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**Permanent**

# **Oxalate Mass Balance during Chemical Cleaning in Tank 6F**

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July 22, 2011

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March 7, 2011

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## LIST OF ACRONYMS

AD	Analytical Development
IC	Ion Chromatography
ICPES	Inductively Coupled Plasma Emission Spectroscopy
ICPMS	Inductively Coupled Plasma Mass Spectrometry
LWO	Liquid Waste Organization
SMP	Submersible Mixer Pumps
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site

## 1.0 SUMMARY

The Savannah River Remediation (SRR) is preparing Tank 6F 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 to determine whether the tank is ready for closure.

SRR 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. Analysis of the anions showed the measured oxalate removed from Tank 6F to be approximately 50% of the amount added in the oxalic acid. To close the oxalate mass balance, the author collected solid samples, leached them with nitric acid, and measured the concentration of cations and anions in the leachate.

The conclusions from this work follow.

- Approximately 65% of the oxalate added as oxalic acid was removed with the decanted liquid.
- Approximately 1% of the oxalate (added to the tank as oxalic acid) formed precipitates with compounds such as nickel, manganese, sodium, and iron (II), and was dissolved with nitric acid.
- As much as 30% of the oxalate may have decomposed forming carbon dioxide.

The balance does not fully account for all the oxalate added. The offset represents the combined uncertainty in the analyses and sampling.

## 2.0 INTRODUCTION

SRR is preparing Tank 6F 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 6F, SRR estimated a sludge heel of 5,984 gallons remained after mechanical sludge removal.<sup>1</sup> To remove this sludge heel, SRR performed chemical cleaning. The chemical cleaning included two oxalic acid strikes, a spray wash, and a water wash.

SRR conducted the first oxalic acid strike as follows. Personnel added 110,830 gallons of 8 wt% oxalic acid to Tank 6F and mixed the contents of Tank 6F with two submersible mixer pumps (SMPs) for approximately four days. Following the mixing, they transferred 115,903 gallons of Tank 6F material to Tank 7F. The SMPs were operating when the transfer started and were shut

down approximately five hours after the transfer started. SRR collected a sample of the liquid from Tank 6F and submitted it to SRNL for analysis.<sup>2</sup> Mapping of the tank following the transfer indicated that 2,400 gallons of solids remained in the tank.

SRR conducted the second oxalic acid strike as follows. Personnel added 28,881 gallons of 8 wt% oxalic acid to Tank 6F. Following the acid addition, they visually inspected the tank and transferred 32,247 gallons of Tank 6F material to Tank 7F.<sup>3</sup> SRR collected a sample of the liquid from Tank 6F and submitted it to SRNL for analysis.<sup>2</sup> Mapping of the tank following the transfer indicated that 3,248 gallons of solids remained in the tank.

Following the oxalic acid strikes, SRR performed Spray Washing with oxalic acid 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 4,802 gallons of 8 wt % oxalic acid to Tank 6F through the spray mast installed in Riser 2, added 4,875 gallons of oxalic acid through Riser 7, added 5,000 gallons of deionized water into the tank via Riser 2, and 5,000 gallons of deionized water into the tank via Riser 7. Following the Spray Wash, they visually inspected the tank and transferred 22,430 gallons of Tank 6F material to Tank 7F.<sup>4</sup> SRR collected a sample of the liquid from Tank 6F and submitted it to SRNL for analysis.<sup>2</sup>

Following the Spray Wash and transfer, SRS added 113,935 gallons of well water to Tank 6F. They mixed the tank contents with a single SMP and transferred 112,699 gallons from Tank 6F to Tank 7F.<sup>4</sup> SRR collected a sample of the liquid from Tank 6F and submitted to SRNL for analysis.<sup>2</sup> Mapping of the tank following the transfer indicated that 3,488 gallons of solids remained in the tank.

The volume of sludge remaining after the second acid strike is larger than the volume remaining after the first acid strike. The volume of sludge remaining after the water wash was larger than the volume remaining after the second acid strike. There are several plausible explanations for these observations. The differences could be from uncertainty in determining the volume of the sludge remaining. The “sludge” contains solid sludge particles as well as entrained liquid. If the amount of entrained liquid increased, the sludge volume would increase. Metal oxides (e.g., hematite or nickel oxide) have a larger density than metal oxalates. If the addition of oxalic acid changed the insoluble metal compounds from metal oxides to metal oxalates, their volume would increase.

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.

The analysis of the liquid samples showed the measured oxalate concentration to be much less than the concentration of oxalic acid added to the tank (see Table 1).<sup>2</sup>

**Table 1.** Anion Analysis of Tank 6F Liquid Samples

<u>Species</u>	<u>Strike 1 (mg/L)</u>	<u>Strike 2 (mg/L)</u>	<u>Spray Wash (mg/L)</u>	<u>Water Wash (mg/L)</u>
Oxalate	44,363 ± 4,436	51,000 ± 5100	24,600 ± 2460	1884 ± 188
Expected oxalate	79,200	79,200	42,200	1,760

### 3.0 EXPERIMENTAL WORK

SRNL received a solid sample from Tank 6F. Personnel performed a nitric acid leach of the sample to attempt to quantify the amount of oxalate present. They performed the leach as follows.

#### 3.1 REAGENT PREPARATION

Personnel prepared ~ 200 mL of 0.25 M nitric acid. We selected the nitric acid concentration based on SRNL's Alternative Enhanced Chemical Cleaning Studies.<sup>5</sup>

#### 3.2 SAMPLE PREPARATION

They placed ~ 0.2 g of Tank 6F sludge into each of two poly bottles. They added ~ 20 grams of nitric acid to each bottle, gently mixed the bottles, allowed the bottles to sit for one hour, collected two samples from each bottle, filtered the samples with a 0.45 μ syringe filter, and submitted the samples to Analytical Development (AD) for analysis by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) and Ion Chromatography (IC). These samples are referred to as Sample 1 and 2.

Following analysis of these samples, we performed a second leach on the remaining solids (Referred to as Samples 11 and 12). For this leach, we decanted the supernate from the bottles, added ~ 40 grams of nitric acid to each bottle, gently mixed the bottles, allowed the bottles to sit for one hour, collected two samples from each bottle, filtered the samples with a 0.45 μ syringe filter, and submitted the samples to AD for analysis by ICP-ES and IC.

### 4.0 RESULTS

Table 2 shows the results from the analysis of the acid leach solutions. The concentrations listed in the table are the average of two replicates. The results show a large amount of oxalate in the first leach samples (Samples 1 and 2). In addition, these samples show large amounts of nickel, manganese, sodium, and iron. Nickel is known to form a precipitate with oxalate.<sup>6</sup> Previous XRD analyses of these solids showed the presence of nickel oxalate.<sup>7</sup> Manganese, iron (II), and iron (III) also will form precipitates with oxalate.<sup>7</sup> The sodium concentration in the first leach is of the same magnitude, but lower, than the iron, manganese, and nickel concentrations. The sodium is likely from the dissolution of sodium oxalate or sodium bioxalate. If the nickel and manganese are present as oxalate compounds, the solid samples should contain one mole of oxalate for each mole of nickel or manganese. If the sodium is present as sodium oxalate, the solid samples will contain two moles of sodium per mole of oxalate. If the sodium is present as sodium bioxalate, the solid samples will contain one mole of sodium per mole of oxalate. The iron could be present as an iron oxalate or as an iron oxide, such as hematite, maghemite, or

goethite. The XRD analysis showed the primary crystalline iron compounds to be hematite, maghemite, and goethite.<sup>7</sup> Therefore, the moles of oxalate should be greater than the moles of nickel plus manganese plus sodium, and less than the moles of nickel plus manganese plus sodium plus iron. Considering the uncertainty in the data, there is good agreement between the molar concentrations of manganese, nickel, and oxalate.

**Table 2. Tank 6F Nitric Acid Leach Results**

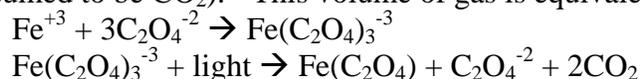
Process Sample	Sample 1	Sample 2	Sample 11	Sample 12
Concentration in Process Sample (g/kg)				
Fe	24	27	13.5	10.7
Mn	6	7	7.2	4.5
Ni	22	23	31.1	18.9
Na	2	2	0.3	0.2
Oxalate	63	72	<10	<10
Concentration in Process Sample (Mole/kg)				
Fe	0.43	0.48	0.24	0.19
Mn	0.12	0.12	0.13	0.08
Ni	0.37	0.39	0.53	0.32
Na	0.09	0.10	0.01	0.01
Fe+Mn+Ni+Na	1.01	1.09	0.92	0.60
Oxalate	0.71	0.82	<0.11	<0.11
Amount Leached (Mole)				
Fe	11,097	12,400	6,303	4,987
Mn	3,000	3,129	3,399	2,118
Ni	9,584	10,264	13,788	8,349
Oxalate	18,550	21,212	<2840	<2950
Fraction of Species in Solids Following Chemical Cleaning Dissolved				
Fe	33%	36%	19%	15%
Mn	62%	64%	70%	44%
Ni	46%	49%	66%	40%
Oxalate <sup>i</sup>	8%	9%	<1%	<1%

The analysis of Samples 11 and 12 shows a significant reduction in the amount of oxalate, nickel, manganese, sodium, and iron dissolved. The result suggests that little oxalate would be recovered by an additional nitric acid leach, and most of the insoluble oxalate has been recovered by the first leach. The results show the addition of dilute nitric acid was effective in dissolving additional iron, manganese, and nickel, and might be effective in dissolving species that have low solubility in oxalic acid, such as plutonium.

Table 2 shows that a small fraction of the oxalate was dissolved by the nitric acid, and minimal oxalate dissolved in the second leach. The second leach dissolved additional iron, manganese, and nickel. To determine the fate of the oxalate, we performed an oxalate balance.

<sup>i</sup> Oxalate fraction is fraction of "missing oxalate"

In Test 1 (50 °C, Mixing) of the Tank 6F Oxalic Acid Cleaning Simulant Test, 55 L of gas was generated (assumed to be CO<sub>2</sub>).<sup>8</sup> This volume of gas is equivalent to 2.08 moles CO<sub>2</sub>. Since



2.08 moles of CO<sub>2</sub> could be produced from 1.04 moles of oxalate. The test solution contained 7656 mL of 8 wt % (0.92 M) oxalic acid, which is equivalent to (7.656 L)(0.92 mole/L) = 7.04 moles oxalate. Dividing 1.04/7.04 = 0.15 yields the amount of CO<sub>2</sub> gas generated is 15% of potential theoretical yield from oxalic acid decomposition. Another mechanism for carbon dioxide generation is the acidification of carbonate. The feed in Test 1 contained 0.32 moles of carbonate. The maximum amount of carbon dioxide the carbonate could form is 0.32 moles, approximately 15% of the carbon dioxide formed.

In Actual Waste Test 1 (50 °C, Mixing), the calculated volume of gas generated from adding 100,000 gallons of 8 wt % oxalic acid is 184,000 ft<sup>3</sup>.<sup>9</sup> Since SRR added 110,830 + 28,881 + 9677 = 149,388 gallons of 8 wt % oxalic acid to Tank 6F, they could have produced (184,000 ft<sup>3</sup>)(1.49)(28.317 L/ft<sup>3</sup>) = 7.76 x 10<sup>6</sup> L of CO<sub>2</sub>. This volume is equivalent to 2.93 x 10<sup>5</sup> moles of CO<sub>2</sub>. The equivalent amount of oxalate would be 1.46 x 10<sup>5</sup> moles. The amount of oxalate added to Tank 6F (in the oxalic acid) is 4.58 x 10<sup>7</sup> grams or 5.20 x 10<sup>5</sup> moles of oxalate. The fraction of oxalate that could have decomposed to CO<sub>2</sub> is 1.46/5.20 = 0.28. According to Actual Waste Test data, 28% of oxalate added would decompose to form CO<sub>2</sub>. The amount of carbonate in the feed for this test is not known.

In the simulant and actual waste tests, the feed slurry was exposed to light which is needed for the decomposition reaction. While the interior of Tank 6H is dark, it is exposed to high doses of radiation, which may help the oxalate decomposition reaction.

The mass balance for Tank 6F is shown below.

- 5.20 x 10<sup>5</sup> moles of oxalate added to the tank based on the volumes and concentration of oxalic acid added to the tank.
- 1.46 x 10<sup>5</sup> moles of oxalate decomposed to form CO<sub>2</sub> based on the CO<sub>2</sub> generation measured in the actual waste test conducted at 50 °C.
- 3.74 x 10<sup>5</sup> moles of oxalate remaining after subtracting the oxalate that decomposed from the oxalate added to the tank.
- 3.25 x 10<sup>5</sup> moles of oxalate removed in liquid based on analysis of the liquid samples.
- 0.49 x 10<sup>5</sup> moles of oxalate remained in the tank following chemical cleaning. This amount is ~9% of the amount of oxalate added to the tank. Of the oxalate calculated to be remaining in the tank following chemical cleaning, approximately 10% (5000 moles) was dissolved by the nitric acid leach. The amount of oxalic acid remaining in the solids and removed by the nitric acid leach was ~1% of the oxalate added to the tank.

This mass balance shows approximately half (63%) of the oxalate added to Tank 6F was dissolved and removed with the liquid. Approximately 1% of the added oxalate formed precipitates with species such as nickel, manganese, and iron (II) and dissolved after nitric acid leaching. These streams leave about 35% of the added oxalate unaccounted for. As much as

30% of the oxalate may have decomposed to form carbon dioxide, which would leave about 5% of the added oxalate unaccounted for.

## 5.0 CONCLUSIONS

The conclusions from this work follow.

- Approximately 65% of the oxalate added as oxalic acid was removed with the decanted liquid.
- Approximately 1% of the oxalate (added to the tank as oxalic acid) formed precipitates with compounds such as nickel, manganese, sodium, and iron (II), and was dissolved with nitric acid.
- As much as 30% of the oxalate may have decomposed forming carbon dioxide.

## 6.0 REFERENCES

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