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Pitting Factor Criteria for localized corrosion inhibition of liquid radioactive waste stored in Hanford double shell tanks

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ABSTRACT

Liquid radioactive waste stored in carbon steel double shell tanks (DSTs) at Hanford has a comprehensive chemistry control program to prevent general corrosion, stress corrosion cracking (SCC) and other types of localized corrosion. Currently, the chemistry control program inhibits general corrosion and localized corrosion due to nitrate concentrations using sodium hydroxide to raise pH over 12. However, future streams may increase the concentration of aggressive species (e.g., chloride, fluoride, and sulfate) and may decrease the pH of the waste to 10. Using a statistically designed matrix of cyclic potentiodynamic polarization (CPP) tests, the chemistry control program is being optimized. Additionally, immersion tests were performed to measure open circuit potential (OCP) and weight change corrosion rates for partially and completely immersed coupons. Pitting factor criteria of 1 to 2 representing borderline conditions were studied to provide limits for the chemistry control program.

Key words: electrochemical testing, pitting corrosion, Hanford, liquid radioactive waste

INTRODUCTION

Several millions of gallons of radioactive waste are currently stored in single shell tanks (SSTs) and double shell tanks (DSTs) at Hanford Site in Washington State, USA. The underground tanks were fabricated of carbon steel. Liquid waste stored in the waste tanks will be retrieved for stabilization into a glass form for permanent storage. However, construction on the large-scale vitrification facility to manage operations for waste will take decades before coming online.[1] The slow progress of developing the vitrification facility, will extend the SSTs and DSTs service lifetimes that already have reached over 60 years for oldest SSTs. To maintain tank integrity, the tanks have a comprehensive corrosion control and monitoring program to mitigate potential corrosion mechanisms.

The liquid waste is currently being inhibited by maintaining alkaline conditions using sodium hydroxide and the reliance upon radiolysis that converts the aggressive specie, nitrate, into the inhibiting specie, nitrite. A set of limits have been obtained and were presented in a previous publication.[2] Currently waste at the tanks are maintained above 1 M hydroxide to help mitigate stress corrosion cracking (SCC), general and pitting corrosion, and the temperatures are lower than 50 °C.[3]

The SSTs liquid waste of suspected tanks that leaked have been transferred to DSTs and this waste may have impacted waste chemistry already in DSTs. 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. Additionally, the waste will need to be inhibited and continuously monitored due to the chemical and/or radiolytic reactions that may occur inside the tank. For this reason, the corrosion control program is being revised to ensure it can continue to inhibit corrosion degradation mechanisms, be more comprehensive for anticipated changes that can occur in the waste and to extend service lifetimes of the tank until eventual removal of waste and closure.

Testing was performed to determine the limits for pitting corrosion and results were presented in previous papers.[2,4] This paper serves as a continuation of that work in which a corrosion critical ratio or pitting factor (PF), as it will be referred in this document, was determined and validated with statistical analysis. Additional testing was performed including long term immersion tests of partially and completely immersed coupons that will be described. The goal is to develop a more inclusive chemical control program for prevention of localized forms of corrosion, which can affect the integrity of the tanks and cause leaks. The PF would be utilized as a tool for setting corrosion control limits based on concentration of statistical significant species.

EXPERIMENTAL PROCEDURE

Materials Tested

Carbon steel coupons, fabricated from Association of American Railroads(1) Tank Car (AAR TC 128) steel, were used for the tests. This steel 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 material was used in two forms: in coupons of dimensions 2 inch (5.08 cm) long, 1 inch (2.54 cm) wide and 0.063 inch (0.16 cm) thick (Metal Samples CO101(3)) for immersion testing; and "bullet" electrodes with dimensions 0.188 inch (0.477 cm) diameter and 1.25 inch (3.175 cm) long (Metal Samples EL400(4)) for electrochemical testing. Table 1 shows the chemical composition of the steel. 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 1: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

Solutions Tested

Simulants with reagent grade chemicals were prepared. The chemicals used are listed in Table 2. Sodium bicarbonate was only added when the pH was adjusted to 10.

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(1) Association of American Railroads, 425 3rd Street SW, Washington, DC 20024

(2) ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959

(3) Trade name

(4) Trade name

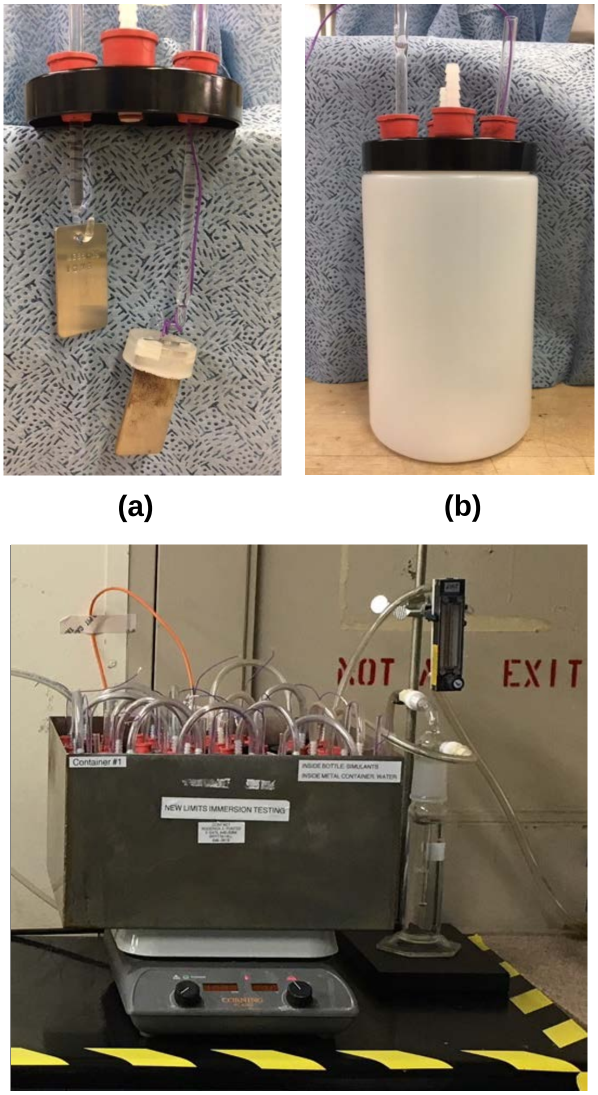
Table 2: Chemicals used in Simulants.

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

Immersion testing

One (1) L capacity polypropylene (PP) bottles were used. The caps of the bottles were modified to maintain corrosion test specimens, provide humidified air flow and to insert reference electrode, pH and temperature probes at given times. . Two coupons were tested in each bottle. One coupon was connected to a purple wire and mounted with epoxy (EpoKwick® from Buehler). Open Circuit Potential (OCP) measurements were measured from the completely immersed coupon. The other coupon was partially immersed to investigate the corrosion behavior at the Liquid Air Interface (LAI). The coupons were polished to a 600-grit finish and prior to immersion, they were rinsed with distilled water and acetone. Figure 1(a) shows a picture of the coupons mounted on a glass holder for partial and complete immersion. This configuration was placed in the PP bottle as shown in Figure 1 (b). In each of the PP bottles, 600 mL of the simulant was added. The PP bottles were placed in a water bath inside a stainless-steel container. The container was placed on top of a hotplate for temperature control. Temperature was maintained at 35 °C. Air was supplied at a flow rate of 10 sccm to a bubbler that humidified the air and circulated it through the PP bottles. Figure 1 (c) displays all the PP bottles that were placed in the water bath. Styrofoam pellets, which floated on the water, were used to minimize water evaporation. Steady state conditions were maintained for four months. Water was added periodically to the bath to maintain the same level. Make-up distilled water was added occasionally to the PP bottles to maintain the LAI level. At the end of testing the coupons were removed and cleaned using ASTM G1[5] C.3.1 solution to obtain weight losses and to inspect visually for areas of corrosion.



(a) (b)

(c)

Figure 1Immersion test setup showing (a) the configuration of the coupons for LAI and complete immersion, (b) the coupons inside the PP bottle and (c) the stainless-steel vessel on top of hot plate and water bubbler for delivering humidified air.

Electrochemical testing

An electrochemical cell with a one (1) L volume capacity was used. The glass cell consisted of two graphite rods used as a counter electrode, a saturated calomel electrode (SCE) used as a reference electrode and a glass holder with the carbon steel electrode used as the working electrode. Approximately 700 mL of simulant was added to the electrochemical cell to conduct a test. Each test was replicated with a different working electrode and fresh solution. The cell was placed on a hotplate with a thermocouple for controlling the temperature to 35 °C. A potentiostat was used to perform the electrochemical testing and prior to use, it was qualified by performing ASTM G5 standard.[6] The electrochemical test protocol consisted of a two-hour OCP monitoring period, followed by cyclic potentiodynamic polarization (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. The potential was returned to OCP to complete the test. In some cases where the CPP test did notprovide a conclusive repassivation potential, as in the case of mixed hysteresis, a modified ASTM G192[7] test for pitting corrosion in carbon steels[8] 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 being manually stopped either because 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 potential at which the current density was less than the forward scan passive current density was defined as the repassivation potential and it was considered a pass if the repassivation potential was found to be higher than 200 mV vs. OCP. On the other hand, if the current density exceeded the passive current density and approached the initial OCP, the test was determined to be a fail.

Statistical design for electrochemical testing

The statistical design and analysis criteria for the tests were detailed in an earlier publication.[2] The binary response for logistic approach of pass or fail from CPP results was utilized again as the dependent variable. The concentration of species including hydroxide, nitrate, nitriteand chloride were the independent variables since they were statistical significant for localized corrosion.[2]

RESULTS

Electrochemical testing, using interior points determined by statistical design, are presented in Table 3. The interior points consisted of additional 15 tests, which were also compositions utilized for the coupon tests. The hydroxide level at 0.0001 M indicates a pH of 10, which was adjusted by adding sodium bicarbonate. After testing, 7 of those tests indicated a pass. Hysteresis is used to identify the CPP response and was explained in previous paper.[2] For this publication, mixed hysteresis with a asterisk (*) was used to identify a positive hysteresis with a closed loop. The logistic approach was added to previous statistical analysis of Plackett-Burman and Box-Behnken designs and the augmented statistical design.[2] From the total of 95 tests, a linear regression model fit was developed. The obtained PF is shown in Equation 1.

$$\text{PF}: \frac{\text{Inhibitor species}}{\text{Aggressive species}} = \frac{8.5[\text{OH}^-]+2.4[\text{NO}_2]}{[\text{NO}_3]+19.6[\text{Cl}^-]} \quad \textbf{(1)}$$

Table 3: Test conditions and results of testing using statistical approach from interior points

Test	Hydroxide (M)	Nitrite (M)	Nitrate (M)	Chloride (M)	Sulfate (M)	Carbonate (M)	Bicarbonate (M)	CPP Hysteresis	Logistic Approach	Pitting on Sample?
1	0.3	1.2	0	0	0.2	0.1	0	Negative	Pass	No
2	0.3	0	0	0	0	0.1	0	Negative	Pass	No
3	0.3	1.2	0	0.4	0.2	0.1	0	Positive	Fail	Yes
4	0.3	1.2	0	0	0	0.1	0	Negative	Pass	No
5	0.3	1.2	5.5	0.4	0	0.1	0	Positive	Fail	Yes
6	1.2	1.2	0	0	0.2	0.1	0	Negative	Pass	No
7	0.3	0	5.5	0.4	0.2	0.1	0	Positive	Fail	Yes
8	0.3	0	5.5	0.4	0.2	0.1	0	Positive	Fail	Yes
9	0.3	0	5.5	0.4	0.2	0.1	0	Positive	Fail	Yes
10	0.3	0	0	0.4	0	0.1	0	Mixed	Fail	Yes
11	0.0001	1.2	0.8	0	0.2	0.075	0.025	Negative	Pass	No
12	0.0001	0.9	0.6	0.025	0.16	0.075	0.025	Negative	Pass	No
13	0.0001	0.6	0.4	0.05	0.12	0.075	0.025	Mixed*	Pass	Yes
14	0.0001	0.3	0.2	0.075	0.08	0.075	0.025	Positive	Fail	Yes
15	0.0001	0	0	0.1	0.04	0.075	0.025	Positive	Fail	Yes

*positive hysteresis with closed loop

A PF greater than 1 indicates that there is less susceptibility to localized corrosion and a PF less than 1 indicates the contrary. The PF was utilized to predict the outcomes of the coupon immersion tests. The 10 conditions that were determined to test are listed in Table 4. Each condition was tested in a PP bottle and maintained for four months at steady-state conditions.

Table 4: Test conditions and pitting factor obtained for the immersion tests

Test	Hydroxide (M)	Nitrite (M)	Nitrate (M)	Chloride (M)	Sulfate (M)	Carbonate (M)	Bicarbonate (M)	PF
1	0.0001	0	0.153	0.049	0.2	0.075	0.025	0.001
2	0.0001	0.6	0.154	0.050	0.2	0.075	0.025	1.28
3	0.0001	1.2	0.023	0.058	0.2	0.075	0.025	2.49
4	0.0001	1.2	0.797	0.005	0.2	0.075	0.025	3.23
5	0.1	0.6	0.452	0.073	0.2	0.1	0	1.22
6	0.1	1.2	0.076	0.094	0.2	0.1	0	1.95
7	0.3	0	0.715	0.135	0.2	0.1	0	0.76
8	0.3	1.2	2.201	0.042	0.2	0.1	0	1.80
9	0.6	0	2.444	0.144	0.2	0.1	0	0.97
10	0.6	1.2	4.224	0.018	0.2	0.1	0	1.75

Figure 2 shows the OCP transients during the four months. As observed the most active OCP was maintained at a range of -440 to -495 mV vs SCE for Solution 1. Most of the OCP transients were maintained at a range of -200 to -400 mV mV vs. SCE. There were two instances in which the OCP started to drift in the noble potential direction but after approximately 600 hours quickly shifted to more negative potentials and were in the same range as others (Solutions 3 and 6).

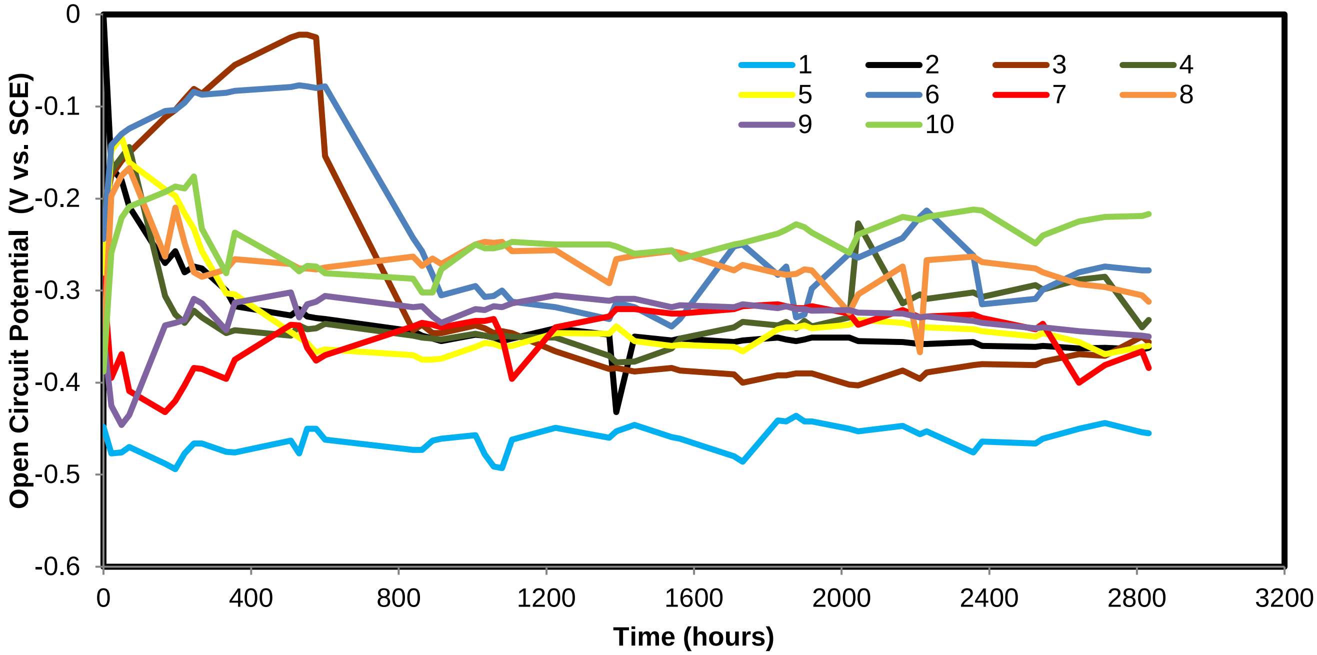
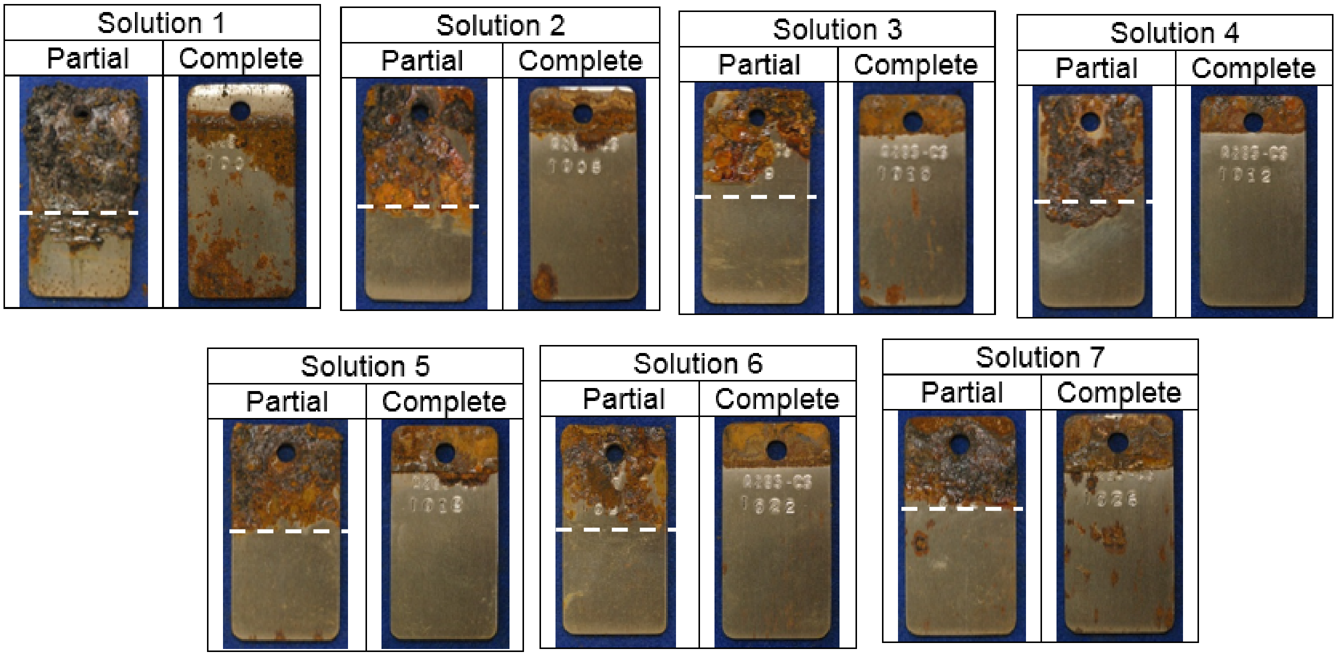
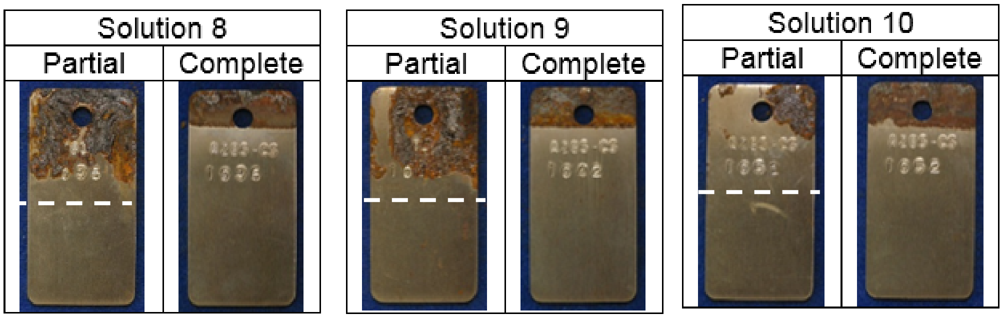


Figure 2: OCP transients versus time of completely immersed coupons in solution

After four months, the coupons were removed from solution. The mounted coupons with the wire were removed from the epoxy and pictures were taken. Pictures of the partially and completely immersed coupons are shown in Figure 3. The coupons were classified as high and low corrosion sustained. All partially immersed coupons showed the appearance of vapor space corrosion and the completely immersed coupons showed crevice corrosion attack in the mounted area. The coupons exposed in solution 1 had the highest level of corrosion. In particular, the coupon partially immersed showed a very aggressive LAI and vapor space attack. In contrast, the coupons exposed in solution 10 had the lowest level of corrosion. This correlates to the OCP transient observed in Figure 2, which the most noble corresponded to solution 10 and the most active corresponded to solution 1. This result was expected given the low inhibitor level in solution 1 and the high inhibitor level in solution 10. Or stated another way, the low pitting factor for solution 1 produced a high degree of corrosion, while the high pitting factor for solution 10 produced a low degree of corrosion.



High Corrosion



Low corrosion

Figure 3: Pictures of partial and complete immersed coupons after long term testing prior to cleaning

Corrosion rates were calculated using the mass loss of the coupons and the complete area of the coupon. The results are listed in Table 5. It was noted that coupons subjected at a partial level had higher corrosion rates from the testing than completely immersed. This was likely due to two factors: 1) depletion of hydroxide inhibitor at the liquid air interface, and 2) condensation of water in the vapor space and correlates to a more aggressive LAI and vapor corrosion attack than immersed. The corrosion rates for solution 1 correlated well with the OCP transients, as they were 13.13 and 1.86 mpy for the partially and completely immersed coupon, respectively. In addition, the lowest corrosion rates were observed for Solution 10.

Table 5: Mass loss and corrosion rates of partial and complete immersed coupons

Test	mass loss (g)		Corrosion rate (mpy)	
	Partial	Complete	Partial	Complete
1	2.4015	0.3402	13.13	1.86
2	0.7999	0.0601	4.37	0.33
3	0.4572	0.0552	2.50	0.30
4	0.2141	0.0413	1.17	0.23
5	0.4122	0.0796	2.25	0.44
6	0.4030	0.0314	2.20	0.17
7	0.3663	0.0516	2.00	0.28
8	0.1118	0.0133	0.61	0.07
9	0.1882	0.0170	1.03	0.09
10	0.0461	0.0057	0.25	0.03

Borderline conditions were observed in cases where pitting factor is between 1 and 2 in most of the testing with a mixed hysteresis result in CPP tests. Because of the mixed hysteresis, it is difficult to assign a pass or fail criterion and a modified ASTM G192 test was performed as a result. To investigate this range, 15 tests were selected with the corresponding PF between 1 and 2 and greater than 2, and hydroxide concentrations from 0.0001 M (i.e., pH 10) to 0.6 M. The concentration of species as well as the response in CPP tests are summarized in Table 6. Sodium sulfate and Total Inorganic carbon (TIC) were maintained at 0.2 and 0.1 M, respectively. As before, the modified G192 test was utilized to interpret the mixed hysteresis result to determine if a condition was a pass.

Table 6: Test conditions and results of testing from selected test with PF between 1 and 2 and above

Test	Hydroxide (M)	Nitrite (M)	Nitrate (M)	Chloride (M)	PF	CPP Hysteresis	Logistic approach	Pitting on Sample?
1	0.0001	0.6	0.3	0.04	1.33	Mixed	Pass	Yes
2	0.0001	1.2	0	0.05	2.94	Positive	Pass	Yes
3	0.0001	1.2	2	0	1.44	Mixed	Pass	Yes/No
4	0.1	0	0.2	0.02	1.44	Mixed*	Fail	Yes/No
5	0.1	0.6	0.3	0.06	1.55	Negative	Pass	Yes/No
6	0.1	1.2	0.5	0.05	2.52	Mixed*	Pass	No
7	0.1	1.2	2.5	0.005	1.44	Mixed	Pass	Yes/No
8	0.3	0	0.1	0.08	1.53	Negative	Pass	No
9	0.3	0.6	0.07	0.1	1.97	Mixed*	Pass	Yes
10	0.3	1.2	0.5	0.15	1.58	Negative	Pass	Yes/No
11	0.3	1.2	2.5	0.05	1.56	Mixed	Pass	No
12	0.6	0	0.6	0.05	3.23	Mixed	Pass	Yes/No
13	0.6	0.6	0.001	0.25	1.33	Mixed*	Pass	Yes
14	0.6	1.2	0.001	0.3	1.36	Negative	Pass	No
15	0.6	1.2	5.5	0.01	1.40	Negative	Pass	Yes/No

*positive hysteresis with closed loop

For tests between PF 1 and 2 and slightly above, 9 of the 15 results showed mixed hysteresis with 7 of those results resulting in samples that pitted and did not pit during duplicate runs. After running modified ASTM G192 tests, most of the tests showed a passing category with just one fail. Even though, the use of a modified ASTM G192 test was needed for determination of pass or fail, it seems that for PF higher than 1, a pass is the most likely response with above 90% of success for the 15 tests performed.

CONCLUSIONS

Electrochemical tests, and long-term (up to four months) immersion testing, with partially and completely immersed coupons were utilized to determine the susceptibility to carbon steel pitting corrosion in a radioactive waste environment. The partially immersed coupons were used to investigate corrosion at the liquid air interface. It was observed that coupons exposed at the liquid air interface had corrosion rates by a factor of 7 times higher than its counterpart that was completely immersed, for the case of solution 1, which is is low on nitrite and hydroxide. The OCP trends show significant activity during the complete four months for this solution while others were kept between a range of -200 to -400 mV vs. SCE during most of the exposure. The PF was re-calculated using a total of 95 tests including 15 interior points tests that were described in this publication. In comparison, with the previous equation obtained, only the coefficients corresponding to hydroxide and the chloride increased slightly. However, there was not a significant effect in prediction of susceptibility towards localized corrosion. The PF showed a prediction of 93% of the 95 tests performed. This high percentage continues to provide confidence for the efficacy of the PF to predict localized corrosion susceptibility for the waste chemistry. The results of the tests indicated that conditions with PF greater than 2 typically benign toward carbon steel, while at conditions with PF less than 1 the material is susceptible to pitting. For PF between 1 and 2, the behavior is marginal although most of the tests indicated a benign condition per the modified ASTM G192 test.

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