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Pitting Corrosion Inhibition of Carbon Steel in Simulated Liquid Radioactive Waste at Elevated Hydroxide Concentrations

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ABSTRACT

Liquid radioactive waste is stored in underground double shell tanks (DSTs) constructed carbon steel at the Hanford site. A comprehensive chemistry control program to prevent stress corrosion cracking (SCC) and other types of localized corrosion exists. The program mostly relies on the addition of sodium hydroxide to raise the pH of the waste and radiolysis to form nitrite for inhibition. It is desirable to define the borderline conditions of the current chemistry control program to be aware and prevent conditions conducive to pitting corrosion. These conditions may occur due to anticipated future waste streams that can change the chemistry of the waste in these tanks. The current corrosion control program primarily inhibits against localized corrosion due to nitrate. Electrochemical testing was utilized determine the borderline conditions for pitting to optimize the chemistry control program for DSTs. A statistically designed set of borderline conditions at high hydroxide concentration with different aggressive species (e.g., chloride, sulfate) in addition to nitrate was tested.

Key words: radioactive waste, carbon steel, pitting corrosion, electrochemical testing

INTRODUCTION

The Hanford Site located in Washington state has a legacy of millions of liters of nuclear waste from research programs. The liquid waste is stored in underground storage tanks in which 149 are single shell tanks (SST) and 28 double shell tanks (DST). The liquid waste will be retrieved for stabilization and it will likely take a few more decades due to the construction process of the vitrification facility. In the meantime, tank integrity is being closely monitored for all the tanks because most of them are approaching their design lifetimes. Additionally, a corrosion control program is in place to maintain the waste chemistry to mitigate corrosion mechanisms that can affect the integrity of the tank for general and localized corrosion.

By understanding the potential degradation mechanisms, the tank service lifetime can be extended until final disposition of the waste and eventual closure of the tank.

To prepare the liquid waste for eventual stabilization by vitrification or grout formulation, the waste is being retrieved from SSTs that are suspected leakers and transferred to DSTs. This transference of waste can impact the waste chemistry of the DST. Initial projections suggest that the waste chemistry of the DSTs may shift to a broader range of pH and higher aggressive anion concentrations (e.g., chloride, sulfate, etc.) than the wastes that are presently stored. Therefore, in conjunction with this evaluation, the corrosion control program is being assessed to ensure that it is robust and can adjust to these anticipated changes.

The present corrosion program is shown in Table 1. The liquid waste is inhibited against corrosion of carbon steel by addition of sodium hydroxide to raise the pH and reliance on radiolysis to deplete nitrate ion into nitrite, which inhibits corrosion. The limits were developed based on laboratory testing. Currently the focus has been on waste temperatures lower than 50 °C since the temperatures of DST at Hanford are typically less than this temperature[1]. Presently, the liquid waste at the tanks is maintained above 1 M hydroxide, which can mitigate stress corrosion cracking (SCC), pitting corrosion and general corrosion. However, the process changes mentioned before, and the potential for hydroxide depletion within the interstitial liquid of the waste solids, may challenge these requirements in the future.

Table 1: Double-Shell Tank Waste Chemistry Limits for Corrosion Control

For $[NO_3^-]$ Range	**Variable**	**For Waste Temperature (T) Range**		
		T < 167 °F (75 °C)	**167 °F (75 °C) $\leq$ T $\leq$ 212 °F (100 °C)**	**T > 212 °F (100 °C)**
$[NO_3^-] \leq 1.0M$	$[OH^-]$	$0.010M \leq [OH^-] \leq 8.0M$	$0.010M \leq [OH^-] \leq 5.0M$	$0.010M \leq [OH^-] \leq 4.0M$
	$[NO_2^-]$	$0.011M \leq [NO_2^-] \leq 5.5M$	$0.011M \leq [NO_2^-] \leq 5.5M$	$0.011M \leq [NO_2^-] \leq 5.5M$
	$[NO_3^-]/([OH^-] + [NO_2^-])$	< 2.5	< 2.5	< 2.5
$1.0M < [NO_3^-] \leq 3.0M$	$[OH^-]$	$0.1([NO_3^-]) \leq [OH^-] < 10M$	$0.1([NO_3^-]) \leq [OH^-] < 10M$	$0.1([NO_3^-]) \leq [OH^-] < 4.0M$
	$[OH^-] + [NO_2^-]$	$\geq 0.4([NO_3^-])$	$\geq 0.4([NO_3^-])$	$\geq 0.4([NO_3^-])$
$[NO_3^-] > 3.0M$	$[OH^-]$	$0.3M \leq [OH^-] < 10M$	$0.3M \leq [OH^-] < 10M$	$0.3M \leq [OH^-] < 4.0M$
	$[OH^-] + [NO_2^-]$	$\geq 1.2M$	$\geq 1.2M$	$\geq 1.2M$
	$[NO_3^-]$	$\leq 5.5M$	$\leq 5.5M$	$\leq 5.5M$

Previous testing had been performed to address apparent gaps of the corrosion control program that address stress corrosion cracking[2]. Results from the previous paper[3] and this paper are trying to determine conditions conducive to pitting corrosion. The testing program specifically targets gap regions such as the pH range between 10 and 13.5 and will address chloride concentrations up to 0.4 M and sulfate concentrations up to 0.2 M. The goal is to develop a more comprehensive chemistry control program to prevent pitting corrosion of carbon steel that can affect the integrity of Hanford tanks due to changes in waste chemistry. This paper shows how elevated hydroxide concentrations can affect pitting corrosion at gap regions targeted. A critical pitting factor was utilized to aide in the prediction of chemical compositions that enable pitting corrosion.

EXPERIMENTAL PROCEDURE

Materials Tested

Legacy carbon steel electrodes were fabricated from Association of American Railroads[1] Tank Car (AAR TC) 128 Steel since it approximates the chemistry and microstructure of the vintage steel from which the tanks were fabricated UNS K02401 (i.e., American Society for Testing and Materials (ASTM) [2] A515 Grade 60 carbon steel). The electrodes were in the form of "bullets" with dimensions 0.188 inch (0.477 cm) diameter and 1.25 inch (3.175 cm) long (Metal Samples EL400[3]). Table 2 shows the chemical composition measured for the steel used. All elemental compositions except for Mn and Si meet the ASTM specification. The Mn is greater than the maximum allowed of 0.9 wt.%, while the Si is less than the required range.

Table 2:Chemical Composition of AAR TC 128 Steel (wt.%)

	C	**Mn**	**P**	**S**	**Si**	**Fe**
Specification	0.24 (max.)	0.9 (max.)	0.035 (max.)	0.04 (max.)	0.13 to 0.33	Balance
Measured	0.212	1.029	0.012	0.013	0.061	Balance

Before testing, the electrode was polished to a 600-grit finish and examined to ensure a homogeneous surface free of defects. Then, the electrode was rinsed with distilled water and acetone. A glass holder was used to attach the electrode to a stainless-steel rod and it was insulated with a PTFE fixture (i.e., Metal Samples MI2604[3]).

Solutions Tested

Simulants were prepared using reagent grade chemicals. Tests were conducted at 35 °C with pH higher than 13. Table 3 shows the chemical species and the chemical used to simulate the concentration. Total Inorganic Carbon (TIC) concentration was maintained at 0.1 M and depending on pH requirements the solution was adjusted by using sodium bicarbonate.

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
TIC	Sodium carbonate
	Sodium bicarbonate

Test Apparatus and Set-up

Approximately 700 mL of simulant was added into a corrosion cell. Two carbon graphite rods were used as counter electrode. A saturated calomel electrode was used as the reference electrode. The corrosion

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

cell was placed on top of a hotplate with temperature control. The glass holder with the carbon steel electrode was placed into solution as the working electrode. A Gamry® REF600 potentiostat was used to perform the electrochemical testing and prior to use, it was qualified by performing ASTM G5 standard[4]. The electrochemical testing consisted of a two hour open circuit potential (OCP) monitoring period, followed by a cyclic potentiodynamic polarization (CPP) test. The CPP test was conducted by applying a potential ramp from -50 mV vs. OCP up to a vertex threshold current of 1 mA/cm^2 at a scan rate of 0.167 mV/s. The potential was returned to OCP to complete the test. Duplicate tests were run for each solution condition. In some cases, ASTM G192 tests[5] were performed consisting on three steps. The first step, potentiodynamic, the potential was applied -100 mV vs. OCP up to a threshold current density of 50 µA/cm^2 and a second step, galvanostatic, will maintain the threshold current density for four hours. For the third and final step, the potential is decrerased in a stepwise manner 10 mV every two hours until the current density is less than the current density of the forward potentiodynamic sweep. The potential at which the current is less than the passive current density, and does not increase with time was the repassivation potential.

STATISTICAL DESIGN AND ANALYSIS OF TESTS

Placket-Burman and Box-Behnken statistical designs were used for major variables affecting pitting corrosion. The details of this testing are presented in a previous conference paper[3]. The independent variables used are presented in Table 4. The dependent variable was changed as a binary response of pass (0) or fail (1) using CPP results. The binary response allows the use of logistic regression to perform the statistical analysis of the data. The equation for the probability of fail is given by the equation below,

$$P(1)=\frac{1}{1+e^{\mathrm{lin}(0)}} \tag{1}$$

where lin(0) is the linear model as a function of a pass test. The linear function is shown below,

$$\mathrm{lin}(0)= A + B[\mathrm{Nitrite}]+ C\,[\mathrm{Chloride}]+ D\,[\mathrm{Nitrate}]+ E\,[\mathrm{Sulfate}]+ F[\mathrm{Hydroxide}]+ G\,[\mathrm{Temperature}] \tag{2}$$

The results from the Plackett-Burman and Box-Behnken statistically designed tests were used to produce an augmented statistical design for hydroxide concentration of 1.2 M. The results of this matrix were combined to identify the chemical species that are statistically significant and create an equation to identify pass or fail by the independent variables that affect corrosion phenomena of carbon steel. The commercial package JMP® v. 11.1.1 from SAS Institute Inc. was used to design the test matrix and to analyze statistically the significant variables. The independent variables that can affect corrosion are displayed in Table 4 with maximum and minimum concentration of chemical species and temperature. The maximum values of the variables correspond to maximum conditions observed in the Hanford waste tanks.[1]

Table 4: Variables and Constants for Anticipated Stream Conditions for Plackett-Burman Test Series

Independent Variables		
	Minimum	**Maximum**
Hydroxide (M)	0.0001	0.6
Nitrite (M)	0.0	1.2
Nitrate (M)	0.0	5.5

Chloride (M)	0.0	0.4
Sulfate (M)	0.0	0.2
TIC (M)	0.1	
Temperature (°C)	20	50

RESULTS

The augmented statistical designed series for 1.2 M hydroxide produced 27 tests and is presented in Table 5. Three experiments (gray shaded in table) correspond to median concentration of species with different concentration of sulfate to statistically “anchor” this test with the combined Plackett-Burman and Box-Behnken tests and determine the significance of sulfate towards pitting corrosion.

Table 5: Augmented statistical design with chemical compositions and temperature

Test	Temperature (°C)	Hydroxide (M)	Nitrite (M)	Nitrate (M)	Chloride (M)	Sulfate (M)	Carbonate (M)
1	35	1.2	0	3.75	0	0.13	0.1
2	35	1.2	0	4.75	0	0.07	0.1
3	35	1.2	0	3.1	0.08	0.09	0.1
4	35	1.2	0	2.42	0.16	0.08	0.1
5	35	1.2	0	4.5	0.2	0.03	0.1
6	35	1.2	0	0.94	0.24	0.01	0.1
7	35	1.2	0	0.26	0.32	0.17	0.1
8	35	1.2	0	4.75	0.35	0.07	0.1
9	35	1.2	0	0	0.4	0.02	0.1
10	35	1.2	0.6	4.74	0.08	0.02	0.1
11	35	1.2	0.6	5.32	0.15	0	0.1
12	35	1.2	0.6	3.31	0.16	0.2	0.1
13	35	1.2	0.6	2.68	0.24	0.05	0.1
14	35	1.2	0.6	4.92	0.28	0.06	0.1
15	35	1.2	0.6	1.26	0.32	0.01	0.1
16	35	1.2	0.6	0.63	0.4	0.17	0.1
17	35	1.2	0.6	5.32	0.4	0.01	0.1
18	35	1.2	1.2	4.01	0.16	0.15	0.1
19	35	1.2	1.2	4.17	0.21	0.01	0.1
20	35	1.2	1.2	3.4	0.24	0.1	0.1
21	35	1.2	1.2	1.99	0.32	0.09	0.1
22	35	1.2	1.2	4.57	0.32	0.13	0.1
23	35	1.2	1.2	1.38	0.4	0.01	0.1
24	35	1.2	1.2	4.17	0.4	0.01	0.1
25	35	0.3	0.6	2.75	0.2	0.15	0.1
26	35	0.3	0.6	2.75	0.2	0.07	0.1

27	35	0.3	0.6	2.75	0.2	0.05	0.1

Electrochemical testing was performed for each test to obtain a CPP graph and identify if the sample passes or fails the test. Figures 1 and 2 shows the typical results with a definite pass or fail categorization in a CPP and the corresponding picture showing if pitting corrosion developed.

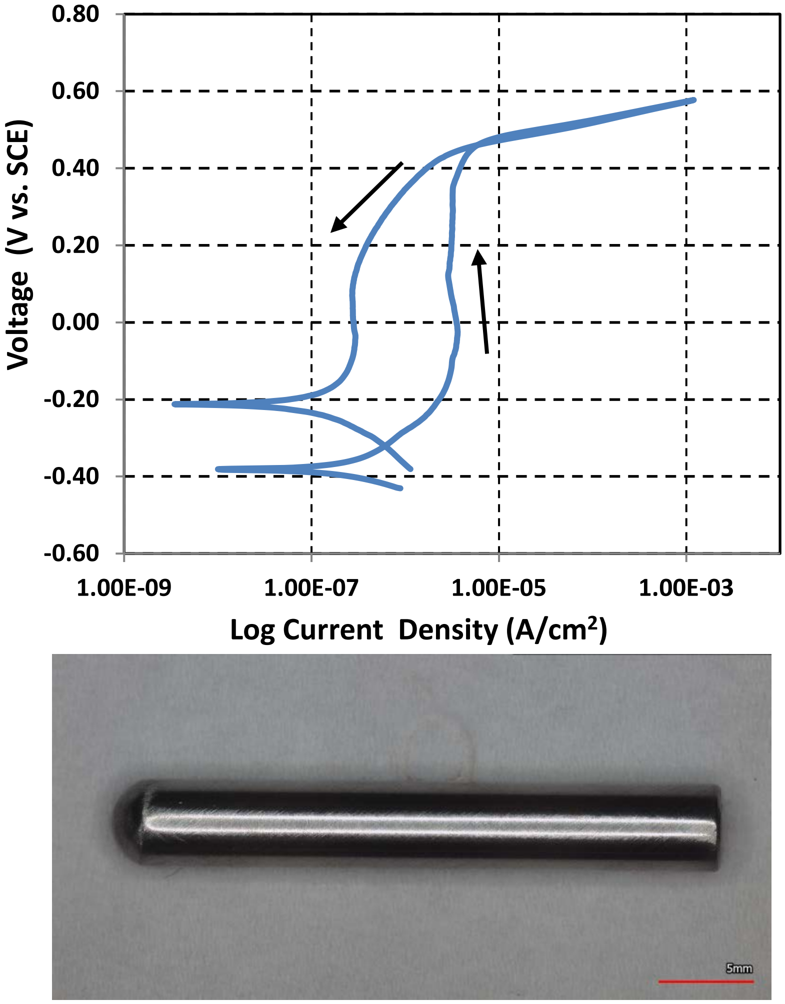

Figure 1: Cyclic potentiodynamic polarization scan and picture for sample for conditions described in Test 1

The CPP diagram in Figure 1 corresponds to negative hysteresis. Negative hysteresis is defined by the current density for the reverse scan being less than that for the forward scan. Most of the tests showed negative hysteresis and are categorized as a pass. The CPP results showed in Figure 2 is the opposite case. This case is categorized a definite fail showing positive hysteresis. For this instance, the current density for the reverse scan is greater than that for the forward scan and completes the cycle with an open loop. The sample can show various degrees of localized corrosion from minor to severe attack.

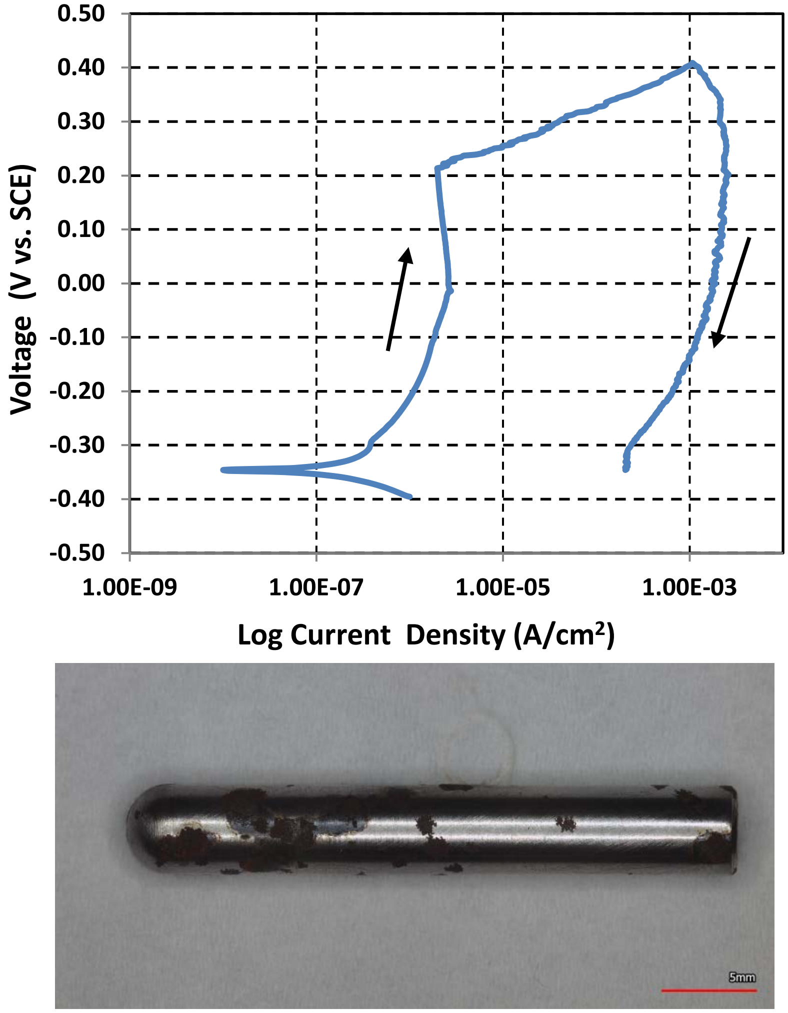

Figure 2: Cyclic potentiodynamic polarization scan and picture for sample for conditions described in Test 25

There can be some occurrences in which the return scan has a lower current density than the forward scan and at some point, intersects the forward scan at more than one point. The hysteresis was defined as mixed. In these cases, it corresponds to some conditions in which localized corrosion is at the borderline for pitting corrosion and cannot be categorized as definite pass or fail.

To address cases when mixed hysteresis occurs and categorize them as pass or fail, a different electrochemical test was used. This test is known as the Tsujikawa-Hisamatsu Electrochemical (THE) method derived from the two Japanese researchers that developed the technique[6]. The technique has been adapted as an ASTM standard with codification G192[5] and can be used to determine repassivation potentials. In this case, it was used to provide a definite categorization of pass or fail for borderline cases that showed mixed hysteresis. Two cases were used as an example and are shown in Figure 3. Figure 3 (a) and (b) shows the CPP graph and picture for Test 8 and 22, respectively.

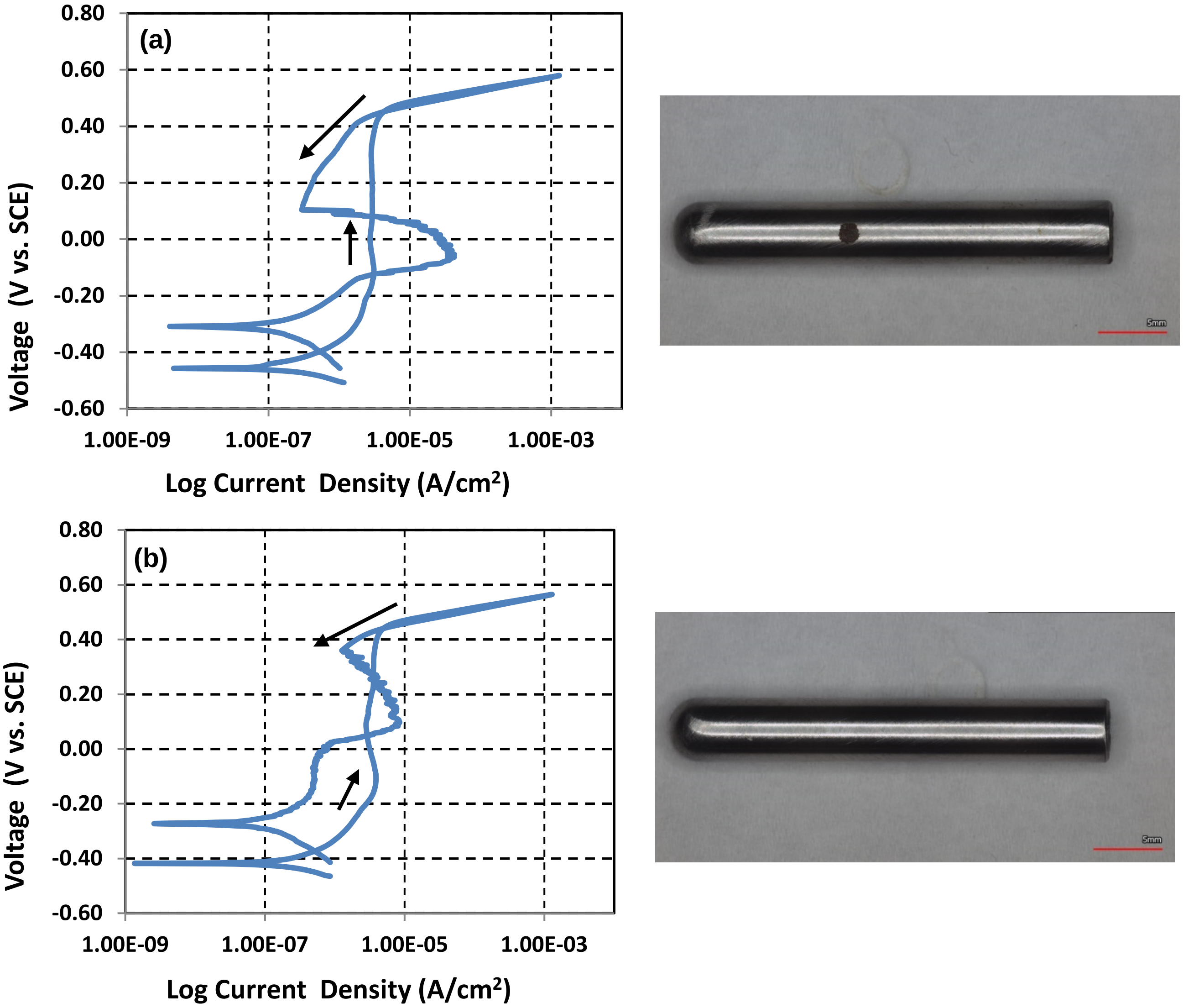

Figure 3: Cyclic potentiodynamic polarization scan and picture on right side for sample for conditions described in (a) Test 8 and (b) Test 22

As observed in Figure 3, the two CPP has very similar features. OCP are approximately 39 mV different and the reverse scan intersected the forward scan twice. Also, the transpassive potentials were approximately 420 mV. However, observing the picture of the bullets, the bullet of Test 8 has a pitting region while the bullet of Test 22 is free of localized corrosion.

Due to the mixed hysteresis results, the ASTM G192 method was utilized to categorize the test as a definite pass or fail. Other tests also presented mixed hysteresis, however in this paper we are showing the results of these two tests as examples, which showed a different response using this electrochemical testing method. The ASTM G192 method consists of three electrochemical techniques that will be performed in sequences. These techniques are 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 decays to a value less than the passive current density defined by the forward scan. Results are shown in Figures 6 and 7 for cases for fail and pass, respectively. The potentiostatic is shown in (a) and the G192 plot in 9 (b). The G192 plot consist of two graphs recording current density at the top and voltage at the bottom as function of time.

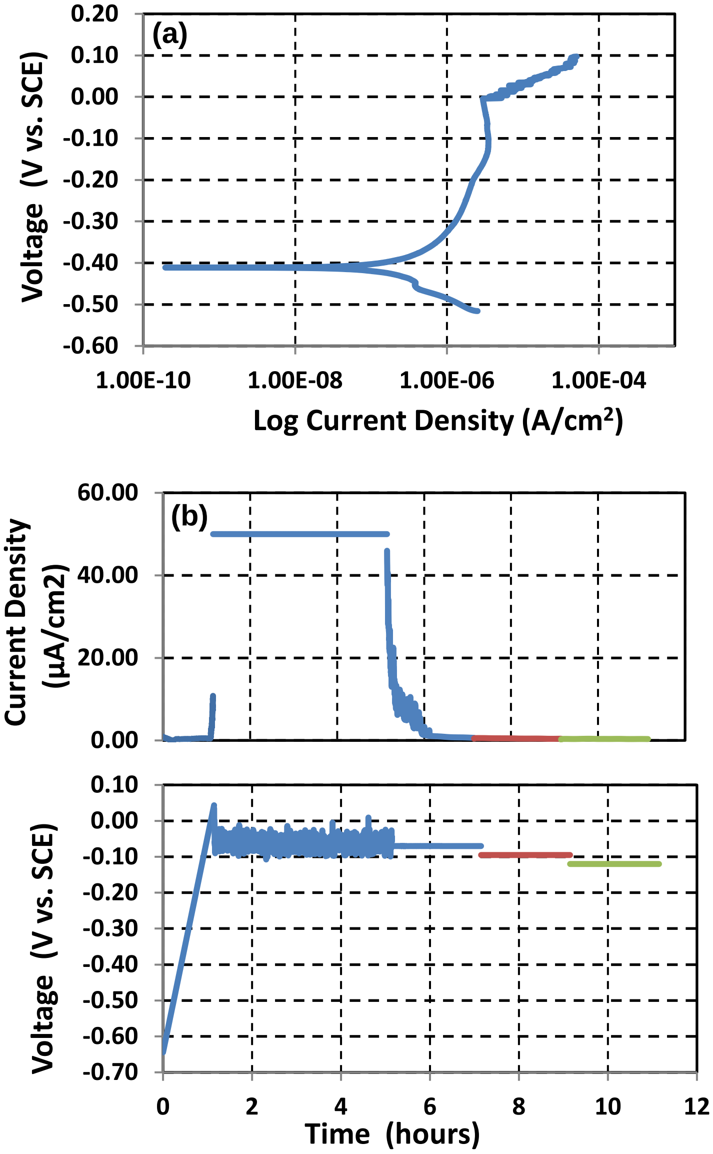

Figure 4: Potentiodynamic (a) and G192 test plot (b) for conditions described in Test 8

Figure 6 (a) shows the potentiodynamic scan for the electrode exposed to simulant in Test 8. As observed, the current increases after reaching 0 mV vs SCE. The galvanostatic current maintained the voltage lower than 0 mV and for 4 hours there was a considerable degree of noise in the data as shown in Figure 6 (b). This allowed the pits to form and grow in small regions of the bullet sample. As the potential was decreased stepwise, the current decayed significantly to almost 0 µA/cm^2 after just three potentiostatic steps. Since the potential started below 0 mV, the repassivation potential is negative and close to the OCP and corresponded to a fail determination. Compared to Figure 7 (a) in which the potential increased to almost 500 mV vs SCE. Additionally, after the galvanostatic period of 4 hours (Figure 7 (b)), the current decreased to almost 0 µA/cm^2 in only three steps, as well. Though, in this case, the repassivation potential is close to 400 mV which is almost 800 mV greater than the OCP. For this situation, the test is categorized as a pass.

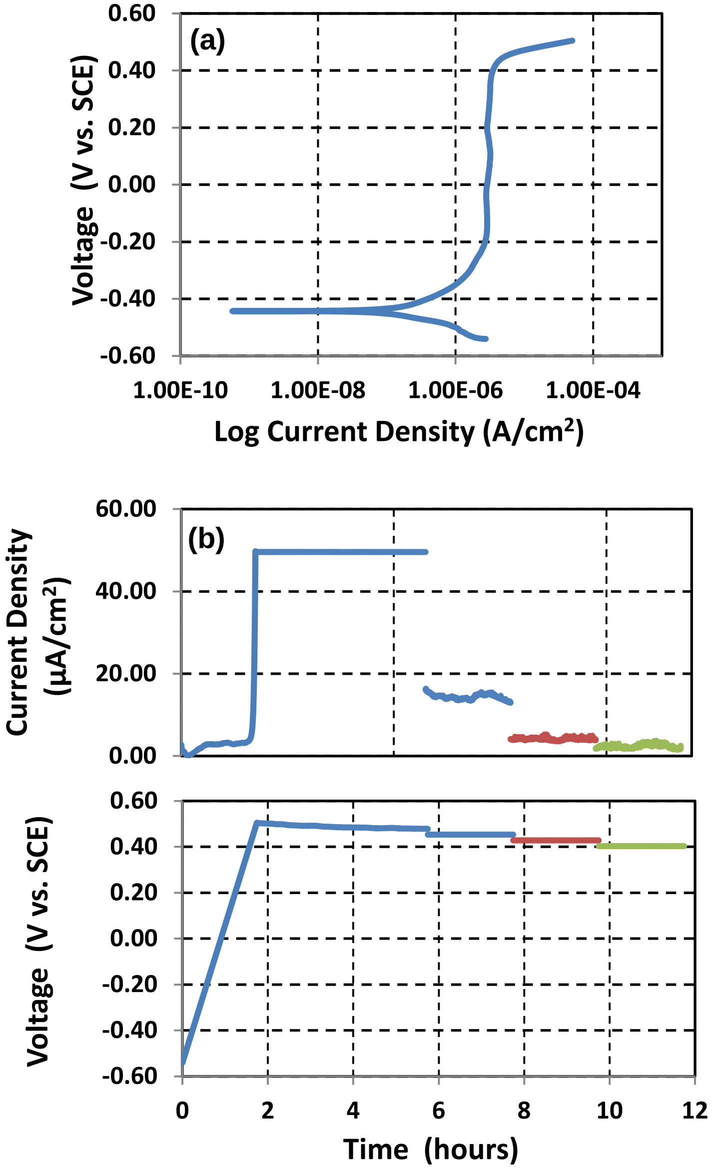

Figure 5: Potentiodynamic (a) and G192 test plot (b) for conditions described in Test 22

Table 6: Results from CPP tests

Test	Hysteresis	Logistic Approach	Pitting on Sample?
1	Negative	Pass	No
2	Negative	Pass	No
3	Negative	Pass	No
4	Negative	Pass	No
5	Negative	Pass	No
6	Mixed	Fail	Yes
7	Negative	Pass	No
8	Mixed	Fail	Yes
9	Negative	Pass	No
10	Negative	Pass	No
11	Negative	Pass	No
12	Negative	Pass	No
13	Negative	Pass	No
14	Mixed	Fail	Yes
15	Negative	Pass	No
16	Negative	Pass	No
17	Mixed	Fail	Yes
18	Negative	Pass	No
19	Negative	Pass	No
20	Negative	Pass	No
21	Negative	Pass	No
22	Mixed	Pass	No
23	Negative	Pass	No
24	Negative	Pass	No
25	Positive	Fail	Yes
26	Positive	Fail	Yes
27	Positive	Fail	Yes

Table 6 shows the results of the 27 tests with type of hysteresis, pass or fail determination in logistic approach mode and if the specimen showed pits. Only 6 cases were fails and from those only 3 were definite fails showing open-loop positive hysteresis. Using multiple regression, least squared analysis a linear model fit was developed for the logistic approach from the combined results of Plackett-Burman and Box-Behnken with the augmented design model for 1.2 M hydroxide. The linear coefficients and p values are shown in Table 7. The significance of the variable was determined using T statistics, where coefficients with p values less than 0.05 are considered statistically significant. The statistically significant coefficients continue to be nitrite, chloride, nitrate and hydroxide (shaded in gray) compared to previous paper[3].

Table 7: Coefficients for Equation 1 fit to the combined statistical analysis test matrices.

Species	Coefficient	P value
Intercept	-0.78	0.8424
Nitrite (M)	3.79	0.0126
Chloride (M)	-20.98	0.0005
Nitrate (M)	-1.38	0.0022
Hydroxide (M)	9.12	0.0003
Sulfate (M)	15.75	0.0875
Temperature (°C)	0.020	0.8424

The coefficients also indicate if the chemical species is an inhibitor or aggressive species. If the coefficient is positive, the chemical species inhibit localized corrosion towards carbon steel and if it is negative, it is considered and aggressive species. Analyzing the statistical model with only the significant variables, new coefficients are obtained. The coefficients are shown in Table 8. Equation 3 was defined as the critical pitting ratio,

$$\text{Critical Pitting Ratio}: \frac{\text{Inhibitor species}}{\text{Aggressive species}} = \frac{6.2[OH^-]+2.4[NO_2]}{[NO_3]+15.3[Cl^-]} \tag{3}$$

where a ratio higher than 1 indicates dominance of inhibitor species and no predisposition to pit and a ratio lower than 1 indicates dominance of aggressive species, therefore the specimen may pit.

The critical pitting ratio was calculated for each of the 27 tests of the test matrix. The calculated value is presented in Table 9 and a comparison with the prediction from the pitting ratio and the actual test result was made. In 25 of the 27 cases (93% correct), the critical pitting ratio criteria were correct. Also in one of those instances the pitting critical ratio is very close to 1. This clearly indicates that the critical pitting ratio, using the coefficients of the significant variables, is useful for predicting localized corrosion of carbon steel. Further testing will continue to develop a framework to have higher assurance in the critical pitting ratio and develop more comprehensive chemical control limits.

Table 8: Coefficients for Equation 1 fit using only statistical significant variables to determine critical pitting ratio the combined statistical analysis test matrices.

Species	Coefficient
Nitrite (M)	2.81
Chloride (M)	-17.56
Nitrate (M)	-1.15
Hydroxide (M)	7.12

Table 8: Critical Pitting Ratio calculation and prediction of fail/pass categorization from the augmented statistical analysis test matrix

Test	Pitting Critical Ratio	Predictive Logistic Approach	Match with Logistic Approach?
1	1.98	Pass	Yes
2	1.57	Pass	Yes
3	1.72	Pass	Yes
4	1.53	Pass	Yes
5	0.98	Fail	No
6	1.61	Pass	No
7	1.44	Pass	Yes
8	0.74	Fail	Yes
9	1.22	Pass	Yes
10	1.49	Pass	Yes
11	1.17	Pass	Yes
12	1.54	Pass	Yes
13	1.40	Pass	Yes
14	0.96	Fail	Yes
15	1.44	Pass	Yes
16	1.32	Pass	Yes
17	0.78	Fail	Yes
18	1.60	Pass	Yes
19	1.40	Pass	Yes
20	1.46	Pass	Yes
21	1.50	Pass	Yes
22	1.09	Pass	No
23	1.38	Pass	Yes
24	1.00	Fail/Pass	-
25	0.57	Fail	Yes
26	0.57	Fail	Yes
27	0.57	Fail	Yes

CONCLUSIONS

Electrochemical testing using CPP and ASTM G192 methods was used to define critical chemical concentrations for inhibiting and aggressive species for waste simulants of Hanford tanks. By designing a statistical matrix covering elevated concentration of hydroxides, the test results previously obtained from Plackett-Burman and Box-Behnken matrices were combined to establish the statistical significance of the independent variables. It was determined that nitrate, nitrite, chloride and hydroxide continue to be statistically significant. Using a logistic approach regression model, coefficients were obtained from the statistically significant species. The coefficients were used to obtained a critical pitting ratio relation to identify if carbon steel in the exposed simulant would be susceptible to pitting corrosion. The efficacy of the critical pitting ratio was demonstrated to predict localized corrosion of carbon steel.

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REFERENCES

1. B. S. Holmesmith, “Caustic Limits Report-For Period Ending March 23, 2015”, RPP-13639, Rev. 11, Washington River Protection Solutions, Richland, WA, July 2015.
2. L. M. Stock, J. R. Follett, and E. C. Shallman, “Specifications for the Minimization of the Stress Corrosion Cracking Threat in Double-Shell Tank Wastes,” RPP-RPT-47337, Washington River Protection Solutions, Richland, WA, March 2011.
3. R. E. Fuentes, B. J. Wiersma, K. D. Boomer and A. J. Feero, “Inhibition of Pitting Corrosion in Simulated Liquid Radioactive Waste”, CORROSION/2017, Paper No. 9689, NACE International, Houston, TX, 2017.
4. ASTM Standard G5-14, “Standard Reference Test Method for Maiking Potentiostatic and Potentiodynamic Measurements”, West Conshohocken, PA.
5. ASTM Standard G192-08 (2014), “Standard Test Method for Determining the Crevice Repassivation Potential of Corrosion-Resistant Alloys Using a Potentiodynamic-Galvanostatic-Potentiostatic Technique”, West Conshohocken, PA.
6. S. Tsujikawa and Y. Hisamatsu, Corrosion Engineering (Japan), 29, 37 (1980).