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Tank Closure,
Chemical
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Retention:
Permanent

Analysis of Samples from Tank 5F Chemical Cleaning

Michael R. Poirier
Samuel D. Fink

December 9, 2009

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808
Prepared for the U.S. Department of Energy Under
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LIST OF ACRONYMS

CVAA	Cold Vapor Atomic Absorption Spectroscopy
IC	Ion Chromatography
ICPES	Inductively Coupled Plasma Emission Spectroscopy
ICPMS	Inductively Coupled Plasma Mass Spectrometry
LWO	Liquid Waste Organization
PuTTA	Plutonium Thenoyl Trifluoroacetone Scintillation
SMP	Submersible Mixer Pumps
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

1.0 SUMMARY

The Savannah River Site (SRS) is preparing Tank 5F for closure. The first step in preparing the tank for closure is mechanical sludge removal. Following mechanical sludge removal, SRS performed chemical cleaning with oxalic acid to remove the sludge heel. Personnel are currently assessing the effectiveness of the chemical cleaning.

SRS personnel collected liquid samples during chemical cleaning and submitted them to Savannah River National Laboratory (SRNL) for analysis. Following chemical cleaning, they collected a solid sample (also known as "process sample") and submitted it to SRNL for analysis. The authors analyzed these samples to assess the effectiveness of the chemical cleaning process.

The conclusions from this work follow.

- With the exception of iron, the dissolution of sludge components from Tank 5F agreed with results from the actual waste demonstration performed in 2007. The fraction of iron removed from Tank 5F 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 approximately 26 kg of barium, 37 kg of chromium, and 37 kg of mercury.
- Most of the radioactivity remaining in the residual material is beta emitters and ^{90}Sr.
- The chemical cleaning removed more than ~90% of the uranium isotopes and ^{137}Cs.[i]
- The chemical 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.
- The chemical cleaning removed more than 90% of the aluminum, calcium, and sodium from the tank.
- The cleaning operations removed 61% of lithium, 88% of non-radioactive strontium, and 65% of zirconium. The ^{90}Sr and non-radioactive strontium were measured by different methods, and the differences in the fraction removed are not statistically significant.
- Chemical cleaning removed 10 – 50% of the barium, chromium, iron, magnesium, manganese, and silicon.
- Chemical cleaning removed only ~1% of the nickel.

SRNL makes the following recommendations to remove the remaining sludge and activity in Tank 5F and to improve sludge heel removal in cleaning of future tanks

- When performing chemical cleaning on future waste tanks, ensure the pH of the acid is less than 2 before removing the acid from the tank.

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[i] Note that the values cited in this report are based on a single sample of the liquid during each oxalic cleaning and water wash phase and solids samples from a single location following the water wash. Therefore, relatively large variability may be associated with the specific values. However, the reported values are useful for understanding the effect of chemical cleaning in Tank 6F and for deriving general conclusions.

- Prior to performing chemical cleaning for future tanks, collect a sludge sample and have SRNL analyze it for key contaminants. This provides a baseline for comparison, which allows a better evaluation of the efficiency of future chemical cleaning activities.
- Future work should include analysis of the solid samples by a method such as X-ray diffraction (XRD) to identify the specific compounds of the key contaminants.
- During chemical cleaning, mix the tank as soon as it contains sufficient liquid. The mixing will promote contact between the acid and sludge, improving the dissolution rate. The mixing will also suspend particles not dissolved by the acid.
- The sludge heel should be washed after completion of mechanical cleaning to reduce the liquid ionic strength prior to starting chemical cleaning. Reducing the ionic strength will increase the oxalate solubility.

2.0 INTRODUCTION

Savannah River Remediation (SRR) is preparing Tank 5F 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 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 5F, a sludge heel with estimated volume of 3,453 gallons remained after mechanical sludge removal. (The volumes of sludge in Tank 5F and the volumes of acid and water added are from a Liquid Waste Organization (LWO) document. The volumes reported in this document use the same number of significant figures as the LWO document).[1]

SRR developed a process, Chemical Cleaning, to remove these sludge heels using oxalic acid. They developed a flowsheet based on SRNL testing and LWO modeling.[2,3,4] The flowsheet washes the sludge with well water prior to chemical cleaning to reduce the ionic strength and increase the oxalate solubility. The flowsheet employs one strike with 8 wt % oxalic acid at an acid:sludge ratio of 20:1, followed by two strikes with 8 wt % oxalic acid at an acid:sludge ratio of 13:1. The tank is mixed to promote sludge dissolution and the liquid pumped to Tank 7F. Following the acid strikes, a Water Wash is performed to remove residual acid from the tank walls and cooling coils. Following each acid/water addition, SRR collects liquid samples and submits them to SRNL for analysis of cations, anions, and radionuclides.[5] Following the Water Wash, SRR collects solid samples and submits them to SRNL for analysis of cations and radionuclides.[6]

The Tank 5F chemical cleaning included two oxalic acid strikes, a Spray Wash (with oxalic acid and water), and a Water Wash. The cleaning protocols did not wash the sludge prior to Oxalic Acid Strike 1.

The first oxalic acid strike used the following protocol. Personnel added 67,468 gallons of 8 wt % oxalic acid to Tank 5F. Following the oxalic acid addition, they added 43,177 gallons of well water and mixed the contents of Tank 5F with two submersible mixer pumps (SMPs) for approximately four days. Following the mixing, SRR transferred 111,381 gallons of Tank 5F material to Tank 7F. The SMPs were operating at the start of the transfer and turned off when the liquid level dropped. The transfer lasted approximately 13 hours, with the SMPs operating for the first 6 hours.[1] Personnel collected a sample of the liquid from Tank 5F and submitted to SRNL for analysis.[7] Mapping of the tank following the transfer indicated that 2,745 gallons of solids remained in the tank.[1]

The second oxalic acid strike proceeded as follows. SRR added 32,743 gallons of 8 wt % oxalic acid to tank 5F. Following the acid addition, personnel visually inspected the tank and transferred 30,891 gallons of Tank 5F material to Tank 7F.[8] They collected a sample of the liquid from Tank 5F and submitted to SRNL for analysis.[7] Mapping of the tank following the transfer indicated that 3,592 gallons of solids remained in the tank.[8]

Following the oxalic acid strikes, SRR 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. SRR conducted the Spray Wash as follows. Personnel added 4,821 gallons of 8 wt % oxalic acid to Tank 5F through the spray mast installed in Riser 7 and 4,824 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, personnel visually inspected the tank and transferred 26,224 gallons of Tank 5F material to Tank 7F.[9] They collected a sample of the liquid from Tank 5F and submitted it to SRNL for analysis.[7]

Following the Spray Wash and transfer, SRR added 99,230 gallons of well water to Tank 5F, mixed the tank contents with a single SMP, and transferred the liquid from Tank 5F to Tank 7F.[9] Personnel collected a sample of the liquid from Tank 5F and submitted it to SRNL for analysis.[7] Mapping of the tank following the transfer indicated that 3,300 gallons of solids remained in the tank.

Following the Water Wash, SRR personnel collected a solid sample and submitted it to SRNL 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.

3.0 SAMPLES RECEIVED AND ANALYZED

SRNL received liquid samples following Oxalic Acid Strike 1, Oxalic Acid Strike 2, the Spray Wash, and the Water Wash. They analyzed the samples for pH using pH paper, for density gravimetrically, and for turbidity.[7] Following these analyses, they filtered subsamples, diluted them to reduce the dose, 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 received one solid sample from Tank 5F. The sample mass was only a few grams, and it contained no free liquid. Therefore, there is no analysis of free liquid for Tank 5F. SRNL prepared two subsamples. One of the subsamples was digested by the aqua regia method and the other by the peroxide fusion method. The samples were analyzed 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).

4.0 RESULTS

4.1 ANALYTICAL RESULTS

Table 1 shows the measured pH and density of the liquid samples following the oxalic acid strikes, the Spray Wash, and the Water Wash in Tank 5F. 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.

Table 1. 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 2, Table 3, Table 4, and Table 5 show the measured composition of the liquid samples collected during chemical cleaning. Table 2 shows the cation concentrations in the samples. With the exception of iron, the data show a significant decrease in the concentration of the major cations in the liquid samples (Al, Ca, Mn, Na, Si, and U) 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. These potential causes are discussed later in the report.

Table 2. Cation Analysis of Tank 5F 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

Comparing the composition of the liquid following the Spray Wash with the liquid following the Second Acid 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 is likely 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 3 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 5F prior to the addition of oxalic acid. Prior to chemical cleaning, the liquid in Tank 5F contained 0.852 M NO_3. If the initial sludge volume was 3453 gallons and the sludge was 50% supernate, the tank contained 5569 moles of NO_3^-. Since the volume of oxalic acid added was 431,300 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).

Table 3. Anion Analysis of Tank 5F 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_2^-	<380	< 338	< 328	< 323
NO_3^-	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

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 Tank 5F chemical cleaning demonstration.[2] In that test, researchers observed $FeC_2O_4*H_2O$ precipitate. In addition to precipitating as ferrous oxalate, the oxalate could be present as iron bioxalate ($FeHC_2O_4^{+2}$). Studies by Christodoulou et al. found $FeHC_2O_4^{+2}$ to be the dominant iron compound in oxalic acid between pH 1 and 3.[10] SRNL personnel should analyze solid samples from the sludge remaining in Tank 5F by X-Ray Diffraction (XRD) to determine the specific compounds remaining in the tank. A second plausible explanation, which would apply to Strike 1, is that the high pH (pH = 4) would decrease the oxalate solubility. Finally, the oxalate may have precipitated with the nickel present in Tank 5F. Work by Garcia-Clavel et al. showed the reaction of nickel compounds with oxalic acid formed $NiC_2O_4*2H_2O$.[11] Analysis of a Tank 5F sludge sample by XRD could confirm the presence of nickel oxalate hydrate.

Table 4 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 4. ICPMS Analysis of Tank 5F 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

Table 5 shows the radionuclide concentrations in the samples. The largest contributors to radioactivity are ^{90}Sr (and beta) and ^{137}Cs. The contributions to the total activity for the 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 concentrations will be the same. Therefore, the beta activity should be at least twice the ^{90}Sr activity. Discussions with the radiochemists who performed the analysis suggest this result could be due to solid particles in the sample. The samples were filtered, and a simple calculation shows a single ^{90}Sr particle with radius of 120 μ or 1000 ^{90}Sr particles with radius of 12 μ would be needed to explain the high ^{90}Sr concentration measured. We are uncertain of the reason for 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.

Table 5. Radionuclide Analysis of Tank 5F 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	$7.7 \times 10^{3} \pm 1.1 \times 10^{3}$	$< 1.6 \times 10^{4}$	$4.6 \times 10^{3} \pm 1.5 \times 10^{3}$	$1.1 \times 10^{4} \pm 4.9 \times 10^{3}$

The Process Sample contained ~ 70 wt % solids. Table 6 shows the concentration of cations in the Process Sample collected following chemical cleaning in Tank 5F. The table shows the composition of a Tank 5F sludge sample collected in 2006 before chemical cleaning for comparison.[2] Since that sample was collected prior to mechanical sludge removal and mechanical sludge removal may not have removed all species proportionally (i.e., faster settling constituents may increase as mechanical sludge removal progresses), the sample 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.

Table 6. Cations Analysis of Tank 5F Process Sample[c]

	Aqua Regia		Peroxide Fusion		Tank 5F
	Sample	AD Blank	Sample	AD Blank	2006 Sludge Sample
Species	mg/kg	mg/kg	mg/kg	mg/kg	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%

Previous SRNL testing of the chemical cleaning process showed minimal (~1%) dissolution of nickel.[2] In addition, work by Garcia-Clavel et al. showed the reaction of nickel compounds with oxalic acid formed $NiC_2O_4*2H_2O$.[11] 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 relative nickel concentration (due to a loss of soluble species) results from a 50% decrease in sludge mass.

Table 7 shows the concentration of select uranium, neptunium, and plutonium isotopes measured by ICP-MS. The sum of the concentrations of the uranium isotopes (<1336 mg/kg and <2235 mg/kg) is consistent with the uranium concentration measured by ICP-ES (< 1560 mg/kg and <7940 mg/kg). The data show the uranium concentration in the Process Sample is significantly less than the measured concentration in the Tank 5F sludge prior to chemical cleaning, indicating good removal of uranium by chemical cleaning.

4.2 MASS BALANCE

SRNL performed a mass balance of the radionuclides and nonradionuclides measured in the cleaning samples and process sample. Equation [1] describes the mass balance.

initial amount = amount removed + amount remaining

$$V_i x_i = V_1 x_1 + V_2 x_2 + V_{spray} x_{spray} + V_{water} x_{water} + V_{proc\text{-}sol} x_{proc\text{-}sol} + V_{proc\text{-}liq} x_{proc\text{-}liq} \quad [1]$$

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 [1] can be solved to determine x_i. Table 10 shows the volumes of sludge and liquid used to perform the mass balance.[1]

Table 7. Radionuclide Analysis of Tank 5F Process Sample (in dpm/g)

	Aqua Regia		Peroxide Fusion		Tank 5F
	Sample 1	AD Blank	Sample 1	AD Blank	2006 Sample
Species	dpm/g	dpm/g	dpm/g	dpm/g	dpm/g
^{60}Co	$2.4 \times 10^{7} \pm 1.2 \times 10^{6}$	$< 5.8 \times 10^{5}$	$2.4 \times 10^{7} \pm 1.2 \times 10^{6}$	$< 5.6 \times 10^{5}$	3.1×10^{7}
^{90}Sr	$1.3 \times 10^{10} \pm 1.1 \times 10^{9}$	$< 1.6 \times 10^{7}$	$1.2 \times 10^{10} \pm 9.5 \times 10^{8}$	$< 1.7 \times 10^{7}$	8.1×10^{10}
^{99}Tc	$< 4.0 \times 10^{3}$	$< 4.7 \times 10^{3}$	$< 5.2 \times 10^{3}$	$< 4.9 \times 10^{3}$	2.9×10^{4}
^{137}Cs	$1.1 \times 10^{8} \pm 5.5 \times 10^{6}$	$< 5.7 \times 10^{5}$	$7.7 \times 10^{7} \pm 3.9 \times 10^{6}$	$1.3 \times 10^{6} \pm 1.8 \times 10^{5}$	2.3×10^{9}
Alpha	$< 2.3 \times 10^{8}$	$< 8.1 \times 10^{6}$	$< 2.28 \times 10^{8}$	$< 8.1 \times 10^{6}$	1.3×10^{9}
beta	$2.1 \times 10^{10} \pm 2.1 \times 10^{9}$	$< 2.0 \times 10^{7}$	$1.9 \times 10^{10} \pm 1.9 \times 10^{9}$	2.4×10^{7}	n.m.
$^{239+240}$Pu	$2.3 \times 10^{7} \pm 1.1 \times 10^{6}$	$< 5.1 \times 10^{4}$	$2.4 \times 10^{7} \pm 1.5 \times 10^{6}$	$< 2.1 \times 10^{5}$	1.9×10^{7}
^{238}Pu	$5.9 \times 10^{6} \pm 3.1 \times 10^{5}$	$5.9 \times 10^{4} \pm 2.2 \times 10^{4}$	$6.3 \times 10^{6} \pm 4.2 \times 10^{5}$	$2.8 \times 10^{5} \pm 3.8 \times 10^{4}$	4.3×10^{6}
^{241}Am	$1.5 \times 10^{8} \pm 7.5 \times 10^{6}$	$2.2 \times 10^{5} \pm 3.8 \times 10^{4}$	$1.4 \times 10^{8} \pm 7.0 \times 10^{6}$	$1.0 \times 10^{5} \pm 2.0 \times 10^{4}$	1.1×10^{8}
^{243}Am	$3.7 \times 10^{6} \pm 4.4 \times 10^{5}$	$< 1.0 \times 10^{5}$	$3.5 \times 10^{6} \pm 4.2 \times 10^{5}$	$3.9 \times 10^{5} \pm 1.0 \times 10^{5}$	7.4×10^{5}
^{242m}Am	$3.2 \times 10^{5} \pm 5.1 \times 10^{4}$	1.1×10^{3}	$4.2 \times 10^{5} \pm 7.5 \times 10^{4}$	$< 1.9 \times 10^{3}$	3.2×10^{5}
^{243}Cm	$< 6.4 \times 10^{5}$	$< 2.1 \times 10^{6}$	$< 1.1 \times 10^{6}$	$< 1.7 \times 10^{5}$	n.m.
^{245}Cm	$< 1.4 \times 10^{6}$	$< 5.3 \times 10^{5}$	$< 1.0 \times 10^{6}$	$< 2.1 \times 10^{5}$	n.m.
^{247}Cm	$< 5.9 \times 10^{5}$	$< 7.7 \times 10^{4}$	$< 2.6 \times 10^{5}$	$< 4.4 \times 10^{4}$	n.m.
^{249}Cf	$< 5.8 \times 10^{5}$	$< 8.4 \times 10^{4}$	$< 2.7 \times 10^{5}$	$< 5.2 \times 10^{4}$	n.m.
^{251}Cf	$< 4.2 \times 10^{5}$	$< 1.4 \times 10^{5}$	$< 4.2 \times 10^{5}$	$< 5.7 \times 10^{4}$	n.m.
^{242}Cm	$2.7 \times 10^{5} \pm 4.2 \times 10^{4}$	$9.3 \times 10^{2} \pm 5.4 \times 10^{2}$	$3.5 \times 10^{5} \pm 6.1 \times 10^{4}$	$< 1.5 \times 10^{3}$	2.7×10^{5}
^{244}Cm	$7.6 \times 10^{6} \pm 1.2 \times 10^{5}$	$3.1 \times 10^{4} \pm 1.4 \times 10^{4}$	$1.1 \times 10^{7} \pm 1.7 \times 10^{6}$	$1.2 \times 10^{5} \pm 3.0 \times 10^{4}$	8.5×10^{6}
^{241}Pu	$2.8 \times 10^{7} \pm 4.1 \times 10^{6}$	$< 2.4 \times 10^{4}$	$2.9 \times 10^{7} \pm 4.3 \times 10^{6}$	$< 4.5 \times 10^{4}$	1.8×10^{7}
^{154}Eu	$6.8 \times 10^{7} \pm 3.4 \times 10^{6}$	$< 5.9 \times 10^{5}$	$6.5 \times 10^{7} \pm 3.2 \times 10^{6}$	$< 6.0 \times 10^{5}$	n.m.
^{155}Eu	$1.0 \times 10^{7} \pm 1.4 \times 10^{6}$	$< 1.1 \times 10^{6}$	$1.1 \times 10^{7} \pm 1.1 \times 10^{6}$	$< 1.1 \times 10^{6}$	n.m.

n.m. not measured

Table 8 and Table 9 show the concentration of radionuclides in the process sample collected following chemical cleaning in Tank 5F. The tables show the composition of a Tank 5F sludge sample collected before chemical cleaning for comparison.[2] 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.

Table 8. Radionuclide Analysis of Tank 5F Process Sample (in dpm/g)

	Aqua Regia		Peroxide Fusion		Tank 5F
	Sample 1	AD Blank	Sample 1	AD Blank	2006 Sample
Species	dpm/g	dpm/g	dpm/g	dpm/g	dpm/g
^{60}Co	$2.4 \times 10^{7} \pm 1.2 \times 10^{6}$	$< 5.8 \times 10^{5}$	$2.4 \times 10^{7} \pm 1.2 \times 10^{6}$	$< 5.6 \times 10^{5}$	3.1×10^{7}
^{90}Sr	$1.3 \times 10^{10} \pm 1.1 \times 10^{9}$	$< 1.6 \times 10^{7}$	$1.2 \times 10^{10} \pm 9.5 \times 10^{8}$	$< 1.7 \times 10^{7}$	8.1×10^{10}
^{99}Tc	$< 4.0 \times 10^{3}$	$< 4.7 \times 10^{3}$	$< 5.2 \times 10^{3}$	$< 4.9 \times 10^{3}$	2.9×10^{4}
^{137}Cs	$1.1 \times 10^{8} \pm 5.5 \times 10^{6}$	$< 5.7 \times 10^{5}$	$7.7 \times 10^{7} \pm 3.9 \times 10^{6}$	$1.3 \times 10^{6} \pm 1.8 \times 10^{5}$	2.3×10^{9}
Alpha	$< 2.3 \times 10^{8}$	$< 8.1 \times 10^{6}$	$< 2.28 \times 10^{8}$	$< 8.1 \times 10^{6}$	1.3×10^{9}
beta	$2.1 \times 10^{10} \pm 2.1 \times 10^{9}$	$< 2.0 \times 10^{7}$	$1.9 \times 10^{10} \pm 1.9 \times 10^{9}$	2.4×10^{7}	n.m.
$^{239+240}$Pu	$2.3 \times 10^{7} \pm 1.1 \times 10^{6}$	$< 5.1 \times 10^{4}$	$2.4 \times 10^{7} \pm 1.5 \times 10^{6}$	$< 2.1 \times 10^{5}$	1.9×10^{7}
^{238}Pu	$5.9 \times 10^{6} \pm 3.1 \times 10^{5}$	$5.9 \times 10^{4} \pm 2.2 \times 10^{4}$	$6.3 \times 10^{6} \pm 4.2 \times 10^{5}$	$2.8 \times 10^{5} \pm 3.8 \times 10^{4}$	4.3×10^{6}
^{241}Am	$1.5 \times 10^{8} \pm 7.5 \times 10^{6}$	$2.2 \times 10^{5} \pm 3.8 \times 10^{4}$	$1.4 \times 10^{8} \pm 7.0 \times 10^{6}$	$1.0 \times 10^{5} \pm 2.0 \times 10^{4}$	1.1×10^{8}
^{243}Am	$3.7 \times 10^{6} \pm 4.4 \times 10^{5}$	$< 1.0 \times 10^{5}$	$3.5 \times 10^{6} \pm 4.2 \times 10^{5}$	$3.9 \times 10^{5} \pm 1.0 \times 10^{5}$	7.4×10^{5}
^{242m}Am	$3.2 \times 10^{5} \pm 5.1 \times 10^{4}$	1.1×10^{3}	$4.2 \times 10^{5} \pm 7.5 \times 10^{4}$	$< 1.9 \times 10^{3}$	3.2×10^{5}
^{243}Cm	$< 6.4 \times 10^{5}$	$< 2.1 \times 10^{6}$	$< 1.1 \times 10^{6}$	$< 1.7 \times 10^{5}$	n.m.
^{245}Cm	$< 1.4 \times 10^{6}$	$< 5.3 \times 10^{5}$	$< 1.0 \times 10^{6}$	$< 2.1 \times 10^{5}$	n.m.
^{247}Cm	$< 5.9 \times 10^{5}$	$< 7.7 \times 10^{4}$	$< 2.6 \times 10^{5}$	$< 4.4 \times 10^{4}$	n.m.
^{249}Cf	$< 5.8 \times 10^{5}$	$< 8.4 \times 10^{4}$	$< 2.7 \times 10^{5}$	$< 5.2 \times 10^{4}$	n.m.
^{251}Cf	$< 4.2 \times 10^{5}$	$< 1.4 \times 10^{5}$	$< 4.2 \times 10^{5}$	$< 5.7 \times 10^{4}$	n.m.
^{242}Cm	$2.7 \times 10^{5} \pm 4.2 \times 10^{4}$	$9.3 \times 10^{2} \pm 5.4 \times 10^{2}$	$3.5 \times 10^{5} \pm 6.1 \times 10^{4}$	$< 1.5 \times 10^{3}$	2.7×10^{5}
^{244}Cm	$7.6 \times 10^{6} \pm 1.2 \times 10^{5}$	$3.1 \times 10^{4} \pm 1.4 \times 10^{4}$	$1.1 \times 10^{7} \pm 1.7 \times 10^{6}$	$1.2 \times 10^{5} \pm 3.0 \times 10^{4}$	8.5×10^{6}
^{241}Pu	$2.8 \times 10^{7} \pm 4.1 \times 10^{6}$	$< 2.4 \times 10^{4}$	$2.9 \times 10^{7} \pm 4.3 \times 10^{6}$	$< 4.5 \times 10^{4}$	1.8×10^{7}
^{154}Eu	$6.8 \times 10^{7} \pm 3.4 \times 10^{6}$	$< 5.9 \times 10^{5}$	$6.5 \times 10^{7} \pm 3.2 \times 10^{6}$	$< 6.0 \times 10^{5}$	n.m.
^{155}Eu	$1.0 \times 10^{7} \pm 1.4 \times 10^{6}$	$< 1.1 \times 10^{6}$	$1.1 \times 10^{7} \pm 1.1 \times 10^{6}$	$< 1.1 \times 10^{6}$	n.m.

n.m. not measured

Table 11 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 (< 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. The table also shows most of the activity remaining in the tank is in the sludge rather than in the liquid.

Table 12 shows the fraction of each species removed from Tank 5F 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.

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

Table 9. Radionuclide Analysis of Tank 5F Process Sample (in mCi/kg)

	Aqua Regia		Peroxide Fusion		Tank 5F
	Sample 1	AD Blank	Sample 1	AD Blank	2006 Sample
Species	mCi/kg	mCi/kg	mCi/kg	mCi/kg	mCi/kg
^{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 10. Volumes of Sludge and Liquid in Tank 5F during Chemical Cleaning

V_1	421,600 L
V_2	116,900 L
V_{spray}	99,300 L
V_{water}	375,600 L
$V_{proc\text{-}sol}$	12,491 L
$V_{proc\text{-}liq}$	30,772 L

When the chemical cleaning process started in Tank 5F, the Project did not need to understand mercury removal by oxalic acid addition, so the mercury concentration in the liquid samples was not measured. After the process sample showed a very high mercury concentration, the Project became interested in mercury removal by chemical cleaning.

The liquid in the process samples collected from Tank 6F contained 2.33 mg/L of mercury.[12] If the Tank 5F liquid samples contained 2.33 mg/L of mercury, 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.

If the remaining iron, manganese, and nickel are present as oxalates (FeC_2O_4, MnC_2O_4, and NiC_2O_4), they would be bound with 138,000 moles of oxalate. Based on the oxalate analyses of the liquid samples following Strike 1, Strike 2, and the Spray Wash, the amount of added oxalate that is not in the liquid phase is 145,000 moles. The difference is ~ 5%. SRNL should analyze a sample of sludge from Tank 5F to identify the specific chemical compounds present.

Table 11. Amount of Material Removed from Tank 5F

Species	Strike 1 (kg)	Strike 2 (kg)	Spray Wash (kg)	Water Wash (kg)	Remaining Solid (kg)	Remaining Liquid (kg)
Al	271	20.9	11.8	4.2	32	0.3
Ba	2.3	1.2	0.49		26	
Ca	75	5.9	2.8	2.0	7.6	0.2
Cr	6.9	1.3	0.9	0.8	37	0.1
Fe	1430	460	383	109	4800	8.9
Li	3.8	1.3	1.1		< 3.9	
Mg	6.3	1.4	0.9	0.5	9.7	
Mn	658	83	39	41	872	3.3
Na	1533	136	40	30	40.5	2.5
Ni	12.8	0.9	0.9		2140	
Si	151	10.4	5.0		477	
Sr	17.6	1.2	0.6		2.7	
U	2860	181	84	82	< 39	6.7
Zr	29.9	12.2	8.7	0.8	28	
Hg	n.m.	n.m.	n.m.	n.m.	37	n.m.
Sum	7,055	918	578	270	8572	22
^{234}U					< 0.3	
^{235}U	19.2	1.1	0.5	1.0	0.4	0.1
^{237}Np	1.0	0.1		0.1	0.5	
^{238}U	2639	170	75	171	44	14
^{239}Pu	0.6				2.9	
	(dpm)	(dpm)	(dpm)	(dpm)	(dpm)	(dpm)
^{60}Co	1.5×10^{14}				6.0×10^{14}	
^{90}Sr	1.3×10^{18}	1.1×10^{17}	5.5×10^{16}	2.3×10^{16}	3.1×10^{17}	1.8×10^{15}
^{99}Tc		3.4×10^{10}	4.7×10^{10}		$< 1.1 \times 10^{11}$	
^{137}Cs	7.2×10^{16}	7.4×10^{15}	2.5×10^{15}	1.4×10^{15}	2.3×10^{15}	1.2×10^{14}
Alpha		1.1×10^{15}	5.6×10^{13}		$< 5.7 \times 10^{15}$	
Beta	8.4×10^{17}	2.3×10^{17}	9.5×10^{16}	5.0×10^{16}	4.9×10^{17}	4.1×10^{15}
$^{239/240}$Pu	2.7×10^{13}	7.5×10^{12}	3.1×10^{12}	6.3×10^{11}	5.8×10^{14}	5.2×10^{10}
^{238}Pu	5.5×10^{12}	2.4×10^{12}	6.1×10^{11}		1.5×10^{14}	
^{241}Am	3.2×10^{13}				3.6×10^{15}	
^{243}Am					9.0×10^{13}	
^{242m}Am	1.3×10^{11}				9.3×10^{12}	
^{243}Cm					2.1×10^{13}	
^{245}Cm					3.0×10^{13}	
^{247}Cm					1.1×10^{13}	
^{249}Cf					1.1×10^{13}	
^{251}Cf					1.0×10^{13}	
^{242}Cm	1.0×10^{11}				7.7×10^{12}	
^{244}Cm	3.2×10^{12}		4.6×10^{11}	4.1×10^{12}	2.3×10^{14}	
^{241}Pu	n.m.	n.m.	n.m.	n.m.	7.1×10^{14}	n.m.
^{154}Eu	n.m.	n.m.	n.m.	n.m.	1.7×10^{15}	n.m.
^{155}Eu	n.m.	n.m.	n.m.	n.m.	2.7×10^{14}	n.m.
Sum	2.2×10^{18}	3.5×10^{17}	1.5×10^{17}	7.4×10^{16}	8.2×10^{17}	6.0×10^{15}

n.m. not measured

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. The data in Table 12 shows a slight difference in the removal of cold strontium compared with ^{90}Sr (88% versus 83%). Cold strontium and ^{90}Sr are measured by different methods (ICPES and radiochem, respectively), and the differences are not statistically significant. Table 12 shows differences in the plutonium removal. The ICPMS method shows 17% removal, while the radiochemical method (PUTTA) method shows 5 – 6% removal. The PUTTA method has a lower analytical uncertainty and is considered more accurate.

Table 12. Fraction Removed and Amount Remaining in Tank 5F

Species	Fraction Removed	Amount Remaining
	(%)	(kg)
Al	90	33
Ba	14	26
Ca	92	8
Cr	21	37
Fe	33	4,830
Li	61	4
Mg	48	10
Mn	48	875
Na	98	43
Ni	1	2,138
Si	26	477
Sr	88	3
U	99	46
Zr	65	28
Hg	n.m.	37
	(%)	(Ci)
^{234}U	n.m.	<1.6 Ci (< 0.3 kg)
^{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	20	273
^{90}Sr	83	143,000
^{99}Tc	41	0.1
^{137}Cs	97	1,100
Alpha	17	2,600
Beta	71	227,000
$^{239/240}$Pu	6	263
^{238}Pu	5	69
^{241}Am	1	1,650
^{243}Am	n.m.	41
^{242m}Am	1	4
^{243}Cm	n.m.	10
^{245}Cm	n.m.	14
^{247}Cm	n.m.	5
^{249}Cf	n.m.	5
^{251}Cf	n.m.	5
^{242}Cm	1	3
^{244}Cm	2	103
^{241}Pu	n.m.	324
^{154}Eu	n.m.	752
^{155}Eu	n.m.	121

n.m. not measured

4.3 COMPARISON WITH CHEMICAL CLEANING DEMONSTRATIONS

Table 13 shows the process conditions for chemical cleaning in Tank 5F (Strike 1), and compares them with the conditions in Tank 6F and the demonstrations.[2,3] The pH during Strike 1 in Tank 5F was 4 rather than the target of 1 – 2. The iron in the simulant demo was ferric hydroxide. The iron in the actual waste demonstration, Tank 5F, and Tank 6F contained a variety of iron compounds, and likely included magnetite and hematite. The oxalic acid concentration in Tank 5F was less than the concentration in the demonstrations and in Tank 6F. The mixing differed from the demonstrations, also. In the demonstrations, mixing started 2 days after oxalic acid addition started and continued for approximately 7 days. In Tank 5F, 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 demonstration was minutes.

Table 13. Comparison of Conditions for Tank 5F Chemical Cleaning and Cleaning Demonstrations

	Simulant Demo	Actual Waste Demo	Tank 5F	Tank 6F
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 14 shows the fraction of select species dissolved during the first oxalic acid strike in Tank 5F and compares it with the results from the SRNL demonstrations.[2,3] In general, there is good agreement between the chemical cleaning in Tank 5F and the demonstrations. The one species that does not show good agreement is iron. The difference in iron dissolved could be from increased corrosion during the demonstrations, from the high pH during the first oxalic acid strike in Tank 5F (pH 4), or from different iron compounds in Tank 5F compared with the demonstrations.

Table 14. Comparing Oxalic Acid Dissolution in Tank 5F with SRNL Demonstrations

Species	Tank 5F	Actual Waste Demonstration[2]	Simulant Demonstration[3]
Fe	21%	62%	99%
U	89%	73%	100%
Mn	40%	40%	43%
Ni	0.6%	0.1%	0.6
Na	88%	96%	96%
Al	81%	84%	n.m.
^{238}Pu	3.5%	2.9%	n.m.
$^{239/240}$Pu	4.4%	3.2%	n.m.

n.m. *not measured*

The test vessels used in the demonstrations contained carbon steel coupons to measure the corrosion rate during the chemical cleaning process.[2,3] Since the demonstrations were scaled to have a similar sludge to carbon steel surface area as Tank 5F (see Table 15), the fraction of the iron dissolved from corrosion in Tank 5F during Strike 1 should be comparable to the fraction dissolved during the demonstrations. The average measured corrosion rate in the simulant demonstration conducted at 50 °C was 21 mpy (0.021 in/yr).[3] Given a tank liquid volume of 431,300 L (42 inches), the carbon steel surface area is 11,520 ft^2.[13] Assuming the carbon steel has a density of 7.8 g/mL and contains 99% iron[14], the amount of iron that would dissolve from corrosion in one week is calculated with equation [2].

$$(0.021\ \text{in/yr})(1\ \text{yr}/52\ \text{wk})(1\ \text{wk})(11{,}520\ \text{ft}^2)(12\ \text{in/ft})^2 = 670\ \text{in}^3$$

$$670\ \text{in}^3\ (2.54\ \text{cm/in})^3\ (1\text{L}/1000\ \text{cm}^3) = 11\ \text{L}$$

$$11\ \text{L}\ (7.8\ \text{kg/L})\ (0.99) = 85\ \text{kg of iron from corrosion}$$

$$85\ \text{kg}/431{,}300\ \text{L}\ (10^6\ \text{mg/kg}) = 197\ \text{mg Fe/L from corrosion} \qquad [2]$$

The concentration of iron that could be in the sample from corrosion (197 mg/L) is significantly less than the amount measured in the sample following Strike 1 (3385 mg/L). The calculation shows the amount of iron dissolved from corrosion (85 kg) would be ~6% of the amount of iron removed in the first strike (1460 kg). Therefore, decreased corrosion is not the reason for the reduction in the fraction of iron removed.

Table 15. Geometrical and Process Conditions in Tank 5F 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 5F (nominal)	0.56	11.8	8.8
Tank 5F (actual)	0.3	9.6	32

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 5F than in the demonstrations, the dissolution rate and fraction dissolved could be significantly different.[15] The iron in the simulant demonstration was added as ferric hydroxide.[3] The Chemical Cleaning Flowsheet assumed the iron to be ferric hydroxide.[4] The iron in the actual waste demonstration and Tank 5F likely contained a variety of iron compounds. SRNL analysis of Tank Farm historical sludge samples shows the iron to be primarily magnetite and hematite according to Dr. Michael Hay. 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.[16] Torres et al. investigated the dissolution of hematite and magnetite by oxalic acid and found magnetite to be more readily dissolved than hematite with oxalic acid.[17] Lee et al. investigated the dissolution of iron oxide by oxalic acid and found that goethite and lepidocrosite dissolve more rapidly that hematite.[18] Taxiarchou et al.

investigated the dissolution of hematite in oxalic acid solutions and found the dissolution to occur faster under visible light.[19] The sludge in the demonstrations was exposed to visible light, while the sludge in Tank 5F was not. Therefore, if Tank 5F sludge contained iron in the form of hematite, then this would explain the reduction in the fraction of iron removed when compared to the demonstrations.

The liquid sample collected after Strike 1 had a pH of 4 rather than 1 – 2 as measured in the demonstrations. This higher pH reduces the solubility and dissolution of iron. 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.[20] 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.[21] 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 6F, the measured pH of the liquid was 2. The fraction of iron dissolved in Tank 6F was ~ 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.[10]

The mixing in the simulant demonstration differed from the mixing in Tank 5F. In the simulant demonstration, the mixing started ~ 2 days after oxalic acid addition began. Reviewing the data from Test 2 and Test 3 shows a significant increase in the amount of iron and manganese dissolved after mixing started.[3] The mixing improves contact between the acid and sludge and increases the mass transfer rate. Both effects should increase the sludge dissolution rate. Mixing in Tank 5F will also improve the suspension of solid particles not dissolved by the oxalic acid.

Performing a sludge wash prior to oxalic acid addition will reduce the ionic strength of the liquid in the tank, which will increase the oxalate solubility. In addition, the washing will reduce the total base in the tank and help ensure the pH is less than 2 after acid addition.

Oxalic acid effectively removed uranium from Tank 5F, and removed ~ 70% of the ^{237}Np from the tank. The oxalic acid was somewhat effective at removing the ^{99}Tc from the tank. The actual removal may have been better than reported, because the concentration in the process sample was less than the detection limit.

The oxalic acid was not as effective at removing plutonium, americium, and nickel from the sludge heel. The operations were marginally effective at removing manganese. Since mercury was not measured in the liquid samples collected following the oxalic acid strikes, Spray Wash, and Water Wash, we cannot assess the effectiveness of oxalic acid at removing mercury. However, comparing the mercury concentration in the 2006 sample with its concentration in the process sample suggests that the oxalic acid was not effective in removing mercury.

To reduce the amount of ^{239}Pu, ^{241}Am, Hg, Mn, or Ni, a cleaning agent other than oxalic acid needs to be selected. Nitric acid is a plausible acid to dissolve ^{239}Pu, ^{241}Am, Hg, Mn, and Ni, but it is very corrosive to carbon steel. Sodium carbonate is a plausible chemical to dissolve the plutonium and americium.

When performing chemical cleaning on other waste tanks, ensure the pH of the acid is less than 2 before removing the acid from the tank. Prior to performing chemical cleaning, Liquid Waste should collect a sludge sample and have SRNL analyze it for key contaminants to better evaluate the efficiency of chemical cleaning. Washing the sludge prior to the start of chemical cleaning would reduce the ionic strength and increase oxalate solubility. The chemical cleaning process needs sufficient mixing to ensure good contact between the acid and sludge, and to suspend particles not dissolved by the acid.

5.0 CONCLUSIONS

The conclusions from this work follow.

- With the exception of iron, the dissolution of sludge components from Tank 5F agreed with results from the actual waste demonstration performed in 2007. The fraction of iron removed from Tank 5F 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 approximately 26 kg of barium, 37 kg of chromium, and 37 kg of mercury.
- Most of the radioactivity remaining in the residual material is beta emitters and ^{90}Sr.
- The chemical cleaning removed more than ~90% of the uranium isotopes and ^{137}Cs.
- The chemical 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.
- The chemical cleaning removed more than 90% of the aluminum, calcium, and sodium from the tank.
- The cleaning operations removed 61% of lithium, 88% of non-radioactive strontium, and 65% of zirconium. The ^{90}Sr and non-radioactive strontium were measured by different methods, and the differences in the fraction removed are not statistically significant.
- Chemical cleaning removed 10 – 50% of the barium, chromium, iron, magnesium, manganese, and silicon.
- Chemical cleaning removed only ~1% of the nickel.

SRNL makes the following recommendations to remove the remaining sludge and activity in Tank 5F and to improve sludge heel removal in cleaning of future tanks

- When performing chemical cleaning on future waste tanks, ensure the pH of the acid is less than 2 before removing the acid from the tank.
- Prior to performing chemical cleaning for future tanks, collect a sludge sample and have SRNL analyze it for key contaminants. This provides a baseline for comparison, which allows a better evaluation of the efficiency of future chemical cleaning activities.

- Future work should include analysis of the solid samples by a method such as X-ray diffraction (XRD) to identify the specific compounds of the key contaminants.
- During chemical cleaning, mix the tank as soon as it contains sufficient liquid. The mixing will promote contact between the acid and sludge, improving the dissolution rate. The mixing will also suspend particles not dissolved by the acid.
- The sludge heel should be washed after completion of mechanical cleaning to reduce the liquid ionic strength prior to starting chemical cleaning. Reducing the ionic strength will increase the oxalate solubility.

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