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Removing Sludge Heels from Savannah River Site Waste Tanks by Oxalic Acid Dissolution

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ABSTRACT

The Savannah River Site (SRS) will remove sludge as part of waste tank closure operations. Typically the bulk sludge is removed by mixing it with supernate to produce a slurry, and transporting the slurry to a downstream tank for processing. Experience shows that a residual heel may remain in the tank that cannot be removed by this conventional technique. In the past, SRS used oxalic acid solutions to disperse or dissolve the sludge heel to complete the waste removal. To better understand the actual conditions of oxalic acid cleaning of waste from carbon steel tanks, the authors developed and conducted an experimental program to determine its effectiveness in dissolving sludge, the hydrogen generation rate, the generation rate of other gases, the carbon steel corrosion rate, the impact of mixing on chemical cleaning, the impact of temperature, and the types of precipitates formed during the neutralization process.

The test samples included actual SRS sludge and simulated SRS sludge. The authors performed the simulated waste tests at 25, 50, and 75 °C by adding 8 wt % oxalic acid to the sludge over seven days. They conducted the actual waste tests at 50 and 75 °C by adding 8 wt % oxalic acid to the sludge as a single batch. Following the testing, SRS conducted chemical cleaning with oxalic acid in two waste tanks. In Tank 5F, the oxalic acid (8 wt %) addition occurred over seven days, followed by inhibited water to ensure the tank contained enough liquid to operate the mixer pumps. The tank temperature during oxalic acid addition and dissolution was approximately 45 °C. The authors analyzed samples from the chemical cleaning process and compared it with test data.

The conclusions from the work follow..
- Oxalic acid addition proved effective in dissolving sludge heels in the simulant demonstration, the actual waste demonstration, and in SRS Tank 5F.
- The oxalic acid dissolved ~ 100 % of the uranium, ~ 100% of the iron, and ~ 40% of the manganese during a single contact in the simulant demonstration. (The iron dissolution may be high due to corrosion of carbon steel coupons.)
- The oxalic acid dissolved ~ 80% of the uranium, ~ 70% of the iron, ~ 50% of the manganese, and ~ 90% of the aluminum in the actual waste demonstration for a single contact.

- The oxalic acid dissolved ~ 100% of the uranium, ~ 15% of the iron, ~ 40% of the manganese, and ~ 80% of the aluminum in Tank 5F during the first contact cycle. Except for the iron, these results agree well with the demonstrations. The data suggest that a much larger fraction of the iron in the sludge dissolved, but it re-precipitated with the oxalate added to Tank 5F.

- The demonstrations produced large volumes (i.e., 2 – 14 gallons of gas/gallon of oxalic acid) of gas (primarily carbon dioxide) by the reaction of oxalic acid with sludge and carbon steel.

- The reaction of oxalic acid with carbon steel produced hydrogen in the simulant and actual waste demonstrations. The volume produced varied from 0.00002 – 0.00100 ft^3 hydrogen/ft^2 carbon steel. The hydrogen production proved higher in unmixed tanks than in mixed tanks.

INTRODUCTION

The Savannah River Site will remove sludge as part of waste tank closure operations. Typically the bulk sludge is removed by mixing it with "water" to create a slurry, and transporting the slurry to a downstream tank for processing. Experience shows that a residual heel may remain that cannot be removed by this conventional technique. In the past, SRS used oxalic acid solutions to disperse or dissolve the sludge heel to complete the waste removal.[1,2,3] Since the waste tanks and cooling coils are constructed of carbon steel, a significant amount of corrosion may occur due to the acid.

The authors investigated the chemical cleaning process to determine its effectiveness in dissolving sludge, the hydrogen generation rate, the generation rate of other gases, the carbon steel corrosion rate, the impact of mixing on chemical cleaning, the impact of temperature, and the types of precipitates formed during neutralization of the spent acid. Savannah River National Laboratory (SRNL) conducted tests with simulated Tank 5F sludge, tests in which simulated Tank 5F sludge was irradiated, and tests with actual Tank 5F sludge. Following the testing, SRS performed chemical cleaning in two waste tanks. We analyzed supernate samples collected from these tanks to assess extent of dissolution.

This paper discusses the results of the simulant testing, the actual waste testing, and the chemical cleaning in SRS waste tanks. The paper will focus on sludge dissolution and gas generation. A previously published paper describes the corrosion data.[4]

TESTING

Simulant Demonstration

Personnel prepared supernate simulant, sludge simulant, and oxalic acid. They prepared the supernate to match the composition of Tank 7F supernate. (The supernate in Tank 7F was used for mechanical cleaning, or sluicing, operations to remove sludge from Tank 5F prior to start of chemical cleaning.) Table 1 shows the supernate composition. They vacuum filtered the resulting mixture with a 0.45-μm nylon membrane Nalgene® filter, aged it for two days, and

verified the absence of solids before using. They prepared a depleted uranium PUREX sludge simulant with composition shown in Table 2. Table 3 shows the conditions for the tests conducted.

Table 1. Simulated supernate recipe.

| Component	Source	Molarity
NaOH	NaOH	1.0870
$NaNO_3$	$NaNO_3$	0.6300
$NaNO_2$	$NaNO_2$	0.6084
$NaAlO_2$	$Al(NO_3)_3.9H_2O$	0.203
Na_2SO_4	Na_2SO_4	0.098
Na_2CO_3	$Na_2CO_3.H_2O$	0.4396
NaCl	NaCl	0.0163
NaF	NaF	0.0209
Na_2HPO_4	$Na_2HPO_4.7H_2O$	0.0065
$Na_2C_2O_4$	$Na_2C_2O_4$	0.0052
Na_2SiO_3	$Na_2SiO_3.9H_2O$	0.00261
Na_2MoO_4	$Na_2MoO_4.2H_2O$	0.000131
KNO_3	KNO_3	0.01500
CsCl	CsCl	0.00014

Table 2. Simulated Tank 5F sludge target composition (based on equilibrium calculations and Waste Characterization System values).

Component	wt %	Component	wt %
$Al(OH)_3$	11.30	$Ni(OH)_2$	10.02
$BaSO_4$	0.52	$Pr(OH)_3$	0.15
$CaCO_3$	2.36	$SrCO_3$	0.06
CaF_2	0.14	$UO_2(OH)_2$	17.31
$Ca_3(PO_4)_2$		Ag_2CO_3	0.21
$Cr(OH)_3$		$Ba_3(PO_4)_2$	
$Fe(OH)_3$	44.50	$Ca(OH)_2$	1.37
HgO	0.15	$CePO_4·2H_2O$	0.19
$KMnO_4$		$Pu(OH)_4$	0.02
$La(OH)_3$	0.15	$Sr_5(PO_4)_3OH$	0.12
$Mg(OH)_2$	0.37	$ZnCr_2O_4$	0.59
$Mn(OH)_2$	10.01	ZrO_2	0.49

Table 3. Test matrix for process demonstrations with simulated waste.

Test	Dissolution Vessel Temperature (°C)	Oxalic Acid Temperature (°C)	Receipt Vessel Temperature (°C)	Mixing
1	50	50	25	Yes
2	75	50	25	Yes
3	25	25	25	Yes
4	50	25	25	No
5	75	25	25	No
6	25	25	25	No

Figure 1 shows the experimental setup for the simulant chemical cleaning test. The first three tests (Tests 1, 2 and 3, respectively) occurred at 50 °C, 75 °C and 25 °C. These tests included mixing when the vessel liquid height reached the agitator. The second set of tests, Tests 4, 5 and 6, operated at the same temperatures (50 °C, 75 °C and 25 °C, respectively) but with no mixing of the Dissolution Vessel.
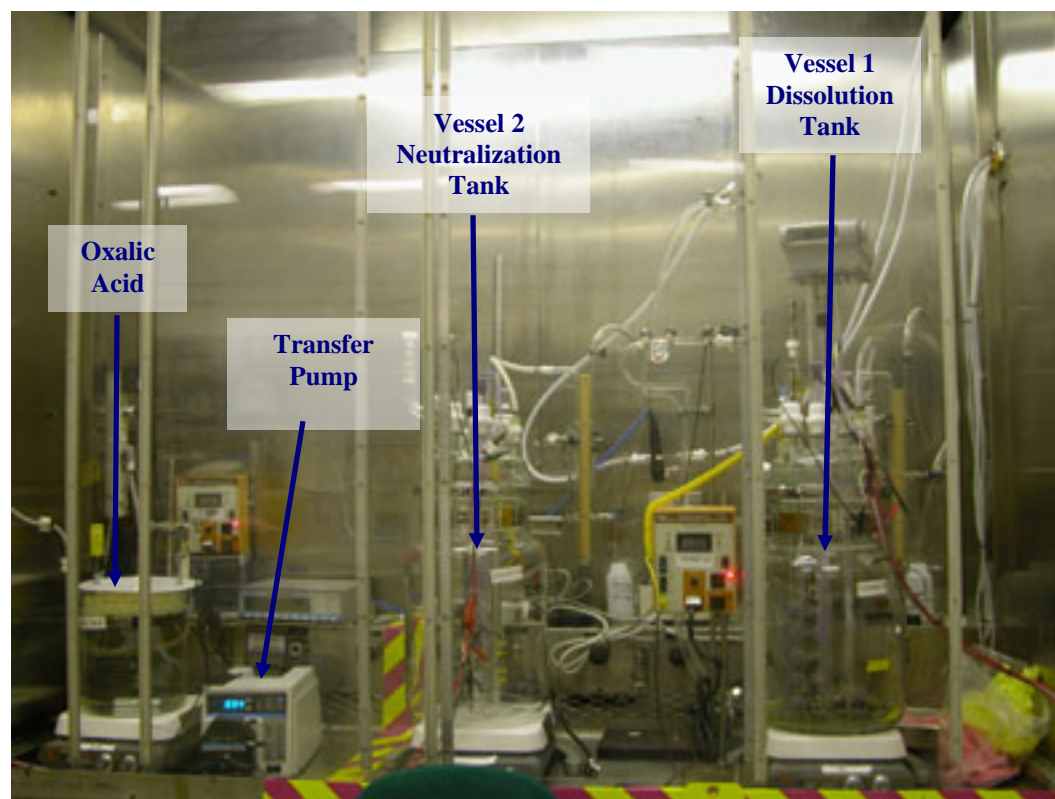
Figure 1. Equipment for chemical cleaning (experimental) demonstrations.

Personnel conducted the simulated sludge chemical cleaning demonstrations as follows. They placed 7656 mL of 8 wt % oxalic acid in a glass vessel. They placed polypropylene beads on top of the oxalic acid and covered the vessel to minimize evaporation. They placed 190 g of simulated sludge containing depleted uranium into a ~ 22 L glass vessel. They added 775.6 g of

simulated salt solution. The ratio of acid to sludge and the ratio of supernate to sludge mimic the values expected in Tank 5F for the cleaning operations.

They purged the vessel with air containing a helium tracer. The flow rates of helium (0.117 cm^3/min) and of air (17 cm^3/min) were controlled by MKS mass flow controllers. The six demonstrations had an average vapor space turnover time of 853 min. The flow rates selected provided a comparable vapor space turnover rate for the current Tank 5F ventilation system.

They heated the oxalic acid and sludge to the target temperatures. Once the oxalic acid and sludge reached the target temperatures, they transferred the oxalic acid to the sludge tank at ~ 0.7 mL/min. This rate was selected so the acid transfer occurred over approximately 7 days, similar to planned duration of oxalic acid transfer for Tank 5F processing.

Initially, the sludge tank mixer remained inactive to mimic the lack of mixing in Tank 5F during the first acid additions until a sufficient liquid level was established to prime the pumps. In tests with mixing, the mixer was turned on after the liquid covered the agitator impeller. This point typically occurred after ~2 days, similar to the timing that may occur in full-scale operation. The mixing conditions – i.e., impeller dimensions and rotational speed – were selected to provide comparable mixing energy as expected in Tank 5F operations with a circulating pump.

Once the oxalic acid addition finished, the contact with sludge continued for ~50 hours. After the 50 hour contact, researchers pumped the vessel contents to a receipt tank that contained 5 L of simulated salt solution. Personnel transferred 1.5 L from the Dissolution Vessel to the Receipt Vessel with the exception of Test 1 and Test 5 in which 3 L was transferred. The reduction in transfer volume for the remaining tests allowed personnel to perform post-dissolution mixing in the Dissolution Vessel to look for any evidence of trapped hydrogen on the solid residues and to assess ability to suspend those residues.

The transfer occurred over ~17.5 hours. This transfer rate approximated the upper range of the transfer rates possible for Tank 5F to Tank 7F transfers with existing equipment. The higher rate is believed more likely to cause massive precipitation and hence the greatest potential to form a floating layer in the receipt tank that might impede gas release. Transfer occurred through a submerged tube into the receipt tank – analogous to the Tank 7F downcomer – with no agitation in the tank. These conditions mimic planned operations in Tank 7F and use of the maximum flowrate provides a greater potential for solids formation. Personnel measured the pH for the receipt tank contents during the transfer.

The temperature of the acid-sludge slurry was monitored during the tests. The pH was measured daily with a pH probe or paper. The pre and post dissolution sludge as well as the spent acid solution were analyzed for metals by ICP-ES and ICP-MS (Inductively-Coupled Plasma - Emission and Mass Spectroscopy). The test sampled a portion of the off-gas stream using an online Agilent Model M300A Micro-GC gas chromatograph (GC) with a Molsieve 5A column for measurement of helium, hydrogen, oxygen, and nitrogen. Personnel added a PoraPlot Q column for measurement of carbon dioxide and nitrous oxide after Test 3. Argon was the carrier gas for the GC.

Actual Waste Demonstration

The actual waste tests occurred via remote handling in the SRNL Shielded Cells. Personnel used a sample of solids collected from Tank 5F and a sample of supernate from Tank 7F. Characterization of these samples is the subject of a separate report.[5]

The reactors were constructed of glass (see Figure 2). A carbon steel coupon was placed in contact with the solution for the duration of each test. Personnel measured corrosion rates of the carbon steel coupon. They measured the gases released from the vessel with an on-line gas chromatograph. The reactor was heated using a heating mantle. The solution temperature was monitored throughout testing.

A purge gas (argon) was introduced directly into the reactor and exited through the top of the reflux condenser. A portion of the off-gas stream was sampled using an Agilent Model M200 Micro-GC gas chromatograph (GC) with a Molsieve 5A column for measurement of helium, hydrogen, oxygen, and nitrogen and a PoraPlot Q column for measurement of carbon dioxide and nitrous oxide. Argon was the carrier gas for the GC.

Given that low flow rates prototypical of planned tank conditions for the addition of the oxalic acid were prohibitive with the available equipment, oxalic acid addition occurred in batch fashion. The tests used an 8 wt % oxalic acid (OA) to sludge/supernate volume ratio of 20:1. For each test a 7 mL portion of sludge/supernate mixture was added to the test reactor through the purge inlet (without purging). A portion of 8 wt % OA was used to rinse the residual sludge/supernate mixture from the container into the reactor before addition of the remainder of the 145 mL of OA solution to the test reactor.

At the completion of the tests the reactor was cooled and the oxalic acid solution filtered through a 0.45 micron filter prior to analysis of the filtrate and residues. A portion of the oxalic acid solution (30 mL) from each test was neutralized via submerged addition to a Tank 7F simulant (50 mL). Solids formation and liquid layer behavior were observed and recorded. Table 4 shows the test conditions.

Table 4. Matrix for actual waste tests.

Test	Dissolution Temperature (°C)	Oxalic Acid Temperature (°C)	Neutralization Temperature (°C)	Mixing
1	50	Ambient	Ambient	Yes
2	75	Ambient	Ambient	Yes

Figure 2. Equipment for Actual Tank 5F Waste Chemical Cleaning Test

Tank Farm Deployment

Prior to the start of chemical cleaning, Tank 5F contained ~ 3400 gallons of sludge. SRS personnel added 69,000 gallons of 8 wt % oxalic acid followed by 45,000 gallons of water to produce 120,000 gallons of 5.8 wt % oxalic acid. They mixed the tank, collected liquid samples, and submitted the samples for analysis. SRNL analyzed these samples for pH, turbidity, cations (by ICP-ES) and anions (by IC).

Relative Scale of Tests to Process

Table 5 shows a comparison of the headspace turnover time, sludge volume to carbon steel surface area ratio, oxalic acid volume to carbon steel surface area ratio, and oxalic acid volume to sludge volume ratio for the tests and for operations in Tank 5F. Tank 5F contains mounds of "moist" solids. During start of an acid cleaning cycle, the tank will also contain a supernate heel. The amount of heel (i.e. supernate) present may vary slightly between cycles. For these process demonstrations with simulated sludge, researchers selected a supernate-to-sludge volume ratio of ~4.

Table 5. Geometrical and process conditions in chemical cleaning tests and in Tank 5F.

Test	Head space volume per purge rate (min)	Sludge* (gal) per ft^2 metal surface area	Oxalic acid (gal) per ft^2 metal surface area	Oxalic acid volume per sludge plus supernate volume	Oxalic acid volume per sludge volume
Actual Waste Test	9.36	0.2	4.2	20.7	47 (dry) 21 (wet)
Simulant Demonstrations (50 °C, mixing)	1052	0.25 (dry) 0.85 (wet)	7.5	8.8	35 (dry) 17.5[#] (wet)
Simulant Demonstrations (others)	853	0.25 (dry) 0.87 (wet)	8.8	8.8	35 (dry) 17.5[#] (wet)
Tank 5F Nominal	853 (1728 for safety limit of 45 scfm)	0.31 (dry) 1.05 (wet)	10.4	9.9	34

* Sludge values are calculated on a "dry" bases accounting only for the sludge mounds (in Tank 5F) or the dry sludge added (in experiments) and on a wet based accounting for the added supernate.

[#] These values assume the starting sludge holds 50 wt % water.

RESULTS

Observations

Simulated Sludge Chemical Cleaning Demonstrations

Figure 3 shows the progression of the test over time. Each of the tests followed a similar pattern with differences in the timing primarily due to different temperatures. There was very little visual difference between the mixing and non-mixing tests other than the formation of large crystals being preferred slightly in the unmixed tests. Visual inspection showed the lower temperature tests (i.e., 25 °C) seemed to promote larger crystal growth. It should be noted that mixing did not start for any of the tests until at least 45 hours after the start of acid addition. At this time, sufficient acid had been added to reduce the pH to <2 and the vessel contents had turned green in color.

The oxalic acid addition led to the formation of white colored solids directly under the acid addition point. As more acid was added, the solids took on a bright yellow color. The liquid level had not reached any of the metal coupons when the yellow colored material first formed. As acid addition continued, the formation of solids spread throughout the vessel. A white colored layer soon was visible across the top of the un-dissolved sludge. The solids then took on a brown or rust color. The brown coloring typically resided on top of the white solids formed. As more acid was added and the pH continued to drop, the solution became an emerald green

color characteristic of iron oxalate (or trisoxalatoiron(III) complex, $Fe(C_2O_4)_3^{3-}$). As acid addition continued the solution became darker moving to an olive green color. After completion of acid addition, the vessels were then allowed to stand for 50 hours to allow the acid to continue dissolving the sludge. In Tests 1-3, mixing persisted during the 50 hour period while the vessel remained unstirred for Tests 4-6.
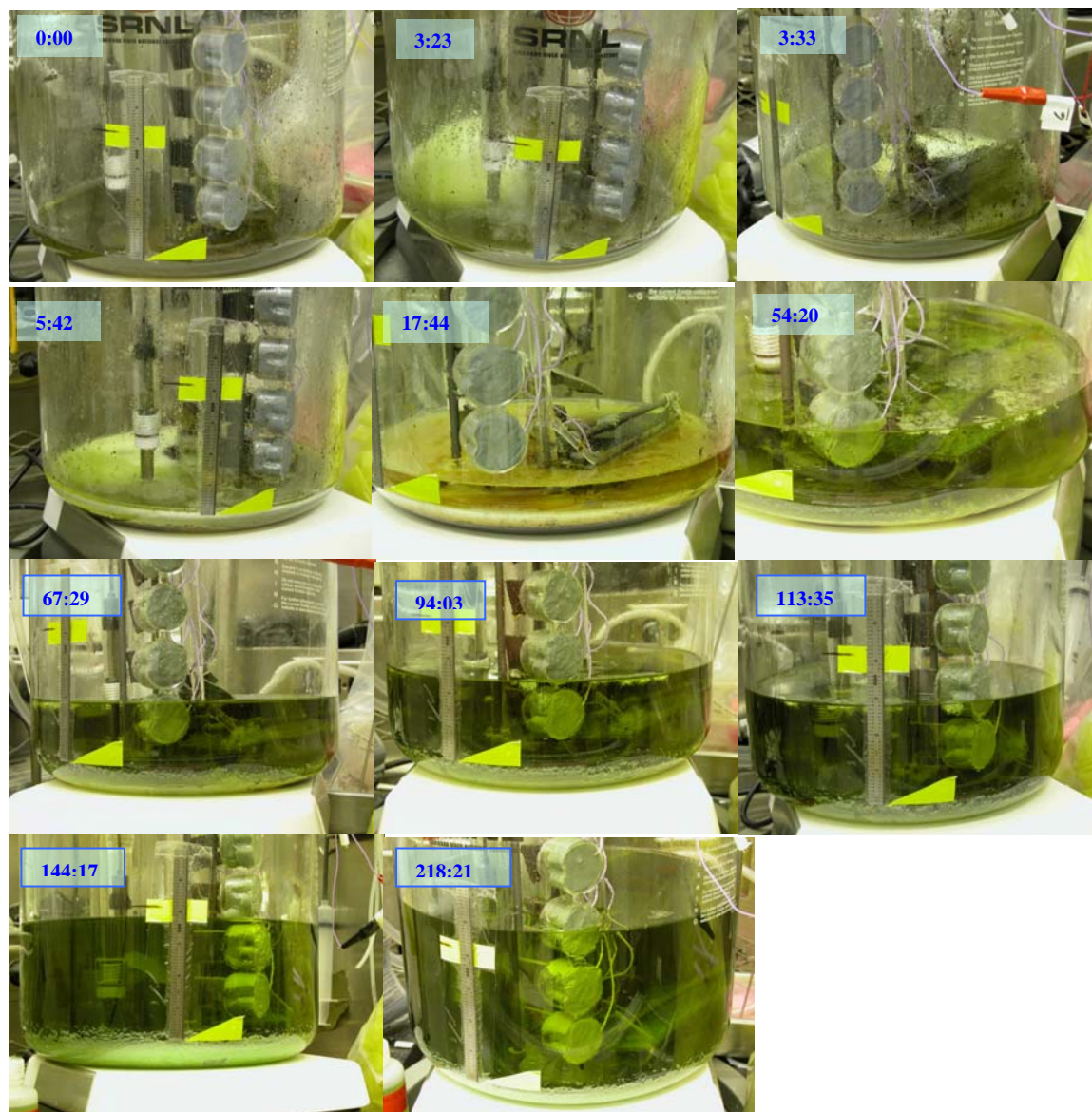
Figure 3. Stages of dissolution in Test 6 (25 °C, unmixed) from start of acid addition.
The highlighted block shows the time (in hours:minutes) since start of the experiment.

Figure 4 shows the daily samples taken during Test 5. The photo shows the color progression from the yellow/brown from the first sample (pH 12, leftmost photo), to the emerald green for the next two samples (pH 6 and 4 respectively). The remaining samples show the migration to a more olive green color (pH 1.5 and less).

Figure 4. Daily samples from Test 5 showing color progression of liquid from left to right.

After completion of oxalic acid addition, the Dissolution Vessel was allowed to stand for 50 hours and then a portion of the vessel contents was transferred to a second vessel containing 5 L of simulated Tank 7F supernate. The Dissolution Vessel contents were transferred at rates that approximately represent the highest available pumping rates of existing Tank 5F equipment.

As the transfer started from the Dissolution Vessel to the Receipt Vessel, the Dissolution Vessel material rapidly rose to the top of the liquid in the Receipt Vessel due to density difference. A brown layer formed on the surface of the Receipt Vessel as the neutralization resulted in the precipitation of the dissolved solids from the Dissolution Vessel solution. Eventually, a channel of the precipitated solids formed around the submerged transfer tube. These "floating" solids sank to the bottom of the vessel within several hours of formation. At the end of the transfer (17-18 hours) almost all of the solids were on the bottom of the vessel.

As the transfer continued, three distinct layers formed in the Receipt Vessel. The limited mixing and the different densities of the acid and Tank 7F simulated solution allowed the various layers to segregate. A layer of the material transferred from the Dissolution Vessel material started to accumulate. Soon, three distinct layers were observed in the Receipt Vessel; the lower supernate layer containing precipitate solids that eventually sank, a middle turbid zone, and an upper layer of the Dissolution Vessel acid. The pH was measured by sampling each layer during the tests. The pH of the lower layer (supernate) was typically +12, the pH of the turbid layer varied depending on the sample but was generally basic (pH 8-10), and the top layer had a low pH (~ 2) when the samples were taken immediately after the transfer was completed. Samples obtained from the top liquid layer 4-5 hours later had reached a pH of 7.

After the transfer from the Dissolution Vessel to the Receipt Vessel, the remaining contents of the Dissolution Vessel were mixed in an attempt to slurry the solids that formed in the dissolution tank. The mixer was increased in stages to 270 rpm, equivalent energy to a submersible mixer pump. The vessel was left to mix for two days. While a significant fraction of material had been suspended, there was also a significant portion of material stuck to the vessel walls and internals.

Actual Waste Tests

Following the oxalic acid contact with the Tank 5F sludge, personnel collected liquid and solid samples, which they analyzed for cations by ICPES and ICPMS. The analyses show significant

fractions of iron, uranium, aluminum, and manganese were dissolved by the oxalic acid. Some of the iron measured in the liquid was from sludge dissolution and some was from carbon coupon corrosion.

Following the chemical cleaning, oxalic acid was contacted with Tank 7F supernate solution. This "neutralization" process produced a large volume of solid particles (~ 2X the original sludge mass). The solid particles consisted of sodium oxalate, as well as iron, uranium, manganese, and aluminum. These precipitated solids appeared different (e.g., color, surface appearance) from the solids in the Tank 5F sludge sample.

The solids remaining from the Dissolution Vessel and the Receipt Vessel were digested by aqua regia and analyzed by ICP-ES for RCRA metals (Ag, Ba, Cd, Cr, and Pb) for disposal purposes and Al, Fe, Mn, Ni, and U for determining material balances. Additionally U concentration was determined by ICP-MS since the emission peak given off using ICP-ES for this particular element overlaps emission peaks and interferes with the detection of other desired elements. Material balances were completed for U, Fe, Mn, and Al to track the extent of dissolution of these elements in the Dissolution Vessel and the precipitation subsequent to transferring into the Receipt Vessel.

At the end of the oxalic acid addition to the Tank 5F sludge, a layer of whites solids with a slight blue color remained at the bottom of the glass (borosilicate glass (DOW 7740) containing silicon, aluminum, boron and sodium). A laser (785 nm) was focused on the solids and the Raman spectrometer detected two different spectra. The Raman spectra indicate the presence of sodium oxalate, iron oxalate and iron hydroxide. (Note that Fe and Mn oxalates are not easily discriminated by the Raman analysis. Hence, the reported iron oxalates may include Mn oxide. The same analytical limitation exists for the respective oxides.) In the same sample, the XRD (X-Ray Diffraction) indicates the presence of calcium oxalate. The products are consistent with the low solubility of iron and calcium in oxalic acid. The presence of sodium oxalate is due to the large concentration of sodium that exceeds the sodium solubility in oxalic acid. Temperature (25 °C to 75 °C) and mixing (no mixing) had no effect on the residues compositions.

In the 50 °C test, personnel added the oxalic acid filtrate to the simulated supernate over the course of a few minutes. This high rate of addition immediately caused the entire solution to become cloudy with precipitated solids throughout the reactor. During this rapid addition, only one liquid layer, with pH 14, resulted after the addition of the solution. In an attempt to make conditions more closely mimic planned operations, the 75 °C neutralization test used a specially modified peristaltic pump to add the oxalic acid filtrate at a slow rate that minimized mixing in the reactor. Two distinct liquid layers occurred during this addition as well as the formation of solids, similar to the behavior observed in the demonstrations with simulated waste. Some solids remained suspended in the liquid layers and collected near the interface of the two liquid layers as well as on the submersed stainless steel tubing used for adding the acid solution. The pH of the top layer measured 3 roughly corresponding to the starting acid filtrate. The pH of the lower layer measured 14 corresponding to the supernate solution. Five minutes after slowly swirling the reactor, the top layer remained pH 3. After continued gentle mixing to combine the liquid layers (i.e., complete the acid-base neutralization), solids remained suspended in the liquid. After standing 25 minutes, a liquid sample from near the top measured pH 8 and suspended

solids persisted. After 50 minutes, suspended solids continued to persist, and the pH remained 8. Technicians used a stir-bar for further agitation with the resultant well-mixed solution measuring pH 14.

Tank 5F Chemical Cleaning

Following the addition of oxalic acid to Tank 5F, SRS personnel mixed the tank for 5 days. After mixing, they transferred the liquid to Tank 7F, collected a sample of the Tank 5F liquid, mixed Tank 7F, and collected a sample of the Tank 7F liquid. Visual inspection and mapping of Tank 5F indicated that the solids volume decreased from 3453 gallons prior to oxalic acid addition to 2745 gallons after oxalic acid cleaning.

Analysis of the Tank 5F sample showed the pH to be 4 and the turbidity to be 134 NTU. The pH is higher than expected. This higher pH could lead to less effective sludge dissolution by the oxalic acid. Analysis of liquid samples showed significant amounts of iron, aluminum, uranium, and manganese.

The liquid analysis showed oxalate concentrations much lower than the amount of oxalic acid added to the tank. This result suggests that the oxalate exceeds its solubility in the Tank 5F liquid and is precipitating with species such as iron.
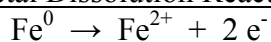
Analysis of the Tank 7F sample showed the pH to be 14, the free OH to be 1.5 Molar, and the turbidity to be 48 NTU.
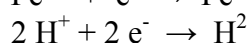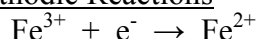
Gas Generation

During the simulant demonstration tests and actual waste tests, personnel purged the vapor space of the Dissolution Vessel with air and a helium tracer. Following its exit from the Dissolution Vessel, the vapor passed through a condenser and a chiller to remove water vapor. Following these processed steps, the vapor phase was analyzed with an online gas chromatograph (GC).

During simulant Tests $1 - 3$, the sum of the measured gases was less than 100%. The likely cause of this offset is carbon dioxide generation. During simulant Tests $4 - 6$ and the actual waste tests, the GC measured carbon dioxide. The generation of CO_2 from corrosion would require consumption of oxygen as indicated below.

- Metal Dissolution Reaction
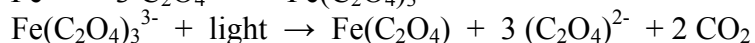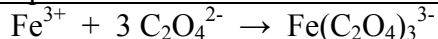 $$Fe^0 \rightarrow Fe^{2+} + 2\ e^-$$

- Cathodic Reactions
    $$Fe^{3+} + e^- \rightarrow Fe^{2+}$$
    $$2\ H^+ + 2\ e^- \rightarrow H^2$$

- Oxygen Consumption
    $$Fe^{2+} + \tfrac{1}{2}\ O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + H_2O$$

- Precipitation and Carbon Dioxide Generation

$$Fe^{3+} + 3\ C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-}$$
$$Fe(C_2O_4)_3^{3-} + light \rightarrow Fe(C_2O_4) + 3\ (C_2O_4)^{2-} + 2\ CO_2$$

In the simulant tests, more gas (carbon dioxide) was produced at 50 °C and 75 °C than at 25 °C. No significant difference is observed in the carbon dioxide produced between 50 °C and 75 °C tests. Good agreement in the amount of carbon dioxide produced is observed between the simulant and actual waste test at 50 °C.

Test 6 shows the gas generation during each of the tests. Since CO_2 productions accounts for most of the gas generated, we normalized the gas generation by the oxalic acid volume in the given test. After performing this normalization, the results agree within an order of magnitude. In the simulant tests, more gas (carbon dioxide) was produced at 50 °C and 75 °C than at 25 °C. No significant difference is observed in the carbon dioxide produce between the 50°C and 75 °C tests. Good agreement in the amount of carbon dioxide produced is observed between the simulant and actual waste test at 50 °C.

Table 6. Gas generation during chemical cleaning tests.

Test	Purge Gas (cm^3)	Gas Volume Generated per unit volume Oxalic Acid	H_2 Generation corrected for sludge (ft^3/kg)	H_2 Generation corrected for metal surface area (ft^3/ft^2)
Simulant: 50 °C, mixed	416,000	7.2	0.00023	0.00018
Simulant: 75 °C, mixed	246,000	11.4	0.00033	0.00028
Simulant: 25 °C, mixed	339,000	3.4	0.00028	0.00023
Simulant: 50 °C, unmixed	345,000	14.2	0.00120	0.00100
Simulant: 75 °C, unmixed	229,000	10.3	0.00050	0.00040
Simulant: 25 °C, unmixed	248,000	3.4	0.00061	0.00051
Actual 50 °C	233,000	13.8	0.00019	0.00007
Actual 75 °C	114,000	2.1	0.00005	0.00002

Table 6 shows the hydrogen generation during each of the tests. Since the hydrogen is produced by a reaction between the oxalic acid and the sludge and by a reaction between the oxalic acid and the metal coupons, we normalized the hydrogen generation rates by each of these parameters. When normalizing by sludge mass, the actual waste and simulant tests results agree well.

The hydrogen generation rates during the simulant tests were higher when the vessel was not mixed. We believe the lack of mixing reduce the transport of oxygen from the vapor space to the carbon steel coupons. The dissolved oxygen causes the corrosion process to form carbon dioxide rather than hydrogen.

SRS Tank Farm personnel used the worst case hydrogen generation rate and gas generation rate to perform the documented safety analysis (DSA) for this process and to design the supplemental

ventilation systems which were used to ensure the tanks were kept under vacuum for contamination control. During the oxalic acid addition and dissolution in Tank 5F, personnel have not observed much hydrogen generation or total gas generation.

Dissolution Efficiency and Kinetics

Table 7 shows the fraction of material dissolved during the tests and compares it with measurements from chemical cleaning in Tank 5F. The uranium dissolution in the simulant demo and the Tank Farm agrees well (~ 100%). The uranium dissolution in the actual waste test was less (~ 80%). The iron dissolution in the Tank Farm is significantly less than in the two demos. The manganese dissolution is approximately the same in all cases.

Table 7. Sludge Dissolution.

Test	Uranium	Iron	Manganese	Aluminum
Test 1 (50 °C w/mixing)	100%	99%	43%	
Test 2 (75 °C w/mixing)	99%	94%	24%	
Test 3 (25 °C w/mixing)	100%	99%	32%	
Test 4 (50 °C w/o /mixing)	99%	96%	33%	
Test 5 (75 °C w/o mixing)	99%	98%	37	
Test 6 (25 °C w/o mixing)	99%	100%	57%	
Actual waste 1	73%	62%	40%	84%
Actual Waste 2	87%	76%	59%	100%
Tank 5F	99.99%	15%	40%	78%

The Tank 5F sample collected had a pH of 4 following acid addition. The samples from the simulant and actual waste tests had a pH of 1 following acid addition. This higher pH in Tank 5F is a likely cause of the lower fraction of iron dissolved in that case. In addition, the Tank 5F sample contained a large fraction of oxalate that was not soluble. This oxalate likely precipitated with iron reducing the fraction in solution. Finally, the simulant and actual waste demos contained carbon steel coupons that corroded and produced iron.

CONCLUSIONS

- Oxalic acid addition proved effective in dissolving sludge heels in the simulant demonstration, the actual waste demonstration, and in SRS Tank 5F.
- The oxalic acid dissolved ~ 100 % of the uranium, ~ 100% of the iron, and ~ 40% of the manganese during a single contact in the simulant demonstration. (The iron dissolution may be high due to corrosion of carbon steel coupons.)
- The oxalic acid dissolved ~ 80% of the uranium, ~ 70% of the iron, ~ 50% of the manganese, and ~ 90% of the aluminum in the actual waste demonstration for a single contact.
- The oxalic acid dissolved ~ 100% of the uranium, ~ 15% of the iron, ~ 40% of the manganese, and ~ 80% of the aluminum in Tank 5F during the first contact cycle. Except for the iron, these results agree well with the demonstrations. The data suggest that a much larger fraction of the iron in the sludge dissolved, but it re-precipitated with the oxalate added to Tank 5F.
- The demonstrations produced large volumes (i.e., 2 – 14 gallons of gas/gallon of oxalic acid) of gas (primarily carbon dioxide) by the reaction of oxalic acid with sludge and carbon steel.
- The reaction of oxalic acid with carbon steel produced hydrogen in the simulant and actual waste demonstrations. The volume produced varied from 0.00002 – 0.00100 ft^3 hydrogen/ft^2 carbon steel. The hydrogen production proved higher in unmixed tanks than in mixed tanks.

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