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CORROSION TESTING OF CARBON STEEL IN OXALIC ACID CHEMICAL CLEANING SOLUTIONS

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ABSTRACT

Radioactive liquid waste has been stored in underground carbon steel tanks for nearly 60 years at the Savannah River Site. The site is currently in the process of removing the waste from these tanks in order to place it into vitrified, stable state for longer term storage. The last stage in the removal sequence is a chemical cleaning step that breaks up and dissolves metal oxide solids that cannot be easily pumped out of the tank. Oxalic acid has been selected for this purpose because it is an effective chelating agent for the solids and is not as corrosive as other acids. Electrochemical and immersion studies were conducted to investigate the corrosion behavior of carbon steel in simulated chemical cleaning environments. The effects of temperature, agitation, and the presence of sludge solids in the oxalic acid on the corrosion rate and the likelihood of hydrogen evolution were determined. The testing showed that the corrosion rates decreased significantly in the presence of the sludge solids. Corrosion rates increased with agitation, however, the changes were less noticeable.

Keywords: carbon steel, radioactive waste tanks, oxalic acid, chemical cleaning

INTRODUCTION

Radioactive liquid waste has been stored in underground carbon steel tanks for nearly 60 years at the Savannah River Site (SRS). The site is currently in the process of removing the waste from these tanks in order to place it into vitrified, stable state for longer term storage. The last stage in the removal sequence is a chemical cleaning step that breaks up and dissolves metal oxide solids that cannot be easily pumped out of the tank. Oxalic acid has been selected for this purpose because it is an effective chelating agent for the solids and is not as corrosive to the carbon steel tank as other acids.

An improved chemical cleaning process is being developed to treat oxalates that are precipitated downstream from the tank that is being cleaned. The process that occurs in the tank that is being cleaned is similar to the previous chemical cleaning technology in that oxalic acid is used for both, but the improved process differs from the previous technology in the following ways: 1) The sludge heel will be washed with water rather than supernate; 2) dilute oxalic acid (i.e., 1 or 2 wt%) is used in place of concentrated oxalic acid (8 wt%); and 3) most of the resultant oxalate is decomposed by an Advanced Oxidation Process (AOP). Reducing the amount of oxalic acid used for dissolution of sludge and the subsequent oxidative destruction of oxalic acid will lead to a reduction of downstream impacts.

Technology gaps to implement the improved process were identified. Corrosion rate data for carbon steel exposed to the chemical cleaning environment were needed to evaluate the degree of degradation that could occur in the treatment tank during this process and the propensity for hydrogen evolution due to the corrosion of carbon steel. The corrosion data included a combination of electrochemical and coupon immersion testing to determine the general corrosion rate, as well as susceptibility to localized corrosion. The electrochemical studies were typically performed to gain a better understanding of the corrosion mechanism. The coupon immersion tests were performed under environmental conditions that were as representative of the actual process as possible. This includes the critical variable of time, which is not considered in the electrochemical tests. The coupons were examined for weight loss and any evidence of localized corrosion. The corrosion rates obtained from these tests will be utilized for estimates for the actual process.

EXPERIMENTAL PROCEDURE

Test Materials

The material for the electrochemical and immersion testing was ASTM A285, Grade C carbon steel (UNS K02200). This material has similar chemical and physical properties as the waste tanks that will be the focus of the initial chemical cleaning operations. The chemical compositions of the as-received coupons are shown in Table 1. The samples were polished to 600 grit finish prior to testing.

Table 1. Chemical Composition (Wt %) of A285 Grade C, Carbon Steel

C	Mn	P	S	Cu	Ni	Cr	Si	Fe
0.18	0.75	0.011	0.008	0.03	0.03	0.06	-	balance

Test Solutions

The test solutions consisted of 2.5 wt.% oxalic acid in contact with solids that were designed to simulate the residual metal oxides in the tank. The primary constituents in the residual oxide solids were iron, aluminum, manganese, nickel, mercury, and silicon. Two solids simulants were tested to represent the range for the ratio of iron to aluminum that exists between solids in different waste tanks. The composition of the solids simulants are shown in Table 2.

Prior to conducting the tests, the solids were contacted with the 2.5 wt.% oxalic acid. As a result a portion of the metal oxide constituents dissolved in the solution. Both the solids and the liquid were added to the vessel for the test. The solution pH after the solids and liquid were contacted remained relatively constant at approximately 1.3. Tests were also conducted in 2.5 wt.% oxalic acid to simulate the situation where there was little or no solids present in the tank and as an experimental control.

Table 2. Composition of Two Metal Oxide Simulant

Species	Concentration (mg/l)	
	Simulant A	Simulant B
Fe	35,000	6,200
Al	10,000	72,000
Mn	4,600	6,400
Si	1,300	300
Hg	1,800	3,200

In addition to the solids composition, the effects of temperature and agitation on the corrosion behavior were investigated. Two test temperatures, 50 and 75 °C, were utilized for cases where the solids slurry was agitated and not agitated.

Experimental Procedures

Electrochemical Tests.

The electrochemical studies were performed utilizing either a Gamry™ or Princeton Applied Research™ (PAR) potentiostat. The oxalic acid/sludge was prepared approximately 12 hours prior to the test and placed in the test cell. The test temperature was maintained by a hot plate that had a temperature controller. Evaporation of the solution during the test was minimized with the use of a condenser. The carbon steel working electrode was a 1.5 cm² rectangle that was anchored in a cold mount epoxy. Graphite rods were utilized for the counter electrodes. A saturated silver-silver chloride (Ag/AgCl) electrode was utilized as the reference electrode. Duplicate tests were performed on separate samples.

The electrochemical tests performed include: 1) Open circuit potential (OCP) measurement, 2) Linear polarization resistance (LPR) measurements, 3) Cathodic polarization, and 4) Cyclic potentiodynamic polarization (CPP). These tests were performed in sequence.

The initial test performed monitored the OCP for 1 to 4 hours. The OCP reflects a measure of the electrochemical activity at the metal surface, i.e., whether it is actively corroding or becoming passive. The test also provides information on the relative stability of the passive film, and whether hydrogen evolution is thermodynamically possible.

The linear polarization resistance (LPR) test was performed once the OCP had stabilized. The LPR technique provides a non-destructive, instantaneous estimate of the uniform or general corrosion rate. The ASTM standard practice was utilized to conduct the test¹. The potential was scanned from -20 mV vs. OCP to +20 mV vs. OCP at a scan rate of 0.17 mV/second and the current response recorded for this test. The test was typically conducted two to four hours after the initiation of the OCP measurements.

Cathodic potentiodynamic polarization studies were performed next. These tests were utilized to investigate the kinetics of the cathodic electrochemical reaction. Based on these studies, it can be determined if hydrogen is indeed being evolved and whether the reaction is transport limited. The cathodic polarization test scans the potential from the OCP to -250 mV vs. OCP at a rate of 0.167 mV/second. Parameters determined from this test included i_0 , the exchange current density, β_c , the cathodic Tafel slope, and α , the transfer coefficient.

Cyclic potentiodynamic polarization (CPP) was the final electrochemical test that was performed. CPP is utilized to investigate the susceptibility of a material to localized corrosion in a given environment. The test was typically conducted 6 to 8 hours after the initiation of the OCP measurements. This test is initiated at a potential 50 mV less than the OCP. The potential was increased to approximately 0.5 V vs reference at a scan rate of 0.167 mV/second to a vertex potential of 0.5 V vs. the reference electrode. The potential was then scanned in the reverse direction back to the OCP. At the conclusion of the test, the current vs. potential plot was evaluated for evidence of passivity or breakdown of passivity. The sample was also visually inspected for evidence of corrosion.

Coupon Immersion Tests

Tests were performed on carbon steel coupons exposed to the two sludge simulants treated with 2.5 wt.% oxalic acid under both non-agitated (or minimal) and continuous vigorous mixing conditions. The coupons were nominally 50 mm long, 25 mm wide, and 6.25 mm thick. The coupons were nominally

56 g. Duplicate samples were tested at each condition and the average corrosion rate for the two samples was reported.

The volumetric ratio of oxalic acid to sludge solids used for the tests was approximately 20:1. The solutions were maintained at a nominal pH 2 or less through periodic refreshment with oxalic acid during the testing if necessary. The test duration was 28 or 30 days and test temperatures were 50 and 75 °C for the tests in 2.5 wt.%.

At the completion of the test, the coupons were removed from the test vessel for visual examination. During this examination, the form of corrosion on each coupon was identified (e.g., general) and differences in the corrosion products were noted. Photographs were taken to document these results. After removal of the corrosion products, the coupons were weighed to determine the resultant weight loss. Corrosion rates were calculated from the weight loss².

Solid samples were collected from the coupon surface and submitted for x-ray diffraction (XRD) analysis for identification. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were also utilized to examine the coupons. A sample of the remaining liquid in the test vessel was also submitted for post-test characterization. Ion chromatography (IC) was performed to identify the concentrations of anions, while inductively coupled plasma emission spectroscopy (ICP-ES) was performed to identify the concentrations of the elements in the final solution.

RESULTS AND DISCUSSION

Electrochemical Tests

Open Circuit Potential (OCP) Monitoring.

The OCP for carbon steel exposed to 2.5 wt.% oxalic acid is shown in Figure 1. The OCP achieves a steady stable potential relatively quickly. The potentials were all less than -0.400 V vs. Ag/AgCl and therefore hydrogen evolution was the likely cathodic reaction.

The effect of temperature and agitation on the OCP for carbon steel was also shown in this figure. At 75 °C, the OCP shifts in the noble direction for a short time before returning to a constant stable value. This shift is likely associated with the formation of the ferrous oxalate film on the surface. There is not a significant difference in the time at which the shift in OCP occurs, which indicates that agitation at this temperature does not have a significant impact on the formation of the ferrous oxalate film. The lower steady state OCP for agitation indicates a higher corrosion rate for the agitated case versus the non-agitated at these initial times.

At 50 °C, the shift in the OCP is not as apparent. However, it should be noted that the OCP is still gradually increasing at the end of 1 hour. The shift in the OCP may have occurred after the OCP measurements were halted. Thus at the lower temperature, the time for complete passivation simply is taking longer. The potential measured at 50 °C was slightly lower than that measured at 75 °C after 1 hour. If the OCP shift were to take place after 1 hour, it seems likely that the steady state OCP for 50 °C test, for both agitated and non-agitated, would be greater than that for the 75 °C test. Thus the corrosion rate at 75 °C, at least initially, would be greater than at 50 °C. As before hydrogen evolution is the likely cathodic reaction at 50 °C as well.

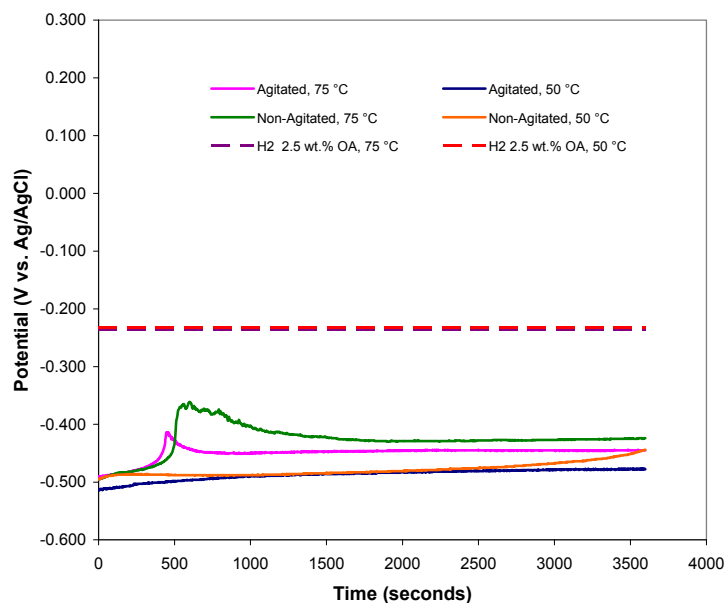


Figure 1. OCP transients for 2.5 wt.% oxalic acid in an agitated and non-agitated solutions at 50 and 75 °C. The dashed line represents the potential below which hydrogen evolution is thermodynamically favored.

Figure 2 shows the effect of temperature and agitation on the OCP transients for the Simulant A/2.5 wt.% oxalic acid mixture. Initially the potential at the steel surface was at a potential where hydrogen evolution was possible. However, after a short period of time the potential shifted dramatically in the positive direction to a potential where hydrogen evolution is not thermodynamically favored. The time at which the shift occurs also depends on agitation and temperature. Higher temperature and agitation shorten the time for the shift to occur. This shift may be due to a dissolved oxidizing species which achieved a critical concentration in the solution at this time. This species may in turn be involved in the cathodic reaction. The shift may also reflect the time it takes to build-up an adherent oxide on the surface. Ferrous oxalate is known to precipitate on the surface of carbon steel at these potentials³.

In two of the four cases, the final OCP after two hours of exposure indicates that hydrogen evolution may be occurring. The OCP for the 50 °C test clearly remains more noble (i.e., greater than) to the equilibrium potential for hydrogen evolution, while the OCP for the 75 °C test after an initial shift decays to approximately the equilibrium hydrogen potential. Agitation appears to result in a more active OCP at both temperatures. This result indicates that the dissolved oxidizing species or the species is more readily available at the surface due to the agitation.

Figure 3 shows the effect of temperature and agitation on the OCP transient in the Simulant B/ 2.5 wt.% oxalic acid mixture. The same potential shift that was observed with Simulant A was observed in this case. The final OCP for all conditions tested indicated that hydrogen evolution was not thermodynamically favored. Initially the potential is at a condition where hydrogen evolution is possible. At this stage the potential for the agitated solution is more positive than that for the solution that is not agitated. However, the potential is continuously increasing in all cases, which indicates that the ferrous oxalate film is forming. The OCP shift occurs earlier in the agitated solutions than for the non-agitated solutions. This observation again reflects the fact that the cathodic reaction is transport controlled and therefore dependent upon the concentration of the electro-active species in solution. Agitation likely promotes the dissolution of these species.

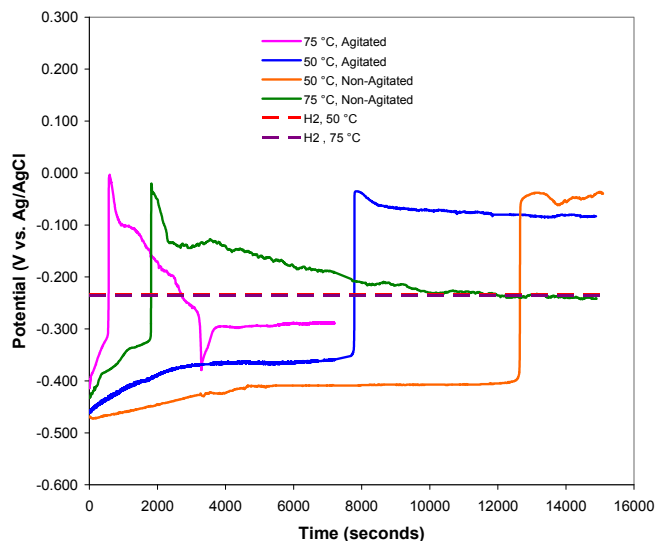


Figure 2. OCP transients for PUREX sludge simulant/2.5 wt.% oxalic acid mixtures.

Figure 3 also shows that the shift in the OCP occurs earlier for the higher temperature tests than the lower temperature tests. For example in the non-agitated condition, the OCP shifted for the 75 °C test shifted approximately 2 hours before the shift was observed at 50 °C. The same is true for the agitated condition, although to a lesser degree. The potential shift also occurred at earlier times for the higher temperature simulant. From these results, it is clear that the higher temperatures result in a more stable oxalate film. This observation again reflects the fact that the cathodic reaction is transport controlled and therefore dependent upon the concentration of the electro-active species in solution. Higher temperatures likely promote the dissolution of these species.

The noticeable difference between the two sludge simulants is that the OCP for the Simulant B remains at a more positive potential, while the OCP for Simulant A decays to a constant value after one hour. These potential shifts are again thought to be associated with the dissolution of an oxidizing species and/or the development of the passive film. In all cases, the OCP remains at more positive values likely due to the presence of electroactive dissolved species that drive the cathodic reactions.

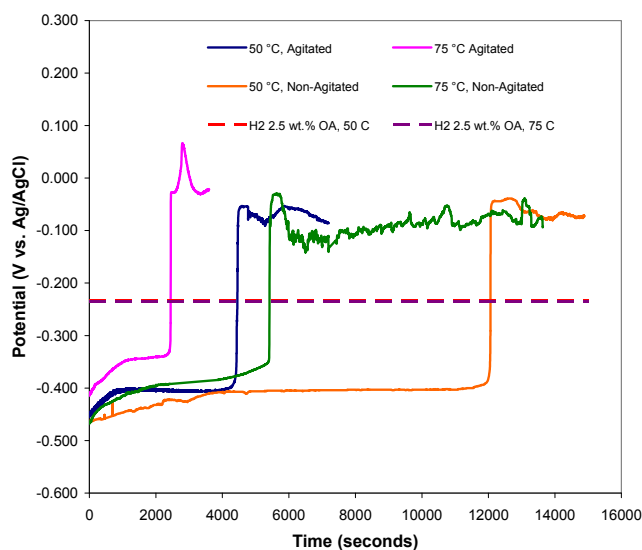


Figure 3. OCP transients for HM sludge simulant/2.5 wt.% oxalic acid mixtures.

LPR Tests.

The results of the LPR tests are shown in Table 3. The corrosion rates measured in the simulant/oxalic acid tests are typically an order of magnitude less than that observed for oxalic acid alone. This result may be due to a difference in the cathodic reaction that occurs in each situation. In the case of oxalic acid, hydrogen evolution is likely involved whereas, for the simulant/oxalic acid environment a dissolved species may be involved in the cathodic reaction. The latter situation may also involve transport control of the cathodic reaction, which depends upon the concentration of the species in solution. The difference may also be attributed to the mechanism by which the passive film forms. A more adherent film may be forming in the presence of the solids simulants.

Table 3. Corrosion Rates Determined from Linear Polarization Resistance Measurements

Test Condition	Corrosion Rate (mm/yr)	
	50 °C	75 °C
Simulant A/Oxalic Acid		
Agitated	0.056	0.18
Not Agitated	0.028	0.051
Simulant B/Oxalic Acid		
Agitated	0.29	0.11
Not Agitated	0.036	0.071
Oxalic Acid		
Agitated	2.4	7.3
Not Agitated	0.13	2.6

The effect of agitation on the corrosion rate is also shown in this table. In general, agitation increased the corrosion rate by a factor of 2 to 10. These results could be explained by the disruption of the ferrous oxalate film by the agitation or the incorporation of other oxides within the oxalate layer.

The results showed that the corrosion rates in the sludge simulant did not have a strong dependence on temperature. Although in most cases, the corrosion rate increased slightly with temperature, in most cases the corrosion rates were likely within a factor of 2 (i.e., within the error of the LPR technique). Thus, the inhibiting mechanism does not appear to be temperature dependent within the range of temperatures tested, at least during the initial stages of exposure.

Cathodic Polarization Tests.

The values for α , β_c and i_0 are summarized in Table 4. The data from tests with agitation are presented to minimize the effects of transport of the electro-active species to the metal surface and emphasize the kinetics of the reaction at the surface. From the table it is observed that for the tests performed in pure oxalic acid, α is between 0.4 and 0.6, which indicates that hydrogen evolution is occurring at the steel surface⁴. On the other hand, α for the solutions with a sludge simulant present are less than 0.4, which indicates that another cathodic reaction, possibly involving a dissolved species, is occurring.

The table also shows that i_0 is significantly lower in the sludge simulants than in pure oxalic acid. The lower exchange current densities reflect lower corrosion rates in the solutions that contain the sludge simulant. This result is in agreement with the LPR measurements discussed previously.

The effect of the addition of the sludge simulant on the cathodic polarization curve is shown in Figure 4. These tests were performed at 75 °C with agitation. These figures clearly show that the cathodic reaction kinetics were significantly slower in solutions that contain sludge simulants than that in the oxalic acid alone. This conclusion is indicated by the lower exchange current densities.

Table 4. Kinetic data obtained from cathodic polarization tests. All data was obtained from tests where the solutions were agitated.

Simulant	Temperature (°C)	OCP (V vs. Ag/AgCl)	β_c (V/decade)	α	$i_o(\mu\text{A}/\text{cm}^2)$
2.5 wt.% oxalic acid	50	-0.463	0.121	0.530	360
2.5 wt.% oxalic acid	75	-0.445	0.115	0.60	550
Simulant B/2.5 wt.% oxalic acid	50	-0.086	0.17	0.377	23
Simulant B/2.5 wt.% oxalic acid	75	0.007	0.212	0.326	15
Simulant A/2.5 wt.% oxalic acid	50	-0.082	0.261	0.246	5
Simulant A/2.5 wt.% oxalic acid	75	-0.228	0.201	0.344	2

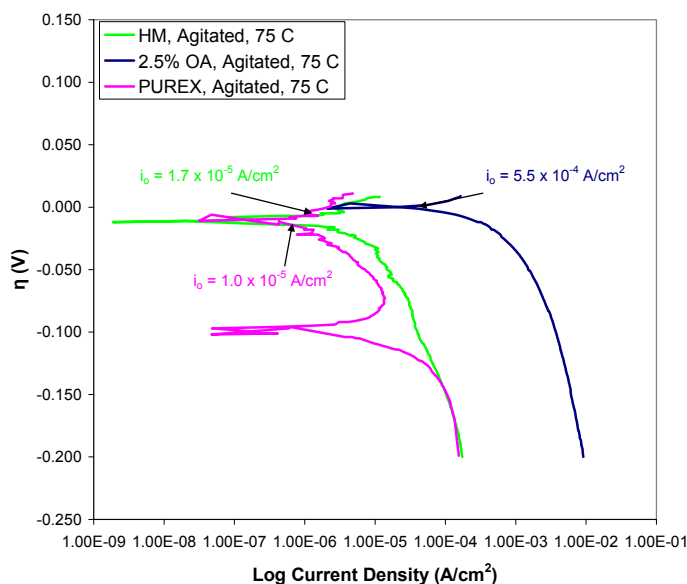


Figure 4. Cathodic polarization curves for the simulants with 2.5 wt.% oxalic acid at 75 °C with agitation. η is the difference between the measure potential and OCP.

The effect of agitation is illustrated in Figure 5. These tests were performed with Simulant B/2.5 wt.% oxalic acid at 50 °C. The exchange current density is approximately an order of magnitude greater for the agitated solution than the non-agitated, indicating that agitation increases the aggressiveness of the solution. The shape of both curves illustrates that at this temperature the cathodic reaction is transport controlled after 0.2 V of polarization. The limiting current density is also nearly an order of magnitude greater for the agitated solution than for the non-agitated. This result suggests that agitation increases the concentration of the aggressive species in solution.

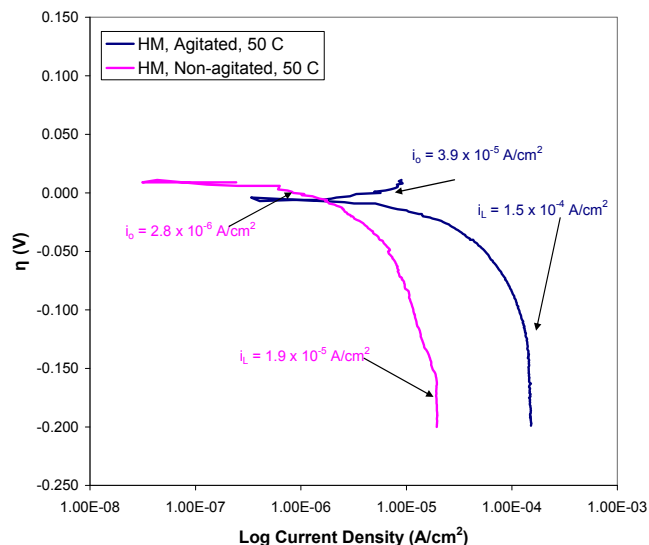


Figure 5. Cathodic polarization curves for HM/2.5 wt.% oxalic acid at 50 °C with and without agitation.

The effect of temperature is illustrated in Figure 6. These tests were performed with Simulant B/2.5 wt.% oxalic acid at 50 °C and 75 °C with no agitation. The exchange current density is approximately a factor of 2 greater for the higher temperature solution, indicating that the solutions are more aggressive at the higher temperature. However, the effect of temperature within the range of these tests is not as great as the effect of agitation. The shape of both curves illustrates that at this temperature the cathodic reaction is transport controlled after 0.2 V of polarization. The limiting current density is also approximately a factor of 2 greater for the 75 °C test than the 50 °C test. This result also suggests that temperature increases the concentration of the aggressive species in solution.

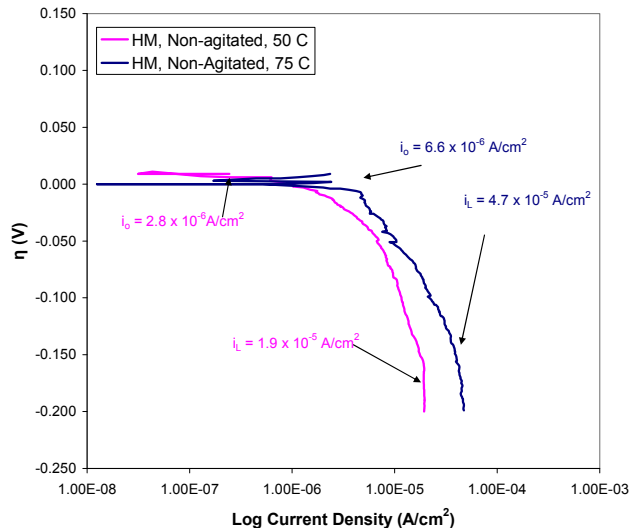


Figure 6. Cathodic polarization curves for HM/2.5 wt.% oxalic acid at 50 °C and 75 °C without agitation.

Cyclic Potentiodynamic Polarization.

Figure 7 shows the results of CPP testing in 2.5 wt.% oxalic acid. The test was performed at 75 °C with agitation. Negative hysteresis was observed indicating no susceptibility to localized attack. A large passive region (approximately 0.6 V) was observed with a passive current density of approximate 1 mA/cm². The breakdown potential was approximately 0.25 V and is indicative of the destruction of the

ferrous oxalate layer. Observation of the samples after testing showed evidence of an oxide or oxalate film on the surface that had been disrupted. However, no evidence of localized attack such as pitting was observed. Therefore, general corrosion of carbon steel with the formation of a passive ferrous oxalate film on the surface occurred.

Figure 8 shows the results of CPP testing in the Simulant A/2.5 wt.% oxalic acid mixture. The tests were performed at 75 °C with agitation. Although the exchange current density was lower than that for oxalic acid, the passive current density and the breakdown potential were the similar. Negative hysteresis was observed on the reverse scan, which indicates little susceptibility to localized corrosion. Observation of the samples after testing showed evidence of an oxide or oxalate film on the surface that had been disrupted. However, no evidence of localized attack such as pitting was observed. Therefore, general corrosion of carbon steel with the formation of a passive ferrous oxalate film would be expected.

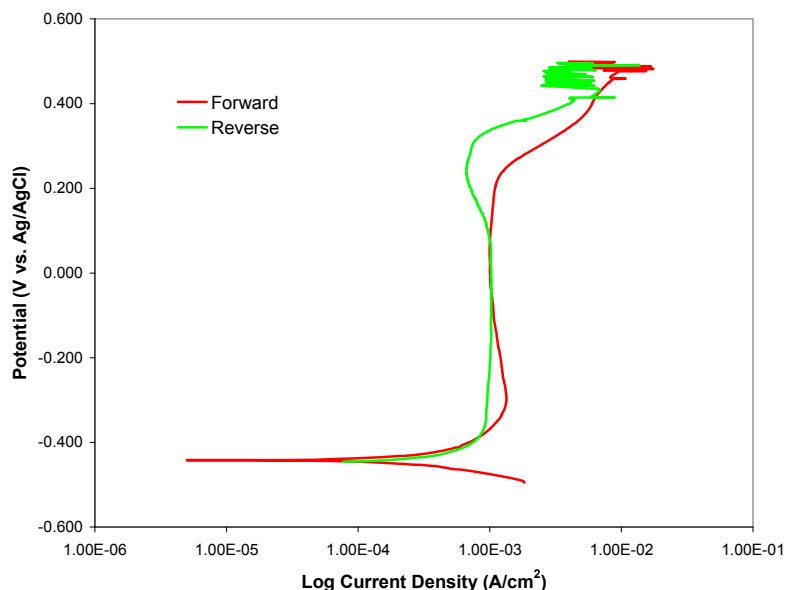


Figure 7. CPP scan in agitated, 2.5 wt.% oxalic acid at 75 °C.

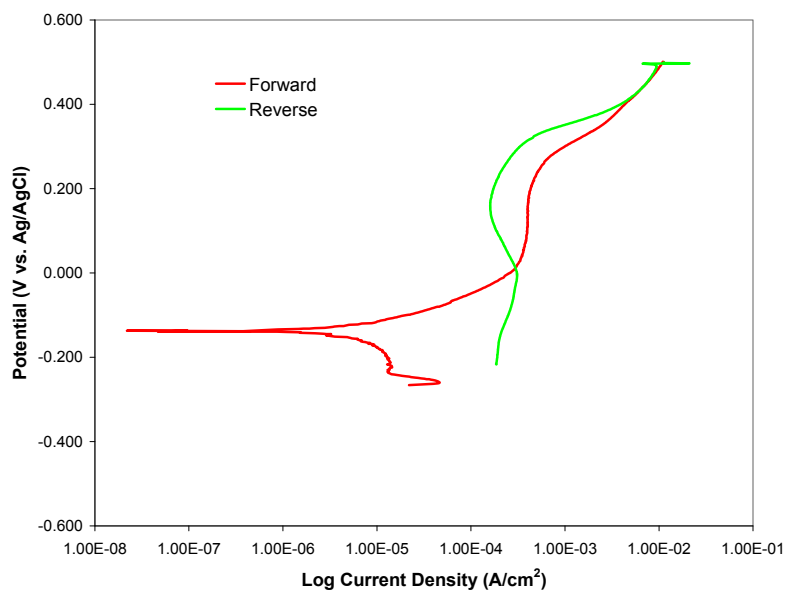


Figure 8. CPP scan in agitated, Simulant A/2.5 wt.% oxalic acid mixture at 75 °C.

Figure 9 shows the results of CPP testing in the Simulant B/2.5 wt.% oxalic acid mixture. The tests were performed at 75 °C with agitation. In this case there is no clear passive current density or breakdown potential. Instead there was a gradual increase in the current density up to the vertex potential. Negative hysteresis was observed initially, however, cross-over was also observed on the reverse scan. This result is unclear and indicates that the Simulant B/2.5 wt.% oxalic acid may result in localized attack. Figure 10 shows the the results of CPP testing in the Simulant B/2.5 wt.% oxalic acid mixture at 75 °C without agitation. This case also did not show any clear passive current density or breakdown potential. Additionally, a slight positive hysteresis was observed on the reverse scan. These two results indicate that carbon steel may be more susceptible to localized attack in Simulant B than in Simulant A. Observation of the samples after testing showed evidence of an oxide or oxalate film with no evidence of localized attack such as pitting. Therefore, this conclusion could not be corroborated within the short term exposure of the electrochemical coupon test.

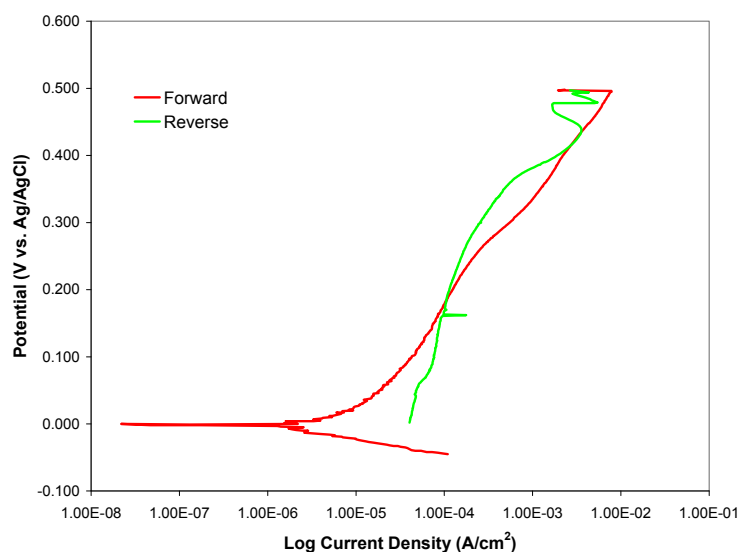


Figure 9. CPP scan in agitated, Simulant B/2.5 wt.% oxalic acid mixture at 75 °C.

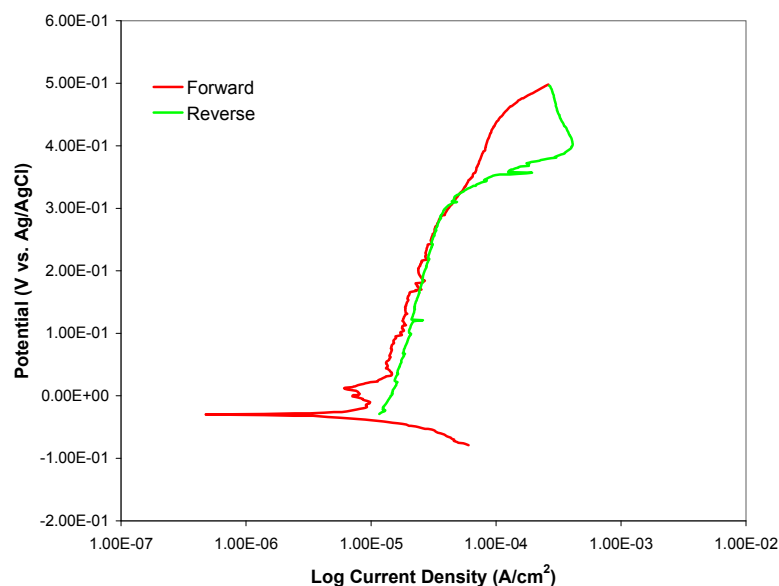


Figure 10. CPP scan in non-agitated, HM/2.5 wt.% oxalic acid mixture at 75 °C.

Coupon Immersion Tests

Solution Characterization.

Color changes in the solids-acid mixtures were observed during the tests. Initially the solids and were a reddish-brown color indicative of the iron present in the solids. The color of the solids and the solution changed to a yellowish green after approximately 1 day at 75 °C and after 6 days at 50 °C. These yellowish solids are likely ferrous oxalate. These changes are likely a result of the dissolution of the solids.

Analyses of the solutions following coupon testing were performed to determine the changes that occurred during the test (See Tables 5 and 6). In general, the dissolved species reflected the initial composition of the sludge simulant. For example, the aluminum concentration in Simulant B/2.5 wt.% oxalic acid was significantly greater than that observed in Simulant A/2.5 wt.% oxalic acid. Likewise, the iron concentration in Simulant A/2.5 wt.% oxalic acid was significantly greater than that observed in Simulant B/2.5 wt.% oxalic acid. Not surprisingly the concentration of dissolved metals increased with temperature, however, the effect of agitation was not as clear. Interestingly, the amount of mercury in solution tended to be higher for Simulant A/2.5 wt.% oxalic acid tended to be greater than that for Simulant B/2.5 wt.% oxalic acid even though the initial concentration of mercury in the sludge was significantly higher for Simulant B.

Table 5. Final solution analyses for the coupon tests in the Simulant A/2.5 wt.% oxalic acid mixture.

Species	Concentration (mg/l)			
	Agitation, 75°C	No Agitation, 75°C	Agitation, 50°C	No Agitation, 50°C
Fe	2400	5400	550	3800
Al	720	840	790	790
Mn	160	310	83	140
Si	25	14	15	10
Hg	2	13	16	2

Table 6. Final solution analyses for the coupon tests in the Simulant B/2.5 wt.% oxalic acid mixture.

Species	Concentration (mg/l)			
	Agitation, 75°C	No Agitation, 75°C	Agitation, 50°C	No Agitation, 50°C
Fe	630	1100	1000	700
Al	2600	3700	840	3300
Mn	270	410	160	320
Si	35	22	23	24
Hg	3	< 1	3	<1

Surface Characterization.

For all three test solutions at all conditions, only ferrous oxalate, at varying degrees of coverage, was typically observed on the surface. The lone exception was the coupon test in Simulant B at 75 °C with no agitation. In this case, reddish-brown deposits were observed along with the ferrous oxalate. The

deposits were in vertically oriented streaks on the coupon. XRD analysis revealed that the reddish deposits were goethite. The Pourbaix diagram indicates that goethite and hematite are unstable at pH 1.2 in a reducing environment and tend to dissolve⁵. The only means by which this could occur would be if the ferrous ion was oxidized to the ferric species. This reaction would need to be polarized by a strong oxidizing agent for this to occur.

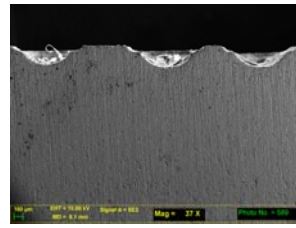
After cleaning, the coupons were examined under a microscope. Coupons exposed to oxalic acid, Simulant A/2.5 wt.% oxalic acid at both temperatures, and Simulant B/2.5 wt.% oxalic acid were smooth and exhibited general corrosion only. The exception occurred for the coupons in the Simulant B/2.5 wt.% oxalic acid at 75 °C, where pitting was observed in the stagnant solution, and pitting with general corrosion occurred in the agitated solution (see Figure 12). The pits in the non-agitated solution had a hemi-spherical morphology. Over time some of the pits coalesced and gave the pit a narrow, oblong appearance. As can be seen by looking at the edge of the coupon (see Figure 13a), the bottom of the pits has a smooth almost polished appearance. The coupons in the agitated solutions not only exhibited hemi-spherical pits, but considerable general attack had also occurred. Vertical grooves appeared to be etched into the surface.

The corrosion morphology for the coupons exposed to Simulant B/2.5 wt.% oxalic acid with no agitation was examined further with the scanning electron microscope (SEM). Energy Dispersive Spectroscopy (EDS) was utilized in tandem with the SEM to identify any species present in and around the pits. Figure 13a is an SEM micrograph of the hemi-spherical pits that were present on the coupon. Some of the corrosion product remained behind in the occluded cell. The coalescence of the spherical pits into an oblong “streak” is also shown. EDS results for the region adjacent to the pits indicated that the primary constituents were iron, carbon and oxygen, which is consistent with the iron oxalate film and also the presence of iron oxide (i.e., goethite). The lighter color is likely the ferrous oxalate and the goethite is likely the darker color. Within the pit, in addition to these constituents, significant quantities of aluminum were also present. Aluminum is one of the primary constituents for Simulant B and may have become entrapped in the corrosion products in the pits. The EDS results also indicate an oxygen peak that has a higher relative intensity than that observed on the exterior of the pit. This suggests that there is a larger fraction of iron and/or aluminum oxide present in the pit. A higher magnification micrograph of the corrosion products in the pits is shown in Figure 13b. Particles on the order of 3 microns or less were observed evenly dispersed on the surface of the corrosion product. EDS identified that these particles contained mercury. This result suggests that mercury was involved in the development of the pits.

Corrosion Rate Determination.

Table 7 shows the corrosion rates determined from the weight loss measurements. The corrosion rates in the simulant-acid mixtures were significantly higher than those measured with the LPR technique. Likewise, no indication of localized attack was observed for the CPP tests, whereas for the coupons localized attack was observed for Simulant B at 75 °C. This disagreement between the electrochemical and the coupon tests is likely a function of exposure time. The longer exposure time allowed more dissolution of the sludge to occur, and hence a more aggressive solution to develop in the case of the coupon tests.

The oxalic acid tests at 75 °C also did not correlate well with the LPR results. In this case, the corrosion rate for the coupons was significantly lower than the LPR test. The lower rate was the result of a more adherent ferrous oxalate film that forms approximately 2 days after the initial exposure. Thus, the initial corrosion rate measured by the LPR test, decreases significantly after approximately 2 days and results in a significantly lower average corrosion rate after 30 days.



(a)



(b)

Figure 12. Cleaned Coupon showing pitting corrosion in (a) HM/2.5 wt.%oxalic acid at 75 °C with no agitation, (b) HM-PUREX/2.5 wt.% oxalic acid at 75 °C with agitation. Magnification was 20X unless shown otherwise.

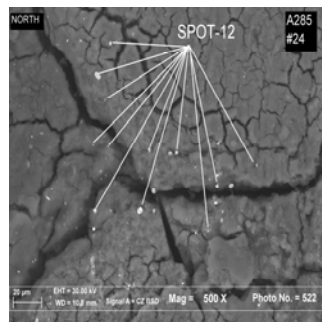
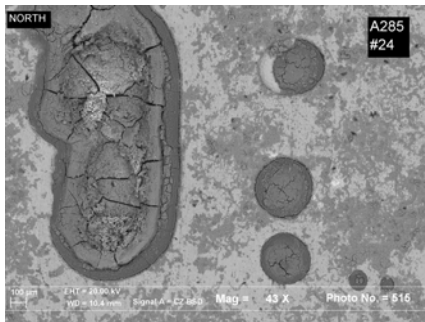


Figure 13. This coupon was tested in Simulant B/2.5 wt.% oxalic acid at 75 °C with no agitation. (a) SEM micrograph showing the hemi-spherical and oblong shaped pits. (b) SEM micrograph showing the mercury particles dispersed with in the corrosion product in side a pit.

Table 7 also shows that the corrosion rate in the non-agitated 2.5 wt.% oxalic acid at 50 °C was approximately 6 to 7 times greater than that observed in the solutions containing sludge simulants at the same temperature. It also appears that the corrosion rate has a stronger dependence on temperature with the oxalic acid than the simulant environments. The lower corrosion rates in the presence of a sludge simulant suggest either a more tenacious oxalate film or the nature and the kinetics of the cathodic reaction have been significantly altered by the presence of dissolved species in the oxalic acid. Based on the observations of the cathodic reactions, it seems likely that the presence of dissolved species.

Table 7. Corrosion Rates Determined from Coupon Immersion Tests

Test Condition	Corrosion Rate (mm/yr)	
	50 °C	75 °C
Simulant A		
Agitated	1.3 ^a	0.51
Not Agitated	0.56	0.84
Simulant B		
Agitated	0.53	1.85 ^b
Not Agitated	0.48	0.48 ^c
Oxalic Acid		
Agitated	2.2	0.53
Not Agitated	3.5	0.58

a – One coupon corroded at 0.66 mm/yr and the other corroded at 2 mm/yr.

b - Pitting along with heavy general corrosion was observed.

c – Pitting was observed.

The results from Table 7 showed that the temperature did not significantly influence the corrosion rate for the non-agitated condition. However, there was significant variability with temperature for the agitated solutions. These differences are more likely a reflection of the variability in the development of the ferrous oxalate film due to the agitation of the solution.

Corrosion Mechanism

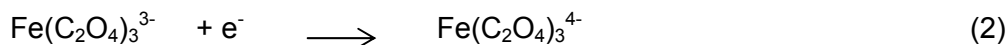
Cathodic Reaction.

Corrosion of steel and dissolution of iron oxides result in a build-up of not only ferrous ions, but ferric oxalate complexes as well in the acidic environment. During the chemical cleaning process, the concentration of ferric species increases due to dissolution of iron oxides such as hematite, magnetite, and iron oxide corrosion products such as goethite or lepidocrocite. These oxides reside in the sludge solids and in a layer of mill scale or corrosion product on the tank wall. Ferric ions may also evolve as ferrous species react with oxygen present in the solution. Ferric oxalate complexes are relatively stable and remain soluble in oxalic acid.

The free ferric ion concentration in oxalate media however, is essentially nil at a pH of 2⁶ as the ferric ion is readily complexed with the oxalate to form a di-oxalatoferrate ($\text{Fe}(\text{C}_2\text{O}_4)_2^-$) ion at a pH of approximately 2. This species may be reduced at cathodic sites. At oxalate concentrations greater than 0.1 M, the reaction proceeds as:



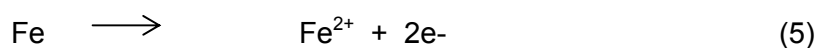
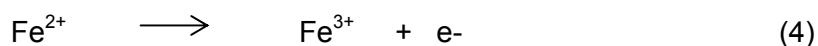
At pH levels between 1 and 1.5 with oxalic acid concentrations of approximately 2.5 wt.% so that in addition to the di-oxalatoferrate complex another iron (III) oxalate complex, the tri-oxalatoferrate species, $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$,^{7, 8} is present in significant quantities. This species has been shown to be reduced according to the following reaction:



Note that in this case ferrous oxalate is not formed as it is for the reaction involving the di-oxalatoferrate complex. Thus, one might suspect that less ferrous oxalate would be present to maintain a passive layer at this condition.

Pitting Mechanism.

Mercury is known to be a strong oxidizing agent and may provide an explanation for the aggressive nature of Simulant B. A mechanism was postulated to explain the occurrence of the localized attack. Iron and aluminum oxides are initially entrapped on the surface of the coupon with the iron oxalate. The mercuric species is adsorbed from the solution by the aluminum oxides⁹. If the temperature is high enough, the aluminum oxide begins to dissolve leaving either a mercuric or mercurous species present on the surface. The presence of the mercury species polarizes the surface at a local site. For example, the mercurous species may be involved in reactions at local sites according to the following reactions.



Note that the ferric ions produced by reaction (3) accelerate the rate of reaction (4) at oxidizing potentials¹⁰. The ferric ion would react with water to form the goethite. The equilibrium potentials for the mercurous and mercuric species are approximately +0.4 V and +0.7 V vs. Ag/AgCl, respectively⁵. These potentials are noble to the equilibrium OCP values that were measured during the tests, and the breakdown potential for ferrous oxalate. Therefore, wherever this reaction occurs on the metal surface, the ferrous oxalate will not form to slow the reaction. Interestingly, the CPP scans were only carried out to +0.5 V vs. Ag/AgCl. No pitting was observed during the short-term electrochemical tests. Given that the equilibrium potential for the mercurous species is within this range, this suggests that the mercuric species is possibly being reduced to mercury. This explanation may also be the reason for the absence of localized attack during these tests. Time could also be a factor as the adsorption rate of the mercuric ion may limit the build-up of a sufficient concentration of species to polarize the local site.

CONCLUSIONS

Corrosion rate data for carbon steel exposed to the ECC treatment tank environment was obtained to evaluate the degree of corrosion that occurs. These tests were also designed to determine the effect of various environmental variables such as temperature, agitation and sludge slurry type on the corrosion behavior of carbon steel. Coupon tests were performed to estimate the corrosion rate during the ECC process, as well as determine any susceptibility to localized corrosion. Electrochemical studies were performed to develop a better understanding of the corrosion mechanism. The tests were performed in a simulant-acid mixture.

The following results and conclusions were made based on this testing:

1. The results of the electrochemical and coupon immersion tests were not in agreement. Dissolution of the solids over time resulted in more aggressive solutions. Hence, the coupons provided a better evaluation of the operable corrosion mechanisms.
2. Electrochemical testing indicated that for oxalic acid/sludge simulant mixtures the cathodic reaction has transport controlled reaction kinetics. The literature suggests that the dissolution of the sludge produces a di-oxalatoferrate ion that is reduced at the cathodic sites. The cathodic reaction does not appear to involve hydrogen evolution. On the other hand, electrochemical tests demonstrated that the cathodic reaction for corrosion of carbon steel in pure oxalic acid involves hydrogen evolution.
3. Agitation of the oxalic acid/sludge simulant mixtures typically resulted in a higher corrosion rates for both acid concentrations. The transport of the ferrous ion away from the metal surface results in a less protective ferrous oxalate film.

4. A mercury containing species along with aluminum, silicon and iron oxides was observed on the interior of the pits formed in the Simulant B/2.5 wt.% oxalic acid simulant at 75 °C. The pitting rates in the agitated and non-agitated solution were 2 mils/day and 1 mil/day, respectively. A mechanism by which the mercury interacts with the aluminum and silicon oxides in this simulant to accelerate corrosion was postulated.

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