

## **Actual-Waste Tests of Enhanced Chemical Cleaning for Retrieval of SRS HLW Sludge Tank Heels and Decomposition of Oxalic Acid - 12256**

Christopher J. Martino\*, William D. King\*, and Edward T. Ketusky\*\*

\*Savannah River National Laboratory, Aiken, SC 29808

\*\*Savannah River Remediation, Aiken, SC 29808

### **ABSTRACT**

Savannah River National Laboratory conducted a series of tests on the Enhanced Chemical Cleaning (ECC) process using actual Savannah River Site waste material from Tanks 5F and 12H. Testing involved sludge dissolution with 2 wt% oxalic acid, the decomposition of the oxalates by ozonolysis (with and without the aid of ultraviolet light), the evaporation of water from the product, and tracking the concentrations of key components throughout the process. During ECC actual waste testing, the process was successful in decomposing oxalate to below the target levels without causing substantial physical or chemical changes in the product sludge.

### **INTRODUCTION**

In support of Savannah River Site (SRS) tank closure efforts, the Savannah River National Laboratory (SRNL) conducted actual-waste testing to evaluate the Enhanced Chemical Cleaning (ECC) process. ECC is an alternative to the baseline 8 wt% oxalic acid (OA) chemical cleaning technology for tank sludge heel removal.[1,2] Chemical cleaning is necessary because mechanical removal of the sludge from the 1 to 1.3 million gallon waste tanks leaves several thousand gallons of residual material adhering to the tank bottom, walls, and cooling coils. The large quantities of sodium oxalate and other metal oxalates formed from the baseline chemical cleaning process impact downstream processes by requiring additional washing during sludge batch preparation and increase the amount of material that must be processed in the tank farm evaporator systems and the Saltstone Processing Facility. ECC was identified by Savannah River Remediation (SRR) as a potential method to minimize the impact of oxalate additions to the SRS Tank Farms without adding additional components to the waste.[3,4,5]

ECC utilizes a more dilute OA to dissolve the sludge heel and an oxidation process to decompose the resulting oxalate. Figure 1 contains a simplified diagram of the ECC process. Sludge is dissolved in the tank being cleaned for closure (the Treatment Tank) by adding 2 wt% OA and mixing the tank contents. OA is used because it is effective at dissolving many of the sludge materials (such as iron and uranium), potentially freeing other sludge components that may not dissolve completely in OA. The mixture of dissolved sludge and suspended insoluble solids is removed from the Treatment Tank and transferred to the ECC reactor. In the ECC reactor, concentrated ozone gas is added to the reactor, resulting in soluble ozone and hydroxyl radicals that aid the decomposition of oxalate ion to carbon dioxide gas. Ultraviolet (UV) light can also be used in the ECC reactor to augment the decomposition of OA.[6,7] The decomposition of oxalic acid inside the ECC reactor causes the pH to increase and the dissolved sludge to precipitate, mostly in the form of metal oxides. The ECC product is pH adjusted to excess hydroxide and sent to an existing Deposition Tank for storage for future waste processing. Optionally, the ECC process can contain an evaporator to remove water from the dilute slurry prior to storage in the Deposition Tank.

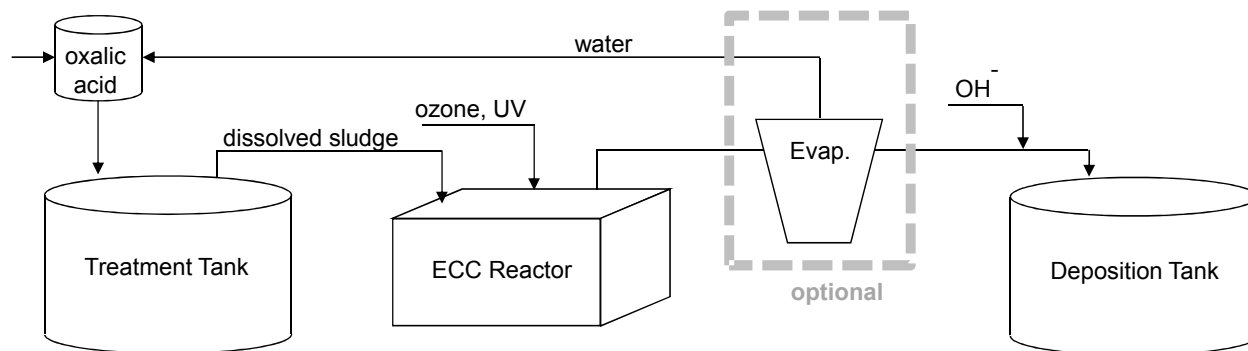


Fig. 1. Simplified Diagram of Enhanced Chemical Cleaning Process Potential Implementation

The primary goals for the ECC actual waste test were to confirm ECC performance with real tank sludge samples, to determine the impact of ECC on fate of actinides and the other sludge metals, and to determine changes, if any, in solids flow and settling behavior. SRNL conducted tests using actual SRS waste material from SRS Tanks 5F and 12H. Testing involved sludge dissolution with batches of 2 wt% OA; the decomposition of the oxalates by ozonolysis with and without the aid of UV light; the evaporation of a portion of the material for water removal; and tracking the concentrations of key components in the Deposition Tank at a variety of storage conditions. The target for the decomposition of oxalate was >99.5% (<100 mg/L oxalate in reactor product).

## METHOD

A series of ECC process experiments utilizing SRS actual-waste sludge was performed in the SRNL Shielded Cells facility. Testing of sludge dissolution, oxalate decomposition, and product evaporation portions of the ECC flowsheet was performed in a single apparatus designed and fabricated by AREVA NP. As seen in Figure 2, the apparatus contained three primary modules, one each for the dissolution of sludge from the Treatment Tank (Dissolution Module), the decomposition of oxalate in an ozone/UV reactor (Decomposition Module), and the removal of water for the recovery of dissolution fluid volume (Evaporator Module). Adjustment of pH and storage of material in the Deposition Tank was investigated outside of the apparatus by holding portions of the material in bottles at applicable Deposition Tank temperatures.

Sludge (48 to 63 grams) was loaded into the Dissolution Module basket. A series of 3.2 L batches of 2 wt% OA was added to the Dissolution Module, recirculated, and heated to 70 °C for 8 hours. Dissolved sludge material (along with some entrained undissolved sludge) was transferred to the Decomposition Module. The series of dissolved sludge batches in the Decomposition Module were recirculated and heated to 70 °C. Ozone was fed to the Decomposition Module through an eductor until the fluid pH and the sample analysis indicate that oxalates have been decomposed to levels less than 100 mg/L. An ozone generator located outside of the Shielded Cells provided 2 L/min of 5 wt% O<sub>3</sub> in O<sub>2</sub> at a pressure of 8 psig. The oxalic acid decomposition was performed with and without the application of UV light to the fluid. Portions of the product from the Decomposition Module are processed in the Evaporator Module, a vacuum evaporation system operating at 70 °C. Evaporated and non-evaporated ECC product slurries were held at temperature (nominally 50 °C) and monitored over the course of several weeks.

The use of actual waste sludge limited the scale of the test, with the Decomposition Module in the test being between 1:2400 and 1:3000 scale when compared to the volume of the planned field implementation.[3,5]

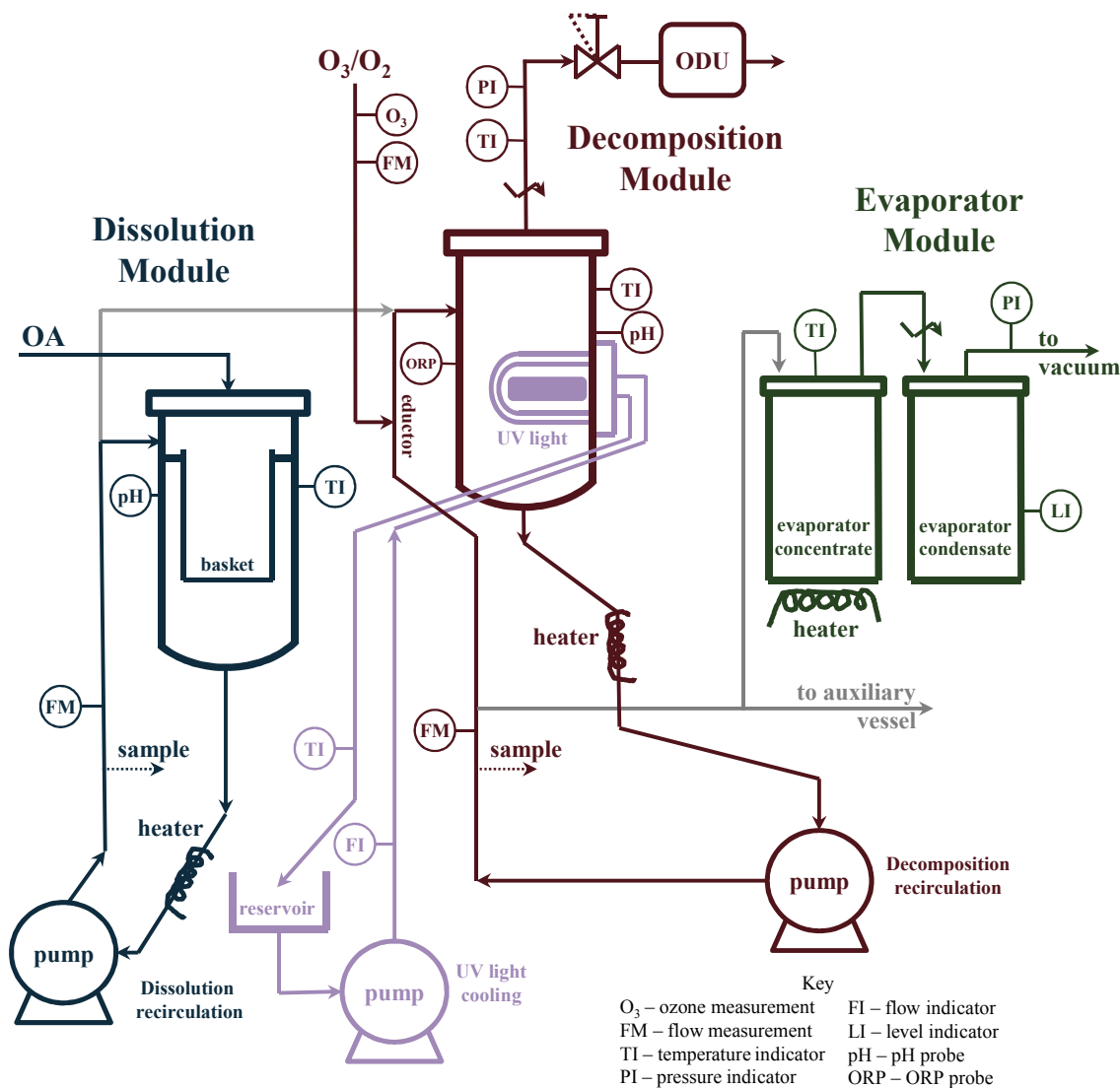


Fig. 2. Schematic of ECC Equipment Main Shielded Cells Skid

Samples are taken from various portions of the ECC process during the actual waste testing. Soluble fractions are approximated by the filtrate that passes through 0.45 micron nylon filters. Sample preparation for soluble fractions is by dilution in 3 M nitric acid and preparation for bulk or insoluble fractions is by aqua regia dissolution. Analysis for metals, radionuclides, and anions are performed at SRNL.

The two actual-waste sludges used in this testing represent the two main types of waste sludge in the SRS Tank Farm. The Tank 5F sludge sample is from the heel of sludge remaining after bulk waste removal from an F-area PUREX waste tank. The Tank 12H material is sludge contained in slurries sampled during bulk waste removal in an H-area HM waste tank. The

primary component of Tank 5F material is iron (as hematite) and the primary component of Tank 12H material is aluminum (as boehmite).[8,9]

Table I contains a description of the different tests performed as part of this actual-waste demonstration of the ECC process. An initial test without sludge was performed by processing a single OA batch in the Decomposition Module. Tests 1 and 2 were performed on the entire ECC process, including sludge dissolution of each waste feed, oxalic acid decomposition without the aid of UV light, and multiple Deposition Tank storage conditions (with and without ECC product evaporation). Tests 3 and 4 used dissolved sludge material from a previous study to gather data on the oxalate decomposition with the aid of UV light.

Table I. Description of Enhanced Chemical Cleaning Actual Waste Tests

Test Number	Waste Tank	Dissolution Study	Oxalate Decomposition	Evaporation Study	UV Light	OA Batches	Storage Conditions
0	None	No	Yes	No	No	1	0
1	12H	Yes	Yes	Yes	No	3	8
2	5F	Yes	Yes	Yes	No	3	8
3	12H	No	Yes	No	Yes	2	1
4	5F	No	Yes	No	Yes	2	1

## RESULTS AND DISCUSSION

### Sludge Dissolution and Removal

Using three OA batches per test, Test 1 showed an approximately 73% removal of Tank 12H sludge and Test 2 showed an approximately 80% removal of Tank 5F sludge. Removal includes both dissolution of soluble components and partial transfer of insoluble solids. The dissolution process was constrained to eight hours per OA batch and thus did not precisely represent the in tank dissolution process. The in-tank dissolution process would effectively be a minimum of three days and a maximum of several months as the waste tank inventory is fed in small batches through the ECC reactor.[3,5]

Table II: Percent Removal during Dissolution of Sludge with 2 wt% Oxalic Acid

	Tank 12H (HM sludge)	Tank 5F (PUREX sludge)
Iron	78%	75%
Aluminum	46%	96%
Manganese	95%	90%
Nickel	68%	69%
Thorium	37%	16%
Strontium	79%	92%
Uranium	99%	99.9%
Plutonium	62%	87%
Americium	26%	73%

Table II contains mass balance information for the removal of sludge during Test 1 (Tank 12H) and Test 2 (Tank 5F) after three batches of OA. Residuals remaining in the Dissolution Module at the conclusion of Test 1 were primarily aluminum (90% of the mass as boehmite) with small amounts of iron and manganese. Residuals remaining at the conclusion of Test 2 were primarily iron (66% of the mass as hematite) with small amounts of manganese and nickel. For both tests, uranium and manganese were removed more efficiently than the bulk sludge material while americium and thorium were more resistant to dissolution than the bulk sludge material.

### **Oxalic Acid Decomposition**

OA decomposition to <100 ppm oxalate in nominal 3.2 L batches of dissolved sludge was accomplished in 8 to 12.5 hours with the application of 5 wt% ozone at 70 °C without the aid of UV light. Similar OA decomposition testing with the aid of UV light was accomplished in 4.5 to 8 hours. The use of UV light appears to speed up the oxalate decomposition rate significantly during the period at the start of each decomposition batch.

As shown in Figures 3 and 4, the pH and oxidation/reduction potential (ORP) were tracked during oxalate decomposition testing. The pH and ORP curves for the three OA batches for only Test 1 are shown, but similar trends were obtained for Tests 2 through 4. The pH correlated well with the progress of OA decomposition. Fluctuations in ORP were noted during periods of high rate of pH change and precipitation of sludge solids. As seen for Test 1, each subsequent batch of dissolved sludge typically requires longer oxalate decomposition times. This is likely due to the higher starting pH, the higher metal content, and the possibly lower soluble oxalate content in the earlier dissolved sludge batches. Note that several metals present in SRS sludge have been shown to heterogeneously or homogeneously catalyze ozone and UV oxidation reactions for the decomposition of organics.[6,7,10,11,12] The oxalate decomposition in the test that did not contain sludge required the longest decomposition time (14 hours).

Tables III through VI contain the measurement of the soluble components in the Decomposition Module samples for each test and OA batch taken at various times after the start of application of ozone. Timing of the intermediate samples was based on changes observed in the pH. The initial sample and earliest Decomposition samples have the highest solubilities of many components. Samples from the end of the decomposition process typically had the lowest soluble level of sludge components, indicating that sludge is precipitating as the oxalate is decomposing and the pH is increasing.

During the ECC testing without UV light, approximately 5 moles of ozone was fed to the Decomposition Module for every mole of oxalate decomposed. This molar ratio was higher than the 3:1 ozone to oxalate ratios and lower than that were attained during simulant testing.[5] The less efficient utilization of ozone in this testing may be due to several factors. Some ozone feed conditions were lower than the process baseline conditions, including the concentration (5 wt% versus the baseline 10 wt%) and pressure (8 psi versus the baseline 10 psi). The ozone generator was located an extended distance from the apparatus in the Shielded Cells, potentially allowing a portion of the ozone to decompose prior to introduction to the Decomposition Module. The Decomposition Module recirculation rate was not optimized and was maintained at the maximum capability of the recirculation pump.

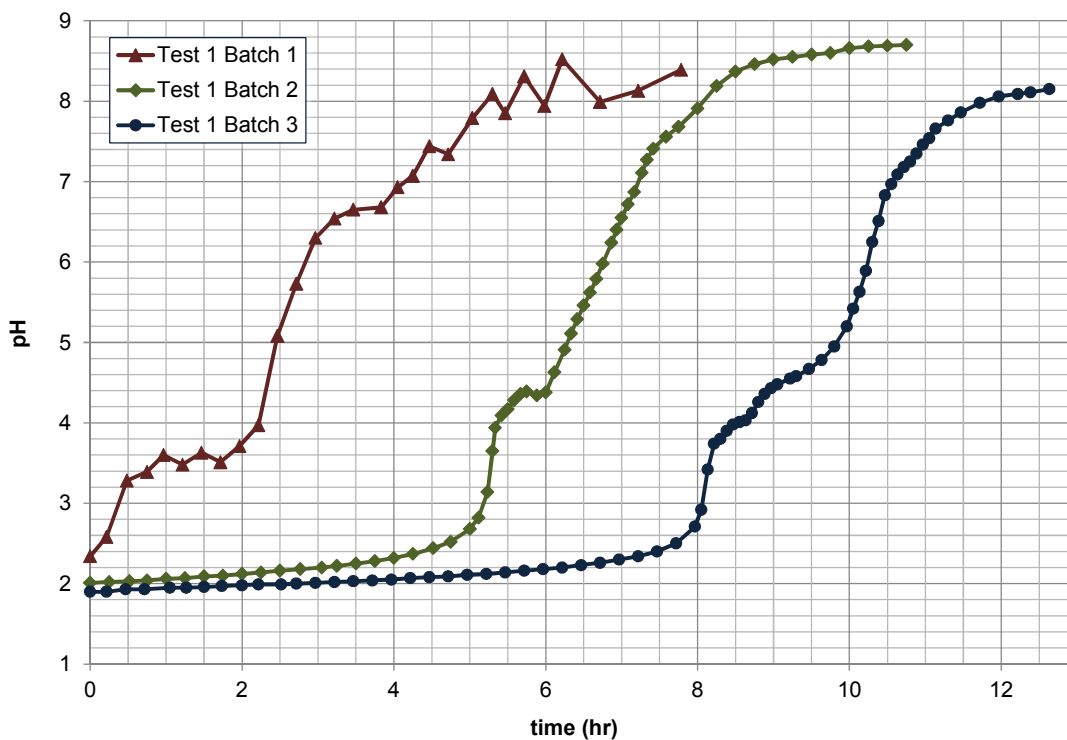


Fig. 3. Measured pH Change during the Oxalate Decomposition Process for Tank 12H Dissolved Sludge (No UV Light)

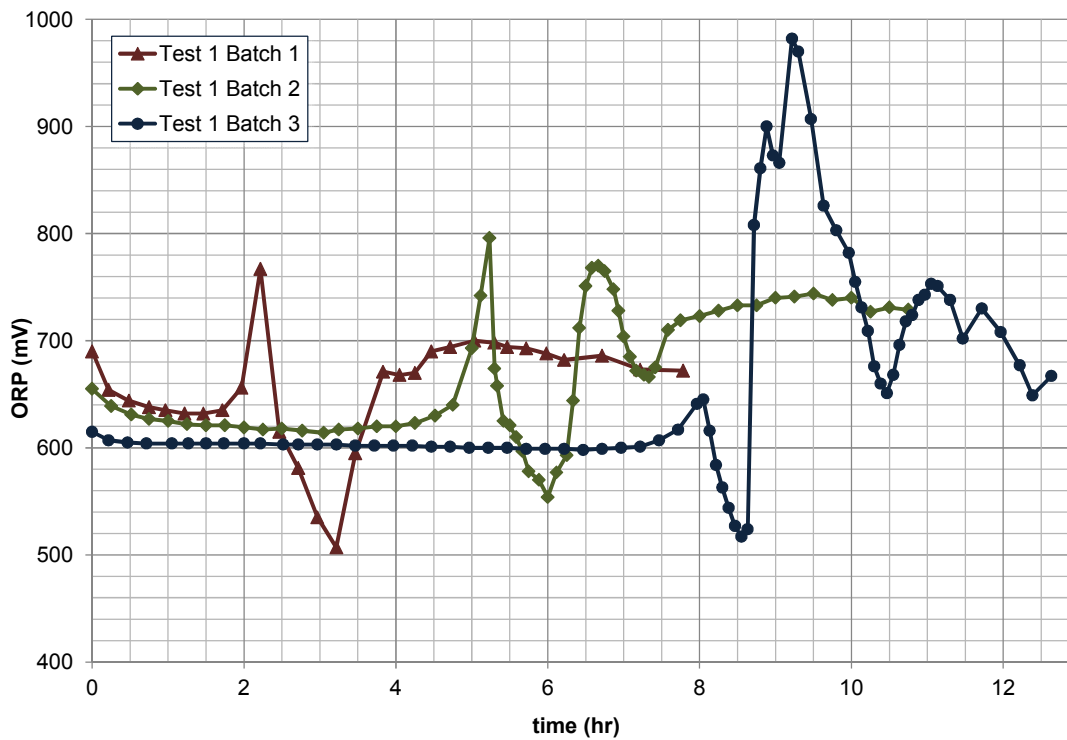


Fig. 4. Measured ORP during the Oxalate Decomposition Process for Tank 12H Dissolved Sludge (No UV Light)

Table III. Measurement of Soluble Components during the ECC Oxalate Decomposition Process (Tank 12H Sludge, No UV Light)

analyte	units	initial	1st sample	2nd sample	3rd sample	final sample
Test 1, Batch 1						
time	hr	0.0	1.1	4.6	--	7.6
pH	--	2.34	3.48	7.34	--	8.39
ORP	mV	690	632	694	--	672
Oxalate	mg/L	8.05E+03	1.49E+03	4.00E+02	--	<4.79E+01
Al	mg/L	2.35E+02	1.32E+02	3.51E+00	--	2.93E+01
Fe	mg/L	4.43E+02	3.62E+00	3.39E-01	--	4.97E-01
Mn	mg/L	3.21E+02	3.90E-01	9.92E-01	--	3.20E+00
Th-232	mg/L	1.55E+01	3.34E-01	1.63E-02	--	<1.91E-02
U-235	mg/L	1.43E+00	1.20E+00	4.81E-01	--	6.30E-01
U-238	mg/L	8.08E+01	6.37E+01	2.54E+01	--	3.38E+01
Pu-238	dpm/mL	6.46E+06	4.21E+06	2.06E+06	--	2.20E+06
Pu-239/240	dpm/mL	3.46E+05	2.20E+05	1.04E+05	--	1.13E+05
Sr-90	dpm/mL	1.28E+08	--	--	--	8.17E+05
Test 1, Batch 2						
time	hr	0.0	3.5	6.8	--	10.8
pH	--	2.01	2.25	5.98	--	8.70
Oxalate	mg/L	1.50E+04	2.88E+03	7.12E+02	--	<4.98E+01
Al	mg/L	2.19E+02	2.71E+02	9.09E+01	--	1.51E+01
Fe	mg/L	1.97E+02	2.64E+02	1.12E+01	--	5.51E-01
Mn	mg/L	1.00E+02	1.48E+02	3.27E+00	--	2.09E+00
Th-232	mg/L	1.09E+01	1.24E+01	1.11E-01	--	<9.08E-03
U-235	mg/L	4.25E-01	5.67E-01	3.89E-01	--	<5.34E-02
U-238	mg/L	2.33E+01	2.85E+01	2.09E+01	--	2.64E+00
Pu-238	dpm/mL	1.73E+06	2.33E+06	1.72E+06	--	2.48E+05
Pu-239/240	dpm/mL	8.53E+04	1.20E+05	8.94E+04	--	1.25E+04
Sr-90	dpm/mL	5.21E+07	--	--	--	1.68E+05
Test 1, Batch 3						
time	hr	0.0	4.2	8.5	10.3	12.5
pH	--	1.90	2.07	3.98	6.25	8.11
ORP	mV	615	602	527	676	649
Oxalate	mg/L	1.84E+04	5.67E+03	6.59E+02	1.85E+02	<3.96E+01
Al	mg/L	1.94E+02	2.73E+02	2.85E+02	2.47E+01	2.10E+00
Fe	mg/L	7.36E+01	1.65E+02	9.36E+01	7.09E-01	6.99E-01
Mn	mg/L	2.45E+01	7.71E+01	6.43E+01	5.85E-01	2.27E+00
Th-232	mg/L	1.38E+01	1.69E+01	6.87E+00	2.12E-02	<9.37E-03
U-235	mg/L	7.92E-02	2.39E-01	2.09E-01	1.34E-01	<9.37E-03
U-238	mg/L	4.09E+00	1.27E+01	1.14E+01	6.84E+00	2.53E-02
Pu-238	dpm/mL	5.12E+05	1.36E+06	1.14E+06	9.72E+05	7.30E+03
Pu-239/240	dpm/mL	2.49E+04	6.99E+04	6.02E+04	5.08E+04	<6.45E+02
Sr-90	dpm/mL	1.54E+07	--	--	--	7.82E+05

Note: "--" indicates that data is not available.

Table IV. Measurement of Soluble Components during the ECC Oxalate Decomposition Process (Tank 5F Sludge, No UV Light)

analyte	units	initial	1st sample	2nd sample	3rd sample	final sample
Test 2, Batch 1						
time	hrs	0	2.5	5.1	9.7	10.9
pH	--	2.20	--	--	--	--
Oxalate	mg/L	3.75E+03	3.13E+02	6.51E+02	<8.93E+01	<7.82E+01
Al	mg/L	2.95E+02	2.70E+02	3.87E+01	2.82E+01	2.81E+01
Fe	mg/L	2.72E+03	8.47E+02	5.46E+01	5.48E+00	5.08E+00
Mn	mg/L	8.77E+02	7.24E+02	1.80E+01	4.61E+00	4.11E+00
U-235	mg/L	1.17E+01	9.93E+00	6.05E+00	5.36E+00	4.58E+00
U-238	mg/L	1.72E+03	1.45E+03	8.84E+02	7.38E+02	6.73E+02
Pu-238	dpm/mL	4.13E+04	3.58E+04	1.94E+04	7.40E+03	7.37E+03
Pu-239/240	dpm/mL	1.27E+05	3.68E+04	8.36E+03	5.46E+03	4.88E+03
Sr-90	dpm/mL	1.15E+09	--	--	--	1.56E+07
Test 2, Batch 2						
time	hrs	0	3.5	5.0	--	7.6
pH	--	1.27	3.20	6.38	--	8.52
Oxalate	mg/L	1.04E+04	<8.94E+01	4.04E+02	--	<8.20E+01
Al	mg/L	7.04E+01	1.56E+02	2.59E+01	--	5.69E+00
Fe	mg/L	1.42E+03	8.29E+02	3.60E+00	--	4.59E+00
Mn	mg/L	1.75E+02	2.88E+02	4.81E-01	--	1.74E+00
U-235	mg/L	1.33E+00	3.78E+00	2.33E+00	--	3.30E-01
U-238	mg/L	1.85E+02	5.79E+02	3.64E+02	--	4.99E+01
Pu-238	dpm/mL	4.10E+04	7.16E+04	3.15E+04	--	4.42E+03
Pu-239/240	dpm/mL	3.89E+04	4.80E+04	1.83E+04	--	2.79E+03
Sr-90	dpm/mL	1.83E+08	--	--	--	2.58E+06
Test 2, Batch 3						
time	hrs	0	3.3	5.8	7.3	8.6
pH	--	1.20	1.46	2.71	6.45	7.84
Oxalate	mg/L	1.61E+04	<9.57E+01	<9.29E+01	<9.50E+01	<7.98E+01
Al	mg/L	2.56E+01	6.91E+01	7.18E+01	1.88E+00	<1.54E+00
Fe	mg/L	8.17E+02	1.45E+03	7.42E+02	4.49E+00	1.72E+00
Mn	mg/L	8.14E+01	1.56E+02	1.57E+02	2.33E-01	3.61E-01
U-235	mg/L	2.82E-01	1.27E+00	1.50E+00	1.53E-01	<1.85E-02
U-238	mg/L	4.38E+01	2.01E+02	2.06E+02	2.44E+01	1.24E+00
Pu-238	dpm/mL	3.11E+04	8.61E+04	6.23E+04	2.01E+04	6.43E+02
Pu-239/240	dpm/mL	2.24E+04	4.79E+04	3.00E+04	1.01E+04	<3.46E+02
Sr-90	dpm/mL	7.78E+07	--	--	--	7.65E+05

Note: "--" indicates that data is not available.



Table V. Measurement of Soluble Components during the ECC Oxalate Decomposition Process (Tank 12H Sludge, with UV Light)

analyte	units	initial	1st sample	2nd sample	3rd sample	final sample
Test 3, Batch 1						
time	hr	0.0	1.2	2.5	5.0	7.9
pH	--	1.65	3.12	3.98	6.04	7.95
Oxalate	mg/L	2.83E+04	7.64E+03	6.04E+03	1.42E+03	1.33E+02
Al	mg/L	1.57E+03	1.56E+03	7.30E+02	1.38E+02	<1.70E+00
Fe	mg/L	3.65E+02	3.08E+02	9.47E+00	4.84E+00	<4.93E-01
Mn	mg/L	2.51E+02	2.38E+02	2.15E+00	7.16E-01	2.03E+00
Th-232	mg/L	2.78E+00	2.67E+00	<7.23E-02	<6.86E-02	<7.70E-02
U-235	mg/L	9.82E-01	9.04E-01	7.40E-01	5.70E-01	6.97E-02
U-238	mg/L	6.61E+01	6.17E+01	4.80E+01	3.77E+01	3.11E+00
Pu-238	dpm/mL	1.31E+06	1.17E+06	1.60E+05	1.56E+05	2.03E+04
Pu-239/240	dpm/mL	8.05E+04	6.44E+04	8.91E+03	9.52E+03	1.45E+03
Sr-90	dpm/mL	1.61E+08	--	--	--	1.03E+06
Test 3, Batch 2						
time	hr	0.0	1.3	3.4	4.4	6.4
pH	--	1.13	1.25	2.73	4.16	6.26
Oxalate	mg/L	8.54E+03	2.70E+03	3.58E+02	<8.95E+01	<1.00E+02
Al	mg/L	5.27E+02	5.15E+02	5.00E+01	<1.49E+00	<1.66E+00
Fe	mg/L	1.37E+02	1.31E+02	5.00E+00	<4.30E-01	6.47E-01
Mn	mg/L	4.38E+01	4.23E+01	1.71E+00	<2.42E-01	<2.71E-01
Th-232	mg/L	6.83E+00	3.27E+00	7.36E-02	<6.72E-02	<7.51E-02
U-235	mg/L	1.62E-01	1.26E-01	1.05E-01	<4.48E-02	<5.01E-02
U-238	mg/L	8.34E+00	7.37E+00	4.34E+00	<4.48E-02	<5.01E-02
Pu-238	dpm/mL	5.72E+05	2.86E+05	8.30E+04	<7.38E+02	1.76E+04
Pu-239/240	dpm/mL	2.73E+04	1.15E+04	5.53E+03	<7.61E+02	1.37E+03
Sr-90	dpm/mL	2.75E+07	--	--	--	1.97E+07

Note: "--" indicates that data is not available.

Table VI. Measurement of Soluble Components during the ECC Oxalate Decomposition Process (Tank 5F Sludge, with UV Light)

analyte	units	initial	1st sample	2nd sample	3rd sample	final sample
Test 4, Batch 1						
time	hr	0.0	0.7	1.4	2.1	5.5
pH	--	1.35	2.48	4.14	6.09	8.53
Oxalate	mg/L	1.40E+04	4.53E+03	2.80E+03	1.99E+03	1.12E+02
Al	mg/L	3.03E+02	3.10E+02	2.86E+02	1.57E+02	3.36E+01
Fe	mg/L	1.02E+03	7.66E+02	1.07E+02	1.45E+01	3.40E+00
Mn	mg/L	2.82E+02	2.44E+02	3.79E+01	3.68E-01	1.89E+00
U-235	mg/L	9.28E+00	6.98E+00	7.19E+00	6.83E+00	4.41E+00
U-238	mg/L	1.29E+03	1.08E+03	1.18E+03	1.04E+03	6.31E+02
Pu-238	dpm/mL	1.34E+05	4.22E+04	8.33E+03	8.87E+03	5.24E+03
Pu-239/240	dpm/mL	3.17E+04	1.84E+04	3.22E+03	4.25E+03	3.01E+03
Sr-90	dpm/mL	8.51E+08	--	--	--	1.02E+08
Test 4, Batch 2						
time	hr	0.0	1.2	1.6	2.0	4.5
pH	--	1.11	3.13	4.85	6.69	8.41
Oxalate	mg/L	1.00E+04	4.70E+02	1.96E+02	<9.45E+01	<9.56E+01
Al	mg/L	3.11E+01	1.75E+01	1.65E+01	3.24E+00	4.92E+00
Fe	mg/L	6.69E+01	6.13E+01	5.46E+00	1.62E+00	2.72E+00
Mn	mg/L	1.97E+01	1.37E+01	1.91E+00	<2.55E-01	4.96E-01
U-235	mg/L	5.79E-01	3.08E-01	3.29E-01	1.47E-01	5.50E-02
U-238	mg/L	8.59E+01	4.14E+01	4.61E+01	1.85E+01	3.47E+00
Pu-238	dpm/mL	3.60E+04	3.44E+04	5.61E+03	7.55E+03	1.43E+03
Pu-239/240	dpm/mL	1.13E+04	9.31E+03	1.60E+03	2.83E+03	1.05E+03
Sr-90	dpm/mL	1.62E+08	--	--	--	3.41E+06

Note: "--" indicates that data is not available.

### **Down-Stream Impacts**

The ECC test with actual SRS waste sludge was necessary to determine if soluble concentrations of actinides exiting the ECC process were increased to outside of the normal range potentially affecting criticality safety for storage and down-stream processing. Testing showed that, for the Deposition Tank storage conditions that included pH adjustment to approximately 1 M free hydroxide, the soluble concentrations of actinides and other metals in the ECC product were returned to nearly the same level for each test regardless of storage time, storage temperature, and contact with other tank sludge material. Use of the ECC Evaporator generally led to slightly higher soluble component concentrations in the Deposition Tank storage tests.

Typical actinide solubilities in SRS Tank Farm supernatant liquids range from about 6 to 60 mg/L for uranium and less than 1 mg/L for plutonium [13,14]. In this testing, the concentration of uranium was as high as 1700 mg/L after sludge dissolution and was as high as 680 mg/L after oxalate decomposition. The concentration of Pu was as high as 2.7 mg/L after sludge dissolution and as high as 0.88 mg/L after oxalate decomposition. Thus, in some cases, the

soluble uranium and plutonium concentrations at intermediate stages of the ECC process were above or near the expected maximum Tank Farm levels. However, adjustment of pH back to 1 M free hydroxide and Deposition Tank storage of material for two weeks allowed return of these concentrations to within expected Tank Farm levels. After pH adjustment and two weeks of holding time, the liquid-phase uranium concentrations were 18 to 86 mg/L in and liquid-phase Pu concentrations were 0.03 to 0.22 mg/L for Tank 12H and 0.001 to 0.004 mg/L for Tank 5F. Thus, this testing shows that the ECC process should result in soluble concentrations of uranium and plutonium in the Deposition Tank that are near the expected concentration ranges for SRS Tank Farm storage.

Rheological measurements of the ECC products, even for conditions receiving evaporation, revealed that the slurries had low yield stresses due to the low weight percent solids content. Settling of the solids in the pH adjusted ECC product slurries was comparable to the control samples and was fast enough as to not likely delay downstream processing in the SRS Tank Farm.

## CONCLUSIONS

During ECC actual waste testing, the introduction of ozone was successful in decomposing oxalate to below the target levels. This testing did not identify physical or chemical changes in the ECC product sludge that would impact downstream processing. The results from these tests confirm observations made by AREVA NP during larger scale testing with waste simulants.[5] This testing, however, had a decreased utilization of ozone, requiring approximately 5 moles of ozone per mole of oxalate decomposed.

Decomposition of oxalates in sludge dissolved in 2 wt% OA to levels near 100 ppm oxalate using ECC process conditions required 8 to 12.5 hours without the aid of UV light and 4.5 to 8 hours with the aid of UV light. The pH and ORP were tracked during decomposition testing. Sludge components were tracked during OA decomposition, showing that most components have the highest soluble levels in the initial dissolved sludge and early decomposition samples and exhibit lower soluble levels as OA decomposition progresses.

The Deposition Tank storage conditions that included pH adjustment to approximately 1 M free hydroxide tended to bring the soluble concentrations in the ECC product to nearly the same level for each test regardless of storage time, storage temperature, and contact with other tank sludge material.

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