SAVANNAH RIVER SITE TANK CLEANING:
CORROSION RATE FOR
ONE VERSUS EIGHT PERCENT OXALIC ACID SOLUTION - 11413

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ABSTRACT

Until recently, the use of oxalic acid for chemically cleaning the Savannah River Site (SRS) radioactive waste tanks focused on using concentrated 4 and 8-wt% solutions. Recent testing and research on applicable dissolution mechanisms have concluded that under appropriate conditions, dilute solutions of oxalic acid (i.e., 1-wt%) may be more effective. Based on the need to maximize cleaning effectiveness, coupled with the need to minimize downstream impacts, SRS is now developing plans for using a 1-wt% oxalic acid solution.

A technology gap associated with using a 1-wt% oxalic acid solution was a dearth of suitable corrosion data. Assuming oxalic acid's passivation of carbon steel was proportional to the free oxalate concentration, the general corrosion rate (CR) from a 1-wt% solution may not be bound by those from 8-wt%. Therefore, after developing the test strategy and plan, the corrosion testing was performed. Starting with the envisioned process specific baseline solvent, a 1-wt% oxalic acid solution, with sludge (limited to Purex type sludge-simulant for this initial effort) at 75°C and agitated," the corrosion rate (CR) was determined from the measured weight loss of the exposed coupon. Environmental variations tested were: a) Inclusion of sludge in the test vessel or assuming a pure oxalic acid solution; b) acid solution temperature maintained at 75° or 45°C; and c) agitation of the acid solution or stagnant. Application of select electrochemical testing (EC) explored the impact of each variation on the passivation mechanisms and confirmed the CR. The 1-wt% results were then compared to those from the 8-wt%.

The immersion coupons showed that the maximum time averaged CR for a 1-wt% solution with sludge was less than 25-mils/yr for all conditions. For an agitated 8-wt% solution with sludge, the maximum time averaged CR was about 30-mils/yr at 50°C, and 86-mils/yr at 75°C. Both the 1-wt% and the 8-wt% testing demonstrated that if the sludge was removed from the testing, there would be a significant increase in the CR. Specifically, the CR for an agitated 1-wt% pure oxalic acid solution at 45 or 75°C was about 4 to 10 times greater than those for a 1-wt% solution with sludge. For 8-wt% at 50°C, the effect was even larger. The lower CRs suggest that the cathodic reactions were altered by the sludge. For both the 1-wt% and 8-wt% solution, increasing the temperature did not result in an increased CR. Although the CR for a 1-wt% acid with sludge was considered to be non-temperature dependent, a stagnant solution with sludge resulted in a CR that was greater at 45°C than at 75°C, suggesting that the oxalate film formed at a higher temperature was better in mitigating corrosion. For both a 1 and an 8-wt% solution, agitation typically resulted in a higher CR.

Overall, the testing showed that the general CR to the SRS carbon steel tanks from 1-wt% oxalic acid solution will remain bounded by those from an 8-wt% oxalic acid solution.

INTRODUCTION

In order to begin closing the Savannah River Site (SRS) non-compliant radioactive waste tanks, the waste must be removed from the tanks. In spite of the various internal obstructions for most tanks, the bulk can be readily removed using available mechanical agitation methods tied to existing slurry transport capabilities. With a goal of maximizing waste removal, additional methods, especially for sludge, may be required. The sludge consists of mostly precipitated common metal hydro(oxides) such as hematite (Fe_2O_3), Gibbsite ($Al(OH)_3$), Boehmite ($AlO(OH)$, Nickel Oxide (NiO), Manganese Oxide (MnO_2), and other common industrial metal oxides making up normally greater than 90-wt% of the total solids mass, with the radioactive component being a small part of the total mass. In order to leave less-than-residual quantities of waste and approach decontamination levels, chemically aided waste removal methods may be required. Of the removal agents, oxalic acid is preferred because of its combined dissolution and chelation properties, as well as its ability to inhibit carbon steel corrosion.

The concentration of oxalic acid is the main difference between the "new technologies" and the historical application of oxalic acid. Commercial and SRS testing [1, 4, & 15] have both concluded that, under appropriate conditions, dilute oxalic acid solution (e.g., 1-wt%) can dissolve/digest more of the routine metal hydro-oxide found in sludge, compared to concentrated oxalic acid solution (i.e., 8-wt%).

A significant technology gap associated with using 1-wt% oxalic acid solution is a defendable CR. Most corrosion data was determined using either a 4-wt% or an 8-wt% oxalic acid solution. As such, little corrosion data exists for using dilute oxalic acid solution. Since the corrosion inhibition qualities of oxalic acid solution are often attributed to the concentration of oxalate $(C_2O_4)^{-2}$ and ferrous (Fe^{+2}) ions, depending on the passivation kinetics, the CR for a 1-wt% solution may be greater than that for an 8-wt% solution [1].

Using the 8-wt% corrosion test as a guide, a test plan was developed for the 1-wt% solution. The CR would be determined by measuring the weight loss of immersion coupons, under varied environmental conditions. The conditions were: 1) a temperature of either 45°C, or 75°C; 2) either vigorously agitated, or stagnant; and, 3) either exposure to 1-wt% pure oxalic acid solution, or to a 1-wt% oxalic acid solution containing sludge (simulant). With the accelerated nature of the electrochemical testing, the impacts caused by varying temperature, mixing, and presence of sludge were investigated. The specific EC testing included:

1)	Open-circuit potential monitoring (OCP) – to determine the preferred cathodic reaction and if H_2 evolution was occurring.
2)	Linear polarization resistance testing (LPR) – to provide an instantaneous CR and enable confirmation of the immersed coupon CR.
3)	Cathodic polarization testing (CP) – to enable the cathodic reaction kinetics to be investigated.
4)	Anodic polarization (AP) – to evaluate the stability and effectiveness of the passive film.

BACKGROUND AND THEORY

For a metal, the relationship between pH, potential, and stability can be graphically shown using a Pourbaix diagram. A Pourbaix diagram for iron in water, shown by Figure 1, identifies were:

1)	Iron is stable and will not corrode.
2)	Soluble ferric (Fe^{+3}) compounds form, while allowing corrosion.
3)	Insoluble ferrous (Fe^{+2}) compounds form, while inhibiting corrosion.
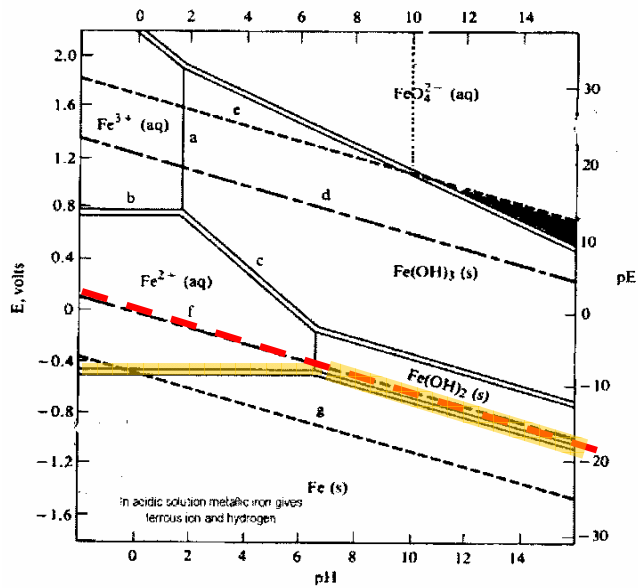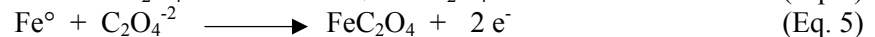
Figure 1. Pourbaix diagram for iron in water [3].

Figure 1 shows the regions of stability for iron, Fe^{+2} and Fe^{+3} ions, and oxide corrosion products. The double lines separate species related by redox equilibrium for iron, the oxidized species, and the corrosion products; it represents iron corroding into Fe^{+2} (Equation 1). Hydrogen (H_2) evolution is shown by line (f). As shown by the diagram, H_2 evolution may occur during the corrosion of iron to Fe^{+2} (Equation 2).

$$Fe^{\circ} \longrightarrow Fe^{2+} + 2e^{-} \qquad \text{(Eq. 1)}$$
$$2\,H^{+} + 2e^{-} \longrightarrow H_2 \qquad \text{(Eq. 2)}$$

Commonly, the corrosion of iron with oxalic acid is over-simplified. That is, iron simply reacts with oxalic acid to form Fe^{+2} oxalate [5-8] and H_2 gas. Following this logic, passivation would occur if the Fe^{+2} oxalate film built-up near the metal surface, which would occur only after the area has become supersaturated with oxalate and Fe^{+2} ions. Equation 3 shows this reaction. Recent electrochemical testing [4 & 7], however, indicates that during chemical cleaning, hydro-oxalate ($HC_2O_4^{-}$) will be a significant reactant. Equation 4 shows the hydro-oxalate reaction. At elevated pH conditions, Equation 5 becomes the thermodynamically favored reaction.

$$Fe^{\circ} + H_2C_2O_4 \longrightarrow FeC_2O_4 + 2H^{+} + 2\,e^{-} \qquad \text{(Eq. 3)}$$
$$Fe^{\circ} + HC_2O_4^{-} \longrightarrow FeC_2O_4 + H^{+} + 2\,e^{-} \qquad \text{(Eq. 4)}$$
$$Fe^{\circ} + C_2O_4^{-2} \longrightarrow FeC_2O_4 + 2\,e^{-} \qquad \text{(Eq. 5)}$$

An obvious weakness in Figure 1 is the failure to account for oxalic acid. Figure 2 shows a Pourbaix diagram for iron in water, extended to include the three regions of stability for oxalic acid.
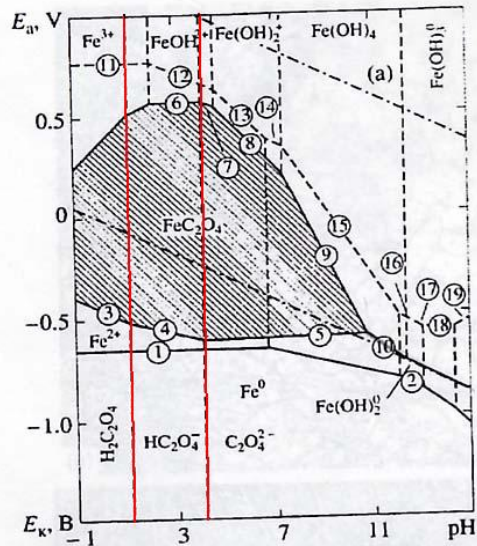
Figure 2. Iron-Oxalic Acid-Water Pourbaix Diagram [15].

As shown in Figure 2, at a pH < 1.25, oxalic acid is thermodynamically stable. At a pH between 1.25 and 4, hydro-oxalate is preferred. While at a pH > 4, oxalate is thermodynamically preferred. A second feature shown in Figure 2 is the region of stability for Fe^{+2} oxalate, indicated by the crosshatched area. For a 1-wt% oxalic acid solution, with a pH of aprox.1.1 [5], the solution would contain 50% stable oxalic acid and 50% hydro-oxalate. Thus, Equations (3) and (4) would both be occurring at the metal surface, forming the Fe^{+2}-oxalate film. Based on maintaining a pH between 1.5 and 2 during dilute chemical cleaning, Equation (1) would combine with hydro-oxalate. The resulting reaction is shown by Equation 6 [4].

$$2\ Fe^{\circ}\ +\ HC_2O_4^- \longrightarrow FeC_2O_4\ (s)\ +\ Fe^{2+}\ +\ H^+\ +\ 4\ e^- \qquad (Eq.\ 6)$$
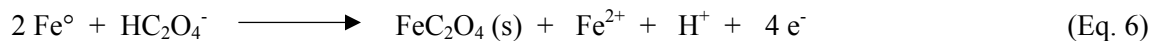
The Fe^{+2} oxalate film forms at the metal surface and mitigates corrosion. The inhibition properties of the film largely depend on its porosity, which primarily depend on its formation rate. At high CR (e.g., 75°C), a tightly adherent film with strong passivation properties is created. Other factors which impact film formation include:

1) Agitation – Mixing the solution decreases the concentration of Fe^{+2} at the metal surface, by transporting them into the bulk solution, creating a less adherent more porous film.
2) Oxidation – Oxidation of Fe^{+2} to become Fe^{+3} (e.g., by mercury, nitrate, permanganate) increases the anodic electrochemical potential, creating a less adherent, more porous film.

For pure oxalic acid, the cathodic reaction that occurs is either hydrogen evolution:

$$2\ H^+\ +\ 2e^- \longrightarrow H_2\ (g) \qquad (Eq.\ 7)$$

and/or, oxygen reduction:

$$O_2 + 4H^+ + 4e^- \qquad 2H_2O \qquad (Eq.\ 8)$$

Hydrogen evolution is favored at de-aerated, stagnant, high temperature conditions [17]. Oxygen evolution on the other hand is more favored in the lower temperature and agitated conditions where oxygen solubility is greater.

Impacts of Temperature and Agitation in Pure Oxalic Acid Solution
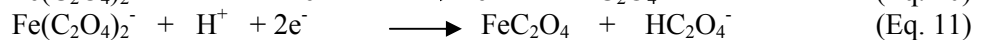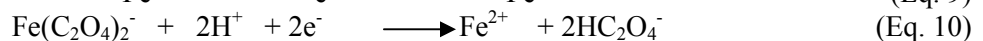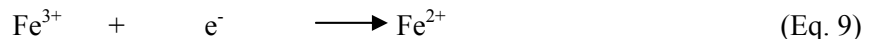
The effects of temperature and mixing on the CR can largely be explained in terms of their effect on the cathodic reaction .Table 1 summarizes the effects of temperature and agitation on the cathodic reaction, film formation rate, and ultimately on the CR.

Table 1. Impact of Temp and Agitation on Film and Corrosion Rates

Temp	Agitation	Mechanisms and Impacts to Film	Corrosion Rate
75°C	stagnant	Cathodic reaction is H_2 evolution – Initial CR depletes H^+ near the surface CR becomes controlled by H^+ transport to surface Initial CR caused build-up of Fe^{+2} at the metal surface No agitation to disperse the Fe^{+2} resulting in tightly adherent film	Decreased
75°C	mixing	Cathodic reaction is H_2 evolution - Convection maintains H^+ near the surface Electrode kinetics control CR H_2 evolution disrupts film formation, Less precipitate at surface Loosely adhered film results in elevated CR	Elevated
45°C	stagnant	H_2 is the primary cathodic reaction With decreased temp, O_2 has small increased role in the corrosion Lower temp resulting in a slower cathodic reaction rate H^+ concentration does not deplete rapidly CR controlled by the electrode reaction kinetics H_2 evolution disrupts the formation of Fe^{+2} oxalate film Loosely adhered Fe^{+2} oxalate film resulting in elevated CR	Elevated
45°C	mixing	H_2 is the primary cathodic reaction Because decreased temp, O_2 has small increased role in the corrosion Lower temp resulting in a slower cathodic reaction rate H^+ concentration does not deplete rapidly Electrode kinetics at the surface control the CR	Elevated

Impact of Sludge

Conditions during chemical cleaning are more complex than those summarized in Table 1. For example, chemicals such as nitrate, chloride, sulfate, and mercury are present, changing the film formation dynamics. In addition, the dissolution of the sludge would result in a build-up of not only Fe^{2+}, but also Fe^{+3}. In the presence of Fe^{3+}, the cathodic reaction shown by Equation 9 can also occur. At a pH~2, Fe^{3+} complexes with oxalate forming a di-oxalatoferrate ion, $Fe(C_2O_4)_2^-$. The $Fe(C_2O_4)_2^-$ is reduced at cathodic sites. If the oxalate concentration were < 0.1 M, the reaction would proceed as shown by Equation 10. At increased oxalate concentrations, the reaction would proceed as shown by Equation 11.

$$Fe^{3+} \; + \; e^- \; \longrightarrow \; Fe^{2+} \qquad \text{(Eq. 9)}$$
$$Fe(C_2O_4)_2^- \; + \; 2H^+ \; + 2e^- \; \longrightarrow Fe^{2+} \; + 2HC_2O_4^- \qquad \text{(Eq. 10)}$$
$$Fe(C_2O_4)_2^- \; + \; H^+ \; + 2e^- \; \longrightarrow \; FeC_2O_4 \; + \; HC_2O_4^- \qquad \text{(Eq. 11)}$$

Once sludge dissolution begins, the oxalate ion concentration would decrease. With the increased Fe^{+2} at the metal surface, the initial film formation rate would also increase. Once the initial film formed, the CR would decrease compared to that for a pure 1-wt% oxalic acid solution. This is summarized by Table 2.

Table 2. Film Formation and Corrosion Rates with Sludge

Condition	Mechanisms and Impacts to Film	Corrosion Rate
Oxalic acid with sludge	Ferric ions increased initial CR proportional to their concentration Due to increased Fe^{+2} & Fe^{+3} at the metal surface, film formation increases Film formed quickly, decreasing the CR	Decreased compared to pure oxalic acid solution

EXPERIMENTAL

Immersion Coupon Testing Similarities

The immersion coupons used for the corrosion testing with the 1-wt% oxalic acid solution were ASTM A285, Grade Carbon steel (UNS K02200), while the coupons used for the 8-wt% solutions were ASTM A537 Class 1 carbon steel. The different coupons were considered to be interchangeable in oxalic acid solution based on previous corrosion studies [4]. Although the exposure of the coupons associated with the 8-wt% oxalic acid testing was about 9-14 days, the exposure of the coupons for the 1-wt% oxalic acid testing lasted up to 30-days.

Both the 1 and the 8-wt% testing exposed coupons to pure oxalic acid solutions or oxalic acid solutions containing sludge. Sludge from a PUREX simulant recipe was used for the 1-wt% testing, while sludge from two alternate recipes was used for the 8-wt% corrosion testing. All three of the sludge recipes were similar, with all three of the resultant sludge types considered representative of typical SRS PUREX sludge (i.e., without the radionuclides). The main differences between the sludge types for 1-wt% and 8-wt%, is that the sludge for 1-wt% testing, contained small direct solid additions of hematite and boehmite [16].

During the 1-wt% pure oxalic acid solution testing, the pH was maintained at about 1.0, while for the 1-wt% oxalic acid solution with sludge the pH was maintained at 2.0. Similarly, with the 8-wt% pure oxalic acid solution testing, the initial pH was about 0.7, while with the 8-wt% oxalic acid solution containing sludge, the initial pH was at about 1.0. Table 3 summarizes different environmental conditions considered during the testing.

Table 3. Test Matrix of Different Conditions Tested

Environmental Factors	Tested Condition
Temperature	Low: 45°C for 1-wt%, 50°C for 8-wt%
	High 75°C
Acid Solution	1-wt% Pure Oxalic Acid Solution
	1-wt% oxalic acid solution with sludge
Mixing	Agitated
	Stagnant

Electrochemical Test Equipment

The electrochemical tests were conducted via a Gamry™ potentiostat, in a 1-liter PAR electrochemical test cell. A hot plate with a controller maintained the temperature during the testing. A condenser minimized the evaporation losses. The carbon steel working electrodes were either a 5-cm^2 cylinder or a 1.5-cm^2 rectangle, anchored in a cold mount. The counter electrodes were either a carbon graphite rod or

a stainless steel mesh. Saturated silver-silver chloride (Ag/AgCl) electrodes were used as the reference electrodes. The software used to collect the information was CorrWare™ for Windows™.

RESULTS AND DISCUSSION

Coupon Analysis

Photographs of the post-test coupons are shown in Figure 3. Coupons that were exposed to sludge simulant were covered with ferrous oxalate and what appeared to be particles from the sludge. In general, higher temperatures and agitation appeared to increase the thickness of the oxalate film and the density of the sludge particles on the coupons that were exposed to the PUREX and HM simulants. The opposite appeared to be true for the coupons exposed to the oxalic acid solution.   The solid layer that formed on the coupons that had been exposed to oxalic acid at 45 °C was thicker and looser than that that formed on the coupon at 75 °C.

Conc & Temp	Acid w/Sludge, Mixing	Acid w/Sludge, Stagnant	Pure Acid, Stagnant
1-wt%, 75°C			
1-wt%, 45°C			
8-wt%, 75°C	Not Available	Not Available	
8-wt%, 50°C	Not Available	Not Available	

Figure 3. Exposed corrosion coupons.

The general CRs were calculated using the weight loss formula shown in Equation 12 [4]:

$$CR = \frac{3.45 \times 10^6}{A \times T \times \rho} \, w \qquad\qquad (Eq.12)$$

where:
CR is the general corrosion rate in mils/yr
w is the measured weight loss of the immersed coupon in grams
A is the area of the immersed coupon, in cm^2
T is the coupon exposure time, in hours
ρ is the density of the immersed coupon, in g/cm^3

The immersion coupon testing determined that 25-mils/yr was an upper bound estimate of the CRs from 1–wt% oxalic acid solution with sludge. For this solution with sludge, temperature did not appear to have

a significant effect on the CRs. This was in direct contrast to the results from 8-wt% oxalic acid testing, where temperature directly influenced the CRs. This difference suggests that the cathodic reaction for an 8-wt% oxalic acid solution were different from those that occurred with a 1-wt% oxalic acid solution with sludge.

The CRs from a 1-wt% pure oxalic acid solution had a strong dependence on temperature, compared to the CRs from a 1-wt% oxalic acid solution with sludge, which were determined to be non-temperature dependent. Under stagnant conditions, the CRs for 1-wt% pure oxalic acid solution at 45°C were greater than the corresponding CRs at 75°C. The CRs in a stagnant 1-wt% pure oxalic acid solution at 45°C were almost 5 times larger than the corresponding CRs from 1-wt% oxalic acid solution with sludge.

For both 1- and 8-wt%, the CRs were lower from the acid solutions containing sludge vs. the pure acid solutions. For 8-wt%, the CRs for 8-wt% pure acid increased with increasing temperature and agitation. Specifically, with agitation, the CRs for 8-wt% pure oxalic acid solution were about 30-mils/yr at 50°C and about 86-mils/yr at 75°C. Under stagnant conditions, the CRs for the same solution (8-wt% pure oxalic acid solution) decreased to about 24-mils/yr at 50°C and about 36-mils/yr at 75°C. For 1-wt% with sludge, the lower CR was because sludge dissolution produces di-oxalatoferrate ions, $Fe(C_2O_4)_2^-$. Since the di-oxalatoferrate ions were reduced at the cathodic sites [15], the cathodic reaction rate would be controlled by diffusion of the ions to the metal surface. For 8-wt% with sludge, the cathodic reaction is likely the reduction of O_2 or ferrate. Both the 1-wt% di-oxalatoferrate ion reduction and the 8-wt% O_2 or ferrate reductions have slower cathodic reaction rates than H_2 evolution. Based on CRs, the 1-wt oxalic acid solution with sludge at 45°C resulted in a passivation film that was less protective than that from pure oxalic acid solution. Agitation typically resulted in larger CRs because the Fe^{+2} ions from the metal surface would be transferred into the bulk of the solution, resulting in a less protective Fe^{+2} oxalate film.

Electrochemical Testing

Open-circuit potential monitoring (OCP) monitors potential to identify if H_2 evolution is the preferred cathodic reaction.

Figure 4 shows the Pourbaix diagram for water. With the measured potential, the Pourbaix diagram was used to determine if corrosion could evolve H_2. Specifically, if the potential during corrosion, $E_{corr,}$ was below the bottom line, H_2 evolution would be possible.
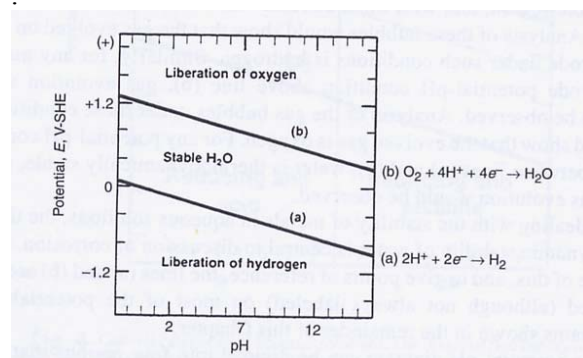.

Figure 4. Pourbaix diagram for water [4]

As shown by Equation 13, the H_2 generation was calculated based on the Nernst Equation [9]:

$$E = E° - 2.303 \frac{RT}{F} *pH \qquad\qquad (Eq.13)$$

where:
$E°$ is the standard potential for H_2 ($E° = 0.0$-V)
R is the ideal gas constant
T is the temperature
F is the Faraday constant.

Table 4 shows the measured potentials of the solution in terms of a normal H_2 electrode and in terms of a saturated Ag/AgCl reference electrode. As can be seen, the presence of sludge decreases the E_{H2} values, while temperature and agitation have very small effects on the E_{H2} values. Starting with an agitated 75°C 1-wt% oxalic acid solution with sludge, the effects the different environmental conditions were electrochemically tested. The results are as follows. The OCP values were compared to the Table 4 E_{H2} values to determine if H_2 evolution was thermodynamically preferred.

Table 4. Hydrogen Evolution Potential (E_{H2}) Values for Corrosion Tests

Sludge	Temp (C)	E_{H2} (mV vs. NHE)	E_{H2} (mV vs. Ag/AgCl)
A	B	C	D=C-197 mv
1-wt% OA	45	-70	-267
1-wt% OA	75	-76	-273
1-wt% OA w/Sludge	45	-127	-324
1-wt% OA w/Sludge	75	-139	-336
8-wt% OA	50	NA	NA
8-wt% OA	75	NA	NA
8-wt% OA w/Sludge	50	-55	-252
8-wt% OA w/Sludge	75	-51	-248

NA= Not Available.

Sludge - Under agitated conditions, at 75°C, a 1-wt% solution with sludge had a potential greater than - 0.34 mV, showing that H_2 evolution was not preferred. Theoretically, removing the sludge from the starting case (i.e., using a 1-wt% pure acid solution) would decrease the potential to around -0.47 mv, indicating that H_2 evolution would be preferred. In general, this showed that at 75°C not considering the effect of sludge, would over-predict a preference for H_2 evolution.

Temperature – Assuming an agitated 1-wt% acid solution containing sludge, and decreasing the temperature from the starting case to 45°C, would decrease the potential to below E_{H2}, such that H_2 evolution would become preferred. This shows that as the temperature decreases, H_2 evolution would become preferred. The importance that sludge has on increasing the potential will also decrease. That is, the potential of a 1-wt% pure oxalic acid solution vs. the potential of a 1-wt% oxalic acid solution with sludge, are similar.

Agitation – At 75°C, under agitated conditions, a 1-wt% oxalic acid solution with sludge had a potential of -0.32 mV, slightly above $E_{H2,}$ such that H_2 evolution would not be preferred. However, if stagnant, H_2 evolution would be preferred. At 45°C for a 1-wt% solution with sludge, switching from an agitated solution to a stagnant solution resulted in a slight decrease in potential. Since H_2 generation was preferred with sludge even when agitated, H_2 generation would remain preferred under stagnant conditions.

Figure 5 shows an example of the the impact of temperature and agitation on the potential in a 1-wt% oxalic acid solution containing sludge. Agitation increased the potential at both temperatures, indicating that a dissolved oxidizing species, or species soluble with Fe^{+2}, was becoming readily available at the

metal surface. Temperature also increased the potential, indicating the formation n of a more adherent film.
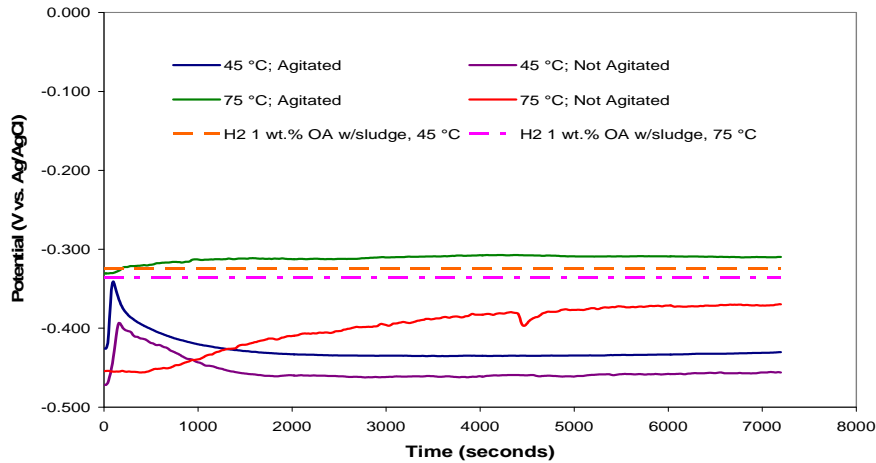

Figure 5. OCP transients for 1- wt% oxalic acid solution with sludge.

Linear polarization resistance (LPR) was used to provide a confirmation of the CRs generated from immersed coupon testing. The test is based on the fact that when the potential is closely polarized to the E_{corr}, the current density, i_{corr}, increases linearly with the potential. Stern and Geary first demonstrated this based on the relationship between the corrosion current, i_{corr} and the polarization resistance, R_p. Refer to Equation 14 [11].

$$i_{corr} = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)R_p}$$ (Eq.14)

where:
β_a is the anodic Tafel slope
β_c is the cathodic Tafel slopes

The software packages for the potentiostats used in this testing assumed the Tafel slope to be 0.120-V to calculate the corrosion current, i_{corr}. Starting with an agitated 75°C 1-wt% oxalic acid solution with sludge, the effects the different environmental conditions were evaluated. With the corrosion current calculated, instantaneous CRs were calculated using Equation 15 [11].

$$CR = 0.13 * \frac{i_{corr} E_w}{\rho}$$ (Eq.15)

where:
E_w is the equivalent weight of iron (27.9 g/equivalent)
ρ is the density of iron (7.86 g/cm^3).

Sludge - Testing showed that CRs of agitated 1-wt% pure oxalic acid solutions at 45 or 75°C were about 4 to 10 times greater (respectively), compared to those for 1-wt% oxalic acid solutions with sludge. This unique behavior is indicative of the preferred cathodic reactions being impacted by the presence of the sludge.

Agitation - For an agitated 1-wt% oxalic acid solution with sludge at 75°C, the measured CRs were about 26 mils/yr. Stagnant, the CRs decreased to about 13 mils/yr. This could be explained by agitation transferring the Fe^{+2} ions from the metal surface into the bulk of the solution, resulting in a less protective Fe^{+2} oxalate film, resulting in an increased CR.

Temperature - For an agitated 1-wt% acid solution with sludge, the CR at 75°C was about 26 mils/yr, while at 45°C, it was about 18 mils/yr. For a stagnant 1-wt% acid solution with sludge, the CR at 75°C was about 13 mils/yr, while at 45°C the CR was 8 mils/yr. Since the differences in the CRs were within potential error associated with linear polarization measurements, the inhibiting mechanism for 1-wt% oxalic acid solution with Sludge did not appear to be strongly temperature dependent.

pH –The CRs for a agitated and stagnant 1-wt% oxalic acid solution with sludge at 45°C were compared to an agitated and stagnant 8-wt% oxalic acid solution with sludge at 50°C, the CRs for both agitated cases were around 18 mils/yr, while for both stagnant were approximately 7-mils/yr.
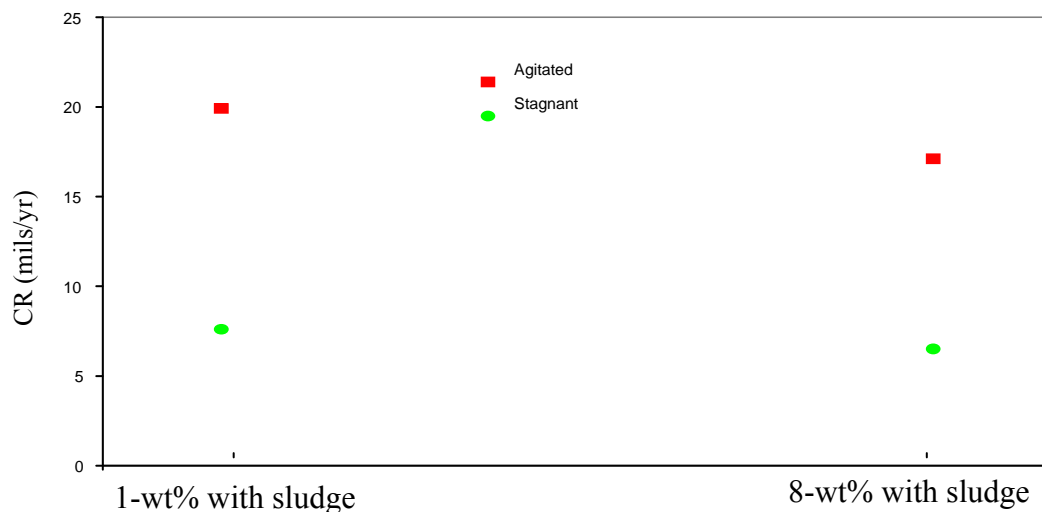

Figure 6. Corrosion rate for 1 and 8-wt% oxalic acid solution with Sludge.

<u>Cathodic polarization (CP)</u> scans the potentials of a working electrode towards more negative, so the cathodic reaction kinetics can be investigated. At potentials close to equilibrium, the relationship between potential and current is expressed by the Tafel expression, shown in Equation 16 [4].

$$\eta = \beta \log (i/i_0) \tag{Eq.16}$$

where:
η is the over voltage
β is the slope of the line
i is the measured current density at the applied potential, E in A/cm^2
i_0 is exchange current density, in A/cm^2, representing the current density when there are equal forward and reverse reactions at electrode equilibrium

The Tafel equation applies within the region of applied current density, below i, but above i_0, the exchange current density. The cathodic Tafel slope, β was determined by finding the slope of the linear portion of the graph at current densities between $2x10^{-5}$ and 1×10^{-3}-A/cm^2 [5]. In the case of 1-wt% oxalic acid, the slope was $1x10^{-3}$-A/cm^2. However, for 1-wt% oxalic acid solution with Sludge, the current density was less. Thus, the linear portion of the graph was fitted to determine β. The exchange

current density, i_0 was determined by extrapolating the Tafel slope line until it intersected at $\eta = 0$. The dominant term controlling the CR in oxalic acid solutions is the H_2 overvoltage from the cathodic areas of the metal. H_2 overvoltage is the difference in potential between a cathode with H_2 evolution and an H_2 electrode at equilibrium. To determine if the cathodic reaction was indicative of H_2 evolution, Equation 17 was used [5].

$$\alpha = 2.3 \ R \ T/(\beta \ F) \qquad \qquad (Eq.17)$$

where:

α is the transfer coefficient

R is the universal gas constant equal to 1.99-cal/mole-k

T is the temperature in K

F is the Faraday constant equal to 23,061-cal /V-equivalent

Starting with an agitated 1-wt% oxalic acid solution with sludge at 75°C, the effects from the different environmental conditions were evaluated using CP. Values for α, β and i_0 are shown in Table 5.

Table 5. Kinetic Data Obtained from Cathodic Polarization Tests

Sludge	Temp (°C)	OCP (V)	β (V/decade)	α	$i_0(\mu A/cm^2)$
1-wt% OA	45	-0.440	0.139	0.454	163
1-wt% OA	75	-0.465	0.146	0.473	543
1-wt% OA w/Sludge	45	-0.435	NA	NA	15
1-wt% OA w/Sludge	75	-0.300	0.588	0.117	70
8-wt% OA w/Sludge	50	-0.40	0.080	NA	NA
8-wt% OA w/Sludge	75	-0.20	0.140	NA	NA

NA – Not Available

Sludge - From Table 5, for an agitated 1-wt% oxalic acid solution with sludge at 75°C, β was 0.58 V/decade, while without the sludge β was 0.15 V/decade. The large Tafel slope at 75°C suggests that the cathodic reaction was being controlled by transport of the active species to the cathode.

For iron and steel, α is typically between 0.4 and 0.6 if H_2 evolution is occurring. At 75°C α was 0.12, indicating an alternate cathodic reaction was occurring, while at 45°C α was 0.47, indicating H_2 evolution at the metal surface. The lower i_0 reflects the lower CRs for oxalic acid solutions with sludge.

Temperature – The i_0 of 70 $\upsilon A/cm^2$ at 75°C only slightly decreased to 15 $\upsilon A/cm^2$ at 45°C. This confirmed that for the 1-wt% oxalic acid solution with sludge the LPR appropriately predicted limited effect temperature changes would have on the CR.

The behavior of a 1-wt% oxalic acid solution with sludge at 45°C was of particular interest. Although the OCP was not significantly different between the pure acid and the acid solution containing sludge, i_0 was significantly lower. This may have been caused by inhibition by an oxalate layer, or by a cathodic reaction different from H_2 evolution. Figure 7 shows that that the cathodic reaction kinetics were significantly slower in 1-wt% oxalic acid solutions with sludge.
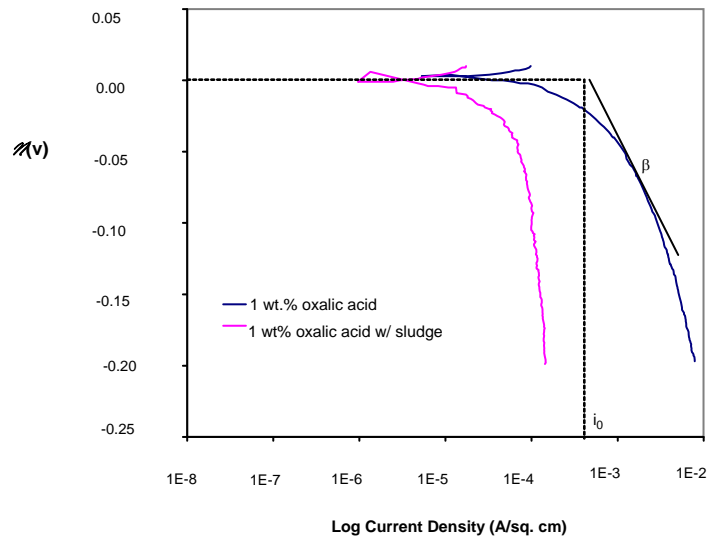
Figure 7. Cathodic polarization curves for 1-wt% with Sludge at 75 °C with agitation.

<u>Anodic Polarization (AP)</u> uses current responses that occur during forward scans to identify film breakdown. In particular, the breakdown potential, E_b, is where the current increases rapidly with a negligible change in potential. This correlates to a decrease in the film's inhibition properties. In addition, the passive current density, I_p provides an indication of the passivation nature of the film, where a lower I_p indicates a more protective film.

Sludge - Figure 8 shows the anodic polarization scans for a 1-wt% pure oxalic acid solution and a 1-wt% oxalic acid solution containing sludge, both agitated and at 75 °C. Although they had similar OCPs (around -0.34 mV), the passive current density, I_p for the 1-wt% pure oxalic acid solution was slightly lower than the 1-wt% oxalic acid solution containing sludge, indicating a more protective film. A breakdown potential at 0.200 V was observed for the 1-wt% pure oxalic acid solution due to the destruction of the oxalate film. A similar breakdown was observed for the 1-wt% oxalic acid solution containing sludge; however, it occurred at ~ 0.05 V. The smaller breakdown potential and higher passive current density indicate that the oxalate film for the 1-wt% oxalic acid solution containing sludge was not as protective. Given that the oxalate film was not as protective, the decreases in the CRs were due to a change in the cathodic kinetics. That means that even though the H_2 evolution was thermodynamically possible based on OCP, another anodic reaction was responsible for the decreased CR. A likely candidate for the cathodic reaction is the reduction of the di-oxalatoferrate ion.
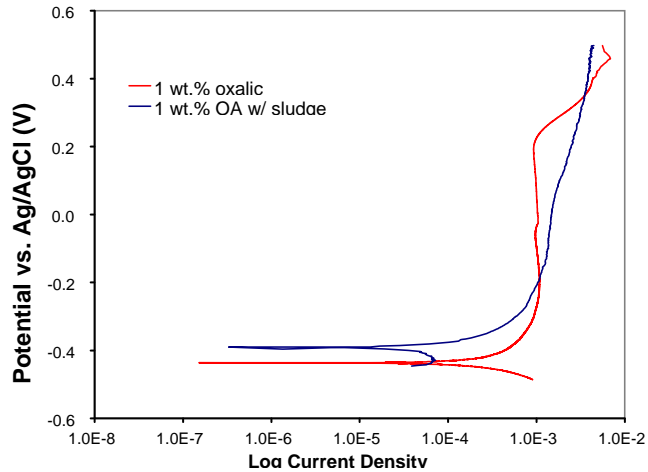
Figure 8. Anodic polarization scans for the 1-wt% oxalic acid at 75 °C with mixing.

The proximity of the breakdown potential, E_b to E_{corr} indicates that the oxalate film will not be very stable in these solutions. That means that is there should there be a relatively small change in the potential from OCP, the film would be more susceptible to breaking down, leading to higher CR.

CONCLUSIONS

To resolve the gap associated with the scarcity of corrosion data for 1-wt% oxalic acid solution, "additional corrosion" testing was initiated. The strategy and tests were largely based on recent 8-wt% testing. Starting with the baseline condition, "an agitated 1-wt% oxalic acid solution at 75°C with sludge," the CRs were determined by measuring the weight loss of exposed coupons. Electrochemical testing (EC) was used to explore the impact of varied conditions on the passivation mechanisms and to confirm the CRs. The conditions varied were: a) if sludge included in the test vessel; b) if testing should be performed at 75 or 45°C; and, b) if the solution should be agitated or stagnant. The 1-wt% results were then compared to those from 8-wt%.

Based on EC, because of H_2 evolution being the result would be a significant increase in CRs. The CRs of agitated 1-wt% pure oxalic acid solutions at 45 or 75°C would be about 4 to 10 times greater (respectively), compared to those for a 1-wt% solution with sludge. Although the CR for 1-wt% acid with sludge were considered to be non-temperature dependent, a stagnant solution with sludge resulted in a CR that was greater at 45°C, than at 75°C, suggesting that the oxalate film formed at higher temperatures was better in mitigating corrosion. The lower CRs for the 1-wt% solution with sludge, suggest that the cathodic reactions were altered by the sludge.

The immersion coupon testing showed that the maximum time averaged CR for a 1-wt% solution with sludge was less than 25-mils/yr for all conditions. For an agitated 8-wt% solution with sludge, the maximum time averaged CR was about 30-mils/yr at 50°C, and 86-mils/yr at 75°C. If stagnant, the CR decreased to 24–mils/yr and 36–mils/yr, respectively. As such, the CRs for 1-wt% oxalic acid with sludge are considered bounded by those for 8-wt% oxalic acid with sludge.

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