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ANALYSIS OF THE PITTING FACTOR FOR PREDICTING LOCALIZED CORROSION OF LIQUID RADIOACTIVE WASTE AT ELEVATED TEMPERATURES

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ABSTRACT

Millions of liters of liquid radioactive waste are stored in double shell tanks (DSTs) at Hanford Site. The DSTs were constructed of carbon steel from 1968 to 1986 and have a comprehensive chemical control program which mostly relies on hydroxide additions, thus preventing localized corrosion specially stress corrosion cracking (SCC). Most of the radioactive waste is now below 50 ºC and the pitting factor was determined to provide limits in the control program using significant chemical species in the waste. However, several tanks have reached temperatures up to 75 ºC, so the pitting factor equation may not be adequate to address localized corrosion conditions at higher temperatures than 50 ºC. Using statistical analysis, a series of electrochemical tests were designed and developed to account for the increase in temperature at different chemistries and at lower pH than 13. Additionally, testing was performed to differentiate between the contribution of the halides (i.e., chloride and fluoride) in the PF equation since we have only been focusing on chloride. Cyclic potentiodynamic polarization (CPP) was used to identify regions of localized corrosion susceptibility at different concentration of statistically significant chemicals in the waste and expanded to temperatures up to 75 ºC. Using the results of this study, the pitting factor was analyzed and validated for elevated temperatures.

Key words: electrochemical testing, cyclic potentiodynamic polarization, Hanford, liquid radioactive waste

INTRODUCTION

The Hanford Site in Washington State currently stores millions of liters of radioactive waste in DSTs that were constructed between 1968 and 1986. A chemistry control and monitoring program was established to mitigate corrosion during their service. The tanks were fabricated of carbon steel and the liquid waste inhibits the metal by additions of sodium hydroxide and from nitrite that is converted from nitrate by radiolysis. Currently most of the liquid waste that is inside the tanks is above 1 M hydroxide and temperatures are lower than 50 ºC.[1] The current composition for the supernate and interstitial liquid present in the DSTs are given in Table 1.[2]

Waste transfers from older single shell tanks to DSTs, may shift the waste chemistry towards higher concentrations of aggressive species such as chloride, fluoride and sulfate and lower the pH. Thus, the tanks may become more susceptible to localized attack such as pitting and/or SCC. Since 2014, SRNL has been conducting corrosion testing to establish a new waste chemistry envelope for pitting corrosion mitigation. The testing culminated with the development of a pitting factor (PF) that predicts pitting susceptibility based on a relative ratio of inhibitor to aggressive corrosion species.[3,4]

Electrochemical testing presented in this publication is a continuation of the testing that has been performed for the past five years. The work began with the utilization of Plackett-Burman and Box-Behnken statistically designed tests to determine the significant variables that affect pitting corrosion of carbon steel.[3-5] For this publication, testing was performed to differentiate between the contribution of the halides (i.e., chloride and fluoride) in the PF equation. Previous forms of the PF assumed that the influence of fluoride and chloride on pitting corrosion were equivalent. Testing was initiated to test the hypothesis that the chloride ion was more aggressive toward carbon steel than the fluoride ion. Furthermore, testing at elevated temperatures (i.e., temperatures over 50 up to 75 ºC) was performed to expand the temperature range for which PF model was valid.

Table 1
Range of concentrations of significant chemicals in the supernate and interstitial liquid of Hanford DST

Chemical Constituent	Concentration Range (M)	
	Supernate	Interstitial
Hydroxide	0.42 - 5.85	0.00 - 5.21
Nitrite	0.21 - 3.10	0.27 - 3.25
Nitrate	0.39 - 3.83	0.06 - 4.74
Chloride	0.01 - 0.32	0.00 - 0.41
Fluoride	0.00 - 0.22	0.00 - 0.73

EXPERIMENTAL PROCEDURE

Electrodes shaped in a “bullet” form with dimensions 0.187 inch (0.477 cm) diameter and 1.250 inch (3.175 cm) long (Metal Samples EL400(1)) were used for the testing. The electrodes were fabricated using Association of American Railroads(2) Tank Car (AAR TC 128) steel, which was used as a surrogate for the actual waste tank steel. The tanks at Hanford were built using UNSK02401 carbon steel (i.e., American Society for Testing and Materials (ASTM)(3) A515[6] Grade 60 carbon steel). Table 2 shows the chemical composition of the surrogate and the nominal composition of the A515 Grade 60 steel . All elemental compositions except for Mn and Si meet the specification for ASTM A515 Grade 60. The Mn is greater than the maximum allowed of 0.9 wt.%, while the Si is less than the required range.

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(1) Trade name
(2) Association of American Railroads, 425 3rd Street SW, Washington, DC 20024
(3) ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959

Table 2
Chemical Composition measured of AAR TC 128 Steel (wt.%) compared to ASTM A515 Grade 60 specification

	C	**Mn**	**P**	**S**	**Si**	**Fe**
Specification	0.24 (max.)	0.90 (max.)	0.025 (max.)	0.025 (max.)	0.13 to 0.45	Balance
Measured	0.212	1.029	0.012	0.013	0.061	Balance

The coupons were tested in various simulants prepared with reagent grade chemicals. Table 3 lists the chemicals used. Sodium bicarbonate was only added when the pH was adjusted to 10.

Table 3
Chemicals used in Simulants

Chemical component	**Chemical used**
Hydroxide	Sodium Hydroxide
Nitrite	Sodium Nitrite
Nitrate	Sodium Nitrate
Chloride	Sodium Chloride
Sulfate	Sodium Sulfate
Total Inorganic Carbon	Sodium carbonate
	Sodium bicarbonate

For electrochemical testing, a one (1) L glass cell was used. The glass cell had ports to accommodate different electrodes: counter, reference and working, as well as a thermocouple for temperature control. Approximately 700 mL of simulant was added to the glass cell and placed on top of a hotplate for controlling the temperature. The counter electrode consisted of two graphite rods electrically connected through a wire attached with alligator clip-ends. The reference electrode was a saturated calomel electrode (SCE) and was placed in a glass bridge that contained the same test solution. The working electrode contained the "bullet" shaped electrode with a polytetrafluoroethylene gasket and sealed using a stainless-steel rod placed inside a glass holder. A potentiostat was used to perform the electrochemical testing and prior to use, it was qualified by performing ASTM G5 standard.[7] The electrochemical test protocol consisted of a two-hour open circuit potential (OCP) monitoring period, followed by CPP. The CPP test was conducted by applying a potential ramp from -50 mV vs. OCP to a vertex threshold current of 1 mA/cm^2 at a scan rate of 0.167 mV/s and returned to 0 mV vs. OCP. In some cases where the CPP test did not provide a conclusive repassivation potential, as in the case of mixed hysteresis, a modified ASTM G192[8] test for pitting corrosion in carbon steels[9] was performed. For this test, a potentiodynamic scan was first performed. The potential was applied at -100 mV vs. OCP and scanned in the noble direction until the measured current density was 50 μA/cm^2. This was followed by a galvanostatic hold at this current density for four hours. For the third and final step, the potential is decreased in stepwise manner 10 mV every two hours until the current density was less than the passive current density measured on the forward scan or the current density exceeded the passive current density while the potential was nearing the initial OCP.

The experimental statistical design and analysis is detailed in an earlier conference proceeding[4]. The logistic approach continued to be used in this case to provide a "pass" or "fail" condition as the dependent variable. The logistic approach was added to previous statistical analysis of Plackett-Burman and Box-Behnken designs and the augmented statistical design. The PF equation, that was obtained from a total of 95 tests performed, was used as a framework to develop a fluoride coefficient in the aggressive species for its significance in pitting corrosion (equation 1). Also, to establish changes for increasing temperature up to 75 ºC. For this equation, the sum of the chloride and fluoride concentrations (i.e., $[Cl^-]+[F^-]$) were considered as total halide concentration.

$$PF = \frac{\text{Inhibitor species}}{\text{Aggressive species}} = \frac{8.5[OH^-]+2.4[NO_2^-]}{[NO_3^-]+19.6[\text{Halide}]} \quad \textbf{(1)}$$

From the ratio of inhibitor versus aggressive, a ratio less than 1 indicates that there is susceptibility to localized corrosion and a ratio higher than 1 indicates the contrary. The PF is used to predict susceptibility of localized corrosion depending on concentration of significant species.

RESULTS

Electrochemical experiments to determine the aggressive effects of fluoride and chloride were performed to establish the coefficients for the PF equation. Table 4 shows the statistically designed matrix to establish those coefficients. A total of fifteen experiments were designed at 35 ºC with different chemistries. The limits for fluoride and chloride was up to 0.3 and 0.4 M, respectively. Other species present at constant values included sulfate (0.2 M) and carbonate (0.1 M).

Table 4
Simulant chemistries to determine fluoride effects

Test	Hydroxide (M)	Nitrite (M)	Nitrate (M)	Chloride (M)	Fluoride (M)	Target pH	PF
1	4	2	0	0.4	0.3	>12	2.84
2	4	2	0	0.4	0.3	>12	2.84
3	0.0001	2	4	0.4	0.3	10	0.27
4	0.0001	2	4	0.4	0.3	10	0.27
5	4	0	4	0.4	0	>12	2.88
6	4	0	4	0.4	0	>12	2.88
7	4	2	0	0	0.3	>12	6.62
8	4	2	0	0	0.3	>12	6.62
9	4	0	4	0	0.3	>12	3.45
10	4	2	0	0	0	>12	N/A
11	4	0	4	0.4	0	>12	2.88
12	4	2	4	0	0	>12	9.73
13	0.0001	2	4	0.4	0.3	10	0.27
14	0.0001	2	4	0.4	0.3	10	0.27
15	4	0	0	0.4	0.3	>12	2.48

As calculated from equation 1, the PF ranged from 0.27 to 9.73. The results from this testing are presented in Table 5. The concentration of fluoride species was included in this table because of changes in concentration were needed due to solubility of fluoride into solution. By adjusting the fluoride additions at the end with small quantities, the fluoride concentration that was soluble was recorded and if precipitation started to occur more additions of fluoride were halted. The highlighted values correspond to new concentration of fluoride in solution.

Table 5 also includes the CPP results as well as the observations of pitting and no pitting. CPP hysteresis was used to identify the CPP response and to categorize a “pass” or “fail” determination. A “pass” is indicated if negative hysteresis is observed and the sample does not show any signs of localized corrosion. In contrast, a “fail” is indicated by a positive hysteresis. The sample may also show various degrees of localized corrosion from minor to severe attack.

Eleven (11) CPP responses indicated negative hysteresis, corresponding to a “pass”, and one (1) indicated positive hysteresis corresponding to a “fail”. Mixed hysteresis occurs when the return scan has less current density at a given potential and then increase in current density intersecting the forward scan once or multiple times. This case will be presented with an example later in this publication. From the table (Table 5), mixed hysteresis with an asterisk (*) was used to identify a positive hysteresis with a closed loop that was differentiated from a “pass” or “fail” at the potential the reverse cycle intersects the forward cycle (i.e., repassivation potential (RP)). The result is a “pass”, when the difference between RP and OPC is more than 200 mV and it is a “fail” when the difference is less than 200 mV. An example of a CPP with a positive hysteresis closed loop is shown in Figure 1 from the results of Test 4. From this CPP, the RP is -167 mV vs. SCE and the OCP is -247 mV vs. SCE, thus the difference is 80 mV and considered a “fail”. The pictures after tests, inserted into the CPP graph shows small pits around the shank and nose. For this set of tests, all the conditions matched the pitting factor prediction.

Logistic regression was performed with results from this test and adding the results of pitting factor between 1 and 2[4]. The coefficients were added into the pitting factor and the resulting equation with the specific contributions of fluoride and chloride is shown in equation 2. The contribution of chloride for the equation is approximately 3 times greater than fluoride.

$$\text{Pitting Factor}= \frac{\text{Inhibitor Species}}{\text{Aggressive Species}} = \frac{8.1\,[OH^-]+1.6\,[NO_2^-]}{[NO_3^-]+16.7\,[Cl^-]+5.7\,[F^-]} \qquad \textbf{(2)}$$

Table 5
Test results of testing from statistically design tests to investigate fluoride effects

Test	Fluoride (M)	CPP Hysteresis	Logistic Approach	Pitting on Sample?
1	0.02	Negative	Pass	No
2	0.02	Negative	Pass	No
3	0.3	Positive	Fail	Yes
4	0.3	Mixed*	Fail	Yes
5	0	Negative	Pass	No
6	0	Negative	Pass	No
7	0.3	Negative	Pass	Yes
8	0.26	Negative	Pass	Yes
9	0.14	Negative	Pass	Yes
10	0	Negative	Pass	No
11	0	Negative	Pass	No
12	0	Negative	Pass	No
13	0.3	Mixed*	Fail	Yes
14	0.3	Mixed*	Fail	Yes
15	0.22	Negative	Pass	No

*positive hysteresis with closed loop

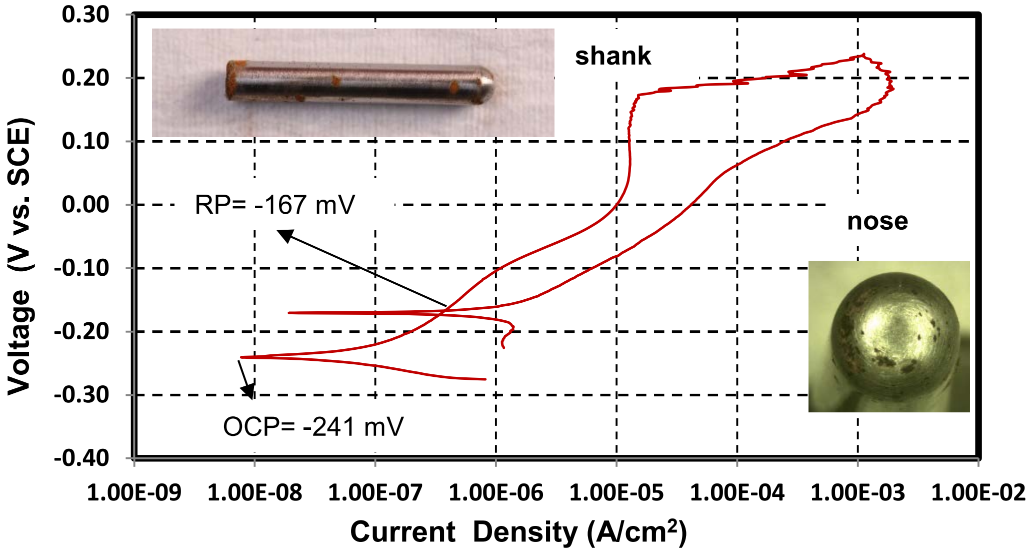

Figure 1: CPP results of Test 4. Inserted are pictures of the "bullet" coupon after test

The PF was validated up to 50 ºC, since up to a maximum of 50 ºC the temperature was not statistically significant. To validate the PF equation at temperatures up to 75 ºC, a statistical experimental design was created using twenty one (21) experiments to cover the same chemistry envelope as before, adding 75 ºC as a factor. Table 6 lists the concentration of species for the test, as well as the corresponding PF using equation 2. It is listed also the results of the CPP data, "fail" and "pass" category from the logistic approach and if there was pitting in the sample after test.

The results from the twenty-one (21) tests showed that seven were "passes" with negative hysteresis and ten (10) were "fails" with positive hysteresis with an open loop. There were two (2) cases with mixed hysteresis and another two (2) with positive hysteresis with closed loop. The tests with positive hysteresis closed loop were less than 200 mV difference between RP and OCP. An example of mixed hysteresis is presented in Figure 2, for test 2. As observed, the reverse scan current density was lower than the passive current density initially, but after approximately 200 mV vs. SCE the current density "crossed-over" and became greater than the passive current density. To determine if this is a "pass" or a "fail" category, a modified ASTM G192[9] test was performed. The modified ASTM G192 method consisted of three electrochemical techniques performed in sequence. These techniques were a potentiodynamic period, followed by a galvanostatic period that allows pits to appear and grow if the conditions are conducive for pitting and, finally, a potentiostatic stepwise reduction until repassivation is achieved or the current goes toward The results for this test are presented in Figure 3. The potentiostatic is shown in (a) and the G192 plot in (b). The G192 plot consist of two graphs recording current density at the top and voltage at the bottom as function of time. For this case, the potentiostatic reached the limit current density at approximately 100 mV vs. SCE. Then, after the period of four hours and after the first potentiostatic step for two hours, the voltage went down to -160 mV vs. SCE which is less than 200 mV of the OCP (OCP is -273 mV vs. SCE and the difference is 113 mV) which is categorized as a "fail".

Table 6
Test conditions and results using statistical approach at a temperature of 75 °C

Test	Hydroxide (M)	Nitrite (M)	Nitrate (M)	Chloride (M)	Fluoride (M)	Sulfate (M)	PF	CPP Hysteresis	Logistic Approach	Pitting on Sample?
1	0.0001	1.2	2.75	0	0	0.2	0.68	Mixed*	Fail	Yes
2	0.0001	0.48	3.3	0	0.3	0.12	0.15	Mixed	Fail	Yes
3	0.0001	0	0	0.2	0.3	0.2	0.00	Positive	Fail	Yes
4	0.0001	0	5.5	0.4	0	0.1	0.00	Positive	Fail	Yes
5	0.0001	1.2	0	0.4	0.15	0	0.25	Positive	Fail	Yes
6	0.0001	1.2	5.5	0.4	0.3	0.2	0.13	Positive	Fail	Yes
7	0.24	0.72	2.2	0.16	0	0	0.63	Positive	Fail	Yes
8	0.48	0.96	5.5	0.32	0.06	0.2	0.48	Mixed	Fail	Yes
9	0.6	0	0	0	0	0	N/A	Negative	Pass	Yes
10	0.6	0.6	2.75	0.2	0.15	0.1	0.83	Positive	Fail	Yes
11	0.6	0.6	2.75	0.2	0.15	0.1	0.83	Positive	Fail	Yes
12	0.6	0.6	2.75	0.2	0.15	0.1	0.83	Mixed*	Fail	Yes
13	0.6	0.6	2.75	0.2	0.15	0.1	0.83	Positive	Fail	Yes
14	0.72	0.24	0	0.4	0.12	0.16	0.84	Negative	Pass	Yes
15	0.96	0	4.4	0.24	0.24	0.04	0.79	Positive	Fail	Yes
16	1.2	0	5.5	0	0	0.2	1.76	Negative	Pass	No
17	1.2	1.2	0	0	0.3	0.1	6.74	Negative	Pass	No
18	1.2	1.2	1.1	0.08	0.18	0.08	3.33	Negative	Pass	No
19	1.2	1.2	5.5	0.2	0	0	1.30	Negative	Pass	No
20	1.2	0.6	0	0.4	0	0.2	1.59	Negative	Pass	No
21	1.2	0	2.75	0.4	0.3	0	0.87	Positive	Fail	Yes

*positive hysteresis with closed loop

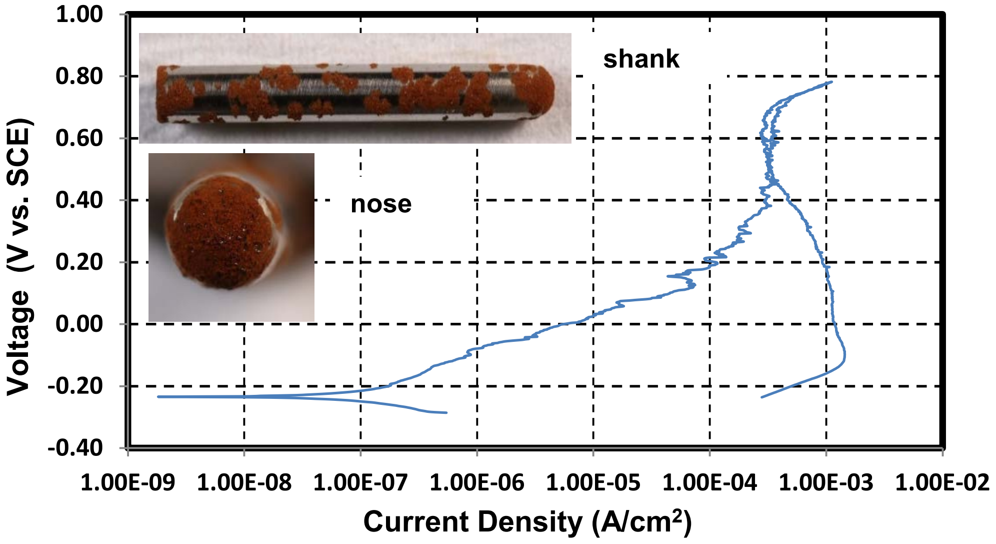

Figure 2: CPP results of Test 2. Inserted are pictures of the “bullet” coupon after test

Thus, temperature remains a statistically non-contributing variable to the PF model and no changes to equation 2 were required. In general, the PF equation that was utilized to predict pitting susceptibility at temperatures of 50 °C and less also predicted pitting susceptibility for 75 °C. That is, PFs greater than 1 predicted no pitting susceptibility, while PFs less than 1 typically predicted pitting susceptibility, although in some cases “pass” conditions were observed. An example of this was observed for Test 14 on Table 6. In this case, the CPP curve exhibited negative hysteresis, although tiny pits were observed on the surface of the electrode. These pits are typically non-propagating and thus this case is considered a “pass”. The model conservatively predicted that a condition was vulnerable to pitting when the test did not indicate the vulnerability.

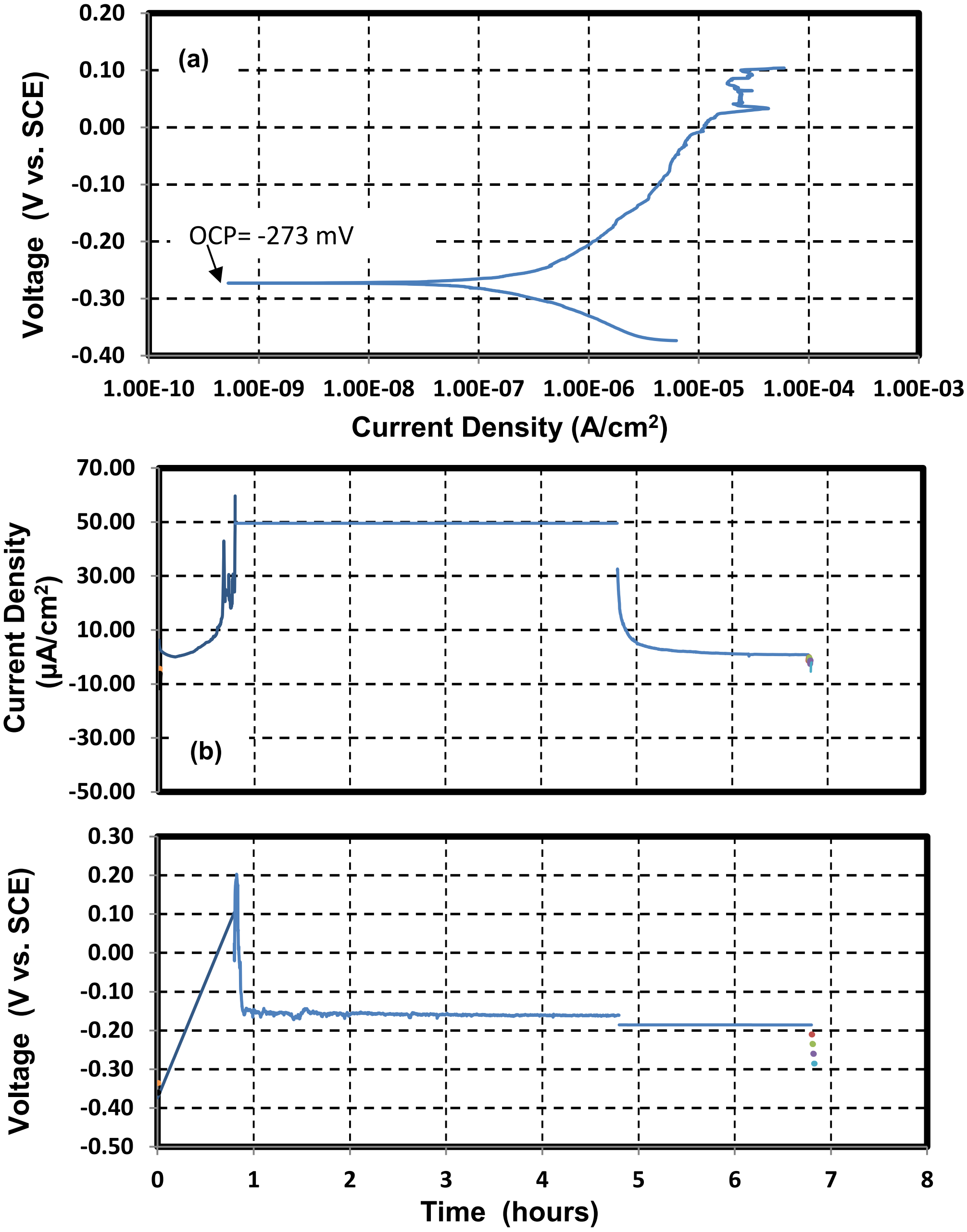

Figure 3: Potentiodynamic (a) and G192 test plot (b) for Test 2

CONCLUSIONS

Electrochemical testing was performed to determine the effect of fluoride on pitting of carbon steel and to expand the temperature limit to 75 ºC for the PF equation. Fifteen tests (15) were performed to aid in determining the fluoride effects to the PF equation, targeting fluoride up to 0.3 M and chloride up to 0.4 M. The statistical analysis resulted in a new PF equation with an additional coefficient for fluoride where the contribution of pitting corrosion is about three times more significant for chloride than fluoride. At temperatures up to 75 ºC, twenty-one (21) tests were performed obtained from a statistical design to determine the impact of temperature in the PF equation. The results showed that for most tests, the PF prediction using the equation developed for temperatures less than 50 °C matched the results. In conclusion, at elevated temperatures the PF equation is still valid and can be used efficiently to predict vulnerability towards localized corrosion of carbon steel for liquid radioactive waste environments with similar chemistry.

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