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Removal of Sludge Heels in Savannah River Site Waste Tanks with *Oxalic* Acid

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The Savannah River Site (SRS) is preparing two tanks for closure. The first step in preparing the tank for closure is mechanical sludge removal. In mechanical sludge removal, a liquid such as inhibited water or salt solution is added to the tank, the liquid is mixed with the sludge to form a slurry, and the slurry is transported from the tank. Mechanical cleaning removes a large fraction of the sludge in the tank, but it leaves a sludge heel of several thousand gallons. SRS employs chemical cleaning to remove this sludge heel. In chemical cleaning, oxalic acid is added to the tank to dissolve the sludge, and the liquid, containing the dissolved sludge, is transported from the tank.

The authors conducted demonstrations of the chemical cleaning process with simulated SRS waste and actual SRS waste to assess the effectiveness of oxalic acid in dissolving SRS sludge. Following these demonstrations, SRS conducted chemical cleaning in two waste tanks (referred to as Tank A and Tank B). During chemical cleaning, the authors analyzed samples to assess the effectiveness of the chemical cleaning in removing the sludge heel.

The conclusions from this work follow. With the exception of iron, the dissolution of sludge components from Tank A agreed with results from the actual waste demonstration performed in 2007. The fraction of iron removed from Tank A by chemical cleaning was significantly less than the fraction removed in the SRNL demonstrations. The likely cause of this difference is the high pH following the first oxalic acid strike. The dissolution of sludge components from Tank B agreed with results from the actual waste demonstration performed in 2007. The fraction of plutonium removed from Tank B by chemical cleaning was slightly higher than the fraction removed in the SRNL demonstrations. Most of the sludge mass remaining in the tank is iron and nickel. The remaining sludge contains significant amounts of barium, chromium, and mercury. Most of the radioactivity remaining in the residual material is beta emitters and ^{90}Sr. The chemical cleaning removed a large fraction of the uranium, aluminum, calcium, sodium, strontium, and cesium. The chemical cleaning was not effective at removing nickel, mercury, plutonium, americium, and curium.

Keywords chemical cleaning; oxalic acid; sludge

INTRODUCTION

The Savannah River Site (SRS) is preparing two waste tanks,[1] Tank A and Tank B for closure. The first step in preparing the tank for closure is mechanical sludge removal. In mechanical sludge removal, personnel add liquid (e.g., inhibited water or supernate salt solution) to the tank to form a slurry. They then mix the liquid and sludge with pumps, and transfer the slurry to another tank for further processing. Mechanical sludge removal effectively removes the bulk of the sludge from a tank, but is not able to remove all of the sludge. In Tank A, a sludge heel of ~3,500 gallons remained after mechanical sludge removal. In Tank B, a sludge heel of ~6,000 gallons remained after mechanical sludge removal

SRS developed a process, Chemical Cleaning, to remove these sludge heels using oxalic acid. They developed a process based on testing (with simulated SRS sludge and actual SRS sludge) and modeling (1,2). The process adds oxalic acid to the tank, mixes the tank with pumps to promote sludge dissolution, and transfers the liquid, containing dissolved sludge components, to another tank for subsequent processing. The process utilizes multiple acid strikes and a water wash to remove residual oxalic acid from the tank. Following each acid/water addition, personnel collect liquid samples and analyze them for cations, anions, and radionuclides. Following the water wash, personnel collect solid samples and analyze them for cations and radionuclides.

This paper describes the simulant demonstration, the actual waste demonstration, and the chemical cleaning process in Tank A and B.

MATERIALS AND METHODS

Simulant Demonstration

Personnel performed simulant testing in the following manner. They prepared supernate simulant, sludge

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[1] In this paper, we refer to the tanks as Tank A and Tank B. Tank A and Tank B are not the actual names of the Tank. A third tank is referred to as Tank C.

simulant, and oxalic acid. They prepared the supernate to match the composition present in Tank A prior to chemical cleaning. Table 1 shows the supernate composition. The sodium hydroxide and aluminum nitrate are added first, and react to form sodium aluminate ($NaAlO_2$ or $NaAl(OH)_4$) and sodium nitrate. After that reaction is complete, the other compounds are added in order of increasing solubility. They vacuum filtered the simulant 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. Tanks A and B contain PUREX sludge. Table 3 shows the conditions for the tests conducted. They performed the tests at 25, 50, and 75°C.

Figure 1 shows the experimental setup for the simulant chemical cleaning test. The first three tests (Tests 1–3, respectively) occurred at 25°C, 50°C and 75°C. These tests included mixing when the vessel liquid height reached the agitator. The second set of tests, Tests 4–6, operated at the same temperatures (25°C, 50°C and 75°C, respectively) but with no mixing of the Dissolution Vessel. In the tests where mixing occurred, the mixing started ~48 hours after the start of oxalic acid addition.

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 A for the cleaning operations.

TABLE 1
Simulated supernate recipe

Component	Source	Molarity
NaOH	NaOH	1.09
$NaNO_3$	$NaNO_3$	0.63
$NaNO_2$	$NaNO_2$	0.61
$NaAlO_2$	$Al(NO_3)_3 \cdot 9H_2O$	0.20
Na_2SO_4	Na_2SO_4	0.098
Na_2CO_3	$Na_2CO_3 \cdot H_2O$	0.44
NaCl	NaCl	0.016
NaF	NaF	0.021
Na_2HPO_4	$Na_2HPO_4 \cdot 7H_2O$	0.0065
$Na_2C_2O_4$	$Na_2C_2O_4$	0.0052
Na_2SiO_3	$Na_2SiO_3 \cdot 9H_2O$	0.0026
Na_2MoO_4	$Na_2MoO_4 \cdot 2H_2O$	0.00013
KNO_3	KNO_3	0.015
CsCl	CsCl	0.00014

TABLE 2
Simulated Tank A sludge target composition (based on equilibrium calculations and waste characterization system values)

Component	wt%	Component	wt%
$Al(OH)_3$	11.3	$Pr(OH)_3$	0.15
$BaSO_4$	0.52	$SrCO_3$	0.06
$CaCO_3$	2.36	$UO_2(OH)_2$	17.3
CaF_2	0.14	Ag_2CO_3	0.21
$Fe(OH)_3$	44.5	$Ca(OH)_2$	1.37
HgO	0.15	$CePO_4 \cdot 2H_2O$	0.19
$La(OH)_3$	0.15	$Pu(OH)_4$	0.02
$Mg(OH)_2$	0.37	$Sr_5(PO_4)_3OH$	0.12
$Mn(OH)_2$	10.0	$ZnCr_2O_4$	0.59
$Ni(OH)_2$	10.0	ZrO_2	0.49

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 the planned duration of oxalic acid transfer for Tank A processing.

Initially, the sludge tank mixer remained inactive to mimic the lack of mixing in Tank A 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. The mixing conditions – i.e., impeller dimensions and rotational speed – were selected to provide comparable mixing energy (defined as power per unit volume) as expected in Tank A operations with a circulating pump.

Once the oxalic acid addition finished, the contact with the 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.

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	25	25	25	Yes
2	50	50	25	Yes
3	75	50	25	Yes
4	25	25	25	No
5	50	25	25	No
6	75	25	25	No

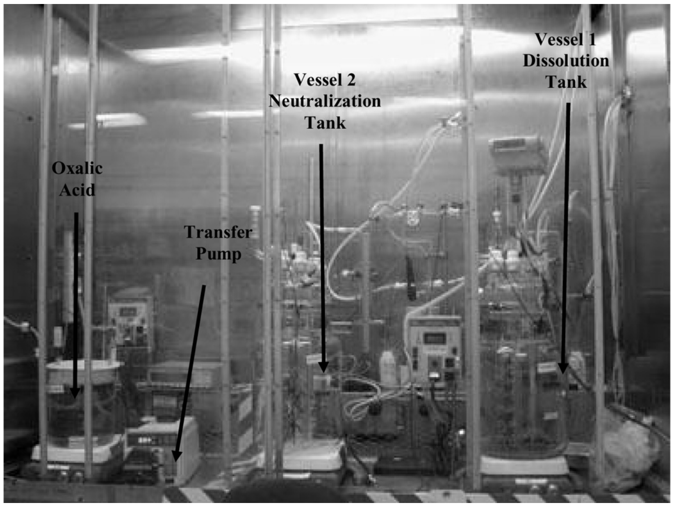

FIG. 1. Equipment for chemical cleaning (experimental) demonstrations.

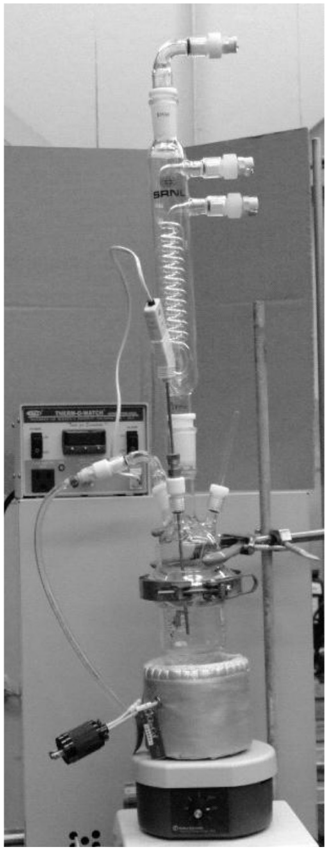

FIG. 2. Equipment for actual Tank A waste chemical cleaning test.

Actual Waste Demonstration

The actual waste tests occurred via remote handling in the Savannah River National Laboratory's (SRNL) Shielded Cells. Personnel used a sample of solids collected from Tank A and a sample of supernate from Tank C.

The reactors were constructed of glass (see Fig. 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. The reactor was heated using a heating mantle. The solution temperature was monitored throughout testing. The reactors were mixed with a stir bar rather than an impeller, so the mixing in these tests was less vigorous than in the simulant tests.

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 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% oxalic acid was used to rinse the residual sludge/supernate mixture from the container into the reactor before the addition of the remainder of the 145 mL of oxalic acid solution to the test reactor. Tests occurred at 50 and 75°C.

Tank A Chemical Cleaning

The Tank A chemical cleaning included two oxalic acid strikes, a spray wash, and a water wash. The cleaning did not wash the sludge prior to Oxalic Acid Strike 1.

The first oxalic acid strike used the following protocol. Personnel added 67,000 gallons of 8 wt% oxalic acid to Tank A. Following the oxalic acid addition, they added 43,000 gallons of well water. They mixed the contents of Tank A with two submersible mixer pumps (SMPs) for approximately four days. Following the mixing, they transferred 111,000 gallons of Tank A material to Tank C. The SMPs were operating at the start of the transfer and turned off when the liquid level dropped to a level that caused air to be entrained by the pumps. The transfer lasted approximately 13 hours, with the SMPs operating for the first 6 hours. Personnel collected a sample of the liquid from Tank A for analysis. Visual inspection of the tank following the transfer indicated that 2,700 gallons of slurry remained in the tank.

The second oxalic acid strike proceeded as follows. They added 33,000 gallons of 8 wt% oxalic acid to tank A. Following the acid addition, personnel visually inspected the tank and transferred 31,000 gallons of Tank A material to Tank C. They collected a sample of the liquid from Tank A for analysis. Visual inspection of the tank following the transfer indicated that 3,600 gallons of slurry remained in the tank. This volume of solids is larger than the volume of solids following mechanical sludge removal. The increase could be from insoluble oxalate solids or water contained in the slurry.

Following the oxalic acid strikes, SRS personnel performed spray washing to remove waste collected on internal structures, cooling coils, tank top internals, and tank walls. The acid spray wash was followed by a water spray wash to remove oxalic acid from the tank internals. They conducted the spray wash as follows. They added 5,000 gallons of 8 wt%oxalic acid to Tank A through the spray mast installed in Riser 7. They added 5,000 gallons of oxalic acid through Riser 2. They added 5,000 gallons of deionized water into the tank via Riser 2 and 5,000 gallons of deionized water into the tank via Riser 7. Following the spray wash, they visually inspected the tank and transferred 26,000 gallons of Tank A material to Tank C. They collected a sample of the liquid from Tank A for analysis.

Following the spray wash and transfer, SRS added 99,000 gallons of well water to Tank A. They mixed the tank contents with a single SMP and transferred the liquid from Tank A to Tank C. They collected a sample of the liquid from Tank A for analysis. Mapping of the tank following the transfer indicated that 3,300 gallons of solids remained in the tank.

Following the water wash, SRS collected a solid sample for analysis to assess the effectiveness of the chemical cleaning and to provide a preliminary indication of the composition of the material remaining in the tank.

Tank B Chemical Cleaning

SRS personnel conducted the first oxalic acid strike as follows. They added 111,000 gallons of 8 wt% oxalic acid to tank B. They mixed the contents of Tank B with two SMPs for approximately four days. Following the mixing, they transferred 116,000 gallons of Tank B material to Tank C. The SMPs were operating when the transfer started and were shut down approximately five hours after the transfer started. They collected a sample of the liquid from Tank B for analysis. Mapping of the tank following the transfer indicated that 2,400 gallons of solids remained in the tank.

They conducted the second oxalic acid strike as follows. They added 29,000 gallons of 8 wt% oxalic acid to tank B. Following the acid addition, they visually inspected the tank and transferred 32,000 gallons of Tank B material to Tank C. They collected a sample of the liquid from Tank B for analysis. Mapping of the tank following the transfer indicated that 3,200 gallons of solids remained in the tank.

Following the oxalic acid strikes, SRS performed spray washing to remove waste collected on internal structures, cooling coils, tank top internals, and tank walls. The acid spray wash was followed by a water spray wash to remove oxalic acid from the tank internals. They conducted the spray wash as follows. They added 5,000 gallons of oxalic acid to tank B through the spray mast installed in riser 2. They added 5,000 gallons of oxalic acid through riser 7. They added 5,000 gallons of deionized water into the tank via riser 2 and 5,000 gallons of deionized water into the tank via riser 7. Following the spray wash, they visually inspected the tank and transferred 22,000 gallons of Tank B material to Tank C. They collected a sample of the liquid from Tank B for analysis.

Following the spray wash and transfer, SRS added 114,000 gallons of well water to Tank B. They mixed the tank contents with a single SMP and transferred 113,000 gallons from Tank B to Tank C. They collected a sample of the liquid from Tank B for analysis. Mapping of the tank following the transfer indicated that 3,500 gallons of solids remained in the tank.

Following the water wash, SRS personnel collected a solid sample for analysis to assess the effectiveness of the chemical cleaning and to provide a preliminary indication of the composition of the material remaining in the tank.

SRNL analyzed liquid samples for pH using pH paper, for density gravimetrically, and for turbidity. Following these analyses, they filtered subsamples, diluted them to reduce the dose where necessary, and analyzed them for cations (by Inductively Coupled Plasma Emission Spectroscopy, ICPES), anions (by Ion Chromatography, IC), and radionuclides (by Inductively Coupled Plasma Mass Spectroscopy, ICPMS, liquid scintillation counting, gamma scan, plutonium thenoyl trifluoroacetone (PuTTA) scintillation, ^{90}Sr, ^{99}Tc, and Am/Cm methods).

SRNL analyzed solid samples as follows. They digested the samples by the aqua regia method and/or the peroxide fusion method. They analyzed them for cations (ICPES), anions (IC), mercury (by Cold Vapor Atomic Absorption, CVAA, spectroscopy), and radionuclides (ICPMS, liquid scintillation counting, gamma scan, PuTTA, ^{90}Sr, ^{99}Tc, and Am/Cm methods).

RESULTS

Demonstrations

Table 4 shows the fraction of material dissolved during the demonstrations. During the simulant demonstration, 99–100% of the uranium was dissolved. During the actual waste demonstration, 73–87% of the uranium was dissolved. The uranium dissolution in the actual waste demonstration was less than in the simulant demonstration. The authors analyzed the dissolution data with a statistical program (JMP®). The analysis showed the uranium dissolution in the actual waste demonstration was less than in the simulant demonstration. This difference could be due to differences between the simulant and the actual waste (i.e., differences between the chemical compounds in which the uranium and iron are present), or to differences in the rate at which the oxalic acid was added to the test vessel. In the simulant demonstration, the oxalic acid was added over seven days. In the actual waste demonstration, it was added as one batch.

During the simulant demonstration, 94–100% of the iron was dissolved. During the actual waste demonstration 62–76% of the iron was dissolved. The statistical analysis showed these differences are significant. The differences between the simulant and actual waste demonstrations could be due to differences between the simulant and actual waste or to differences in the rate at which the oxalic acid

TABLE 4
Sludge dissolution

Test	Uranium (%)	Iron (%)	Manganese (%)	Nickel (%)
Simulant Test 1 (25°C w/mixing)	100	99	32	0.2
Simulant Test 2 (50°C w/mixing)	100	99	43	0.6
Simulant Test 3 (75°C w/mixing)	99	94	24	0.06
Simulant Test 4 (25°C w/o mixing)	99	100	57	0.5
Simulant Test 5 (50°C w/o /mixing)	99	96	33	0.2
Simulant Test 6 (75°C w/o mixing)	99	98	37	2.0
Actual Waste 1 (50°C w/mixing)	73	62	40	0.1
Actual Waste 2 (75°C w/mixing)	87	76	59	0.1

was added to the test vessel. The iron in the simulant demonstration was added as iron (III) hydroxide. The iron in SRS sludge samples is primarily hematite and magnetite. Iron (III) hydroxide is more soluble in oxalic acid.

During the simulant demonstration, 24–57% of the manganese was dissolved. During the actual waste demonstration, 40–59% of the manganese was dissolved. The statistical analysis of the data does not show a statistically significant difference in the fraction of manganese dissolved between the simulant and actual waste tests. The data show that more manganese dissolved at 75°C in the actual waste demonstration than at 50°C. Similar results were observed with uranium and iron. This result could be from the increased temperature or from the change in addition method.

During the simulant and actual waste demonstrations, less than 2% of the nickel dissolved. There is good agreement between the simulant and actual waste demonstrations.

Tank Farm Chemical Cleaning

Tank A

Table 5 shows the measured pH and density of the liquid samples following the oxalic acid strikes, the Spray Wash, and the Water Wash in Tank A. The pH following Strike 1 was higher than expected (pH 4 versus pH 1 – 2 expected). This higher pH would reduce the solubility of metals, and therefore, the effectiveness of oxalic acid in dissolving sludge components.

Tables 6–9 show the measured composition of the liquid samples collected during chemical cleaning. Table 6 shows

TABLE 5
Density and pH of liquid samples

Analysis	Strike 1	Strike 2	Spray wash	Water wash
pH	4	2	3	3
Density (g/mL)	1.022 ± 0.004	1.040 ± 0.004	1.016 ± 0.004	0.993 ± 0.004

TABLE 6
Cation analysis of Tank A liquid samples

Species	Strike 1 (mg/L)	Strike 2 (mg/L)	Spray wash (mg/L)	Water wash (mg/L)
Al	644 ± 64.4	179 ± 18	118 ± 12	11 ± 1.1
Ba	6 ± 0.6	10 ± 1	5 ± 0.5	<1.3
Ca	178 ± 17.8	59.0 ± 5.9	28 ± 2.8	5 ± 0.5
Cr	16 ± 1.6	11 ± 1.1	9 ± 0.9	2 ± 0.2
Fe	3385 ± 339	3935 ± 394	3848 ± 385	289 ± 29
Li	9 ± 0.9	11 ± 1.1	11 ± 1.1	<2.7
Mg	15 ± 1.5	12 ± 1.2	9 ± 0.9	1 ± 0.1
Mn	1560 ± 156	708 ± 71	390 ± 39	109 ± 11
Na	3636 ± 364	1163 ± 116	404 ± 40	81 ± 8.1
Ni	30 ± 3.0	8 ± 0.8	9 ± 0.9	<4.4
Si	358 ± 35.8	89 ± 8.9	51 ± 5.1	<16
Sr	42 ± 4.2	11 ± 1.1	6 ± 0.6	<2.4
U	6784 ± 678	1550 ± 155	851 ± 85	218 ± 22
Zr	71 ± 7.1	104 ± 10	88 ± 8.8	2 ± 0.2

TABLE 7
Anion analysis of Tank A liquid samples

Species	Strike 1 (mg/L)	Strike 2 (mg/L)	Spray wash (mg/L)	Water wash (mg/L)
F^-	<380	<338	<328	<323
Formate	<380	<338	<328	<323
Cl^-	<380	<338	<328	<323
NO_3^-	<380	<338	<328	<323
PO_4^{2-}	912 ± 91	<338	<328	<323
PO_4^{2-}	<380	<338	<328	<323
SO_4^{2-}	<380	<338	<328	<323
Oxalate	22,800 ± 2,280	49,100 ± 4,910	24,000 ± 2,400	1,000 ± 100
Br^-	<380	<338	<328	<323
Expected oxalate	38,700	79,200	49,300	1,900

TABLE 8
ICPMS analysis of Tank A liquid samples

Species	Strike 1 (mg/L)	Strike 2 (mg/L)	Spray wash (mg/L)	Water wash (mg/L)
^{234}U	n.d.	<1.3	<1.6	<0.3
^{235}U	46 ± 4.6	9.1 ± 0.9	5.0 ± 0.5	2.7 ± 0.3
^{237}Np	2.3 ± 0.23	0.99 ± 0.1	<1.9	0.4 ± 0.04
^{238}U	6260 ± 626	1450 ± 140	760 ± 76	450 ± 45
^{239}Pu	1.4 ± 0.14	<1.02	<1.6	<0.2

n.d. = not detected.

the cation concentrations in the samples. With the exception of iron, the data show a significant decrease in the concentration of the major cations (Al, Ca, Mn, Na, Si, and U) in the liquid samples following Strike 2 compared to Strike 1. This decrease is likely due to the large fraction of these species being removed during Strike 1 and the small mass remaining in the tank. The iron concentration does not show this decrease in concentration in the Strike 2 sample. The persistent high iron concentration could be due to incomplete iron dissolution during Strike 1 or to carbon steel corrosion.

This incomplete dissolution could be due to the high pH following Strike 1 (pH 4). Xu and Gao investigated the dissolution of iron by oxalic acid and found the amount of iron dissolved decreased significantly (more than an order of magnitude) when the pH increased from 2 to 4 (3). Lee investigated the dissolution of iron oxide by oxalic acid and found the dissolution rate to decrease when the pH was greater than 2.5 (4).

The average measured corrosion rate in the simulant demonstration conducted at 50°C was 21 mpy (0.021 in/yr). Given a tank liquid volume of 431,300 L (42 inches), the carbon steel surface area is 11,520 ft^2 (5). Assuming the carbon steel has a density of 7.8 g/mL and contains 99% iron (6), the amount of iron that would dissolve from corrosion in one week is calculated with Eq. [1].

$$
\begin{aligned}
&(0.021\ \text{in/yr})(1\ \text{yr/52 wk})(1\text{wk})(11,520\ \text{ft}^2)(12\ \text{in/ft})^2 = 670\ \text{in}^3\\
&670\ \text{in}^3(2.54\ \text{cm/in})^3(1\ \text{L}/1000\ \text{cm}^3) = 11\ \text{L}\\
&11\ \text{L}(7.8\ \text{kg/L})(0.99) = 85\ \text{kg of iron from corrosion}\\
&85\ \text{kg}/431,300\ \text{L}(10^6\ \text{mg/kg}) = 197\ \text{mg Fe/L from corrosion}
\end{aligned}
\qquad [1]
$$

The concentration of iron that could be in the sample from corrosion is significantly less than the amount measured in the sample following Strike 1. Therefore, the likely cause of the high iron concentration in the Strike 2 sample is the high pH and incomplete iron dissolution following the addition of oxalic acid to Tank A in Strike 1, reducing the amount dissolved in Strike 1.

Comparing the composition of the liquid following the spray wash with the liquid following the second acid

TABLE 9
Radionuclide analysis of Tank A liquid samples

Species	Strike 1 (dpm/mL)	Strike 2 (dpm/mL)	Spray wash (dpm/mL)	Water wash (dpm/mL)
^{60}Co	$3.6 \times 10^5 \pm 3.8 \times 10^4$	$<1.2 \times 10^5$		$<8.3 \times 10^4$
^{90}Sr	$3.1 \times 10^9 \pm 3.2 \times 10^8$	$9.7 \times 10^8 \pm 7.1 \times 10^7$	$5.6 \times 10^8 \pm 4.1 \times 10^7$	$6.0 \times 10^7 \pm 5.2 \times 10^6$
^{99}Tc	$<3.8 \times 10^3$	$2.9 \times 10^2 \pm 5.0 \times 10^1$	$4.7 \times 10^2 \pm 1.2 \times 10^2$	$<1.0 \times 10^2$
^{137}Cs	$1.7 \times 10^8 \pm 1.6 \times 10^6$	$6.3 \times 10^7 \pm 7.9 \times 10^5$	$2.5 \times 10^7 \pm 1.3 \times 10^6$	$3.8 \times 10^6 \pm 1.1 \times 10^5$
Alpha	$<4.4 \times 10^7$	$<9.2 \times 10^6$	$<5.7 \times 10^5$	$<3.1 \times 10^5$
Nonvolatile beta	$2.0 \times 10^9 \pm 2.0 \times 10^8$	$2.0 \times 10^9 \pm 2.0 \times 10^8$	$9.6 \times 10^8 \pm 9.6 \times 10^7$	$1.3 \times 10^8 \pm 1.3 \times 10^7$
^{226}Ra	$<1.0 \times 10^7$			
^{239,240}Pu	$6.3 \times 10^4 \pm 3.8 \times 10^3$	$6.4 \times 10^4 \pm 4.9 \times 10^3$	$3.1 \times 10^4 \pm 2.7 \times 10^3$	$1.7 \times 10^3 \pm 3.9 \times 10^2$
^{238}Pu	$1.3 \times 10^4 \pm 8.9 \times 10^2$	$2.1 \times 10^4 \pm 2.3 \times 10^3$	$6.1 \times 10^3 \pm 1.7 \times 10^3$	$<2.4 \times 10^2$
^{241}Am	$7.5 \times 10^4 \pm 1.1 \times 10^4$	$<3.8 \times 10^5$	$<3.5 \times 10^4$	$<4.1 \times 10^5$
^{243}Am	$<6.6 \times 10^2$	$<1.5 \times 10^5$	$<3.4 \times 10^4$	$<1.2 \times 10^4$
^{242m}Am	$3.0 \times 10^2 \pm 7.5 \times 10^1$	$<2.0 \times 10^4$	$<3.7 \times 10^3$	$<2.1 \times 10^3$
^{243}Cm	$<2.4 \times 10^3$	$<4.6 \times 10^5$	$<1.3 \times 10^5$	$<1.9 \times 10^4$
^{245}Cm	$<2.0 \times 10^3$	$<3.7 \times 10^5$	$<1.1 \times 10^5$	$<1.6 \times 10^4$
^{247}Cm	$<3.4 \times 10^3$	$<7.5 \times 10^5$	$<2.2 \times 10^5$	$<2.5 \times 10^4$
^{249}Cf	$<3.6 \times 10^3$	$<8.3 \times 10^5$	$<2.4 \times 10^5$	$<2.6 \times 10^4$
^{251}Cf	$<1.9 \times 10^3$	$<4.4 \times 10^5$	$<1.2 \times 10^5$	$<1.7 \times 10^4$
^{242}Cm	$2.4 \times 10^2 \pm 6.2 \times 10^1$	$<1.7 \times 10^4$	$<3.1 \times 10^3$	$<1.7 \times 10^3$
^{244}Cm	$7.7 \times 10^3 \pm 1.1 \times 10^3$	$<1.6 \times 10^4$	$4.6 \times 10^3 \pm 1.5 \times 10^3$	$1.1 \times 10^4 \pm 4.9 \times 10^3$

strike shows a further decrease in the concentration of all of the major cations, except for iron. The iron concentration is approximately the same in the liquid following the Spray Wash and Strike 2. This result could be from the iron reaching its solubility limit. The concentration of the major species is significantly lower in the Water Wash sample than in the Spray Wash sample.

Table 7 shows the anion concentration in the samples. All of the anions are below the detection limit, except for nitrate and oxalate. The nitrate measured in the sample from Strike 1 is likely from the supernate heel remaining in Tank A prior to the addition of oxalic acid. Prior to chemical cleaning, the liquid in Tank A contained 0.852 M NO_3. If the initial sludge volume was 3500 gallons and the sludge was 50% supernate, the tank contained 5600 moles of NO_3^-. Since the volume of oxalic acid added was 431,000 L, the concentration of NO_3 from the heel would be 800 mg/L, which is very close to the measured value (912 mg/L).

The table includes the expected oxalate concentration based on the volume and concentration of oxalic acid added to the tank. The measured concentration is significantly less following Strike 1, Strike 2, and the Spray Wash. One possible explanation for this difference is the oxalate forming a precipitate with iron, as observed in the simulant chemical cleaning demonstration (2). In that test, researchers observed $FeC_2O_4{*}H_2O$ precipitate. A second plausible explanation, which would apply to Strike 1, is that the high pH (pH = 4) would decrease the oxalate solubility. A third explanation is nickel oxalate precipitation.

Table 8 shows the radionuclides measured by ICP-MS. The uranium concentration shows good agreement with the concentration measured by ICP-ES. The uranium concentration shows similar trends as the major cations measured by ICP-ES.

Table 9 shows the radionuclide concentrations in the samples. The largest contributors to radioactivity are ^{90}Sr (and beta) and ^{137}Cs. All other radionuclides are at least an order of magnitude lower. The concentrations of ^{90}Sr and ^{137}Cs in the Strike 2 sample are roughly one-third of the concentrations in the Strike 1 sample. The concentrations in the Spray Wash sample are approximately half of their value in the Strike 2 sample. The concentrations in the Water Wash sample show an additional decrease. The beta radioactivity in the Strike 1 sample is less than the ^{90}Sr activity. ^{90}Sr decays to ^{90}Y with a half-life of 28.78 years, and ^{90}Y decays with a half-life of 3 days. Since ^{90}Sr has a much longer half-life than ^{90}Y, after several ^{90}Y half-lives, their radioactivity will be the same. Therefore, the beta activity should be at least twice the ^{90}Sr activity. We are not sure of the cause of this discrepancy. The beta radioactivity is almost twice the ^{90}Sr activity in the samples from Strike 2, the Spray Wash, and the Water Wash.

The Process Sample contained ~70 wt% solids. Table 10 shows the concentration of cations in the Process Sample

TABLE 10
Cations analysis of Tank A process sample[c]

	Aqua regia		Peroxide fusion		Tank A
Species	Sample mg/kg	AD blank mg/kg	Sample Mg/kg	AD blank mg/kg	2006 sludge sample mg/kg
Al	1290	<67	<4150	<4190	14,400
Ba	1090	<5.4	991	<27	1,820
Ca	303	<16	[b]	[b]	3,470
Cr	[a]	[a]	1470	260	<1,100
Fe	177000	38	209000	844	373,000
Li	<156	<160	<794	<800	796
Mg	409	8.4	367	<20	<850
Mn	34600	<2.1	35200	<10	68,400
Na	1620	<160	[b]	[b]	42,600
Ni	83000	<73	88200	<366	44,500
Si	[a]	[a]	19100	14600	11,800
Sr	108	<80	<397	<400	1,500
U	<1560	<1600	<7940	<8000	100,000
Zr	1110	<4.5	[b]	[b]	3,910
Hg	1480		[b]	[b]	1,290

[a] Peroxide fusion better method for this species.
[b] Aqua regia better method for this species.
[c] Uncertainties are ±10%, except for Hg, which is ±20%.

TABLE 11
ICPMS analysis of Tank A process sample[a]

	Aqua regia		Peroxide fusion		Tank A
Species	Sample 1 mg/kg	AD blank mg/kg	Sample 1 mg/kg	AD blank mg/kg	2006 sludge sample mg/kg
^{235}U	10.4	<2	19.9	<5	598
^{237}Np	17.6	<2	24.2	<5	
^{238}U	1320.0	6	2200	7.81	95,500
^{239}Pu	113.0	<4	117	<10	
^{234}U	<5.9	<6	<14.9	<15	7.51

[a] Uncertainties are ±20%.

collected following chemical cleaning in Tank A. The table shows the composition of a Tank A sludge sample collected in 2006 before chemical cleaning for comparison (1). Since that sample was collected prior to mechanical sludge removal, it may not represent the composition of the sludge prior to chemical cleaning. The process sample shows reduced concentrations of all species, except nickel, silicon, chromium, and mercury. The nickel concentration shows an increase of ~2X, and the mercury concentration shows an increase of ~15%. The aluminum calcium, sodium, strontium, and uranium concentrations in the Process Sample are less than 10% of their values in the sample collected before chemical cleaning.

Previous SRNL testing of the chemical cleaning process showed minimal (~1%) dissolution of nickel (1,2). In addition, work by Garcia-Clavel et al. showed the reaction of nickel compounds with oxalic acid formed $NiC_2O_4{*}2H_2O$ (7). The increase in Ni observed is from the decrease in the amount of sludge remaining. Assuming no change in the mass of nickel in the sludge, a 2X increase in nickel concentration results from a 50% decrease in the sludge mass.

Table 11 shows the concentration of select uranium, neptunium, and plutonium isotopes measured by ICP-MS. The sum of the concentrations of the uranium isotopes (1340 mg/kg and 2230 mg/kg) is consistent with the uranium concentration measured by ICP-ES (<1560 mg/kg and <8000 mg/kg). The data show that the uranium concentration in the Process Sample is significantly less than the measured concentration in the Tank A sludge prior to chemical cleaning, indicating good removal of uranium by chemical cleaning.

Table 12 shows the concentration of radionuclides in the process sample collected following chemical cleaning in

TABLE 12
Radionuclide analysis of Tank A process sample

	Aqua regia		Peroxide fusion		
Species	Sample mCi/kg	Blank dpm/g	Sample dpm/g	Blank dpm/g	Tank A 2006 sample dpm/g
^{60}Co	10.9 ± 0.5	<0.262	11.0 ± 0.55	<0.255	14.1
^{90}Sr	5818 ± 490	<7.05	5455 ± 450	<7.50	36,800
^{99}Tc	<0.002	<0.002	<0.002	<0.002	0.013
^{137}Cs	48.6 ± 2.4	<0.258	35.1 ± 1.8	0.577 ± 0.080	1,050
Alpha	<104	<3.68	<104	<3.66	590
nonvolatile beta	9409 ± 940	<9.00	8591 ± 859	10.7 ± 3.7	n.m.
$^{239+240}$Pu	10.4 ± 0.5	<0.023	10.7 ± 0.54	<0.097	8.64
^{238}Pu	2.68 ± 0.14	0.027 ± 0.01	2.88 ± 0.15	0.126 ± 0.017	1.95
^{241}Am	68.2 ± 3.4	1.01 ± 0.02	64.1 ± 3.2	<1.04	50.0
^{243}Am	1.69 ± 0.20	<0.046	1.58 ± 0.18	0.179 ± 0.048	0.336
^{242m}Am	0.145 ± 0.023	0.001 ± 0.0006	0.191 ± 0.03	<0.001	0.146
^{243}Cm	<0.292	<0.955	<0.486	<0.076	n.m.
^{245}Cm	<0.632	<0.242	<0.459	<0.095	n.m.
^{247}Cm	<0.269	<0.035	<0.116	<0.020	n.m.
^{249}Cf	<0.264	<0.038	<0.124	<0.024	n.m.
^{251}Cf	<0.189	<0.062	<0.192	<0.026	n.m.
^{242}Cm	0.120 ± 0.019	0.0004 ± 0.0002	0.158 ± 0.025	<0.001	0.123
^{244}Cm	3.44 ± 0.05	0.014 ± 0.0063	4.82 ± 0.73	<0.053	3.86
^{241}Pu	12.7 ± 2.6	<0.011	13.2 ± 1.9	<0.020	8.18
^{154}Eu	30.9 ± 1.5	<0.269	29.4 ± 1.5	<0.273	n.m.
^{155}Eu	4.64 ± 0.65	<0.500	5.05 ± 0.68	<0.509	n.m.

n.m. = not measured.

TABLE 13
Density and pH of Tank B liquid samples

Analysis	Strike 1	Strike 2	Spray wash	Water wash
pH	2	2	3	7
Density (g/mL)	1.100 ± 0.005	1.035 ± 0.007	0.996 ± 0.003	1.051 ± 0.001

Tank A. The table shows the composition of a Tank A sludge sample collected before chemical cleaning for comparison. The data show the concentrations of ^{90}Sr and ^{137}Cs to be significantly less (15% and 4%, respectively) than their concentrations in the 2006 sample. The concentrations of ^{60}Co, ^{99}Tc, and alpha show a decrease, but the decrease is not as large. The concentrations of plutonium, americium, and curium are higher in the Process Sample than in the 2006 sample, indicating poor removal.

Tank B

Table 13 shows the measured pH and density of the liquid samples following the oxalic acid strikes, the spray wash, and the water wash in Tank B. The pH following Strike 1 is 2, which agrees with the measured pH following acid addition in the demonstrations ($pH = 1 - 2$) (1,2). The pH following Strike 1 is lower than the pH following Strike 1 in Tank A, which should lead to better sludge removal.

TABLE 14
Cation analysis of Tank B liquid samples

Species	Strike 1 (mg/L)	Strike 2 (mg/L)	Spray wash	Water wash (mg/L)
Al	1031 ± 103	185 ± 18	176 ± 18	21.4 ± 2.1
Ba	11 ± 1.1	5.1 ± 0.5	3.0 ± 0.3	<3.8
Ca	270 ± 27	59 ± 5.9	33 ± 3.3	4.49 ± 0.45
Cr	16 ± 1.6	4.6 ± 0.46	4.6 ± 0.5	<3.66
Fe	11745 ± 1175	2450 ± 245	2864 ± 286	210 ± 21
K	21 ± 2.1	<15	<11	<16.7
La	15 ± 1.5	<2.9	<2.1	<0.813
Li	68 ± 6.8	16.8 ± 1.7	11.6 ± 1.2	<3.20
Mg	34 ± 3.4	9.1 ± 0.9	9.5 ± 1.0	1.69 ± 0.17
Mn	593 ± 59	100 ± 10	85 ± 8.5	25.1 ± 2.5
Na	3000 ± 300	918 ± 92	804 ± 80	644 ± 64
Ni	50 ± 5	7.6 ± 0.76	5.8 ± 0.6	<6.16
P	60 ± 6	11.6 ± 1.2	<21	<14.7
Pb	18 ± 1.8	6.9 ± 0.7	7.6 ± 0.8	<9.28
S	79 ± 7.9	88 ± 8.8	<621	<182
Si	271 ± 27	41 ± 4.1	27 ± 2.7	36.7 ± 3.7
Sr	34 ± 3.4	6.1 ± 0.61	4.1 ± 0.4	<0.73
Ti	9.5 ± 0.95	2.3 ± 0.23	4.4 ± 0.4	<0.816
U	4943 ± 494	1231 ± 123	1426 ± 143	887 ± 89
Zn	3 ± 0.3	<2.2	<1.1	<0.719
Zr	200 ± 20	27.3 ± 2.7	22.6 ± 2.3	1.9 ± 0.2

TABLE 15
Anion analysis of Tank B liquid samples

Species	Strike 1 (mg/L)	Strike 2 (mg/L)	Spray wash (mg/L)	Water wash (mg/L)
F^-	<702	<325	<328	<334
Formate	<702	<325	<328	<334
Cl^-	<702	<325	<328	<334
NO_2^-	<702	<325	<328	<334
NO_3^-	<702	<325	<328	<334
PO_4^{2-}	<702	<325	<328	<334
SO_4^{2-}	<702	<325	<328	<334
Oxalate	44,363 ± 4,436	51,000 ± 5100	24,600 ± 2460	1884 ± 188
Br^-	<702	<325	<328	<331
Oxalate expected	79,200	79,200	42,200	1,760

Table 14–17 show the measured composition of liquid samples collected during chemical cleaning.

Table 14 shows the cation concentrations in the samples. The data show a significant decrease in the concentration of the major cations (Al, Ca, Fe, Mn, Na, Si, and U) in Strike 2 compared to Strike 1. The likely cause of this result is the removal of the cations during Strike 1. Comparing the composition of the liquid following the spray wash with the liquid following the 2nd acid strike shows approximately the same concentration of all of the major cations. The concentration of the major species is significantly lower in the water wash sample than in the spray wash sample. This result is likely due to the removal of the metals in the acid strikes and spray wash and to the higher pH during the water wash.

The iron measured in the samples could be from sludge dissolution or from carbon steel corrosion. The average measured corrosion rate in the simulant demonstration conducted at 50°C was 21 mpy (0.021 in/yr) (2). Given a tank liquid volume of 419,000 L (41 inches), the carbon steel surface area is 11,460 ft^2 (5). Assuming the carbon steel has a density of 7.8 g/mL and contains 99% iron (8), the amount of iron that would dissolve from corrosion

TABLE 16
ICPMS analysis of Tank B liquid sample

Species	Strike 1 (mg/L)	Strike 2 (mg/L)	Spray wash (mg/L)	Water wash (mg/L)
^{234}U	<5	<5	<5	<5
^{235}U	21.0 ± 2.1	5.6	6.8 ± 0.7	3.56 ± 0.71
^{237}Np	<0.7	<0.48	<2	<0.406
^{238}U	4776 ± 478	1132	1340 ± 134	905 ± 181
^{239}Pu	0.9 ± 0.09	<0.9	<1.6	<0.676

TABLE 17
Radionuclide analysis of Tank B liquid samples

Species	Strike 1 (dpm/mL)	Strike 2 (dpm/mL)	Spray wash (dpm/mL)	Water wash (dpm/mL)
^{60}Co	$<1.6 \times 10^5$	$<1.6 \times 10^5$	*	$<7.78 \times 10^4$
^{90}Sr	$2.3 \times 10^9 \pm 2.4 \times 10^8$	$5.6 \times 10^8 \pm 3.9 \times 10^7$	$3.3 \times 10^8 \pm 2.6 \times 10^7$	$2.05 \times 10^7 \pm 4.11 \times 10^4$
^{99}Tc	$<2.5 \times 10^3$	$2.0 \times 10^2 \pm 4.6 \times 10^1$	$4.0 \times 10^2 \pm 7.6 \times 10^1$	$<4.23 \times 10^2$
^{137}Cs–	$5.5 \times 10^7 \pm 7.3 \times 10^5$	$1.6 \times 10^7 \pm 2.8 \times 10^5$	$9.9 \times 10^6 \pm 5.0 \times 10^5$	$4.31\text{x } 10^6 \pm 2.15 \times 10^3$
Alpha	$<4.7 \times 10^7$	$<4.6 \times 10^6$	$<5.5 \times 10^5$	$<3.28 \times 10^5$
Nonvolatile beta	$1.7 \times 10^9 \pm 1.7 \times 10^7$	$1.2 \times 10^9 \pm 1.2 \times 10^8$	$6.9 \times 10^8 \pm 6.9 \times 10^7$	$6.33 \times 10^7 \pm 6.33 \times 10^4$
^{238}Pu	$1.1 \times 10^5 \pm 7.6 \times 10^3$	$1.1 \times 10^4 \pm 1.6 \times 10^3$	$1.1 \times 10^4 \pm 1.5 \times 10^3$	$2.73 \times 10^3 \pm 1.46 \times 10^2$
$^{239/240}$Pu	$1.4 \times 10^5 \pm 9.9 \times 10^3$	$1.8 \times 10^4 \pm 1.9 \times 10^3$	$1.5 \times 10^4 \pm 1.8 \times 10^3$	$3.53 \times 10^3 \pm 1.80 \times 10^2$
^{241}Am	$1.2 \times 10^6 \pm 1.9 \times 10^5$	$<1.5 \times 10^5$	$<2.2 \times 10^4$	$5.58 \times 10^3 \pm 9.44 \times 10^2$
^{243}Am	$2.1 \times 10^4 \pm 4.4 \times 10^3$	$<2.1 \times 10^5$	$<9.6 \times 10^3$	<84.7
^{242m}Am	$2.1 \times 10^3 \pm 6.1 \times 10^2$	$<6.4 \times 10^3$	$<3.5 \times 10^2$	<18.0
^{243}Cm	$<1.6 \times 10^4$	$<6.7 \times 10^5$	$<3.2 \times 10^4$	$<2.46 \times 10^2$
^{245}Cm	$<1.6 \times 10^4$	$<5.5 \times 10^5$	$<2.6 \times 10^4$	$<3.13 \times 10^2$
^{247}Cm	$<7.0 \times 10^3$	$<1.2 \times 10^6$	$<4.5 \times 10^4$	$<3.13 \times 10^2$
^{249}Cf	$<7.2 \times 10^3$	$<1.3 \times 10^6$	$<4.8 \times 10^4$	$<3.49 \times 10^2$
^{251}Cf	$<4.1 \times 10^3$	$<6.6 \times 10^5$	$<2.9 \times 10^4$	$<2.34 \times 10^2$
^{242}Cm	$1.7 \times 10^3 \pm 4.7 \times 10^2$	$<5.3 \times 10^3$	$<2.9 \times 10^2$	<14.9
^{244}Cm	$1.2 \times 10^6 \pm 1.7 \times 10^2$	$<1.7 \times 10^5$	$7.2 \times 10^3 \pm 2.1 \times 10^3$	$9.51 \times 10^2 \pm 2.69 \times 10^2$

*Species not detected.

in one week is calculated with Eq. [2].

$$\begin{aligned}
&(0.021\ \text{in/yr})(1\ \text{yr}/52\ \text{wk})(1\text{wk})(11{,}520\ \text{ft}^2)(12\ \text{in/ft})^2 = 670\ \text{in}^3 \\
&670\ \text{in}^3(2.54\ \text{cm/in})^3(1\ \text{L}/1000\ \text{cm}^3) = 11\ \text{L} \\
&11\ \text{L}(7.8\ \text{kg/L})(0.99) = 85\ \text{kg of iron from corrosion} \\
&85\ \text{kg}/431{,}300\ \text{L}(10^6\ \text{mg/kg}) = 203\ \text{mg Fe/L from corrosion}
\end{aligned} \qquad [2]$$

The concentration of iron that could be in the sample from corrosion is significantly less than the amount measured in the samples following Strike 1, Strike 2, and the Spray Wash. The measured iron concentration in the water wash sample is approximately the same as the concentration calculated in Eq. [1], but the pH of the water wash sample (7) would reduce the corrosion rate.

Table 15 shows the anion concentration in the samples. All of the anions are below the detection limit, except for oxalate. The table includes the expected oxalate concentration based on the volume and concentration of oxalic acid added to the tank. The measured concentration is significantly less following Strike 1, Strike 2, and the Spray Wash.

One possible explanation for this difference is the oxalate forming $FeC_2O_4{*}H_2O$ precipitate. Analysis of Tank B solid samples by X-Ray Diffraction (XRD) showed the dominant compounds in the solid to be hematite, maghemite, nickel oxalate hydrate, and goethite. Hematite and maghemite are iron oxides, and goethite is an iron oxyhydroxide. Therefore, iron oxalate hydrate is not likely to be the cause of the "missing oxalate". Nickel oxalate precipitation could be an explanation.

Table 16 shows the radionuclides measured by ICP-MS. The uranium concentration shows good agreement with the concentration measured by ICP-ES.

TABLE 18
Cations analysis of Tank B process sample[c]

	Aqua regia		Peroxide fusion	
Species	Sample mg/kg	AD blank mg/kg	Sample mg/kg	AD blank mg/kg
Al	3300	<298	3980	<862
Ba	1860	<24	1338	<29
Ca	446	<89	[b]	[b]
Cr	[a]	[a]	535	<431
Fe	166,667	230,000	121,000	2,900
Li	344	<169	<643	<647
Mg	579	<71	415	<22
Mn	23,700	<984	16,700	<37
Na	1,800	<357	[b]	[b]
Ni	104,000	<115	81,000	<138
Si	[a]	[a]	1600	<226
Sr	72	<4	55	<10
U	<2470	<2050	<2507	<2500
Zr	770	<28	[b]	[b]
Hg	7040	18.5	[b]	[b]

[a] Peroxide fusion better method for this species.
[b] Aqua regia better method for this species.
[c] Uncertainty is ±10%, except for Hg which is ±20%.

TABLE 19
ICPMS analysis of Tank B process sample[a]

	Aqua regia		Peroxide fusion	
Species	Sample mg/kg	AD blank mg/kg	Sample mg/kg	AD blank mg/kg
^{235}U	10	<5	8	<5
^{237}Np	9	<5	6	<5
^{238}U	2713	<31	1725	<31
^{239}Pu	74	<9	49	<9
^{234}U	<5	<5	<5	<5

[a] uncertainty is ±20%.

Table 17 shows the radionuclide concentrations in the samples. The largest contributors to radioactivity are ^{90}Sr (and beta) and ^{137}Cs. All other radionuclides are at least an order of magnitude lower. The concentrations of ^{90}Sr and ^{137}Cs in the Strike 2 sample are $1/3 - 1/5$ of the concentrations in the Strike 1 sample. The concentrations in the spray wash sample are $\frac{1}{2}$ of their value in the Strike 2 sample. The concentrations in the water wash sample show an additional decrease. The beta radioactivity in the Strike 1 sample is less than the ^{90}Sr activity. We are unsure of the cause of this discrepancy. The beta radioactivity is approximately twice the ^{90}Sr activity in the samples from Strike 2, the Spray Wash, and the Water Wash.

The process sample contained approximately 70 wt% solids. Table 18 shows the concentration of cations in the process sample collected following chemical cleaning in Tank B. The largest contributors to the sludge mass remaining in Tank B are iron and nickel.

Table 19 shows the concentration of select uranium, neptunium, and plutonium isotopes measured by ICP-MS. The sum of the concentrations of the uranium isotopes (2728 mg/kg by Aqua Regia and 1738 mg/kg by peroxide fusion) is consistent with the uranium concentration measured by ICP-ES (<2470 mg/kg by Aqua Regia and <2507 mg/kg by peroxide fusion).

Table 20 shows the concentration of radionuclides in the process sample collected following chemical cleaning in Tank B. The largest contributors to radioactivity remaining in Tank B (excluding total alpha and total beta) are ^{90}Sr, ^{137}Cs, ^{241}Am, and ^{244}Cm.

TABLE 20
Radionuclide analysis of Tank B process sample

	Aqua regia		Peroxide fusion	
Species	Sample mCi/kg	AD blank mCi/kg	Sample mCi/kg	AD blank mCi/kg
^{60}Co	26.4 ± 0.8	<1.1	17.7 ± 0.5	0.59
^{90}Sr	3091 ± 168	<186	2545 ± 141	<100
^{99}Tc	0.068 ± 0.003	0.0091 ± 0.0023	0.033 ± 0.0015	<0.0033
^{137}Cs	81.8 ± 2.3	<1.18	63.6 ± 1.8	<0.55
Alpha	<450	<20.9	<323	<10.5
nonvolatile beta	7700 ± 450	<45.5	5455 ± 314	<22.7
$^{239/240}$Pu	8.18 ± 0.26	<0.28	5.45 ± 0.17	<0.023
^{238}Pu	6.36 ± 0.20	<0.10	4.14 ± 0.13	0.039
^{241}Am	159 ± 7	<0.15	100 ± 3.1	<0.10
^{243}Am	2.5 ± 0.2	<0.10	1.68 ± 0.12	0.039 ± 0.012
^{242m}Am	0.21 ± 0.04	<0.021	0.18 ± 0.023	<0.002
^{243}Cm	<1.5	<0.73	<0.864	<0.10
^{245}Cm	<1.1	<0.59	<0.546	<0.086
^{247}Cm	<0.31	<0.24	<0.155	<0.064
^{249}Cf	<0.32	<0.25	<0.159	<0.064
^{251}Cf	<0.25	<0.21	<0.114	<0.11
^{242}Cm	0.18 ± 0.03	<0.017	0.146 ± 0.019	<0.0017
^{244}Cm	155 ± 14	0.10 ± 0.031	2105 ± 9.1	0.10 ± 0.017
^{241}Pu	16.8 ± 2.5	<0.041	8.18 ± 1.18	<0.042
^{154}Eu	45.5 ± 1.3	<1.23	32.3 ± 0.91	<0.59
^{155}Eu	10.5 ± 0.9	<2.23	8.18 ± 0.73	<1.14
^{94}Nb	<1.5	<0.91	<0.77	<0.45
^{134}Cs	<1.5	<1.00	<0.82	<0.50

Table 21 shows the analysis of the free liquid collected from the process sample. The table shows the composition of the wash water sample for comparison. Since no material was added to the tank after the wash water sample was collected, the composition of the two samples should be the same. The anion concentrations, except for oxalate, are consistent and less than the detection limit. The oxalate concentration in the process sample liquid is approximately 1/3 the concentration in the wash water sample. The same ratio between concentrations is observed in the radionuclides measured by ICPMS. The concentrations of ^{137}Cs, $^{239/240}$Pu, ^{241}Am· ^{243}Am, and ^{244}Cm are higher (by ~2X) in the process sample. The concentrations of ^{90}Sr and beta are higher in the wash water sample (by ~2X). These differences are larger than the uncertainties in the measurements. We are uncertain of the reason for these differences.

TABLE 21
Analysis of free liquid collected from process sample

Species	Tank B process sample (mg/L)	Tank B water wash sample (mg/L)
F	<466	<334
Formate	<466	<334
Cl	<466	<334
NO2	<466	<334
NO3	<466	<334
PO4	<466	<334
SO4	<466	<334
Oxalate	596	1884
Hg	2.33 ± 0.47	n.m.
Br	<466	<334
U-235	1.1 ± 0.22	3.56 ± 0.71
Np-237	0.1 ± 0.02	<0.406
U-238	248.0 ± 50	905 ± 180
Pu-239	<0.1	<0.676
U-234	<0.075	
	(dpm/mL)	(dpm/mL)
^{90}Sr	$1.1 \times 10^7 \pm 1.2 \times 10^6$	$2.1 \times 10^7 \pm 4.1 \times 10^4$
^{99}Tc	$<2.2 \times 10^2$	$<4.2 \times 10^2$
^{137}Cs	$7.0 \times 10^6 \pm 3.5 \times 10^5$	$4.310^6 \pm 2.2 \times 10^3$
Alpha	$<2.7 \times 10^6$	$<3.3 \times 10^5$
nonvolatile beta	$3.5 \times 10^7 \pm 3.5 \times 10^6$	$6.3 \times 10^7 \pm 6.3 \times 10^4$
$^{239/240}$Pu	$7.3 \times 10^3 \pm 2.6 \times 10^3$	$3.5 \times 10^3 \pm 1.8 \times 10^2$
^{238}Pu	$<1.6 \times 10^3$	$2.7 \times 10^3 \pm 1.5 \times 10^2$
^{241}Am	$1.3 \times 10^4 \pm 2.0 \times 10^3$	$5.6 \times 10^3 \pm 9.4 \times 10^2$
^{243}Am	$3.8 \times 10^3 \pm 6.8 \times 10^2$	<84.7
^{242m}Am	$<1.8 \times 10^1$	<18.0
^{243}Cm	$<3.0 \times 10^3$	$<2.5 \times 10^2$
245Cm	$<2.4 \times 10^3$	$<3.1 \times 10^2$
^{247}Cm	$<4.7 \times 10^3$	$<3.1 \times 10^2$
^{249}Cf	$<4.4 \times 10^3$	$<3.5 \times 10^2$
^{251}Cf	$<2.2 \times 10^3$	$<2.3 \times 10^2$
^{242}Cm	$<1.5 \times 10^1$	<14.9
^{244}Cm	$1.1 \times 10^4 \pm 2.8 \times 10^3$	$9.5 \times 10^2 \pm 2.7 \times 10^2$
^{241}Pu	$<1.6 \times 10^4$	n.m.

n.m. = not measured.

MASS BALANCE

Tank A

The authors performed a mass balance of the radionuclides and nonradionuclides measured in the cleaning samples and process sample. Equation [3] describes the mass balance.

$$\text{initial amount} = \text{amount removed} + \text{amount remaining}$$

$$V_i x_i = V_1 x_1 + V_2 x_2 + V_{spray} x_{spray} + V_{water} x_{water} + V_{proc-sol} x_{proc-sol} + V_{proc-liq} x_{proc-liq} \quad [3]$$

where V_i is the initial volume of sludge in the tank, x_i is the initial concentration of the component in the sludge, V_1 is the volume of material removed from the tank following Acid Strike 1, x_1 is the concentration in the liquid sample following Strike 1, V_2 is the volume of material removed from the tank following Strike 2, x_2 is the concentration in the liquid sample following Strike 2, V_{spray} is the volume of material removed from the tank following the spray wash, x_{spray} is the concentration in the liquid sample following the spray wash, V_{water} is the volume of material removed from the tank following the water wash, x_{water} is the concentration in the liquid sample following the water wash, $V_{proc\text{-}sol}$ is the volume of sludge remaining in the tank following the water wash, $x_{proc\text{-}sol}$ is the concentration in the sludge process sample, $V_{proc\text{-}liq}$ is the volume of liquid remaining in the tank following the water wash, $x_{proc\text{-}liq}$ is the concentration in the liquid remaining in the tank following the water wash (assumed equal to the concentration in the water wash sample). The initial concentration of the component in the sludge (x_i) is unknown. Equation [2] can be solved to determine x_i. Table 22 shows the volumes of sludge and liquid used to perform the mass balance.

Table 23 shows the amount of each component removed during the acid strikes and washes, as well as the amount

TABLE 22
Volumes of sludge and liquid in Tank A during chemical cleaning

V_1	431,300 L
V_2	93,700 L
V_{spray}	87,000 L
V_{water}	400,000 L
$V_{proc\text{-}sol}$	12,491 L
$V_{proc\text{-}liq}$	30,800 L

remaining in the sludge and liquid. The data show a significant decrease (<10%) in the amount of ^{90}Sr and ^{137}Cs removed during Strike 2, the spray wash, and the water wash compared to Strike 1. The data show less of a decrease for plutonium. Comparing the amount of iron removed with the amount expected to be released from corrosion (85 kg, see Eq. [1]) shows most of the iron in the samples following the oxalic acid strikes and the spray wash is from sludge dissolution rather than corrosion. The iron in the water wash sample is of the same order as the amount expected from oxalic acid corrosion, but the corrosion is expected to be lower during the water wash than during the oxalic acid strikes. The table also shows most of the activity remaining in the tank is in the sludge rather than in the liquid.

Table 24 shows the fraction of each species removed from Tank A and the amount remaining in the tank following chemical cleaning. The table shows more than 90% of the aluminum, calcium, sodium, and uranium has been removed from the tank. The fraction of lithium, strontium, and zirconium removed was 50–90%. The fraction of barium, chromium, iron, magnesium, manganese, and silicon removed was 10–50%. Only 1% of the nickel was removed.

TABLE 23
Amount of material removed from Tank A

Species	Strike 1 (kg)	Strike 2 (kg)	Spray wash (kg)	Water wash (kg)	Remaining solid (kg)	Remaining liquid (kg)
Al	278	16.8	10.3	4.5	32	0.3
Ba	2.4	1.0	0.43		26	
Ca	77	5.5	2.47	2.1	7.6	0.2
Cr	7.0	1.1	0.79	0.8	37	0.1
Fe	1460	369	335	116	4800	8.9
Li	3.9	1.0	0.92		<3.9	
Mg	6.5	1.1	0.76	0.6	9.7	
Mn	670	66	33.9	43.5	872	3.3
Na	1570	109	35.1	32.3	40.5	2.5
Ni	13.1	0.8	0.80		2140	
Si	154	8.3	4.4		477	
Sr	18.0	1.0	0.48		2.7	
U	2926	145	74	87	<39	6.7
Zr	30.6	9.8	7.62	0.9	28	
Hg	n.m.	n.m.	n.m.	n.m.	37	n.m.
^{235}U	19.6	0.9	0.44	1.1	0.4	0.1
^{237}Np	1.0	0.1		0.2	0.5	
^{238}U	2700	136	66	182	44	14
^{239}Pu	0.6				2.9	
	(dpm)	(dpm)	(dpm)	(dpm)	(dpm)	(dpm)
^{60}Co	1.6×10^{14}				6.0×10^{14}	
^{90}Sr	1.3×10^{18}	9.1×10^{16}	4.8×10^{16}	2.4×10^{16}	3.1×10^{17}	1.8×10^{15}
^{99}Tc		2.7×10^{10}	4.1×10^{10}		$<1.1 \times 10^{11}$	
^{137}Cs	7.3×10^{16}	5.9×10^{15}	2.2×10^{15}	1.5×10^{15}	2.3×10^{15}	1.2×10^{14}
Alpha		8.6×10^{14}	4.9×10^{13}		$<5.7 \times 10^{15}$	
Beta	8.6×10^{17}	1.9×10^{17}	8.3×10^{16}	5.3×10^{16}	4.9×10^{17}	4.1×10^{15}
$^{239/240}$Pu	2.7×10^{13}	6.0×10^{12}	2.7×10^{12}	6.8×10^{11}	5.8×10^{14}	5.2×10^{10}
^{238}Pu	5.6×10^{12}	1.9×10^{12}	5.3×10^{11}		1.5×10^{14}	
^{241}Am	3.2×10^{13}				3.6×10^{15}	
^{242m}Am	1.3×10^{11}				9.3×10^{12}	
^{242}Cm	1.0×10^{11}				7.7×10^{12}	
^{244}Cm	3.3×10^{12}		4.0×10^{11}	4.4×10^{12}	2.3×10^{14}	

n.m. = not measured.

Most of the mass remaining in the tank is iron and nickel. The remaining sludge contains 26 kg of barium, 37 kg of chromium, and 37 kg of mercury.

The chemical cleaning removed more than 90% of the uranium isotopes and ^{137}Cs. Cleaning removed 70% of the neptunium, 83% of the ^{90}Sr, and 21% of the ^{60}Co. The chemical cleaning removed less than 10% of the plutonium, americium, and curium isotopes. Most of the activity remaining in the tank is from beta emitters and ^{90}Sr.

Tank B

Table 25 shows the volumes of sludge and liquid used to perform the mass balance.

Table 26 shows the amount of each component removed during the acid strikes and washes, as well as the amount remaining in the sludge and liquid. The data show a significant decrease (>90%) in the amount of ^{90}Sr and ^{137}Cs removed during Strike 2, the spray wash, and the water wash compared to Strike 1. The data show less of a decrease for plutonium. Comparing the amount of iron removed with the amount expected to be released from corrosion (85 kg, see Eq. [1]) shows most of the iron in the samples following Strike 1 is from sludge dissolution rather than corrosion. The iron in the Strike 2, spray wash, and the water wash samples is of the same order as the amount expected from oxalic acid corrosion. The table also shows most of the activity remaining in the tank is in the sludge rather than in the liquid.

Table 27 shows the fraction of each species removed from Tank B and the amount remaining in the tank following chemical cleaning. The table shows more than 90% of the aluminum, calcium, sodium, and uranium has been removed from the tank. The fraction of lithium, chromium, magnesium, silicon, and zirconium removed was 50–90%. The fraction of barium, iron, and manganese removed was 10–50%. Only 2% of the nickel was removed. Table 27 shows a difference in the removal of cold strontium (94%) compared to ^{90}Sr (86%). This difference is due to analytical uncertainty.

Most of the mass remaining in the tank is iron and nickel. The remaining sludge contains 21 kg of barium, 4 kg of chromium, and 93 kg of mercury. If the Tank B liquid samples contained 2.33 mg/L of mercury (as measured in the Tank B process sample liquid), the amount of mercury dissolved and removed in the oxalic acid strikes, spray wash, and water wash (1,000,000 L total volume), would be 2.36 kg (2.6%).

The chemical cleaning removed more than 90% of the uranium isotopes. It removed 70% of the neptunium, 86% of the ^{90}Sr, and 86% of the ^{137}Cs. The cleaning removed ~2% of the technetium. The chemical cleaning removed less than 15% of the plutonium, americium, and curium isotopes. The chemical cleaning removed a larger fraction of the plutonium, americium, and curium in Tank B than in Tank A. This improved removal could be from the lower pH in Tank B following Strike 1 or to the plutonium being present in different compounds in Tank B. Most of the activity remaining in the tank is beta and ^{90}Sr.

TABLE 24
Fraction removed and amount remaining in Tank A

Species	Fraction removed (%)	Amount remaining (kg)
Al	90	33
Ba	13	26
Ca	92	8
Cr	21	37
Fe	32	4,830
Li	60	4
Mg	48	10
Mn	48	875
Na	98	43
Ni	1	2,138
Si	26	477
Sr	88	3
U	99	46
Zr	64	28
Hg	n.m.	37
		(Ci)
^{234}U	n.m.	<1.6 Ci
^{235}U	98	0.001 Ci (0.5 kg)
^{237}Np	70	0.38 Ci (0.5 kg)
^{238}U	98	0.019 Ci (58 kg)
^{239}Pu	17	178 Ci (2.9 kg)
^{60}Co	21	273
^{90}Sr	83	141,000
^{99}Tc	37	0.1
^{137}Cs	97	1,100
$^{239/240}$Pu	6	263
^{238}Pu	5	69
^{241}Am	1	1,650
^{243}Am	n.m.	41
^{242m}Am	1	4
^{244}Cm	3	103
^{241}Pu	n.m.	324

n.m. = not measured.

TABLE 25
Volumes of sludge and liquid in Tank B during chemical cleaning

V_1	419,000 L
V_2	109,000 L
V_{spray}	74,500 L
V_{water}	431,000 L
$V_{proc\text{-}sol}$	13,000 L
$V_{proc\text{-}liq}$	30,800 L

TABLE 26
Amount of material removed from Tank B

Species	Strike 1 (kg)	Strike 2 (kg)	Spray wash (kg)	Water wash (kg)	Remaining solid (kg)	Remaining liquid (kg)
Al	421.0	14.6	1.38	9.0	48.1	0.2
Ba	4.5	0.4			21.1	n.d.
Ca	110.4	4.6	0.26	1.9	13.3	0.05
Cr	6.7	0.4	0.04		4.5	n.d.
Fe	4795.8	192.8	22.57	90.5	1898.2	2.2
Li	27.6	1.3	0.09		6.5	n.d.
Mg	13.8	0.7	0.08	0.7	6.6	0.02
Mn	241.7	7.9	0.67	10.8	266.6	0.3
Na	1223.9	72.3	6.33	277.6	24.1	6.6
Ni	20.0	0.6	0.05		1219.0	n.d.
Si	110.4	3.2	0.21	15.8	16.3	0.4
Sr	13.8	0.5	0.03		0.8	n.d.
U	2013.8	96.9	11.23	382.3	32.9	9.1
Zr	81.9	2.2	0.18	0.8	10.2	0.02
Hg	n.m.	n.m.	n.m.	n.m.	93	n.m.
^{235}U	8.6	0.4	54.50	1.5	0.2	0.01
^{237}Np	0.5				0.2	0.001
^{238}U	1950.2	89.1	10.71	380.8	58.6	2.5
^{239}Pu	0.4				1.6	<0.001
	(dpm)	(dpm)	(dpm)	(dpm)	(dpm)	(dpm)
^{60}Co					1.3×10^{15}	
^{90}Sr	9.3×10^{17}	4.4×10^{16}	3.5×10^{16}	8.6×10^{15}	1.6×10^{17}	1.2×10^{14}
^{99}Tc		1.6×10^{10}	4.2×10^{10}		2.9×10^{12}	2.2×10^{9}
^{137}Cs	2.2×10^{16}	1.3×10^{15}	1.0×10^{15}	1.8×10^{15}	4.1×10^{15}	7.2×10^{13}
Alpha		3.6×10^{14}	5.7×10^{13}		2.3×10^{16}	2.8×10^{13}
Beta	7.1×10^{17}	9.2×10^{16}	7.2×10^{16}	2.7×10^{16}	3.8×10^{17}	3.6×10^{14}
$^{239/240}$Pu	5.8×10^{13}	1.4×10^{12}	1.6×10^{12}	1.5×10^{12}	3.9×10^{14}	3.6×10^{10}
^{238}Pu	4.5×10^{13}	8.3×10^{11}	1.2×10^{12}	1.1×10^{12}	3.0×10^{14}	1.6×10^{10}
^{241}Am	4.9×10^{14}			2.3×10^{12}	7.5×10^{15}	7.2×10^{10}
^{243}Am	8.5×10^{12}				1.2×10^{14}	
^{242m}Am	8.5×10^{11}				1.1×10^{13}	
^{242}Cm	7.1×10^{11}				9.4×10^{12}	
^{244}Cm	4.9×10^{14}		7.4×10^{11}	4.0×10^{11}	7.5×10^{15}	

COMPARISON OF CHEMICAL CLEANING PROCESS WITH DEMONSTRATIONS

Table 28 shows the process conditions for chemical cleaning in Tank A (Strike 1), and compares them with the conditions in Tank B and the demonstrations. The pH during Strike 1 in Tank A was 4 rather than the target of 1 – 2. The iron in the simulant demo was ferric hydroxide. The iron in the actual waste demo, Tank A, and Tank B contained a variety of iron compounds, and likely included magnetite and hematite. The oxalic acid concentration in Tank A was less than the concentration in the demos and in Tank B. The mixing differed from the demos, also. In the demonstrations, mixing started 2 days after oxalic acid addition started and continued for approximately 7 days. In Tank A, mixing started 2 days after completion of oxalic acid addition and continued for approximately 4 days. The transfer times were approximately the same in the simulant demo and the Tank Farm. The transfer time in the actual waste demo was minutes.

Table 29 shows the fraction of select species dissolved during the first oxalic acid strike in Tank A and Tank B, and compares it with the results from the SRNL demonstrations (1,2). In general, there is good agreement between the chemical cleaning in Tank A and Tank B and the demonstrations. The one species that does not show good agreement is iron in Tank A. The difference in

TABLE 27
Fraction removed and amount remaining in Tank B

Species	Fraction removed (%)	Amount remaining (kg)
Al	90.2%	48
Ba	18.7%	21
Ca	89.8%	13
Cr	61.2%	4
Fe	72.9%	1900
Li	81.6%	7
Mg	69.9%	7
Mn	49.4%	267
Na	98.1%	31
Ni	1.7%	1219
Si	88.6%	17
Sr	94.4%	1
U	98.4%	42
Zr	89.3%	10
Hg	n.m.	93
	(%)	(Ci)
^{234}U	[a]	<0.1
^{235}U	99.6%	0.001
^{237}Np	71.6%	0.137
^{238}U	97.5%	0.021
^{239}Pu	18.1%	100.2
^{60}Co	[b]	577
^{90}Sr	86.2%	74,147
^{99}Tc	2.0%	1
^{137}Cs	86.3%	1,905
$^{239/240}$Pu	13.7%	178
^{238}Pu	13.6%	138
^{241}Am	6.1%	3,421
^{243}Am	6.5%	56
^{242m}Am	6.9%	5
^{244}Cm	7.1%	3,421
^{241}Pu	6.1%	327

n.m. = not measured.

[a] all samples less than detection limit – fraction removed should be the same as other isotopes.

[b] all samples less than detection limit.

iron dissolved could be from increased corrosion during the demonstrations, from the high pH during the first oxalic acid strike in Tank A (pH 4), or from different iron compounds in Tank A compared with the demonstrations.

The test vessels used in the demonstrations contained carbon steel coupons to measure the corrosion rate during the chemical cleaning process (1,2). Since the demonstrations were scaled to have a similar sludge to carbon steel surface area as Tank 5 (see Table 30), the fraction of the iron dissolved from corrosion in Tank A during Strike 1 should be comparable to the fraction dissolved during the demonstrations. The calculation described in Eq. [1] shows that if the Tank A walls and cooling coils corroded at the same rate as in the demonstrations (0.021 in/yr), the amount of iron dissolved would be $\sim$6% of the amount of iron removed in the first strike ($\sim$2% in Tank B). Therefore, decreased corrosion is not the reason for the reduction in the fraction of iron removed.

In comparing the results from chemical cleaning with the results from the demonstrations, one assumes that the iron is present as the same compounds in both. If the iron is present as different compounds in Tank A and Tank B than in the demonstrations, the dissolution rate and fraction dissolved could be significantly different (9). The iron in the simulant demonstration was added as ferric hydroxide (2). The iron in the actual waste demonstration and Tank A and Tank B likely contained a variety of iron compounds. SRNL analysis of Tank Farm sludge samples shows the iron to be primarily magnetite and hematite. Larsen and Postma investigated the dissolution of iron oxide compounds and found the dissolution rates to vary as much as two orders of magnitude between different iron compounds (10). Torres et al. investigated the dissolution of hematite and magnetite by oxalic acid and found magnetite to be more reactive than hematite with oxalic acid (11). Lee et al. investigated the dissolution of iron oxide by oxalic acid and found that goethite and lepidocrosite dissolve more rapidly that hematite (9). Taxiarchou et al. investigated the dissolution of hematite in oxalic acid solutions and found the dissolution to occur faster under visible light (12). The sludge in the demonstrations was exposed to visible light, while the sludge in Tank A and Tank B was not.

The Tank A liquid sample collected after Strike 1 had a pH of 4 rather than $1-2$ as measured in the demonstrations and Tank B. This higher pH reduces the solubility and dissolution of iron. In addition, the measured oxalate concentration following Strike 1 was less than calculated based on the amount added and the tank liquid volume. This difference is most likely due to oxalate precipitating with iron, sodium, and other cations because of the high pH. Following Acid Strike 1 in Tank B, the measured pH of the liquid was 2. The fraction of iron dissolved in Tank B was $\sim$70%, which agrees with the demonstration better. Therefore, the high pH following Strike 1 is the primary cause of the difference in the fraction of iron dissolved.

The high pH following Strike 1 did not appear to affect the dissolution of aluminum. Work by Christodoulou et al. investigating the dissolution of aluminum by oxalic acid found little effect on aluminum solubility when the pH was increased from 2 to 4 (13).

TABLE 28
Comparison of conditions for Tank A chemical cleaning and cleaning demonstrations

	Simulant demo	Actual waste demo	Tank A	Tank B
Acid addition time	7 days	Batch addition	7 days	9 days
Start mixing	2 days after start of acid addition	Immediately after addition	2 days after completion of acid addition	5 days after completion of acid addition
Mixing time	7 days	7 days	4 days	4.5 days
Mixing power	TTP equivalent	Stir bar	SMP	SMP
Start transfer	50 hours after acid addition complete		4 days after acid addition complete	11.5 days after acid addition complete
Transfer time	17.5 hours	Minutes	13 hours	14 hours
Water source	Deionized water	Deionized water	Well water	Well water
OA temperature	50°C	50°C	35–40°C	35 – 40°C
PH	1	1	4	2
Iron form	Ferric hydroxide	Varied	Varied	Varied
OA concentration	0.9 M	0.9 M	0.44 M	0.9 M

TABLE 29
Comparing oxalic acid dissolution in Tank A with SRNL demonstrations

Species	Tank A (%)	Tank B (%)	Actual waste demonstration (%)	Simulant demonstration
Fe	21	69	62	99%
U	89	80	73	100%
Mn	40	46	40	43%
Ni	0.6	1.6	0.1	0.6%
Na	88	76	96	96%
Al	81	85	84	n.m.
^{238}Pu	3.5	13	2.9	n.m.
$^{239/240}$Pu	4.4	13	3.2	n.m.

n.m. = not measured.

TABLE 30
Geometrical and process conditions in Tank A and Tank B compared to SRNL demonstrations

Test	Sludge/ surface area (gal/ft^2)	Oxalic acid/surface area (gal/ft^2)	Oxalic acid/sludge + supernate volume
Actual Waste	0.1	4.2	20.7
Simulant	0.25	8.8	10.1
Tank A (nominal)	0.56	11.8	8.8
Tank A (actual)	0.3	9.6	32
Tank B (actual)	0.2	9.6	32

The mixing in the simulant demonstration differed from the mixing in Tank A and Tank B. In the simulant demonstration, the mixing started ~2 days after oxalic acid addition began. Reviewing the data from simulant Test 2 and Test 3 shows a significant increase in the amount of iron and manganese dissolved after the mixing started (2). The mixing improves contact between the acid and sludge and increases the mass transfer rate. Both effects should increase the sludge dissolution rate.

CONCLUSIONS

The conclusions from this work follow.

- With the exception of iron, the dissolution of sludge components from Tank A agreed with results from the actual waste demonstration performed in 2007. The fraction of iron removed from Tank A by chemical cleaning was significantly less than the fraction removed in the SRNL demonstrations. The likely cause of this difference is the high pH following the first oxalic acid strike.
- Most of the sludge mass remaining in the tank is iron and nickel.
- The remaining sludge contains significant amounts of barium, chromium, mercury.
- Most of the radioactivity remaining in the residual material is beta emitters and ^{90}Sr.
- The chemical cleaning removed a large fraction of the uranium, aluminum, calcium, sodium, strontium, and cesium.
- The chemical cleaning was not effective at removing nickel, mercury, plutonium, americium, and curium.

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