**This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.** 

**This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.** 

# **EFFECTIVENESS OF USING DILUTE OXALIC ACID TO DISSOLVE HIGH LEVEL WASTE IRON-BASED SLUDGE SIMULANT**

E. Ketusky, Washington Savannah River Company

### **ABSTRACT**

At the Savannah River Site (SRS), near Aiken South Carolina, there is a crucial need to remove residual quantities of highly radioactive iron-based sludge from large select underground storage tanks (e.g., 19,000 liters of sludge per tank), in order to support tank closure. The use of oxalic acid is planned to dissolve the residual sludge, hence, helping in the removal. Based on rigorous testing, primarily using 4 and 8 wt% oxalic acid solutions, it was concluded that the more concentrated the acid, the greater the amount of residual sludge that would be dissolved; hence, a baseline technology on using 8 wt% oxalic acid was developed. In stark contrast to the baseline technology, reports from other industries suggest that the dissolution will most effectively occur at 1 wt% oxalic acid (i.e., maintaining the pH near 2). The driver for using less oxalic acid is that less (i.e., moles) would decrease the severity of the downstream impacts (i.e., required oxalate solids removal efforts).

To determine the initial feasibility of using 1 wt% acid to dissolve > 90% of the sludge solids, about 19,000 liters of representative sludge was modeled using about 530,000 liters of 0 to 8 wt% oxalic acid solutions. With the chemical thermodynamic equilibrium based software results showing that 1 wt% oxalic acid could theoretically work, simulant dissolution testing was initiated. For the dissolution testing, existing simulant was obtained, and an approximate 20 liter test rig was built. Multiple batch dissolutions of both wet and air-dried simulant were performed. Overall, the testing showed that dilute oxalic acid dissolved a greater fraction of the stimulant and resulted in a significantly larger acid effectiveness (i.e., grams of sludge dissolved/mole of acid) than the baseline technology. With the potential effectiveness confirmed via simulant testing, additional testing, including radioactive sludge testing, is planned.

### **IMPLICATIONS**

With a crucial need to remove residual quantities of highly radioactive iron-based sludge from large select underground storage tanks, the use of concentrated oxalic acid as a solvent to help remove residual sludge from High Level Waste (HLW) tanks is planned. Its use, however, will result in additional normally solid oxalates being added to the HLW process. The solids eventually must be removed. Based on chemistry, for every mole of acid used, approximately 1 mole of solid oxalate (i.e., mostly sodium oxalate) will form within the process. Since the downstream impact is ultimately an oxalate removal/disposal issue, using less oxalic acid (i.e., less total moles of oxalic acid) will decrease the severity of the downstream impacts (i.e., required oxalate solids removal efforts).

# **INTRODUCTION**

A baseline technology currently exists for chemically aiding in the removal of residual quantities of sludge from SRS HLW tanks (e.g., approximately 19,000 liters of sludge containing 5,000 kg of (dry) mostly solid metal hydroxides). The baseline technology recommends using 3 batch-contacts of 8 wt% oxalic acid solution in a 20:1 volume ratio of solvent to sludge (Ref. 1). In contrast to the baseline technology, dissolution literature for iron(III) based sludge-type compounds recommends using dilute concentrations of oxalic acid for dissolution (i.e., maintaining the pH around 2 throughout the dissolution) (Ref. 2 & 3).

The baseline technology was developed using the results from over 40+ years of various SRS sludge simulant and radioactive sludge dissolution tests. In addition, tests associated with similar efforts from the U.S. Department of Energy's Hanford Site, were also reviewed. Most of the significant testing completed through 2003 is detailed in *Waste Tank Heel Chemical Cleaning Summary* (Ref. 4). The summary report assesses various agents and tests that have been performed to support sludge dissolution at SRS and make recommendations. Significant oxalic acid laboratory testing included in the summary report is listed in Table 1 (Ref. 4).

<b>Test</b>	<b>Acid</b>	<b>Protocol</b> (contacts/volume/time)
Simulant & Radioactive Sludge <b>Porous Metal Filters</b>	$2.2 \text{ wt\%}$ $4.5 \text{ wt\%}$	Contact $= 1$ Volume ratio = $60:1$ Contact times = $1 & 8$ kess.
Radioactive Sludge <b>Short Term Dissolution Testing</b>	$3 wt\%$ $8 wt\%$ 16 wt%	Contact $= 1$ Volume ratio = $5 & 10:1$ Contact time $= 0.5$ hrs.
Simulant <b>Individual Metals Testing</b>	$4 wt\%$ $8 \text{ wt\%}$	Contact $= 1$ Volume ratios = 10, 20, & 40:1 Contact time $= 6$ hrs.
Radioactive Sludge Long Term Contacts with Sludge	$8 wt\%$	Contact $= 1$ Volume ratios = 40 & 80:1 Contact time $=$ to 186 hrs.
Radioactive Sludge <b>Sludge Digestion Tests</b>	$4 wt\%$	Contact = $1$ Volume ratio $=$ 30:1 Contact time = 1, 7, 9 & 15 hrs.
<b>Hanford Simulant</b>	9 wt%	Contact $= 1$ Volume ratio = $17.5:1$ Contact time $= 216$ hrs.
Simulant Coil Cleaning Testing	$4 wt\%$	Contacts $= 20$ Volume ratio $=$ Spray $Time = 10$ seconds

**Table 1. SRS and Hanford Sludge Dissolution Testing Up Until 2004** 

More recent 4 and 8 wt% oxalic acid dissolution testing was also preformed and is listed in Table 2.

**Table 2. Oxalic Acid Testing After 2003** 

<b>Test</b>	Acid	<b>Protocol</b>
Simulant & Radioactive Sludge 2004 Dissolution Testing (Ref. 5)	$4 wt\%$	Contacts = $1, 2 - 7$ Volume ratio = $2 & 50:1$ Contact time $= 8$ hrs.
Radioactive Sludge Tank 5 Dissolution (Ref. 6)	$8 wt\%$	Contact $=1$ Volume ratio = $10$ to $20:1$ Contact time $=$ 45-50 hrs

Based on the goal to remove sludge to the "maximum extent practical," it was previously concluded that 3 batch contacts of 8 wt% oxalic acid with an acid solution to sludge volume ratio of 20:1 (i.e., a total of about 550,000 liters of 8 wt% oxalic acid) should be used as the baseline technology. This baseline technology equates to less than 486,000 moles of oxalic acid used. The first acid contact is expected to dissolve 70 wt% of the sludge, the second 50 wt%, and the third 30 wt%. For the initial 5,000 kg of solids, 4,500 kg would be dissolved and about 500 kg of sludge solids would remain within the tank (i.e., about 1,893 liters of sludge). The reported effectiveness of the baseline technology is shown in Table 3 (Ref. 1).

Table 5. Eliectrychess of the Daschile Technology						
<b>Method</b>	<b>Sludge Dissolved</b> $(wt\%)$	<b>Acid Effectiveness</b> (grams of sludge dissolved/moles of acid)				
Baseline	$90 \text{ wt\%}$	9.2				

**Table 3. Effectiveness of the Baseline Technology** 

In stark contrast to the baseline technology, other industries recommend using dilute oxalic acid for iron(III) based sludge dissolution and maintain the pH near 2; in particular the primary side of nuclear power plants use concentrated oxalic acid for scale removal up until the 1990s. In fact, both scale removal in nuclear power plants and HLW tank treatment with oxalic acid share much of the same history and testing up until the 1990s.

According to recent studies (Ref.  $2 \& 3$ ) on iron(III)-based sludge dissolution, the preference for oxalic acid dissolution at a pH near 2, is based on having an appropriate ratio of  $H^+$  and  $C_2O_4$  to maximize the effectiveness of the acid. At low pH values (i.e., pH < 1.6), insoluble oxalate compounds form and hinder dissolution. At high pH values  $(i.e., pH > 3.2)$ , the lack of protons hinder dissolution.

The purpose of this research was to determine the potential effectiveness for dissolving representative HLW sludge simulant using 1 wt% oxalic acid (to maintain the pH near 2). Since the fraction of solids dissolved and the amount of oxalic acid used are key parameters, but can be independently misleading, both mass dissolved (wt% sludge dissolved), and acid effectiveness (i.e., grams of sludge dissolved/mole of oxalic acid) for the dilute oxalic acid testing are calculated and compared to the reported values for the baseline technology. Pending positive results, additional testing is justified.

# **BACKGROUND**

The SRS HLW tanks are made of carbon steel, have flat bottoms, and contain kilometers of carbon steel cooling coils. Although many of the tanks continue to be used, most have out-served their original design life and eventually must be emptied. Tanks 1-8 are the first tanks scheduled to be emptied. Tanks 1-8 are approximately 23 meters in diameter and have an approximate  $2.8x10^{+6}$  liter capacity. In emptying the sludge from the tanks, the bulk of the waste is first removed mechanically (e.g., mixing the waste, then transferring the mixture out of the tank). After bulk waste removal, a residual quantity of sludge will remain in the tank (i.e., up to 5,000 kg of mostly solid metal hydroxides, in about 19,000 liters of sludge). To aid in the removal, oxalic acid is planned to be used as a solvent to dissolve the sludge.

In general, the defined baseline technology consists of adding an 8 wt% oxalic acid solution to approximately 19,000 liters of sludge in a volume ratio of 20:1for 3 batch contacts. The acid/sludge mix is agitated for a few days to ensure adequate time is allowed for the acid to react with and dissolve the sludge. After dissolution, the dissolved sludge/spent acid mix is transferred to another tank. Available concentrated supernatant (with a pH  $> 12$ ) or the addition of 50 wt% caustic is used to restore the pH to the normal operating range of the dissolved sludge/spent acid mix (Ref. 1). As a result of the pH restoration to >10, mostly sodium oxalate solids are formed. Since the disposal path for solids is through vitrification, the solids are blended with sludge and washed to the appropriate sodium concentration to support vitrification. Since the sodium concentration is washed to about 1 molar or less, a large fraction of the oxalates will dissolve and be transferred with the wash- water. Refer to Figure 1 (Ref. 1). Since free volume within the HLW process is at a premium, the wash-water would be transferred to the evaporator concentrate receipt tank. Since the evaporator concentrate receipt tank normally has a concentrated sodium concentration in excess of 6 molar, based on oxalate solubility as a function of sodium concentration (Ref. 1), almost all of the sodium oxalate would precipitate and become part of the existing evaporator concentrate receipt tank salt heel. This intentional salting-out in the evaporator concentrate receipt tank keeps the oxalate from being transferred to, or accumulate in undesirable or problematic locations (e.g., inside the evaporator pot). As part of the process of emptying the tanks, this safely stored oxalate will need to be removed from the HLW process.



**Figure 1. Oxalate Solubility as a Function of Sodium Concentration** 

### **MATERIALS AND METHODS**

Both chemical equilibrium modeling and simulant dissolution testing are performed as part of this research.

#### *Chemical Thermodynamic Equilibrium Modeling*

OLI ESP 1.3®, a commercially available chemical thermodynamic equilibrium software program, was used to approximate the initial dissolution of the simplified sludge simulant. The contents of the sludge simulant modeled based on Tanks 1-8 are shown in Table 4.



#### **Table 4. Simplified Sludge for Dissolution Modeling**

Specifically, isothermic equilibrium modeling (at 25ºC and 1 atmosphere) was used to estimate the effect of adding about 530,000 liters of varying concentrations of oxalic acid, ranging from 0 to 8 wt%, to the sludge. The results of this modeling would be restricted to providing only a speculative determination if 1 wt% acid could dissolve  $\geq$ 90% of the sludge.

#### *Simulant Dissolution Testing*

The simulant dissolution testing would be performed using available Tank 8 sludge simulant.

#### *Tank 8 Sludge Simulant*

An existing aged (i.e., > 3 year old) 208 liter drum of iron-based Tank 8 sludge simulant was available from previous mechanical filtration testing. The simulant was based on a

derivative of the same recipe used for the 2004 simulant dissolution testing (Ref. 7). To enable the mechanical filtration testing simulant to be considered non-hazardous, the Resource Concentration Recovery Act (RCRA) metals were removed from the recipe. The barium, chromium, lead, and zirconium were replaced with aluminum. The halide salts (sodium chloride, sodium fluoride, and sodium iodide) were replaced by sodium nitrate (Ref. 7). The resulting sludge simulant constituents are shown in Table 5.

<b>Cations</b>	Dry wt%	<b>Anions</b>	Dry wt%
Al	9.59	CO <sub>3</sub> <sup>2</sup>	5.13
Ca	2.11	NO <sub>2</sub>	5.87
Cu	0.13	NO <sub>3</sub>	1.95
Fe	24.34	OH <sup>-</sup>	24.7
$\bf K$	0.005	$O_2^-$	11.4
Mg	0.12	PO <sub>4</sub> <sup>3</sup>	0.13
Mn	2.73	SO <sub>4</sub> <sup>2</sup>	0.64
Na	7.2		
Ni	2.79		
Si	0.76		
<b>Sr</b>	0.09		
Zn	0.27		

**Table 5. Constituents of SRS Tank 8 Sludge Simulant** 

The pH of the simulant prior to dissolution testing was measured to be approximately 12.4 (i.e., slightly higher than an expected pH value of 9 to 10 at the time of acid treatment). The solids content of the (wet) sludge, based on the density of the solids and the interstitial liquid, was estimated to be about 16 wt% solids.

In an attempt to mimic the effect of density gradients within the heterogeneous simulant, both an air-dried simulant and a wet simulant were used for the dissolution testing. To perform air-drying, the simulant was spread evenly in a 2.5 cm thick layer over a 20 cm x 30 cm polypropylene tray, and allowed to sit at ambient conditions and dry for 24 hours. The air-dried simulant had a typical solids content of around 30% and remained in a gelatinous phase. The density of the air-dried simulant was measured to be 1.26 g/ml, while the initial wet density of the simulant was measured to be 1.17 g/ml.

# *Building the Test Rig*

As part of this effort, based on available equipment and space limitations, an 18-liter stainless steel dissolution test rig was constructed. The size of the rig and the amount of sludge simulant used per batch were based on the ability to process a 208-liter drum of simulant for at least 10 tests of multiple batches, while ensuring that an adequate simulant reserve remained available for additional dissolution testing. The rig was also designed so the dissolution could be monitored real-time by detecting changes in the pH and oxidation-reduction potential (ORP).

The test rig consisted of a small positive displacement pump, an electrical coil heater, a pH/ORP monitor, and a sludge dissolution chamber. The dissolution chamber consisted of a 5-layer screen used to hold the simulant. The 5-layer screen was used to enable an adequate amount of sludge (i.e., <300 grams) to be loaded into the dissolution chamber for each batch. The flow rate of the acid in the rig was measured to be about 3.8 liters/min. A simplified rig flow diagram is shown in Figure 2.



**Figure 2. Simplified Dissolution Rig** 

For sizing, 300 grams of sludge simulant was considered the maximum sludge that would be loaded per dissolution batch. More than 300 grams (spread out on the 5-layer test screen) would be handled by using multiple batches. Moreover, the process was sized to ensure that each dissolution test, including those consisting of multiple batches, could be completed within about 1 week. The rig would be run as a recirculation dissolution process. Recirculation would enable more uniform pH monitoring, and based on transferability would minimize post-dissolution precipitates from being considered nondissolved sludge.

# *Test Protocol*

At ambient temperature, the 5-layer test screen was initially weighed and then loaded with select quantities of wet-sludge simulant (roughly 300 grams) and re-weighed. The loaded screen was placed into the dissolution chamber and 18-liters of 1 wt% oxalic acid were added to the process. The pH was measured and confirmed to be approximately 1.6. The acid was allowed to soak and was then recirculated for select amounts of time (i.e., roughly seven hours of recirculation and twenty-five hours of contact time per batch). Upon observing no further dissolution based on real time monitoring of the ORP, as well as confirmation by visual observation, the 5-layer screen was removed for the final time and weighed to quantify the mass of the remaining simulant.

Since the purpose of the test was limited to showing the efficacy of using 1 wt% oxalic acid, the testing was not performed using replicates, but, instead limited to using single tests of wet and air-dried simulant. Pending a positive outcome, official testing with replicates would be required.

#### **RESULTS**

### *Modeling*

Using OLI Stream Analyzer<sup>®,</sup> the dissolution of approximately 19,000 liters of sludge was exothermically modeled using 530,000 liters of 0 to 8.0 wt% oxalic acid. At chemical thermodynamic equilibrium, the mass of the solids were recorded as shown in Table 6.

							$(wt\%)$					
<b>Oxalic Acid</b>	$\overline{0}$	$0.125 \,   \, 0.25$		0.5		$\overline{2}$	3	$\overline{4}$	5	6	7	8
<b>Solids Mass</b>							(kg)					
Al(OH) <sub>3</sub>	849	849	849	849	472							
CaCO <sub>3</sub>	222											
$CaC2O4.1H2O$		307	273	229	211	257	255	249	242	234	227	220
Cu(OH) <sub>2</sub>	12	$\overline{4}$										
Fe(OH) <sub>3</sub>				3,010 3,010 2,629 1,578								
Mg(OH) <sub>2</sub>	5											
$Mn(OH)$ <sub>2</sub>	201											
MnCO <sub>3</sub>	12	201										
$MnC_2O_4.2H_2O$			188	161	150	190	195	197	196	196	195	194
$Ni(OH)_{2}$	422											
$NiC2O4.2H2O$		814	814	813	813	814	813	813	813	813	813	813
SiO <sub>2</sub>	$\overline{2}$											
SrCO <sub>3</sub>	$\overline{2}$											
Zn(OH) <sub>2</sub>	8	$\overline{2}$										
<b>Total Solids</b>				4,746 5,187 4,753 3,630 1,646 1,261 1,264 1,259 1,251 1,243 1,235 1,227								

**Table 6. Solids after Treatment with 530,000 liters of 0 to 8 wt% Oxalic Acid**

With the equilibrium modeling results showing that 530,000 liters of 1 wt% oxalic acid can dissolve > 90 wt% of the initial sludge, simulant dissolution testing was initiated.

# *Dissolution Testing*

The results of the dissolution testing showed that after 15 hours of recirculation and 46 hrs of contact time, only 15 grams of the original 452 grams of wet-sludge simulant remained. After 29 hours of recirculation and 118 hours of contact time, only 6 grams of the original 1200 grams of air-dried sludge simulant remained. Table 7 shows the dissolution testing results.

Table <i>1</i> , Results of Dilute Dissolution Testing							
<b>Test</b>	<b>Initial</b> <b>Simulan</b> (grams)	<b>Final</b> <b>Simulant</b> (grams)	<b>Mass</b> <b>Dissolve</b> d (grams)	<b>Accumulativ</b> e Contact <b>Time</b> (hours)	<b>Volume of</b> <b>Acid</b> (liters)		
Wet simulant	452	15	437	46	36		
Air-dried simulant	1,200	6	1,194	118	72		

**Table 7. Results of Dilute Dissolution Testing** 

Using Table 7, the wt% dissolved for the wet sludge simulant and the air-dried sludge simulant was calculated using Equation 1, while the acid effectiveness (grams of sludge dissolved/mole of acid) was calculated using Equation 2. The results are shown in Table 8.

$$
wt\% \, \, \, \, dissolved \, \, = \, \frac{\,(\, \, \text{initial} \, \, \text{mass}) - \,(\, \text{final} \, \, \text{mass})}{\, \, \text{initial} \, \, \text{mass}} \times 100\% \tag{Eq.1}
$$

\n
$$
\text{acid} \quad \text{effectiveness} \quad = \quad \frac{\text{grams} \quad \text{of} \quad \text{simulant} \quad \text{dissolved}}{\text{moles} \quad \text{of} \quad \text{oxid} \quad \text{used}} \tag{Eq. 2}
$$
\n

Where the initial mass, final mass, and acid effectiveness (i.e., grams of simulant dissolved per mole of acid) were measured and calculated as part of the dissolution testing. The results using Equation 1 and 2 are shown in Table 8.

<b>Test</b>	Weight <b>Dissolved</b> $(wt\%)$	<b>Mass</b> <b>Dissolve</b> d (grams)	Acid <b>Used</b> (moles)	Acid <b>Effectiveness</b> (grams/mole
Wet Sludge Simulant	96.7	437	4	109.3
Air-Dried Sludge Simulant	99.5	1,194		149.3

**Table 8. Acid Effectiveness for Wet and Air-Dried Simulant** 

Combining the results of the wet-sludge simulant and the air-dried sludge simulant into a single estimate or variability (where the effect from the difference in sludge density is assumed to bound by the difference between the wet and air-dried simulant), Table 9 shows the expected range for sludge dissolved (wt%), and the acid effectiveness (grams of simulant dissolved/moles of oxalic acid).

Table 9. Combined Acid Effectiveness for Twt% on Simulant					
<b>Results</b>	<b>Weight Dissolved</b> $(wt\%)$	<b>Acid Effectiveness</b> (grams /mole)			
Sludge Simulant	$98.1 + 1.4$	$129.3 \pm 20.0$			

**Table 9. Combined Acid Effectiveness for 1wt% on Simulant** 

### **DISCUSSION**

The sludge in Tanks 1-8 contains approximately 50 wt%  $Fe<sub>2</sub>(OH)<sub>3</sub>$ , with aluminum, manganese, and nickel representing most of the remaining metal mass. Based on the size of the metal molecules formed within HLW, it is likely to suspect that the sludge will have many similar dissolution characteristics tendencies as pure Fe(III) (Ref. 4). Reductive dissolution, aided by protonation, along with the ligand complexation, are normally credited for effective iron(III)-based sludge dissolution when using oxalic acid (Ref. 2  $\&$  4). The need to maintain the pH near 2 for iron(III)-based dissolution can be explained by understanding speciation of oxalic acid (Ref. 2).

### *Speciation of Oxalic Acid*

Oxalic acid has two different ionization constants. The reactions are shown as Reaction 1 and Reaction 2 below (Ref. 2).



In oxalic acid solutions, molecules of oxalic acid and its ions  $HC_2O_4$  and  $C_2O_4^2$  co-exist in equilibrium. In an iron(III) system at a pH of 2,  $Fe^{3+}$ ,  $[FeC_2O_4]^+$ ,  $[Fe(C_2O_4)_2]^+$  and  $[Fe(C<sub>2</sub>O<sub>4</sub>O<sub>3</sub>]<sup>3</sup>$  are present and available to react. At this pH, the needed ratios of both H<sup>+</sup> and  $C_2O_4$  are present; with neither free protons nor available  $C_2O_4^2$  lacking, therefore, dissolution can quickly occur. Outside this pH range, however, sludge dissolution will be hindered. That is, at low pH values there is an excess of oxalate ion, therefore insoluble oxalate compounds form. At high pH values there is a lack of protons, so dissolution will be hindered and additional oxalate compounds will form. Figure 3 shows the speciation of the oxalic acid,  $HC_2O_4$  and  $C_2O_4^{2}$  as a function of pH (Ref. 2).



**Figure 3. Speciation of Oxalic Acid** 

This optimum wt% oxalic acid to support dissolution was also evident in the results of the dissolution equilibrium modeling of the simulant.

# *Modeling Discussion*

As shown in Table 10, the equilibrium modeling results confirm that 530,000 liters of 1 wt% oxalic acid can theoretically dissolve > 90 wt% of the sludge-simulant.

<b>Acid</b>							$(wt\%)$						
Oxalic Acid	$\overline{0}$	0.125	0.25	0.5	1	1.4	2	3	4	5	6	7	8
<b>Solids</b>							(kg)						
$\text{Al}_2(\text{OH})_3$	849	849	849	849	472								
CaCO <sub>3</sub>	222												
$CaC2O4$ .1H <sub>2</sub> O	$\theta$	307	273	229	211	230	257	255	249	242	234	227	220
Cu(OH) <sub>2</sub>	12	4											
Fe <sub>2</sub> (OH) <sub>3</sub>	3010	3010	2629	1578									
Mg(OH) <sub>2</sub>	5												
Mn(OH) <sub>2</sub>	201												
MnCO <sub>3</sub>	12	201											
$MnC_2O_4.2H_2O$	0		188	161	150	165	190	195	197	196	196	195	194
Ni(OH) <sub>2</sub>	422												
$NiC2O4.2H2O$	0	814	814	813	813	814	814	813	813	813	813	813	813
SiO <sub>2</sub>	$\overline{2}$												
SrCO <sub>3</sub>	$\overline{2}$												
Zn(OH) <sub>2</sub>	8	$\overline{2}$											
		(moles)											
$ C_2O_4^{-2} $	$\Omega$												6,551 6,318 6,011 5,888 6,030 6,208 6,189 6,148 6,100 6,045 5,997 5,949

**Table 10. Solids at Chemical Equilibrium for Different Acid Concentrations** 

The modeling results also suggest that the quantity of solid oxalate formed (i.e., moles) can be minimized by using some optimal concentration of oxalic acid near 1 wt%. Below this concentration, additional oxalates will form; above this concentration additional oxalates will also form.

# *Dissolution Testing Discussion*

The dissolution testing clearly confirmed that 1 wt% oxalic acid can dissolve as much of the simulant as reported for the use of 8 wt% oxalic acid. Specifically, the testing suggests that dilute oxalic acid can dissolved slightly more sludge (98.1+1.4 wt% of the hydroxides dissolved vs. the reported baseline value of 90 wt%), but also suggests significantly better acid effectiveness (i.e., 129.3+20 grams of sludge dissolved/mole of acid vs. 9.2 grams/mole for the baseline technology). The results of the testing are summarized and compared to the reported values for the baseline technology. Refer to Table 11.

<b>Method</b>	<b>Weight Dissolved</b> $(wt\%)$	<b>Acid Effectiveness</b> (grams /mole)
Dilute Acid	$98.1 + 1.4$	$129.3 \pm 20.0$
<b>Reported Baseline</b>	$90 \text{ wt\%}$	9.2

**Table 11. Comparison of wt% dissolved to the Baseline Technology** 

With this initial testing confirming the potential effectiveness, additional testing, including radioactive sludge testing is planned.

### *Concerns*

In the 2004 sludge dissolution tests, generally a greater fraction of simulant dissolved compared to real waste (Ref. 5). In general, simulant testing showed > 90 percent dissolved, whereas for radioactive sludge in one test only 76 wt% actually dissolved. Therefore, without getting into the myriad of potential reasons for the difference, it is simply noted that simulant may be easier to dissolve than radioactive waste.

Although this effort has shown that 1 wt% oxalic acid is more effective than those reported for the baseline technology, the intent of this effort was limited to serving only as an initial efficacy test. With the positive results from this effort providing justification, additional testing, including using radioactive sludge, is planned.

# **CONCLUSION**

The equilibrium modeling initially confirmed that 1 wt% oxalic acid should theoretically be capable of dissolving the sludge. The dilute oxalic acid dissolution testing confirmed that 1 wt% oxalic acid could effectively dissolve the simulant and also result in a much higher acid effectiveness (i.e., grams of sludge-simulant dissolved per mole of oxalic acid used) than those values reported for the baseline technology. The results of the testing are compared to the reported values for the baseline technology, as shown in Table 12.

<b>Method</b>	<b>Weight Dissolved</b> $(wt\%)$	ັຕມ <b>Acid Effectiveness</b> (grams /mole)
Dilute	$98.1 \pm 1.4$	$129.3 \pm 20.0$
Baseline	90 wt%	9.2

**Table 12. Comparison of wt% dissolved to the Baseline Technology** 

Although the results of this testing have proved to be very successful, this research was performed using sludge simulant. Because of the potential differences in behavior between simulant and real waste (including the noted differences in the 2004 testing), the success of this effort should be cautiously considered. At best, the results of this testing should only be used to provide justification for performing additional simulant and real waste testing.

# **ACKOWLEDGEMENTS**

Special thanks belong to Ray Beatty and Dr. John Remark (from AREVA NP) for suggesting that the use of dilute oxalic acid to dissolve HLW sludge be further investigated. In addition, thanks also belong to Dr. W. King (from the Savannah River National Laboratory), and R. Spires (from Washington Savannah River Company) whom helped greatly in the review and development of the test plans.

# **LITERATURE CITED**

- 1) Pike, J. A., Badheka, N.P., and Ketusky. E.T., "Flowsheet for SRS Waste Tank Heel Removal Using Oxalic Acid, WSRC-TR-2004-00317, Revision 0, November 16, 2004, Washington Savannah River Site, Aiken SC, USA.
- 2) Lee, Sung Oh, Dissolution of Iron Oxides by Oxalic Acid, University of New South Wales, (PhD Thesis) 2005.
- 3) Lee S.O., Oh J.K., Shin B.S., "Dissolution of Iron Oxide Rust Materials Using Oxalic Acid." Journal of the Mining and Materials Processing Institute of Japan, ISSN:0916-1740, VOL.115;NO.11; PAGE.815-819 (1999).
- 4) Barnes, M.J., Adu-Wusu, K., Hobbs, D.T., Bibler, N.E., Ketusky, E.T., Cantrell J.R., Singleton, M., Fondeur F.F., Stallings, M.E., Hamm. B.A., Stevens, W.E., "Waste Tank Heel Chemical Cleaning Summary", WSRC-TR-2003000401, Rev. 0, Sept 9, 2003, Washington Savannah River Site, Aiken SC, USA.
- 5) Stallings, M.E., Hobbs, D. T., Wiersma, B.J., Dissolution of Simulated and Radioactive Savannah River Site High-Level Waste Sludges with Oxalic Acid and Citric Acid Solutions, WSRC-TR-2004-00043, Rev. 0, March 26, 2004, Washington Savannah River Site, Aiken SC, USA.
- 6) Herman, D. T., Wiersma, B.J., Fondeur, F.F., Wittkop, J. C., Pareizs, J.M., Crapse, K.P., Hay, M.S., Poireir, M.R., and Fink, S.D., "Investigating Hydrogen Generation and Corrosion in the Treatment Tank and the Potential Formation of a Floating Layer in Neutralization Tank During Waste Tank Heel Chemical Cleaning," WSRC-STI-2007-00209, Rev. 0., April 30, 2007, Washington Savannah River Site, Aiken SC, USA.
- 7) Poirier, M. R., Recipe for Simulated Tank 8F Sludge Containing No RCRA Metals or Halides, WSRC-TR-2005-00045, Rev. 0, January 14, 2005 Washington Savannah River Site, Aiken SC, USA.

### **WSRC-STI-2008-00353**