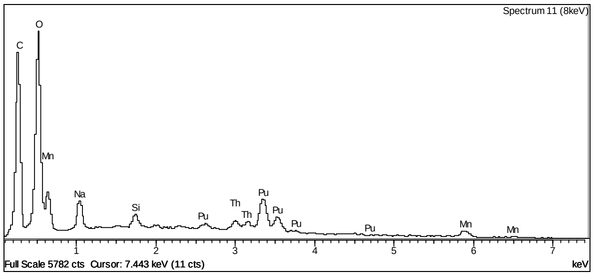


Tank 804 PH-10 Top ADS#3-224688 Poirier 11-17-05 Spot-7 (15keV)



Tank 804 PH-14 Bottom ADS#3-224691 Poirier 11-18-05 Spot-1



Tank 804 PH-14 Bottom ADS#3-224691 Poirier 11-18-05 Spot-11 (8keV)

APPROVAL

Author:

12/2/05
M. R. Poirier, Process Chemistry Science
Date

12/5/05
M. E. Stallings, Process Chemistry Science
Date

Paul Burket
12/5/05
P. R. Burket, Stabilization Science Research
Date

Design Check:

12/5/05
K. Adu-Wusu, Advanced Characterization and Process Research
Date

Customer:

G. J. Zachmann III
12/5/05
G. J. Zachmann III, Chief Engineer
F Canyon Complex Deactivation
Date

Management:

Samuel D. Fink
12/6/2005
S. D. Fink, Process Chemistry Science Manager
Date

12/6/05
J. C. Griffin, Chemical Science & Technology Manager
Date