

## **Evaluation of Sludge Heel Dissolution Efficiency with Oxalic Acid Cleaning at Savannah River Site – 14205**

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### **ABSTRACT**

The chemical cleaning process baseline strategy at the Savannah River Site was revised to improve efficiency during future execution of the process based on lessons learned during previous bulk oxalic acid cleaning activities and to account for operational constraints imposed by safety basis requirements. These improvements were also intended to transcend the difficulties that arise from waste removal in higher rheological yield stress sludge tanks. Tank 12 implemented this improved strategy and the bulk oxalic acid cleaning efforts concluded in July 2013. The Tank 12 radiological removal results were similar to previous bulk oxalic acid cleaning campaigns despite the fact that Tank 12 contained higher rheological yield stress sludge that would make removal more difficult than the sludge treated in previous cleaning campaigns. No appreciable oxalate precipitation occurred during the cleaning process in Tank 12 compared to previous campaigns, which aided in the net volume reduction of 75-80%. Overall, the controls established for Tank 12 provide a template for an improved cleaning process.

### **INTRODUCTION**

SRS stores radioactive material in 45 underground high level waste tanks (6 previously closed). The material is removed through a series of separation processes and the low-level fraction is immobilized in a grout waste form while the high level fraction is disposed in a glass waste form. Of all the components that make up the solid material within these tanks, iron and aluminum are the most abundant chemical constituents. The remaining fraction is mostly composed of sodium, nickel, manganese, uranium, silicon, and other various metal salts and oxides. Methods of waste removal during the operational closure process include a mechanical cleaning approach where large additions of water are added to a tank in a batch process with periods of mixing to aid dissolution of soluble species as well as suspend smaller solids particles that can be removed during transfers out of the waste tank. Tanks high in aluminum content can undergo low temperature aluminum dissolution (LTAD) with caustic chemical to dissolve aluminum species; however, there is negligible impact to other metals. Chemical cleaning with bulk oxalic acid (BOA) can be utilized to treat the residual solids remaining after mechanical waste removal campaigns and potentially LTAD campaigns. The ability to remove residual solids is vital to accelerate closure of these highly radioactive, mostly emptied, storage tanks.

While proven chemical cleaning techniques have been employed over the years to treat the residual solids heel remaining after bulk waste removal campaigns, opportunities for improvement were identified during field execution and subsequent testing to enhance the effectiveness of the chemical cleaning evolution. Previous tanks that have undergone chemical cleaning operations contained Purex waste. Future tanks targeted for closure include tanks that contain H-Modified (HM) waste, known to be higher in mercury and aluminum and have a higher rheological yield stress compared to Purex waste [1]. Tank 12 is one such HM waste tank that recently underwent BOA cleaning utilizing an improved operating strategy. Specific opportunities that were addressed in the improved operating strategy included: 1) increasing the contact rate of the acid with the residual sludge heel, 2) controlling the pH to minimize oxalate precipitation, 3) establishing favorable initial conditions for waste removal, and 4) improving mixing operations during the chemical cleaning evolution [2]. This paper reviews the technical effectiveness of the oxalic acid cleaning process in Tank 12. Overall cost-benefit analyses for implementing bulk oxalic acid cleaning and the downstream impacts of the oxalates on the liquid waste flowsheet at the Savannah River Site will be addressed separately.

## LESSONS LEARNED FROM PREVIOUS CAMPAIGNS

The lessons learned from the previous BOA cleaning campaigns resulted in the following recommendations [3 and 4]:

- The residual heel should be washed with well water prior to starting chemical cleaning in order to reduce the liquid ionic strength in the heel and increase the oxalate solubility.
- Ensure the pH of the acid remains less than 2 to increase oxalate solubility is increased.
- Mix the tank as soon as a sufficient liquid level is reached to support full speed mixing. If possible, continue mixing while transferring waste out of the tank until the minimum mixing level is reached. Mixing helps to promote contact between the acid and residual solids to improve the dissolution rate and also suspends insoluble particles.
- Heat the oxalic acid and maintain the tank temperature to 70°C to promote more effective dissolution and minimize precipitation of oxalates.

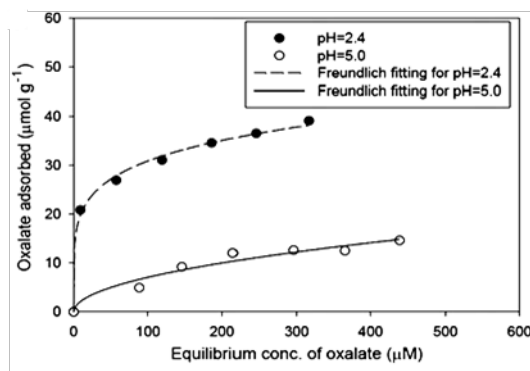
### Washing

One of the methods suggested for improving the overall effectiveness of BOA cleaning is washing the sludge prior to acid cleaning. Washing the sludge heel reduces the ionic strength and increases the oxalate solubility. Appreciable sodium oxalate precipitation has been observed during previous BOA campaigns. Studies have shown that as sodium concentration increases, the oxalate solubility begins to exponentially decrease [5]. As the oxalate solubility decreases, precipitation occurs. If the residual heel contains a high concentration of sodium when BOA is added to the tank, then the predominant reaction observed is the precipitation of sodium oxalate versus the dissolution of the residual heel. Therefore, washing the sludge heel until the starting sodium concentration is reduced to  $[\text{Na}] \leq 0.5 \text{ M}$  promotes better residual heel dissolution [6]. Washing is completed within the envelop of the Corrosion Control Program [7], which allows for temporary suspension of corrosion control requirements (e.g. inhibitor concentrations) during waste removal and tank cleaning efforts while maintaining appropriate wall thickness for structural integrity.

### Maintaining a low pH

During the Tanks 5 and 6 BOA cleaning campaigns, oxalate precipitation was observed during the chemical cleaning process that was not present in the original residual heels. Between 38% and 51% of the theoretical soluble oxalate concentration precipitated and remained in the tank during the Tank 5 BOA cleaning strikes. During the Tank 6 BOA cleaning strikes, between 36% and 44% of the theoretical soluble oxalate precipitated and remained in the tank [8].

As pH increases, the oxalate solubility decreases. Data taken from a literature review shows that the amount of oxalate adsorbed directly correlates to the oxalate solubility, which is a function of pH. As seen in Figure 1, the oxalate solubility significantly increases as the pH drops from 5 to 2.4 [9].



**Figure 1. Relationship between oxalate solubility and pH**

### Mixing

While BOA has been shown to effectively remove residual material from a tank, the maximum amount of residual material removed is proportional to the volume of material contacted by the oxalic acid. A residual heel typically consists of large particles and agglomerations of solids. Unagitated acid reacts only with the top layer of solids due to an inability to dynamically diffuse past these large particles and agglomerations. While acid may slowly dissolve accumulated waste, the pH associated with BOA rises with time due to the dissociation of the acid as well as the dissolution of soluble sludge components in acid (e.g., aluminum and iron). Since an increase in the pH correlates to an increase in the oxalate precipitation, the overall solubility of the acidic solution decreases. Mixing allows better contact with the residual heel and promotes dissolution of soluble material by allowing reactivity before the acid naturally dissociates and oxalates have an opportunity to precipitate. Mixing also allows suspension of undissolved solids, so there is a potential to transfer undissolved solids with associated radiological species out of the tank.

### Temperature

Dissolution using oxalic acid is generally more effective at elevated temperatures (i.e., 70°C), because as the temperature of solution increases, the rate of reaction increases. Of the metal phases present in the high level residual heel, boehmite and hematite are the most difficult aluminum and iron species to dissolve. Studies have confirmed that increasing temperature dissolves sludge faster than lower temperature. Oxalic acid heated to temperatures around 70°C is ideal to dissolve boehmite, while temperatures between 50°C and 70°C are sufficient for hematite dissolution [3, 4, 10, 11, 12, 13].

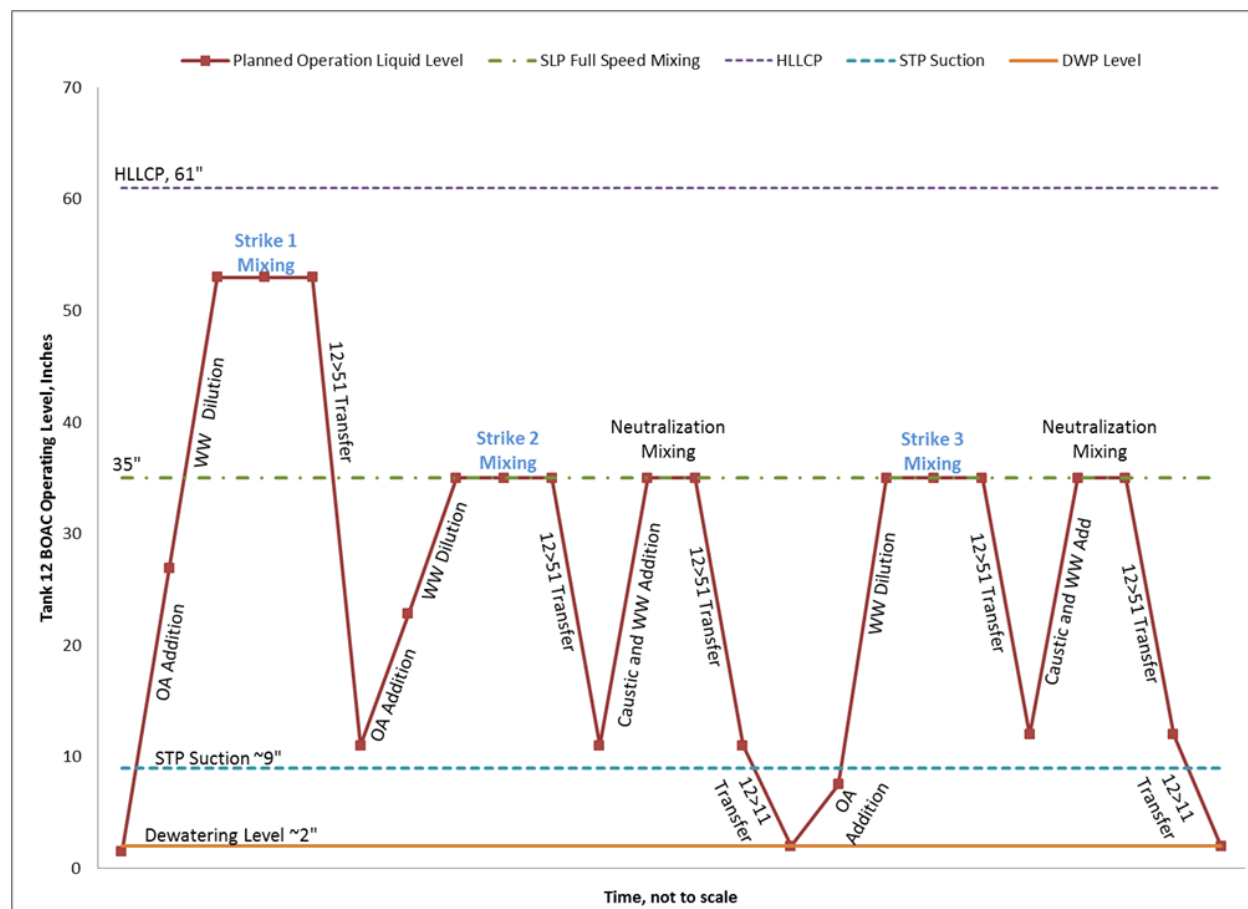
### TANK 12 HISTORY

Tank 12 was placed into service as a receiver for high heat waste in 1956 and continued to receive waste until 1974 [14]. After 1974, Tank 12 was inactive and supernatant evaporated with time and the tank was allowed to dry. Tank 12 was rewet starting in November 2004 in preparation for bulk waste removal efforts (BWRE). Tank 12 BWRE successfully reduced the waste volume from approximately 768 m<sup>3</sup> (203,000 gallons) to approximately 55 m<sup>3</sup> (14,500 gallons). Following BWRE, a low temperature aluminum dissolution campaign was initiated that targeted dissolution of the aluminum component of the remaining waste and ultimately reduced the solids volume to less than 37.9 m<sup>3</sup> (10,000 gallons). In preparation for BOA, the tank underwent a washing campaign to reduce the sodium concentration to less than or equal to 0.5 M. Tank 12 contained 16.7 m<sup>3</sup> (4,400 gallons) of solids prior to BOA [15].

### TANK 12 BOA CLEANING OPERATIONAL STRATEGY

Tank 12 BOA cleaning consisted of three oxalic acid strikes. Each strike was comprised of an addition of 8 wt% oxalic acid followed by an addition of well water to reduce the overall oxalic acid concentration to

less than or equal to 4 wt%. At the completion of each strike and just prior to transferring the acidic material to the neutralization tank (i.e., Tank 51), two dip samples were taken from the tank to be analyzed for dissolved solid species, radiological species, and pH. One sample was sent to the F/H laboratory for analysis and one sample was sent to SRNL for analysis [15]. Except for the radiological analysis, the SRNL results are utilized to evaluate the effectiveness of the BOA cleaning dissolution since a more extensive analysis was provided. The heel in Tank 12 was neutralized to a pH of 7 with caustic and well water following the Strike 2 and 3 acidic transfers out of Tank 12. Neutralization was completed to support dewatering of the tank while remaining within the control set of the safety basis. The intent of dewatering was to transfer as much of the neutralized solution out of Tank 12 as possible following Strike 2 so that the residual material would be exposed to the fresh acid feed during Strike 3 and to facilitate inspections and volume determination. However, the dewatering step did not occur between Strike 2 and 3. Dewatering did occur as intended following Strike 3. The overall operating strategy is summarized below in Figure 2.



**Figure 2. Planned Tank 12 acid cleaning operating strategy**

The lessons learned that were actually implemented during this process included:

- The initial sodium concentration was less than 0.5 M.
- Mixing pumps were turned on to full capacity as soon as possible during all three strikes. Strike 1 was a general mixing campaign designed to dissolve the solid material coating the floor. Conversely, Strikes 2 and 3 had a specific indexed mixing campaign that targeted the immobile mounds.
- pH was monitored throughout the strikes and never exceeded pH 2.

In addition to considering the lessons learned from previous BOA campaigns, operational constraints imposed by the safety basis and physical limitations of Tank 12 impacted the operating strategy.

- A 20:1 volume ratio of 8 wt% oxalic acid to the solids heel could not be exceeded. The 20:1 volume ratio was a safety basis requirement that was tested in laboratory settings; therefore, was treated as a known limit.
- The maximum acid concentration before the mixing pumps were utilized was 4 wt% oxalic acid. A 4 wt% concentration protected the transfer line and tank wall from excessive corrosion.
- Based on corrosion testing, the safety basis limits the temperature of an oxalic acid solution to 60°C during mixing or transfers and 75°C without mixing, which is lower than the ideal temperature discussed in the lessons learned. The heat of reaction between the acid and the sludge could have had a temperature delta as high as 15°C [Ref. 16]. To help protect these temperature limits, the incoming acid to the tank was limited to 55° (+/- 5°). The 55°C limit prevented the temperature of the solution from exceeding 75°C during the acid addition. The dilution water added after acid additions lowered the temperature of the solution and cooling coils were turned on as necessary to protect the 60°C temperature limit during mixing and transfers.
- The Tank 12 transfer pump could not lower material below approximately 0.23 meters (9 inches) due to a cooling coil obstruction. A dewatering pump was utilized to remove waste below this point.
- The maximum operating level within the tank was 1.4 meters (55 inches). This height prevented the annulus pan from overflowing should a leak occur in the tank wall due to corrosion. Protecting this level limited the desired acid addition during Strike 1.
- A minimum fill height of 0.9 meters (35 inches) was needed to run the mixing pumps; this height prevented aerosolization of the material in Tank 12. Additional water was required for Strikes 2 and 3 to bring the fill level to the appropriate height than what was required to merely dilute the 8 wt% oxalic acid to 4 wt%. This level of dilution was deemed acceptable because the benefit to mixing exceeded the impact of the lower wt% acid concentration.
- The dewatering pump could not transfer acidic material to Tank 11 due to an inability to neutralize within the tank per approved controls; therefore, the material was pH adjusted to at least 7 prior to transfer.

TABLE I below provides the general parameters observed for each strike. During Strike 1, the ratio of oxalic acid to the sludge volume was limited to only 15:1 versus the maximum allowed 20:1 due to the maximum operating limit of 1.4 meters (55 inches). The acid concentration was diluted to 4 wt%, and mixing pumps were operated in an oscillating mode. Strike 2 and 3 used conservatively low sludge volume estimates to determine how much acid could be added to the tank to remain within the safety basis limitations. Formal mapping did not occur between the strikes, but inspections were completed through approximately 0.23 meters (9 inches) of supernatant and a conservatively low volume estimate was provided. Only the largest mound was utilized to estimate the total sludge volume remaining in the tank to ensure the 20:1 acid to sludge ratio was not exceeded for Strike 2. For Strike 3 a more rigorous inspection was performed to estimate the volume, but the estimate was still conservatively low. The maximum 20:1 ratio of oxalic acid to the sludge volume was based on the freshly added 8 wt% oxalic acid in addition to the unspent acid that remained in the heel from the previous strike. Additional well water was required to bring the tank level to 0.9 meters (35 inches) to support mixing pump operations for both Strikes 2 and 3, so each respective final acid concentration was approximately 2 wt%.

**TABLE I. General parameters for each strike**

Parameters	Units	Strike 1	Strike 2	Strike 3
Tank Level	m (in)	1.4 (55)	0.9 (35)	0.9 (35)
Initial Sludge Volume	m <sup>3</sup> (gal)	16.7 (4,400)	4.8 (1,263) <sup>a</sup>	4.6 (1,225) <sup>a</sup>
Volume of oxalic acid	m <sup>3</sup> (gal)	244 (64,551)	69 (18,271)	90 (23,899)
Volume of Well Water	m <sup>3</sup> (gal)	258 (68,102)	148 (39,160)	150 (39,540)
Oxalic Acid to Sludge Vol Ratio	N/A	15 to 1	20 to 1	20 to 1
Diluted Oxalic Acid Concentration	wt%	4	2	2
Mixing Campaign	N/A	oscillating	4 sequences (with indexing)	9 sequences (with indexing)

<sup>a</sup> Value is a conservatively low volume assumed to be present at initiation of the strike

### Tank 12 BOA Cleaning Operational Deviations

The process was put on hold due to unforeseen weather delays shortly after Strike 1 was initiated. The mixing pumps were initially turned on for an hour to ensure the 8 wt% oxalic acid was thoroughly mixed with the well water, but the pumps were then shut down and did not resume operation until five days later. This shutdown resulted in a much lower operating temperature within the tank than desired. The two months that Tank 12 underwent BOA cleaning were exceptionally wet months and delays occurred due to rain water in-leakage to support systems such as the diversion boxes used to facilitate tank to tank transfers. Other minor weather delays such as lightning delays and continued rain water in-leakage occurred throughout this time; however, none were as potentially impactful as this initial delay. Strikes 2 and 3 were able to reach a maximum operating temperature of approximately 55° within days of the acid unloading versus the week required for Strike 1.

The dewatering pump was intended to be utilized to remove as much neutralized solution as possible between Strikes 2 and 3. The main purpose of dewatering was to enable a more accurate mapping volume for Strike 3. Dewatering also would have aided in dissolution efficiency by allowing the fresh acid feed during Strike 3 to have direct contact with the remaining solids. Once deployed the dewatering pump did not operate properly with indications that the pump would not prime. Since the solution within the tank was unclouded and modeling indicated minimal impacts to oxalate precipitation, a decision was made to proceed with mapping through approximately 0.23 meters (9 inches) of neutralized solution.

The process was shut down for several weeks following the acidic transfer out of Tank 12 during Strike 3 due to the plugged reheater in the ventilation system. This delay posed minimal impact to the process itself, since the shutdown merely delayed neutralization of the approximate 0.23 meters (9 inch) heel. The pre-washing that occurred prior to BOA reduced the ionic strength of the waste which helped maintain the pH below 2. Therefore, there was minimal risk of oxalates precipitating during the ventilation shutdown.

### TANK 12 BOA CLEANING RESULTS

Tank 12 contained 16.7 m<sup>3</sup> (4,400 gallons) of material prior to initiation of BOA. Mapping completed after BOA showed that approximately 3.8 m<sup>3</sup> (1,000 gallons) of material remained within Tank 12 [Ref. 17]. The cleaning campaign successfully reduced the residual volume by over 77%. At the conclusion of each strike, two dip samples of the spent acid solution were taken. One was sent to SRNL and one was sent to the F/H laboratory for analysis. The SRNL sample was intended to provide a comprehensive analysis of individual solid and radiological species, while the F/H laboratory analysis focused on key anions, the pH of the solution, and the gross beta/gamma and gross alpha contributions.

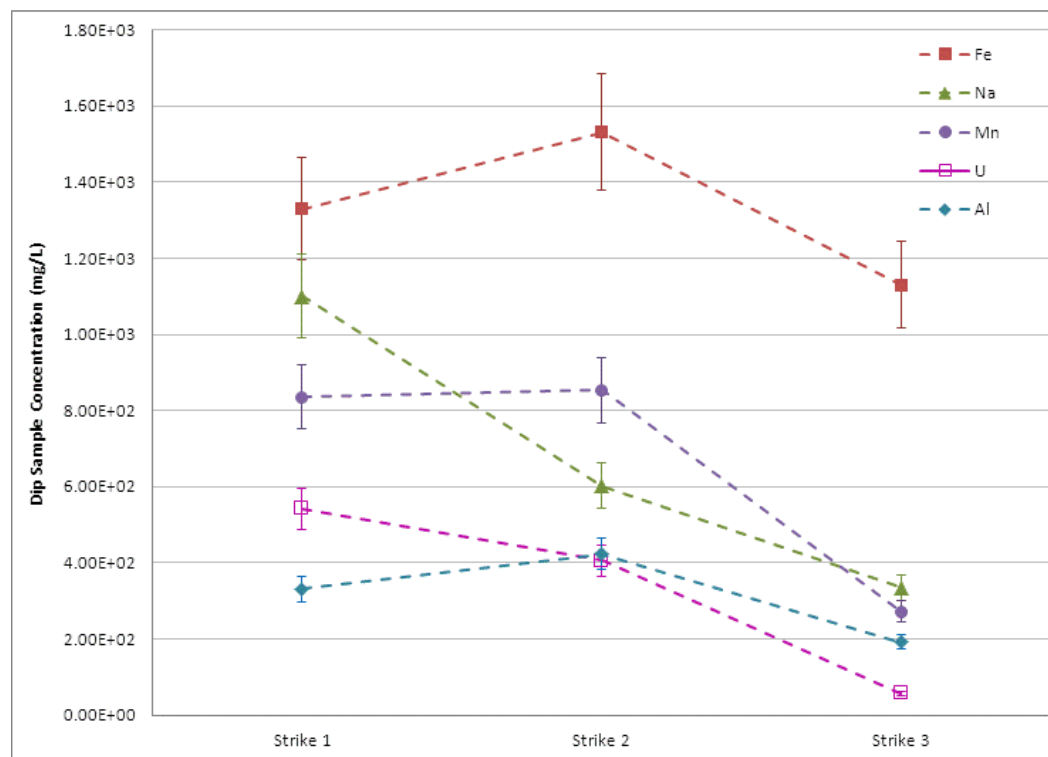
### Dissolved Solids Analysis

The SRNL results of the dip samples obtained at the end of each strike are shown below in TABLE II [18]. The five most prevalent dissolved species are highlighted. Each concentration has a 10% nominal uncertainty for the analytical method utilized to measure the concentration. The total volume of acidic material transferred out of Tank 12 at the completion of each strike is summarized at the bottom of the table. Only the acidic transfers out of Tank 12 are considered. Additional dissolved and/or suspended insoluble solids were likely removed during the neutralized transfers out of the tank following Strike 2 and Strike 3. The additional solids removal cannot be estimated since a dip sample was not pulled prior to the transfer of the neutralized solution out of Tank 12. The insoluble solids potentially removed during the acidic transfers are addressed later in this report.

**TABLE II. Dip sample results**

Species \ Sample ID	Strike 1	Strike 2	Strike 3
	HTF-12-13- mg/L	HTF-12-13- mg/L	HTF-12-13- mg/L
Fe	1.33E+03	1.53E+03	1.13E+03
Na	1.10E+03	6.02E+02	3.36E+02
Mn	8.36E+02	8.53E+02	2.73E+02
U	5.42E+02	4.07E+02	5.84E+01
Al	3.32E+02	4.24E+02	1.92E+02
S	1.40E+02	1.01E+02	8.00E+01
Si	1.34E+02	9.36E+01	3.02E+01
Ca	4.85E+01	5.29E+01	2.24E+01
Zr	1.79E+01	1.40E+01	5.35E+00
Mg	1.71E+01	1.30E+01	4.70E+00
P	1.55E+01	1.31E+01	5.32E+00
Th	1.15E+01	6.78E+00	7.31E+00
K	9.59E+00	9.83E+01	5.20E+00
Li	8.66E+00	4.13E+00	3.74E-01
Cr	6.86E+00	8.06E+00	2.10E+00
Ni	5.42E+00	4.89E+00	3.90E+00
Sr	3.99E+00	3.42E+00	1.43E+00
Cu	3.61E+00	3.70E+00	2.75E+00
Sb	<2.90E+00	<2.90E+00	<2.90E+00
Ba	2.46E+00	3.04E+00	2.95E+00
Gd	<2.35E+00	<2.35E+00	<2.35E+00
B	<1.95E+00	<1.95E+00	<1.95E+00
La	<1.42E+00	<1.42E+00	<1.42E+00
Ti	1.42E+00	1.07E+00	4.40E-01
Sn	<1.16E+00	<1.16E+00	<1.16E+00
Ag	<1.06E+00	<1.06E+00	<1.06E+00
Ce	<1.00E+00	<1.00E+00	<1.00E+00
Pb	<9.80E-01	<1.17E+00	<9.98E-01
Mo	<8.30E-01	<8.30E-01	<8.30E-01
V	<7.10E-01	<7.10E-01	<7.10E-01
Zn	<5.46E-01	<5.31E-01	<4.48E-01
Cd	3.37E-01	2.99E-01	1.27E-01
Co	<2.11E-01	<2.11E-01	<2.11E-01
Be	<1.00E-01	<1.00E-01	<1.00E-01
Transfer Volume (L)	4.34E+05	2.71E+05	2.69E+05

The results of the dip samples show that the highest concentrations of dissolved species are iron, sodium, manganese, uranium and aluminum. The Strike 2 concentrations were generally higher than either Strike 1 or Strike 3, as shown below in Figure 3, but Strike 1 dissolved more solids on a mass basis followed closely by Strike 2. Strike 2 was the first targeted mixing campaign that broke up the largest accumulations within Tank 12; therefore, the relative concentrations of metal species would be higher. The aluminum concentrations were lower than expected. The reduced operating temperature, especially during Strike 1, is the presumed cause for the lower concentrations since 70°C is ideal for boehmite dissolution. The sodium and uranium concentrations decreased during Strikes 2 and 3 indicating that the removal of each species may have been nearing completion. The 10% uncertainty of each measured concentration is shown as an error bar.



**Figure 3. Predominant dissolved species within the dip sample for each strike**

The total mass of dissolved solids was determined by multiplying the concentrations by the total transfer volume. The total mass of dissolved elemental solids removed is between 3.36E+03 kg and 4.10E+03 kg, with an average mass of dissolved solids removed equal to 3.73E+03 kg. The average mass of dissolved solids removed for each strike is 1.99E+03 kg, 1.15E+03 kg, and 5.87E+02 kg for Strike 1, 2, and 3, respectively.

Strike 1 had the largest quantity of solids dissolved but Strike 2 had the higher solids concentrations. Neither piece of information alone indicates which strike was the most efficient since the initial strike conditions were not constant (i.e., there were different ratios of oxalic acid to the sludge volume). The overall efficiency of each strike is defined as the ratio of dissolved solids per mole of oxalic acid available during the strike. The molar oxalic acid concentration of 8 wt% oxalic acid is 0.91 M; therefore, the total moles of oxalic acid available from fresh feed is 0.91 M multiplied by the total volume of oxalic acid added, shown below in TABLE III. Strike 2 also had an unspent acid concentration associated with the 0.3 meter (12 inch) heel left in Tank 12 following Strike 1. Strike 3 did not have an unspent acid



concentration since the heel remaining after Strike 2 was neutralized. The efficiency of each strike was 8.9, 13.5, and 7.1 g of dissolved solids per mole of oxalic acid for Strikes 1, 2, and 3, respectively. The efficiency of Strike 2 was greater than either Strike 1 or Strike 3. The targeting mixing initiated in Strike 2 that broke up the largest mound likely aided in the increase in efficiency between Strike 1 and 2. Solids that had previously been untouched from previous tank processing readily dissolved. The lower temperatures during Strike 1 likely reduced the efficiency somewhat. Strike 3 was less effective because the more soluble species exposed from the Strike 2 indexing already were removed, so the predominant forms treated during Strike 3 were the moderately soluble and insoluble species.

**TABLE III. Overall dissolution efficiency of each strike**

Parameter	Units	Strike 1	Strike 2	Strike 3
Concentration of 8 wt% oxalic acid added	M	0.91	0.91	0.91
Volume of 8 wt% oxalic acid added	m <sup>3</sup> (gal)	244 (64,551)	69 (18,271)	90 (23,899)
Concentration of unspent oxalic acid	M	N/A	0.19	N/A
Volume of unspent oxalic acid	m <sup>3</sup> (gal)	N/A	118 (31,284)	N/A
Moles of oxalic acid	mol	2.22E+05	8.54E+04	8.23E+04
Average mass of solids dissolved	g	1.99E+06	1.15E+06	5.87E+05
Ratio dissolved solids/ mol oxalic acid	g/mol	8.9	13.5	7.1

### Insoluble Solids

The total mass of dissolved solids does not represent the total mass of residual material removed from Tank 12. Suspended insoluble solids were also removed during the transfers out of the tank. While the insoluble solids were not specifically analyzed, the overall wt% fraction within each dip sample was characterized [18]. TABLE IV below shows the calculated wt% insoluble solids seen in each dip sample at the end of each strike as well as the overall slurry density of the sample. Assuming that the dip samples characterized the entire volume of material transferred out of the tank, the total mass of insoluble solids that was removed was determined by multiplying the transfer volume by the slurry density and the wt% insoluble solids. Up to 1.67E+03 kg of insoluble solids were removed during transfers out of the tank. Compared to the average mass of dissolved solids removed from all three strikes, 3.73E+03 kg, the mass of additional insoluble solids that is assumed to have been removed increases the overall mass of sludge solids removed by 45%. This percentage is biased high because mixing was not utilized during the entire transfer and suspended solids may have settled.

**TABLE IV. Wt% insoluble solids and slurry density**

	Strike 1	Strike 2	Strike 3
wt% insoluble solids	0.13%	0.34%	0.06%
Slurry Density (g/mL)	1.014 ± 0.002	1.011 ± 0.002	1.007 ± 0.002

### Radiological Results

Two dip samples were pulled at the end of each strike; one sample was sent to SRNL for analysis and the other was sent to the F/H laboratory for analysis. TABLE V below shows the radiological data from SRNL, which is the upper portion of the table, and the gross beta/gamma and alpha results from the F/H laboratory, which is in the lower portion of the table. SRNL did not measure a gross alpha concentration, but analyzed for the most predominant alpha species that are typically seen in the waste tanks at SRS. The alpha contributors are highlighted in blue. A gross alpha concentration was only detected at the F/H laboratory for the Strike 3 sample. The predominant radiological components removed during BOA

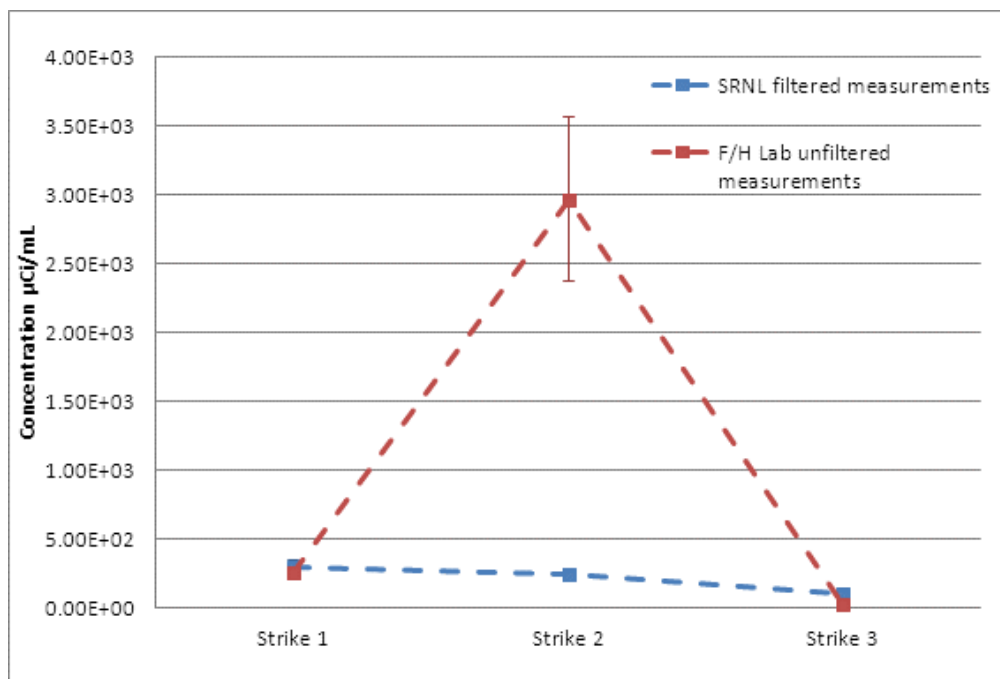
cleaning were beta/gamma contributors. Alpha contributors, such as Pu-238, tend to be associated with insoluble solids that are the most difficult species to remove from a waste tank. Therefore, the results support the overall trend expected for BOA cleaning.

**TABLE V. Radiological data from both SRNL and F/H laboratory**

Species \ Sample ID	Strike 1	Strike 2	Strike 3
	HTF-12-13-102	HTF-12-13-116	HTF-12-13-127
	$\mu\text{Ci/mL}$	$\mu\text{Ci/mL}$	$\mu\text{Ci/mL}$
Co-60	N/A	N/A	8.56E-05
Tc-99	3.24E-04	2.07E-04	1.70E-04
I-129	4.91E-05	3.87E-05	2.64E-05
Eu-154	N/A	3.38E-03	2.72E-03
Th-232	1.05E-06	5.31E-07	7.71E-07
U-233	6.08E-04	5.26E-04	9.71E-05
U-234	5.04E-04	3.49E-04	6.25E-04
U-235	8.04E-06	5.77E-06	9.73E-07
U-236	8.38E-06	4.50E-06	6.47E-07
U-238	1.66E-04	1.21E-04	1.99E-05
Np-237	2.32E-04	1.79E-04	5.92E-05
Pu-238	5.95E-01	3.27E-01	7.48E-02
Pu-239/240	4.31E-02	3.17E-02	6.94E-03
Pu-239	3.15E-02	2.38E-02	7.01E-03
Pu-240	8.77E-03	4.65E-03	2.28E-03
Pu-241	1.42E-01	8.24E-02	1.94E-02
Am-241	3.77E-02	3.44E-02	3.44E-03
Beta/gamma	2.91E+02	2.38E+02	1.01E+02
Species \ Sample ID	200631084	200632293	200632934
	$\mu\text{Ci/mL}$	$\mu\text{Ci/mL}$	$\mu\text{Ci/mL}$
F/H Lab Gross Beta/gamma	2.51E+02	2.97E+03	2.91E+01
F/H Lab Gross Alpha	N/A	N/A	3.74E-02

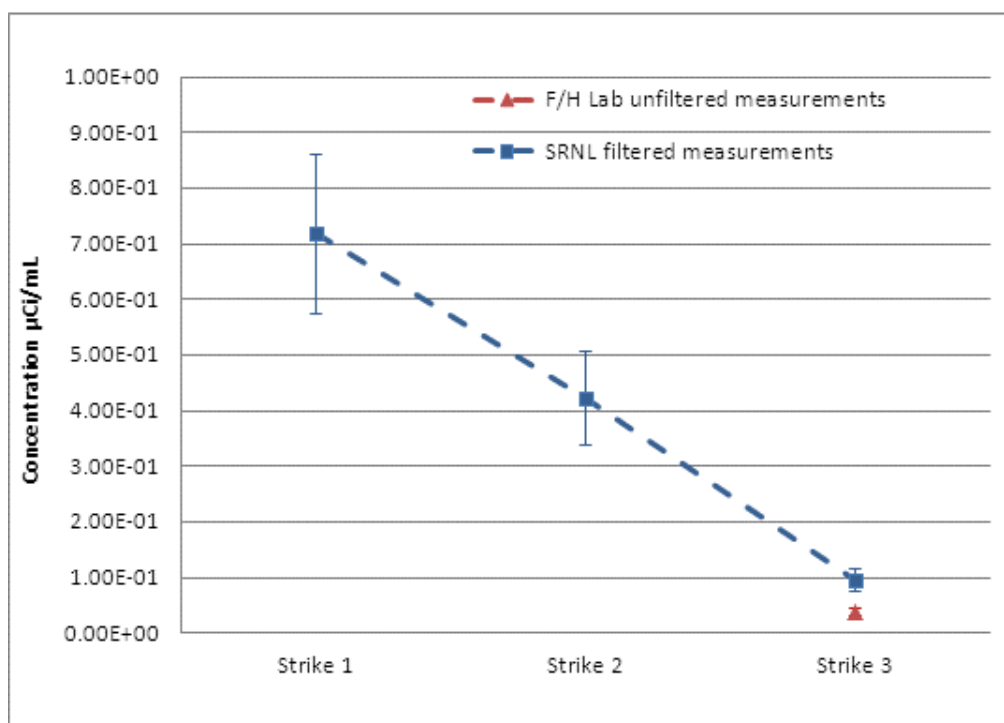
The gross beta/gamma concentrations from each respective lab are considered. The gross alpha concentration that was measured at the F/H laboratory is compared to the summation of all the measured alpha contributors that were measured at SRNL. Both sets of data should reflect similar results since the dip samples were pulled at the same time. Figure 4 shows that the Strike 2 beta/gamma concentration from the F/H laboratory is drastically different than the SRNL results, though. The F/H laboratory did not filter the insoluble solids prior to analyzing the solution, while SRNL filtered every sample prior to analysis. It is plausible that the F/H laboratory sample contained insoluble beta/gamma solids that increased the concentration, while the SRNL results did not include this radiological contribution because the solids were filtered prior to analysis. Of the three strikes, the Strike 2 sample would have the most insoluble solids that impacted the results. Strike 2 was the first targeted mixing campaign that broke up the largest accumulations within Tank 12. The material inside that accumulation had a different chemical composition (i.e., consists of large particles and agglomerations of solids with higher radiological concentrations) since the mound solids remained relatively untouched during the various processing

campaigns, such as low temperature aluminum dissolution with caustic chemicals or washing campaigns with well water. The largest concentration of suspended insoluble radiological solids was expected during this initial accumulations break down. A nominal 20% uncertainty for the analytical method utilized to measure the radiological concentrations was used and is shown as an error bar. Future campaigns should begin indexing the pumps towards the largest accumulations during the first strike rather than solely operating in an oscillating mode. Strike 1 would have had the benefit of dissolving the readily soluble floor material as well as breaking up portions of the large accumulations had some combination of indexing and oscillating mode been utilized instead of merely oscillating, potentially making Strike 1 more effective.



**Figure 4. Gross beta/gamma concentrations from SRNL and F/H laboratory**

Unlike the beta/gamma concentrations, the F/H laboratory only measured a gross alpha concentration during Strike 3. The F/H laboratory reported seeing suspended solids in the Strike 1 and Strike 2 dip samples (none were reported with Strike 3); therefore, insoluble alpha species are expected to also have been removed during the acidic transfers out of Tank 12. Alpha contributors, such as Pu-238, tend to be associated with insoluble solids that are the most difficult species to remove from a waste tank; therefore, the increase in total alpha curies removed based on insoluble solids likely would not be as great as the beta/gamma contribution seen in the Strike 2 dip sample. The trend seen below in Figure 5 indicates that the easier to dissolve alpha species were removed during Strike 1. The insoluble alpha species are likely the predominant radiological species that remains in Tank 12 today, which is consistent with laboratory testing and observations from Tank 5 and 6 chemical cleaning.



**Figure 5. Gross alpha concentrations from SRNL and F/H laboratory**

The BOA cleaning efforts removed mostly beta/gamma species. Considering only the dissolved solids from the SRNL results, between  $1.74\text{E}+05$  and  $2.62\text{E}+05$  Ci of beta/gamma species were removed. Factoring in the suspended solids that were potentially removed in addition to the dissolved solids, as represented by the F/H laboratory data, between  $7.37\text{E}+05$  and  $1.11\text{E}+06$  Ci of beta gamma species were removed. Only the SRNL data was utilized to determine the range of alpha removed since the F/H laboratory data only contained a single gross alpha reading. Between  $3.61\text{E}+02$  and  $5.42\text{E}+02$  Ci of alpha species were removed, which is a low estimate since the SRNL data represents only dissolved solids.

Prior to BOA cleaning efforts, a comprehensive characterization of the residual material was not taken. A single scrape sample of residual floor material was taken and analyzed [19], which is representative of the residual floor material but may not necessarily be representative of the material inside the larger accumulations. In 2011, an analysis was completed of several samples pulled from Tank 12 ranging from 2008 through 2010, which represents varying sludge layers that made up Tank 12 waste prior to any processing from low temperature aluminum dissolution and washing campaigns [20]. This compilation sample likely is more representative of the material inside the accumulations. Therefore, both sets of pre-BOA analyses are used as comparison points for the overall effectiveness of BOA. While neither sample will give a completely accurate estimate for the starting conditions of Tank 12, this analysis will provide reasonable estimations. Final waste characterization of the material remaining in Tank 12 post-BOA cleaning will help close the material balance; however, that information is not currently available. Considering both SRNL and F/H laboratory data, between 45% and 100%<sup>a</sup> of the beta/gamma was removed from Tank 12. The discrepancy in the beta/gamma range was due to the insoluble solids that were not filtered out of the dip sample for F/H laboratory analysis. Near complete removal of beta/gamma

<sup>a</sup> Results actually show that more beta/gamma could have been removed than was originally estimated to be present in the tank.

species is reasonable since the main contributors would be Cs-137/Ba-137 and Sr-90/Y-90, which are fairly soluble, easy to remove species. Between 7% and 9% of the alpha is estimated to have been removed from Tank 12. This range is based solely on the pre-BOA, 2011 compilation sample and the SRNL dip sample. The scrape sample had a much smaller concentration of alpha species, which would overestimate the amount of alpha removed during BOA cleaning. Alpha contributors tend to be associated with insoluble solids that are the most difficult species to remove from a waste tank. Therefore these insoluble particles would not be as prevalent in the residual floor material as they would be in the mound accumulations. The F/H Lab dip sample only measured an alpha concentration during Strike 3; therefore, the total alpha calculated to be removed during BOA cleaning is expected to be underestimated.

### Comparison of Tank 12 BOA Cleaning to Tanks 5 and 6 BOA Cleaning

In 2008, the Tank 5 and 6 BOA cleaning campaigns reduced the solids volume by 4% and 42%, respectively [7]. These campaigns exhibited significant precipitation of non-radiological oxalates. From a radiological standpoint, Tank 5 and 6 BOA cleaning was successful. TABLE VI below shows a comparison of the Tank 12, Tank 5, and Tank 6 campaigns. The higher degree of uncertainty associated with the Tank 12 data is due to the fact that a comprehensive characterization of the residual material was not completed prior to BOA cleaning. Final waste characterization of the material remaining in Tank 12 post-BOA cleaning will help close the material balance. Tank 5 removed 71% of the beta emitters, which was predominantly Sr-90 [3]. A total gamma removal percentage was not determined; however, the amount of Cs-137 removed was measured. Assuming the predominant gamma emitter within the waste was Ba-137, which is in secular equilibrium with Cs-137, it can be inferred that 92% of the gamma was removed. Approximately 17% of the alpha emitters were removed from Tank 5. Tank 6 followed a similar trend: 72% of the beta was removed, 83% of the gamma was removed assuming the predominant species was Ba-137, and 2.5% of the alpha was removed [4]. Compared to these Tanks 5 and 6 BOA cleaning results, Tank 12 was also successful. The Tank 12 campaign did not precipitate an appreciable amount of oxalates as observed in Tanks 5 and 6. Tank 12 is an HM sludge tank known to be higher in mercury and aluminum. The rheology of HM sludge is vastly different than Purex sludge (i.e., Tank 5 and 6 sludge). At lower weight percent solids, HM sludge has a much higher rheological yield stress, which makes removal considerably more difficult. Tank 12 produced comparable radiological removal percentages to Tanks 5 and 6; therefore, the improved BOA cleaning strategy employed during the Tank 12 campaign was a success. Furthermore, the Tank 12 removal percentages for alpha are based solely on soluble alpha removed since an unfiltered sample was not analyzed for gross alpha during Strike 1 and 2. Additional insoluble alpha species are anticipated to have been removed during the acidic transfers out of Tank 12.

**TABLE VI. Radiological comparison between Tank 12, Tank 5, and Tank 6**

Radioactivity	Initial Activity in Tank 12	Activity Removed from Tank 12	Activity Removed from Tank 5	Activity Removed from Tank 6
	Ci	%	%	%
<b>Alpha</b>	8.93E+02 - 5.72E+03 <sup>a</sup>	7 - 9% <sup>b</sup>	17%	2.5%
<b>Beta/Gamma</b>	2.53E+05 - 5.04E+05 <sup>a</sup>	45 - 100% <sup>c</sup>	71 - 92%	72 - 83%

<sup>a</sup> Range is based on both the scrape sample [19] and the 2011 compilation sample [20].

<sup>b</sup> Percentage alpha removed is based solely on the 2011 compilation sample [20] and SRNL dip sample.

<sup>c</sup> Results show that more beta/gamma could have been removed than was originally estimated to be present in the tank.

## CONCLUSIONS

The SRS improved the efficiency of the BOA cleaning process to remove the residual material left in Tank 12. The updated chemical cleaning flowsheet implemented the following improvement controls: the material in Tank 12 was washed prior to BOA cleaning in order to reduce the sodium concentration to less than 0.5 M, the contact rate of the acid with the residual sludge heel was increased by utilizing mixing pumps with targeted mixing strategies to ensure accumulations were broken up, the overall pH of the solution was monitored so that the material could be transferred out of the tank before exceeding pH 2, and the operating temperature was maintained  $< 60^{\circ}\text{C}$  due to tank specific and safety basis related constraints. The operational constraints imposed by the safety basis and physical limitations of Tank 12 did not aid in the dissolution efficiency; however, the improvements that were implemented overcame any disadvantageous influence these constraints might have imposed. The Tank 12 BOA campaign reduced the residual material volume by 77%. Figure 6 below shows a panoramic view of Tank 12 at the conclusion of BOA cleaning, providing an image at the completion of the successful overall waste removal efforts in Tank 12.



**Figure 6. Panoramic Photo of Tank 12 Post BOA Cleaning**

Between 45% and 100% of the beta/gamma emitters and between 7% and 9% of the soluble alpha emitters were estimated to be removed during the cleaning campaign. The radiological removal percentages were comparable to previous BOA cleaning efforts that took place in Tanks 5 and 6. Tank 12 was comprised HM sludge (i.e., the rheological yield stress was greater in Tank 12), yet still managed to produce similar radiological removal percentages to that of the Tank 5 and 6 campaigns indicates marked improvement in the overall cleaning process. Additionally, the suspended insoluble contribution removed is unquantifiable; however, there was evidence proving that some insoluble solids were removed.

Further improvements that could be made in future campaigns include starting the targeted mixing campaign in the first strike rather than beginning in an oscillating mode and improving the temperature controls so that the highest temperature practical is reached. Overall, the controls established for Tank 12 provide a template for an improved cleaning process. This paper reviews the technical effectiveness of the oxalic acid cleaning process in Tank 12. Overall cost-benefit analyses for implementing bulk oxalic acid cleaning and the downstream impacts of the oxalates on the liquid waste flowsheet at Savannah River Site will be addressed separately.



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