This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-09SR22505 with the U.S. Department of Energy.

Enhanced Chemical Cleaning:
Effectiveness of the UV Lamp to Decompose Oxalates - 10502

E. Ketusky, T. Huff, C. Sudduth
Savannah River Remediation, Aiken, SC 29808

S. Jones, J. Remark,
AREVA Federal Services LLC, Charlotte, NC 28262

Mika Sillanpää
Laboratory of Applied Environmental Chemistry, University of Eastern Finland
Mikkeli, Finland

ABSTRACT

Enhanced Chemical Cleaning is a new process scheduled to begin cleaning Savannah River Site High Level Waste Tanks in 2012. It is an improvement over the current chemical cleaning method, in that it minimizes downstream impacts on the High Level Waste System. It is based on a state of the art scale removal process used on the secondary side of nuclear power plants, with modifications to accommodate the unique constraints created by the tanks. Both Enhanced Chemical Cleaning and the scale removal process are founded on dissolving metal oxides/hydroxides using oxalic acid, with subsequent oxalate decomposition via hydroxylation using ozone or peroxide, and UV light as a catalyst. A divergence Enhanced Chemical Cleaning has from nuclear power scale removal is the significantly increased solids concentration during oxalate decomposition. These solids can limit the ability of the UV light to create hydroxyl radicals, either by limiting the ability of the light to penetrate through the solution, or by increasing the fouling rate on the UV light. Both will decrease the overall catalytic effectiveness, thereby decreasing the concentration of formed hydroxyl radicals. The hydroxyl radicals are the driving force behind the oxalate decomposition.

To understand the impact of increased solids, testing was performed using a medium pressure UV light inside an ozone supplied Oxalate Decomposition Reactor. Using a dissolved metal sludge simulant with an initial oxalate concentration greater than 12,000 ppm, and an initial pH of about 2.0, the spent acid solution was recirculated through the reactor, while the UV light was allowed to foul. For the first few hours, the oxalate decomposition rate was about 1,300 ppm/hour. After about 3 hours, enough time for the UV lamp to foul, the oxalate decomposition rate decreased to about 500 ppm/hour. The decomposition rate then remained roughly constant for the next 16 hours. Overall, testing showed that the oxalate destruction rate decreased by about 2.8. Results from very similartests with similar chemistry suggest that the impact should be about 10. Based on the limited reaction pathwayfor the creation of hydroxyl radicals with iron, ozone, and no UV, the discrepancy suggests that initially, at "time zero" the UV light failed to perform up to expectations. It is therefore concluded that regardless of the fouling rate, either the

increased solids concentration is impacting the initial penetrability (i.e. to many solids), or the light is not adequately sized/configured to have the appropriate flux.

INTRODUCTION

At the Savannah River Site there is a goal to close 22 non-complaint (i.e., single shell) High Level Waste Tanks over the next eight years. This is aggressive considering that in the 50 plus years of operation only two Savannah River Site tanks have been closed.

The single shell High Level Waste tanks were constructed from commercial grade carbon steel in the mid-1950's to the early 1960's. In general, their dimensions range from 23 to 26 meters in diameter, 7 to 10 meters high, and the volumetric capacity ranges from 2.8 to 4.9 million liters. Typically, each tank contains an internal labyrinth of cooling coils made from carbon steel, which further complicates waste removal, cleaning, and closure.

Savannah River Site has utilized both mechanical and chemical methods for removing High Level Waste from tanks. The mechanical means, predominantly consisting of mixing/slurrying with ensuing transfer, are used to remove the bulk of the waste. Chemical cleaning is deployed only when residual quantities of solids remain (e.g. less than about 5,000 kg of solids per tank) and mechanical methods are no-longer effective. Chemical cleaning is necessary to support the requirements for closure. At closure, the residual volume of waste solids allowed to remain in a tank is about 50 to 500 kg, depending on the tank. Hypothetically, if spread out evenly on the bottom of the tank, this waste would only be about 0.025 to 0.25 cm thick. The closure requirement for the tanks is primarily driven by the high specific activity of the waste in conjunction with the close proximity to the water table.

Oxalic acid remains the preferred acid for cleaning the metal surfaces because of its combined digesting and chelating effects. Other common acids considered for cleaning include nitric acid and oxalic/citric acid blends. Oxalic acid is preferred over nitric acid due to corrosion concerns; oxalic acid forms a passivation layer on carbon steel surfaces. While both pure oxalic acid and oxalic/citric acid mixtures have been shown to be equally effective in dissolving waste residuals, there are undesirable downstream impacts associated with introducing citric acid into the High Level Waste Sstem. For chemical cleaning, the current process uses 8 wt% concentrated oxalic acid as the solvent. A simplified flow diagram of the current chemical cleaning process is shown in Figure 1.

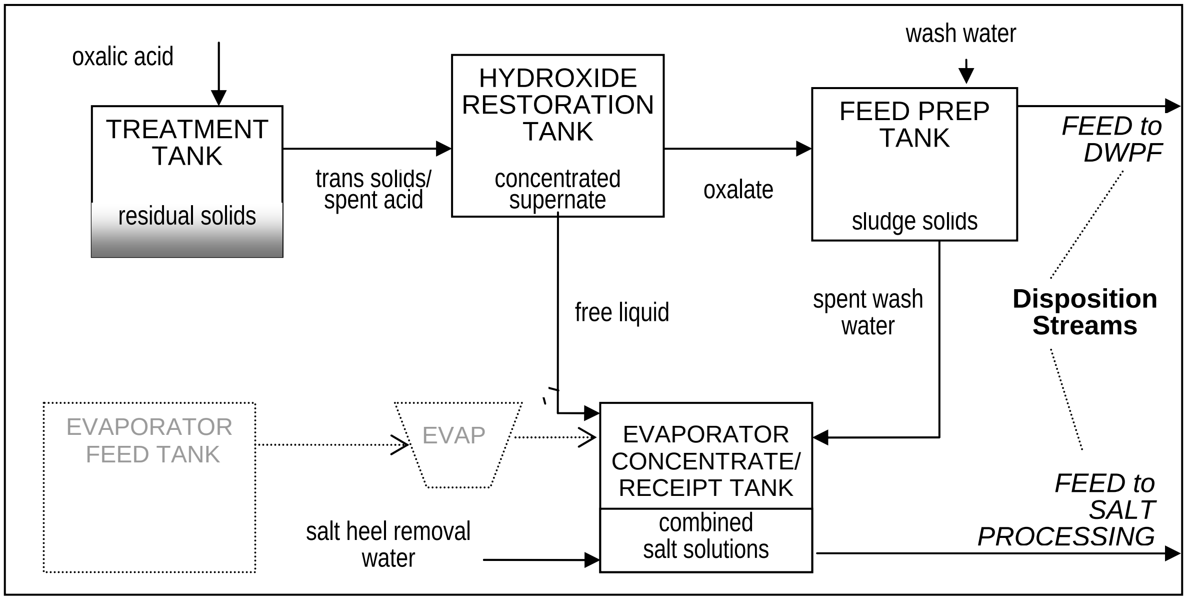

Figure 1. Current Chemical Cleaning Flow Diagram

During the current chemical cleaning process, in three steps, a total of about 380,000 liters of 8 wt% oxalic acid solution is added to the Treatment Tank and slurried. After allowing adequate time for the acid to react with the residual solids, mixing is stopped. The transferable solids/spent acid is transferred out of the Treatment Tank into an existing High Level Waste Tank for hydroxide restoration. The Hydroxide Restoration Tank is pre-staged with adequate quantities of concentrated supernatant to restore the free hydroxide of the waste stream to within High Level Waste System corrosion control parameters. Because of the sodium concentration of concentrated supernatant (e.g. Na >> 5M), large quantities of sodium oxalate precipitate out as a solid.

The solubility of oxalate as a function of sodium concentration is shown as Figure 2.

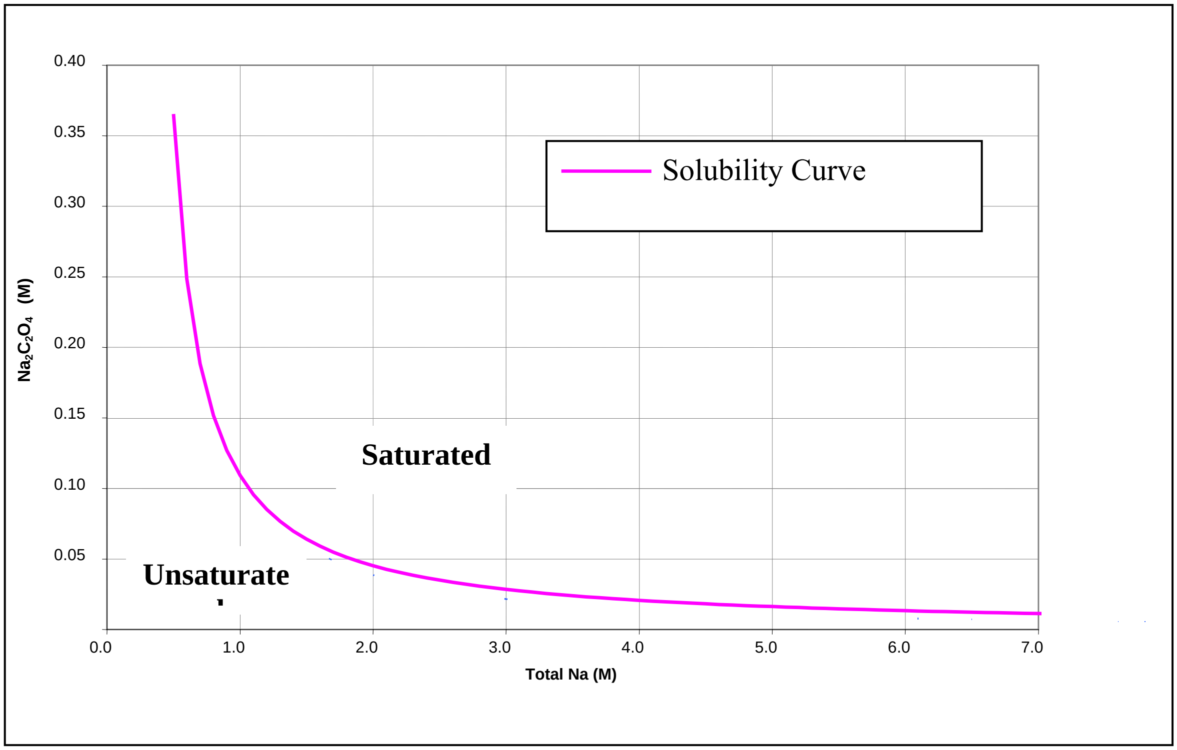

Figure 2. Solubility of Sodium Oxalate vs. Sodium Concentration

Since solids are dispositioned out of the High Level Waste System by vitrification in glass at the Defense Waste Processing Facility (DWPF), the oxalate solids are transferred as slurry to an existing High Level Waste Tank, called the Feed Prep Tank. In the Feed Prep Tank, the oxalate solids are batched with other sludge solids and washed, eventually becoming feed to DWPF. As part of preparing the feed to support DWPF glass standards, the sodium concentration is required to be decreased to Na ≤ 1M through washing. Because of the additional sodium, additional wash cycles are required. Under aggressive schedules to prepare and qualify feed for DWPF, the significant number of additional wash cycles will create feed breaks, with each break extending the required operating life of the entire High Level Waste System. Extending the operating life of the entire High Level Waste System and is considered unacceptable.

During washing, as the sodium is decreased to Na ≤ 1M, a large fraction of the oxalate is solubolized. Since tank space within the High Level Waste System is at a premium, the free liquidin the Hydroxide Restoration Tank, as well as the spent wash water from the Feed Prep Tank containing the washed-out sodium oxalate from DWPF, will be combined in the Evaporator Condensate/Receipt Tank. Under evaporator system conditions, the high sodium concentration (e.g., Na >> 5 M) will cause sodium oxalate to precipitate out and formpart of the tank's sparingly soluble salt heel. Eventually to dissolve theheel (i.e., Na ≤ 0.5 M, immense volumes of water will be necessary creating substantial amounts of additional feed to Salt Processing.

Equation 1 summarizes the primary impacts to the Savannah River Site High Level Waste System from using the current chemical cleaning process.

$$IMPACTS \equiv WashCycles + SaltFeed \qquad \text{(Equation 1)}$$

<u>where:</u>

- WashCycles refers to the number of additional wash cycles required for DWPF feed.
- SaltFeed refers to the additional eventual volume of feed to Salt Processing.

Modeling shows that for every tank treated about 51,000 kg of new sodium oxalate solids will be created for feed to DWPF. In addition, 1.9 million liters of Salt Processing feed will be created. Assuming all of the solid oxalate from cleaning 2 to 3 tanks is added to single DWPF feed batch, 8 to 9 additional DWPF wash cycles, as well as 3.8 to 5.7 million liters of additional feed to Salt Processing, will be required.

Adding less oxalate solids to DWPF each feed would require more feed batches batch (i.e., same total quantity but less per feed batch) and would extended the operating life of the entire High Level Waste System. This is considered unacceptable.

Adding more sodium oxalate to a DWF feed batch would require additional wash cycles, hence, further increasing the likelihood of feed breaks to DWPF. As previously stated, feed breaks would extend the operating life of the entire High Level Waste System, and are considered unacceptable. If more oxalate is added than that from the treatment of 2 or 3 heels, the additional oxalate is simply washed-out of the DWPF feed, nding up instead as feed to Salt Processing.

The envisioned process flowsheet for the Enhanced Chemical Cleaning, which minimizes these impacts, is shown as Figure 3.

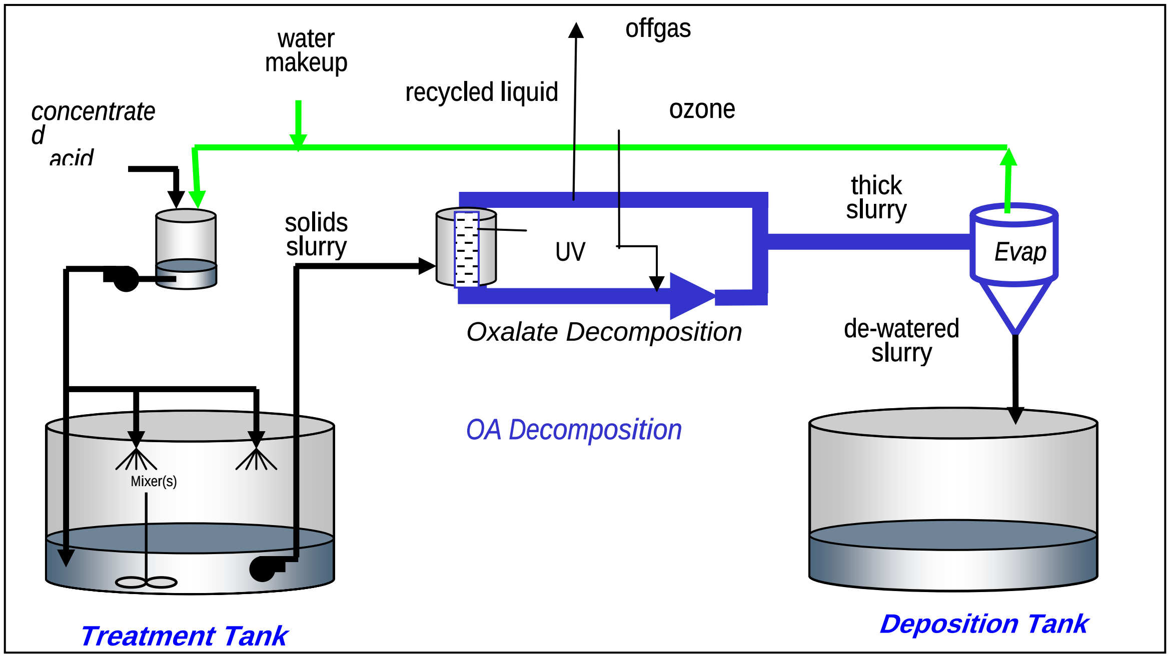

Figure 3. Enhanced Chemical Cleaning Flow Diagram

To achieve maximum dissolution effectiveness during Enhanced Chemical Cleaning, the pH of the Treatment Tank is maintained near 2.0 throughout the cleaning. To maximize solid suspension so that material can be transferred out of the Treatment Tank, additional mixers are added.

The slurry from the Treatment Tank is transferred to the Oxalate Decomposition Reactor. The Oxalate Decomposition Reactor is a key feature of Enhanced Chemical Cleaning where ozone is forced into the slurry and treated with UV light. The light is installed to catalytically aid in formation of hydroxyl radicals. The eactions for the creation of hydroxyl radicals from ozone areshown by Reactions 1A and B.

$$O_3 + H_2O \xrightarrow{hv} H_2O_2 + O_3 \longrightarrow 2 \circ OH \qquad \text{(Reaction 1A)}$$

$$O_3 + H_2O \xrightarrow{hv} 2 \circ OH \qquad \text{(Reaction 1B)}$$

Through hydroxylation, the radicals are aggressively oxidize the oxalate. The resultant carbon dioxide and water vapor are off-gassed, while the newly created metal oxides/hydroxides precipitate out, further increasing the solids concentration within the reactor. After leaving the reactor, a large fraction of the liquid is removed from this thickened slurry through evaporation. The dewatered slurry that contains the metal oxides/hydroxides is transferred into a compliant (i.e., doubled shelled) High Level Waste Tank. The large liquid fraction is removed through evaporation andrecycled back towards the Treatment Tank, where concentrated or dry acid is added to refresh the solvent and continue the cleaning process.

Enhanced Chemical Cleaning diverges from nuclear power scale removal with respect to the planned concentration of solids entering the Oxalate Decomposition Reactor.That is, to maximize cleaning in Enhanced Chemical Cleaning, vigorous agitation is applied to the Treatment Tank, making the solids concentration during Enhanced Chemical Cleaning significantly greater than that in nuclear power scale removal. From a UV perspective, the solids can limit the ability of the UV light to create hydroxyl radicals, either by limiting the ability of the light to penetrate the solution, or by increasing the fouling rate on the UV light. Both ultimately decrease the overall catalytic effectiveness, thereby decreasing the concentration of formed hydroxyl radicals.

A schematic illustrating UV light fouling in the Oxalate Decomposition Reactor is shown in Figure 4.

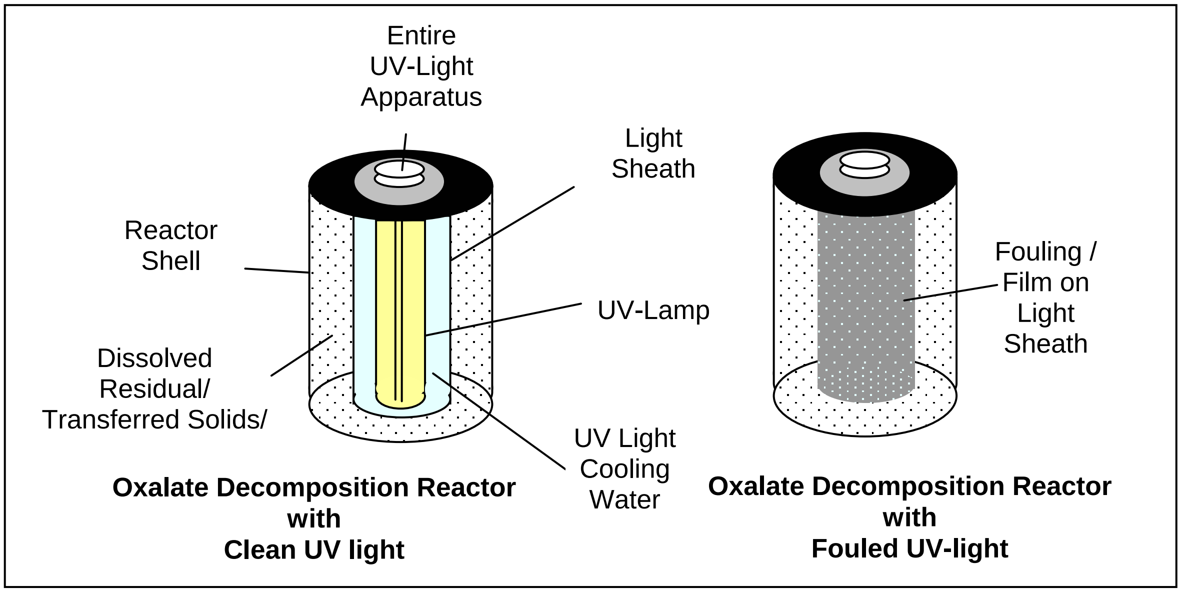

Figure 4. Schematic of UV Light Fouling

Although the effectiveness of the UV light is decreased, because of theincreased metals associated with Enhanced Chemical Cleaning, hydroxyl radicals are created from Fenton-type “dark catalytic” reactions. Oxalate destruction continues in the presence of a significant concentration of ozone and iron in the waste stream.

The objective of this study is to estimate effectiveness of the UV Lamp as a function of time based on the observed oxalate destruction rate.

EXPERIMENTAL

Simulant Recipe

In the presence of ozone, common transition metals such as iron, copper, and manganese are known to act as homogenous catalysts, aiding in the creation of hydroxyl radicals. Largely based on limiting transition metals, a simulant recipe was developed to minimize the creation of hydroxyl radicals. Specifically the simulant would contain no intentionally added copper,manganese, and only minimal quantities of iron, potassium, calcium, and silica. To account for the decrease in transition metals, sodium compounds were mostly used [12].

The problem with only using sodium compounds, however, is that they are very soluble at a pH of 2. Based on Enhanced Chemical Cleaning having an elevated solids concentration, which ultimately hinders the production of hydroxyl radicals, there was a similar need to maintain an elevated concentration of solids. Knowing that in previous sludge dissolution testing, the aluminum proved hard to digest, but was ultimately removed mostly through chelating [6], it was used to account for the solids [12].

Since aluminum is also known to also have the potential to act as a heterogeneous catalyst, concentrations were kept "representative," specifically about 10 wt% above theoretical average sludge concentrations. Small quantities of tungsten and molybdenum, as would be potentially would exist in the waste, were added because of their unique ability to form highly reaction resistant/UV resistant compounds. Refer to Table 1.

Table 1. Simulant Solids Composition Based on Recipe (12)

Form	Total Wt%	Cation Fraction of Mass	Iron / Metal Ratio	Chem. Form for Metal Oxalate
$Al(OH)_3$	39	13.5	40.5	AlC_2O_4
$CaCO_3$	1.2	0.5	1.4	CaC_2O_4
$Fe(OH)_3$	4.9	2.6	7.7	FeC_2O_4
KNO_3	0.14	0.1	0.2	$K_2C_2O_4$
$Na_2MoO_4.2H_2O$	2.2	1.3	3.9	$Na_2C_2O_4$
SiO_2	2.22	1.0	3.1	SiC_2O_4
$Na_2WO_4.2H_2O$	0.37	0.3	0.8	$Na_2C_2O_4$
$NaNO_3$	19.74	5.5	16.5	$Na_2C_2O_4$
NaF	0.21	0.1	0.4	$Na_2C_2O_4$
$Na_2SO_4.10H_2O$	8.47	1.3	4.0	$Na_2C_2O_4$
$Na_3PO_4.12H_2O$	7.13	1.4	4.2	$Na_2C_2O_4$
$Na_2CO_3.H_2O$	14.42	5.5	16.5	$Na_2C_2O_4$

It is important to remember that although dissolution was performed, it was only to provide a source of feed for the decomposition testing.

The simulant was made by the Savannah River National Laboratory, using available reagent grade chemicals.

Physical Properties of Simulant

Similar to sludge in a waste tank, at the time of testing, the drum contained both liquid and solid phases, with varying gradients. For dissolution comparibility/replicability a solids density (i.e., concentration) was chosen. Specifically, the solids in the simulant were spread out in an approximate 2.5 cm thick layer in a polypropylene tray. It was allowed to sit for 24 hours, resulting in an approximately 75% solids concentration. This 75% solids concentration was used for the basis of the dissolution testing [6].

The measured densities of the simulant were 1.69 grams/ml, wet, and 1.05 grams/ml, dry [6]. The buffering capacity was titrated with a 10 gram sample of simulant against a solution of oxalic acid. Another 10 grams was also titrated against a solution of sulfuric acid. The measured buffering capacity required to lower the pH to about 2.0 was determined to be 0.5 grams of oxalic acid per gram of air dried solid[6].

Test Rig and Decomposition Process

A test rig was constructed of stainless steel. It consists of an 18 liter Dissolution Loop, to approximate slurry fed from Enhanced Chemical Cleaning in the Treatment Tank, and a 67 liter Decomposition Loop, which roughly approximated the remaining unit operations associated with the process. The Figure 5 shows the flow diagram of the Decomposition Loop [6].

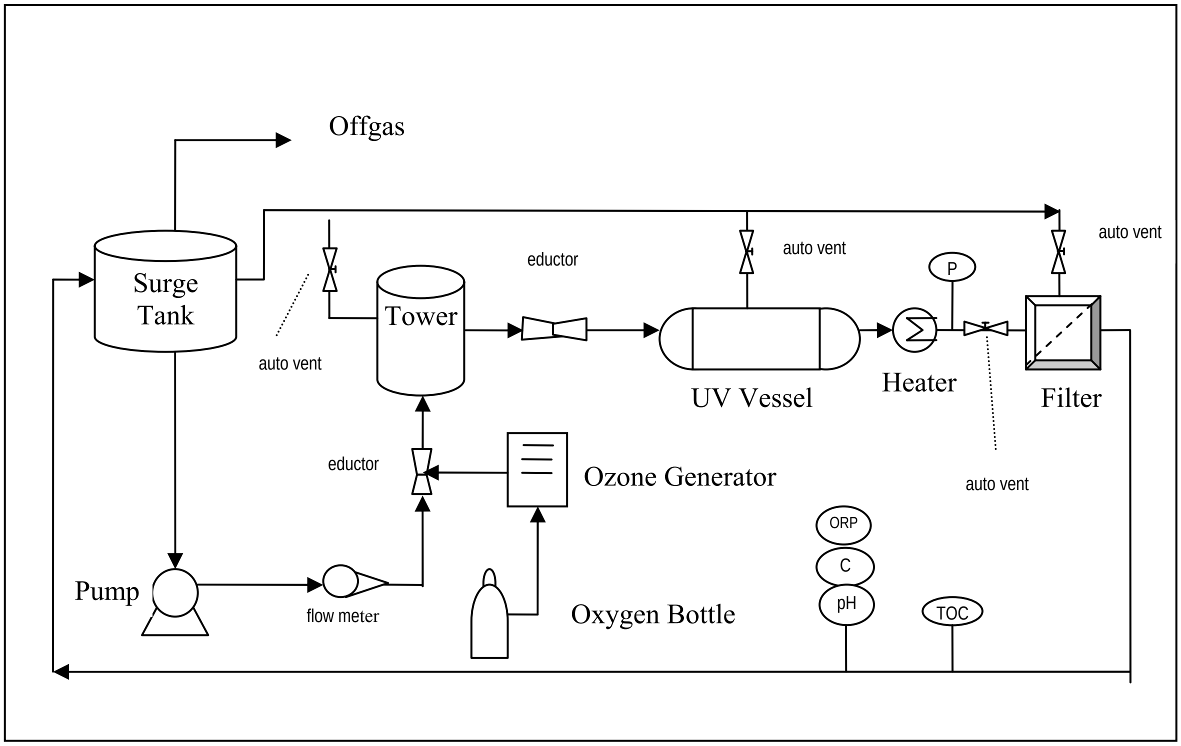

Figure 5. Simplified Flow Diagram of Decomposition Loop

The major components of the decomposition loop used in the testing are [6]:

- One general 15 liter poly vessel (Surge Tank) to allow for level/volume changes within the loop. The vessel also served as a drop tank for the loop's vent lines.
- One fluroplastic 1 gallon per minute magnetic drive pump (Pump).
- Two ½ inch - 1 inch Purfresh Ozone® In-line Contactors (Eductors) to create a relative vacuum to pull the ozone gas into solution.
- One Ozonia Triogen® laboratory ozone generator (Ozone Generator) which uses a corona discharge to provide ozone in excess of 100 g/hour.
- One 10 liter, 3 meter tall vessel made from Schedule 40 stainless pipe (Tower) to keep/separate ozone and carrier gas not dissolved in the solvent.
- One 12 cm UV Vessel containing an Ozonia® 1,500 Watt medium pressure (UV lamp) to provide appropriate spectrum of light in the ultra violet wavelength for oxalate destruction.
- One 6 cm Blak-Ray® sheath (Tube) to separate the waste stream from the UV lamp.
- One 2,000 Watt inline electric (Heater) to provide a heat source to maintain the process temperature at a nominal 70ºC.
- Four 1 inch Plast-O-Matic® Valves PVDF Back Pressure Valve (auto vent) to provide throttling so that the pumping action would create a 10 psig overpressure on the system, enabling more ozone to be maintained in solution than would be possible at atmospheric pressure.

- A Beta-Klean Z2 Series Absolute Rated Rigid Filter Cartridge Filter® (Filter) fitted with 1 micron (nominal) filter cartridges to remove the solids from the liquid.
- Several different commercially available, calibrated instruments (flowmeter, Pressure (P), Temperature ©, pH, EV, Oxidation Reduction Potential (ORP)) used to provide online indication of key process parameters.
- GE Analytical Instruments On-Line TOC Analyzer®, to enable online PPM oxalate approximations based on Total Organic Carbon (TOC).

Testing

Dissolution of 1,200 g of air dried simulant using 18 liters of 5 wt% oxalic acid was performed to provide a concentrated feed (i.e., >> 10,000 ppm of oxalate) to the Decomposition Loop.The Tower, was fed ozone at 60 g/hour. Based on similar testing, the observed ozone solubility limit was about 40 mg/L [6] or 0.0008 moles/L. Initially, when starting the test, the UV lamp (sheath) was clean with no observable film. The UV lamp was not cleaned for the duration of the testing. Oxalate destruction testing continued until, process stream coloration from oxalate was no-longer visible, and verified through online TOC and analytical testing that the oxalate concentration was less than 50 ppm [6].

RESULTS AND DISCUSSION

The initial pH was recorded to be slightly less than 2.0. Starting after about 1 hour, the approximate oxalate concentration in the Decomposition Loop was recorded approximately every hour as shown in Figure 2.

Table 2. Measured Oxalate Concentration In Decomposition Loop

Oxalate Concentration (ppm)	**Time in Decomposition Loop (hr)**
12,200	1
9,700	2
8,400	3
7,800	4
7,100	5
7,100	6
6,100	7
5,500	8
5,100	9
4,800	10
4,200	11
4,100	12
3,600	13
3,100	14
2900	15
2,600	16
2,500	17
2,500	18
2,000	19
2,200	20
1,800	21
1,100	22
900	23
700	24
500	25
40	26

The Table 2 data is plotted as Figure 6.

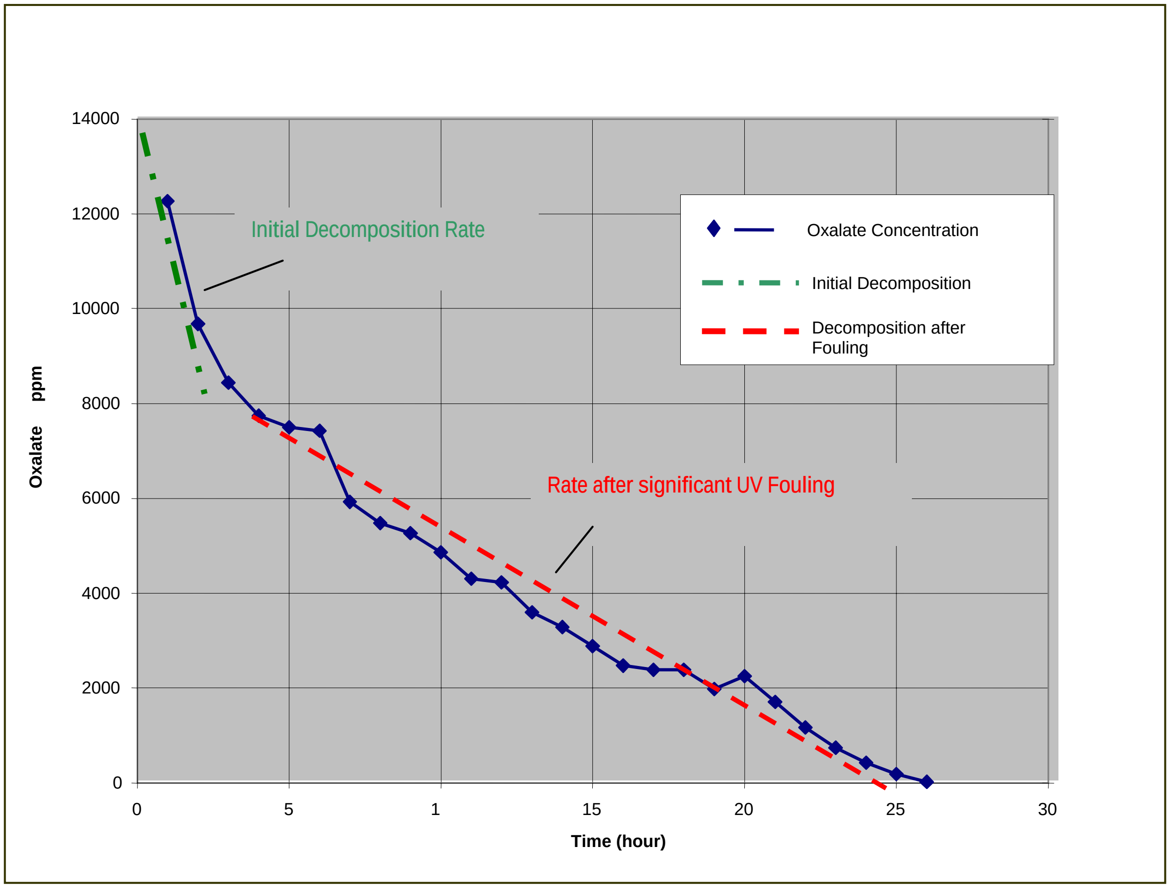

Figure 6: Oxalate Concentration in the Decomposition Loop vs. Time

Importance of Hydroxyl Radical

As shown by the first few points graphed on Figure 6, the initial decomposition rate of the oxalate is very aggressive. Studies have concluded that at a pH ranging from 2 to near neutral conditions, oxalate reacts with a very low rate constant with ozone, $k = 0.04\ M^{-1}s^{-1}$[1], a mid-range rate constant for hydrogen peroxide, $k = 2\ M^{-1}s^{-}1$ [2], and a very high rate constant with hydroxyl radical, $k = 5.3x10^{6}\ M^{-1}s^{-1}$[1]. Therefore the oxalate destruction rate is mostly caused by the availability of hydroxyl radicals. Logically, assuming all other factors equal, the greater the decomposition rate the greater the concentration of available hydroxyl radicals. It can be assumed that initially there is the greatest concentration of hydroxyl radicals, UV lamp is most effective, and the oxalate destruction rate is at a maximum.

Reactions for Hydroxyl Radical

As previously discussed, hydroxyl radicals are produced in ozone/ UV processes by Reactions 2A and 2B

$$O_3 \ + \ H_2O \xrightarrow{hv} H_2O_2 \ + \ O_3 \longrightarrow 2 \circ OH \qquad \text{(Reaction 2A)}$$

$$O_3 \ + \ H_2O \xrightarrow{hv} 2 \circ OH \qquad \text{(Reaction 2B)}$$

Other likely reactions in the Decomposition Loop which can produce hydroxyl radicals include homogenous catalytic type reactions. The Fenton's type reactions will compete for the intermediate peroxide in Reaction2A [3]. The combined Fenton's reaction is shown by Reactions 3A and 3B.

$$Fe(II) \ + \ H_2O_2 \ \longrightarrow \ Fe(III) \ + \ \circ OH \ + OH^- \qquad \text{(Reaction 3A)}$$

$$Fe(III) \ + \ H_2O_2 \ \longrightarrow \ Fe(II) \ + HO_2 / \ O_2{}^- \ + \ H^+ \qquad \text{(Reaction 3B)}$$

Where in Reaction 3A the HO_2/O_2^- represents the perhydroxyl radical. The perhydroxyl radical has an oxidation potential just slightly less than hydrogen peroxide (i.e., an oxidation potential of 1.70 volts compared to 1.77 volts for hydrogen peroxide, compared to 2.05 volts for the hydroxyl radical [1]). Due to this fact, the perhydroxyl radical is considered to have an insignificant impact on the destruction rate of oxalate [3,5, and 11].

Even without the UV light, in an ozonation process with minimal concentrations of Fe (II), the Fe (II) will act as a homogeneous catalyst where ferro-hydroxyl radicals are produced as an intermediate. The ferro-hydroxyl radicals can react and form hydroxyl radicals. This is shown by Reaction 4 [4].

$$Fe^{2+} \ + \ O_3 \ \longrightarrow \ FeO^{2+} \ + \ O_2 \ + \ H_2O \longrightarrow Fe^{3^+} \ + \ \circ OH \ + \ OH^- \ + \ O_2$$

(Reaction 4)

Oxalate Destruction

The overall destruction of oxalate can be qualitatively expressed as Equation 2.

$$[C_2O_4]^{-2} \ + \ \sum \left[\circ OH\right] \ \rightarrow \ products \qquad \text{(Equation 2)}$$

where:

- $[C_2O_4]^{-2}$ is the oxalate that will be decomposed.
- $\Sigma[\bullet OH]$ is the summation of the hydroxyl radicals that will be produced via Reactions 2A, 2B, 3A and 4.
- Products are CO_2 and water.

Expanding to show the each of the individual reactions, results in Equation 3.

$$[C_2O_4]^{-2} + [\circ OH]_{2A+2B+3A+4} \rightarrow products \qquad \text{(Equation 3)}$$

where:

- 2A and 2B are for Reactions 2A and B where the •OH radicals are made from ozone and UV light as a catalyst.
- 3A is for Reaction 3A, which is an Fenton's reaction that uses intermediate peroxide produced in Reaction 2A.
- 4 is Reaction 4, a Fenton's type of reaction that uses iron and ozone.

Assuming the decomposition reactions are all first order, the overall destruction rate with UV, can be expressed as Equation 4.

$$Rate = k[A][B]_{2A} + k[A][B]_{2B} + k[A][B]_{3A} + k[A][B]_4 \qquad \text{(Equation 4)}$$

Without the UV light, Reaction 4 becomes the only means for hydroxyl generation. This is shown by Equation 5.

$$Rate_{noUV} = k[A][B]_4 \qquad \text{(Equation 5)}$$

Rate Constant without UV

Although the ozone concentration is based on the observed ozone solubility limit, and remains an assumed constant (O_3 = 0.0008 moles/L), the concentration of iron decreases as the Decomposition Loop destroys oxalate. The solids are precipitated and then removed via the cartridge filter. The iron concentration can be estimated using Equation 6.

$$[Fe(II)] = [C_2O_4] \times metal/oxalate\ \ ratio \times iron/cation\ \ ratio \qquad \text{(Equation 6)}$$

where:

- $[C_2O_4]$ concentration decreases over time as recorded in Table 2.
- Metal to oxalate mass ratio can be assumed to be about 50/88.
- Iron/cation ratio is determined in Table 1 to be 7.7 %.

Using Equation 6, Table 3 shows the estimated iron concentrations and the measured oxalate concentrations for the 26 hours of Destruction Loop run time decomposition. Refer to Table 3.

Table 3. Iron Concentration as a Function of Time

Decomposition Time	**Oxalate Concentration**		**Metal/Oxalate**	**Iron/Cation**	**Fe(II) Concentration**
(hr)	**(g/l)**	**(M)**	**ratio**	**ratio**	**(M)**
1	12.22	0.14	0.57	0.08	6.08E-3
2	9.73	0.11	0.57	0.08	4.84E-3
3	8.41	0.10	0.57	0.08	4.18E-3
4	7.84	0.09	0.57	0.08	3.90E-3
5	7.12	0.08	0.57	0.08	3.54E-3
6	7.98	0.09	0.57	0.08	3.97E-3
7	6.11	0.07	0.57	0.08	3.04E-3
8	5.49	0.06	0.57	0.08	2.73E-3
9	5.07	0.06	0.57	0.08	2.52E-3
10	4.79	0.05	0.57	0.08	2.38E-3
11	4.16	0.05	0.57	0.08	2.07E-3
12	4.10	0.05	0.57	0.08	2.04E-3
13	3.57	0.04	0.57	0.08	1.78E-3
14	3.08	0.04	0.57	0.08	1.53E-3
15	2.91	0.03	0.57	0.08	1.45E-3
16	2.58	0.03	0.57	0.08	1.28E-3
17	2.50	0.03	0.57	0.08	1.24E-3
18	2.49	0.03	0.57	0.08	1.24E-3
19	1.99	0.02	0.57	0.08	9.88E-4
20	2.20	0.02	0.57	0.08	1.09E-3
21	1.81	0.02	0.57	0.08	8.97E-4
22	1.12	0.01	0.57	0.08	5.55E-4
23	0.92	0.01	0.57	0.08	4.58E-4
24	0.73	0.01	0.57	0.08	3.65E-4
25	0.50	0.01	0.57	0.08	2.47E-4
26	0.04	0.00	0.57	0.08	1.79E-5

As previously shown on Figure 6, the destruction rate after 3 hours was 8,000 ppm / 17 hours or 471 ppm oxalate destroyed per hour. This equates to a destruction rate of approximately 1.45E-6 moles $L^{-1}s^{-1}$. Assuming a first order reaction and dividing by the concentrations of Fe(II) and O_3 and then multiplying by 67 liters to account for the size of the Decomposition Loop, results in a rate constant for the a Fenton's type of reaction (i.e., Reaction 4) of $k = 2.1E+1\ M^{-1}s^{-1.}$

Importance of UV

The actual importance of UV to the destruction rate of oxalate depends on many factors, but because of its overall significance to the environmental and nuclear, is well tested. Based on the destruction rate of a typical oxalate decomposition at a pH = 2, and a temperature of around 70°C, a clean UV light will increase the destruction rate approximately by a factor of 10 [5]. Therefore, assuming a similar impact factor for UV for Enhanced Chemical Cleaning an approximate rate constant should be 2.1 $M^{-1}s^{-1}$, or in terms of destruction rate, 1.45E-7 moles $L^{-1}s^{-}$. Based on Figure 6, the destruction rate with the clean light (i.e., the first 3 hours) was approximately 4,000 ppm / 3 hours or 1,333 ppm oxalate destroyed per hour. This equates to achieving a destruction rate of only 4.2E-6 moles $L^{-1}s^{-1}$, or an increase in the destruction rate by only a factor of 2.8, instead of 10, as predicted by the general studies associated with using ozone/UV in a Fenton's process[5].

CONCLUSION

Through simulant testing, it has been shown that theincreased solids associated with Enhanced Chemicla Cleaning will decrease the oxalate destruction rate by a factor of about 2.8. Results from very similar tests with similar chemistry suggest that the impact should be about 10. Based on the limited reaction pathway for the creation of hydroxyl radicals with iron, ozone, and no UV, the discrepancy suggests that initially, at "time zero" the UV light failed to perform up to expectations. It is therefore concluded that regardless of the fouling rate, either the increased solids concentration is impacting the initial penetrability (i.e. to many solids), or the light is not adequately sized/configured to have the appropriate flux.

Due to the fact that independent multiple tests were not performed and the same initial conditions were not applied, and testing with the light turned off was not actually performed, more detailed testing has been initiated.

REFERENCES

1) T. Garoma and M. D. Gurol, "Modeling Aqueous Ozone /UV Using Oxalic Acid as a Probe Chemical', Environmental Science and Technology, 2005, 39 (20) pp 7964-7969, September 17, 2005.

2) D. Chung, E. Kim, Y. Shim, J Yoo, C. Choi, and J Kim, "Decomposition of Oxalate by Hydrogen Peroxide in Aqueous Solution, ' Journal of Radio-analytical , Nuclear Chemistry Letters, 201: 96, 495-507.

3) Chemical Speciation and Reactivity in Water Chemistry and Water Technology: A Symposium in Honor of James J. Morgan, Pages 608-611 in reprints of Extended Abstracts, Vol 40, No. 2, American Chemical Society, Washington DC, August 20-24, 2000.

4) T. Logager, J. Holeman, K. Sehested, and T. Pedersen, "Oxidation of Ferrous Ions by Ozone in Acidic Acid Solutions," Inorganic Chemistry, 31, 3523-3529, American Chemical Society, 1992.

5) A. El-Raady and T, Nakajima, "Effect of UV Radiation on the Removal of Carboxylic Acids from Water by H2O2 and O3 in the Presence of Metallic Ions," Ozone Science and Engineering, 28: 53-58, February 2006.

6) J. Dennis "Savannah River Site Salt Simulant," AREVA, 51-9077712-000, April 23, 2008.

7) F. Li, J Chen, C. Liu, J. Dong, T. Liu," Effect of iron oxides and carboxylic acids on Photochemical Degradation of Bisphenol, " Biology Fertility Soils, 42: 409-417, January 2006.

8) F. Beltran, F Rivas, and R. Montero de Espinosa, "Iron Type Catalysts for the Coronation of Oxalic Acid in Water," Water Research Volume 39: Issue 15, 3553-3564, September 2005.

9) S. Penkett, B. Jones, K. Brich and A. Eggleton, " The importance of atmospheric ozone and hydrogen peroxide in oxidizing sulfur dioxide in cloud and rainwater,' Atmospheric Environment, Volume 13, Issue 1, 123-137, July 1978.

10) J. Yoo and E. Kim, "Decomposition of Oxalate Precipitates by Photochemical Reaction," Korea Atomic Energy Research Institute, Korea, 2002.

11) R. Zepp, B. Faust and J. Holgne, "Hydroxyl Radical Formation in Aqueous Reaction (pH 3-8) of Iron (II) with Hydrogen Peroxide: The Photo-Fenton Reaction," Environmental Science Technology, Volume 26, 313-319, 1992.

12) R. E. Eibling, “Development of an Insoluble Salt Simulant to Support Enhanced Chemical Cleaning Tests, “WSRC-STI-2008-00079, Rev. 0, April 2008, Washington Savannah River Site, Aiken, SC.