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Development of a Corrosion Control Program for Liquid Radioactive Wastes Stored in Carbon Steel Waste Tanks

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ABSTRACT

Large underground, carbon steel tanks are used for interim storage of liquid radioactive waste at the Hanford site. The Hanford Waste Treatment and Immobilization Plant (WTP) is being constructed to treat the high-level waste (HLW) and low-activity waste (LAW) stored in the tanks. Secondary waste will be generated by condensation and scrubbing of the LAW melter off-gas stream. A portion of this stream, which will contain substantial amounts of chloride, fluoride, ammonia, and sulfate ions, may be returned to the tank farms for storage and evaporation. Presently, there are no restrictions on the halide or sulfate concentrations of this return stream prior to transferring to the carbon steel waste tanks. Prior to initiating the process, the current corrosion control program needs to be updated to account for the susceptibility to pitting corrosion of waste tanks due to the halide content of the secondary waste. Cyclic potentiodynamic polarization tests were utilized to determine the nitrite inhibitor requirements needed to safely receive and store the secondary waste.

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

INTRODUCTION

Weapons, space and medical research programs led by the U. S. Department of Energy have created a legacy of nuclear waste over the past 70 years. At the Hanford site in Richland, WA, the liquid waste is being stored on an interim basis in 149 single shell tanks (SST) and 28 double shell tanks (DST). The final disposition of the liquid waste into a solid vitrified form will likely take several more decades. Understanding potential degradation mechanisms is a key to preserving the structural and leak integrity of the waste tanks, particularly the DSTs, until final disposition of the waste. Presently, the site implements a corrosion control program to maintain the waste chemistry within requirements that mitigate corrosion mechanisms such as stress corrosion cracking, pitting and general corrosion.

With the eventual start-up of the Hanford Waste Treatment and Immobilization Plant (WTP), secondary wastes generated during the Direct Feed Low Activity Waste (DFLAW) portion of the mission may be returned to the DSTs. The tank farm facility is reviewing and evaluating material balance projections to determine the impact of these processes on the waste chemistry. Initial projections suggest that the waste chemistry of the receiving DSTs may shift to a broader range of pH and higher aggressive anion concentrations (e.g., chloride, sulfate, etc.) than the waste compositions that are presently stored. Therefore, in conjunction with this evaluation, a corrosion control program is being developed to ensure that it is robust and can adjust to these anticipated changes.

The present corrosion control program mitigates corrosion of carbon steel due to the nitrate ion by addition of sodium hydroxide to the tanks to raise the pH of the waste and reliance upon radiolysis to deplete the nitrate ion to the nitrite ion, which inhibits corrosion. The inhibitor requirements are exhibited in Table 1. These limits were developed based on laboratory testing that evaluated specific corrosion mechanisms. For nitrate concentrations greater than 1 M, the primary concern is stress corrosion cracking and general corrosion, while for nitrate concentrations less than 1 M pitting and general corrosion are primary corrosion mechanisms of concern. The return waste streams from the WTP are anticipated to contain up to 0.65M chloride ion and 0.25 M fluoride ions and low nitrate ions (<0.82 M nitrate). The testing presented in this paper focuses on determining the inhibitor requirements of the high chloride waste stream compositions that will be returned to the carbon steel DSTs. Previous work[1], indicated the halide control equations for similar waste streams used currently at the Savannah River Site (SRS) are not applicable for the much higher chloride concentrations returned to the tank farm. When extrapolated above the developed SRS limit, the SRS specification over-estimates the amount of nitrite needed to inhibit pitting for the amount of halide predicted to be present in the DFLAW secondary waste.

The work presented in this paper focuses on defining a corrosion model for the anticipated WTP returns that will provide protection from halide pitting corrosion. This was accomplished by employing statistical test matrices and regression analysis to determine the dependent variables and significance of the variables in the recycle steam as they relate to pitting corrosion using cyclic potentiodynamic polarization (CPP) tests.

Table 1.
Hanford Double-Shell Tank Waste Corrosion Chemistry Specification for Nitrate Corrosion Control.

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

EXPERIMENTAL PROCEDURE

Materials Tested

The coupons were fabricated from Association of American Railroads (1) Tank Car (AAR TC) 128 Steel. This steel was selected for testing since it approximates the chemistry and microstructure of UNS K02401 [i.e., American Society for Testing and Materials (ASTM)(2) A515 Grade 60 carbon steel], the steel from which the tanks were fabricated.[2] The AARTC 128 steel was also selected because it was of the same vintage as the tank steel. The chemical composition of the steel is shown in Table 2. The yield strength for the material was greater than 380 MPa and the ultimate tensile strength was greater than 550 MPa. All elemental compositions except for Mn and Si meet the ASTM A515 specification. The Mn is greater than the maximum allowed of 0.9 wt.%, while the Si is less than the required range. The higher Mn could explain the higher than specified tensile properties (e.g., ultimate strength required to be between 415 MPa to 550 MPa).

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

Figure 1 shows the microstructure of the rail car steel as exhibited in the longitudinal and transverse orientation. A banded, ferrite/pearlite matrix was observed. The transverse orientation also exhibited several inclusions, likely manganese sulfide inclusions.

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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

(a) (b)

Figure 1: Microstructure of AAR TC Steel (a) longitudinal, (b) transverse.

Solutions Tested

The secondary waste returned to the DSTs is projected to have a wide range of compositions that results from the range of compositions of the waste treated and immobilized in the DFLAW flowsheet. This range directly impacts the composition of return streams to tank farms. Based on the flowsheet model results received from Hanford tank farms and the WTP Contractors, the composition ranges in Table 3 were used for testing. These values include a ±30% of the maximum and minimum values for the aggressive species (+30%) and inhibitor species (-30%). The tests were conducted at pH of 10 and 40°C.

Table 3.
Variables and Constants for Anticipated Stream Conditions

Independent variable			Dependent Variables	Constants	
	Minimum	Maximum	E_{rp} (V)	Potassium (M)	0.01
Sulfate (M)	0.0	0.45	E_{corr} (V)	pH	10
Chloride (M)	0.01	1.63	E_{rp} - E_{corr} (V)	Temperature (°C)	40
Fluoride (M)[a]	0.0	1.04			
Nitrite (M)	0.0	4.0			
Nitrate (M)	0.01	2.6			
Carbonate (M)[b]	0.0	0.07			
Phosphate (M)[b]	0.0	0.013			

[a] Fluoride was omitted in later test matrices due to solubility issues at high concentration.

[b] These constituents were held constant at the midpoint concentrations for the Box-

Behnkin Test Matrix at 0.035 M for Carbonate and 0.013 M for Phosphate .

Sample Mounting

Carbon Steel electrodes were fabricated to an EL-400 “bullet” design. The electrode is a cylinder 1.250 in. (3.175 cm) in length, 0.188 in. (0.478 cm) diameter, with a hemi-spherical (round) end, with an area of 0.736 in^2 ($4.74 cm^2$). The electrode was mounted using a threaded rod of 316 stainless steel sheathed in a glass tube sealed with a Teflon seal between the electrode and the glass sheath.

Test Apparatus

A 1-liter PAR type cell is used for the test vessel, fitted with two ¼-inch diameter carbon counter electrodes and saturated calomel reference electrode contain in a luggin salt bridge.

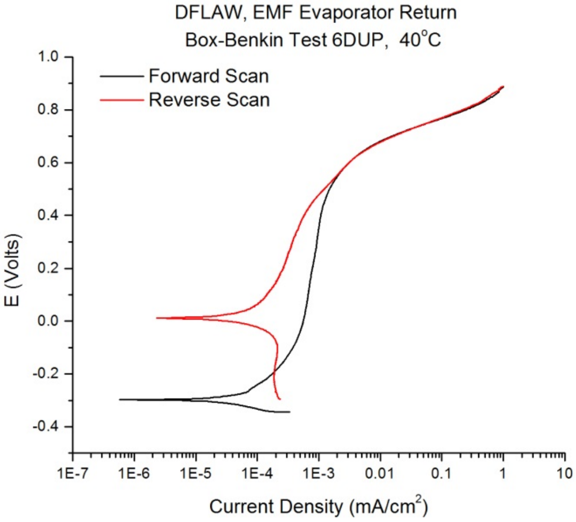
Electrochemical Testing and Analysis

Cyclic Potentiodynamic Polarization (CPP) tests were performed using parameters similar to the ASTM-G 61 method[3] that have been specified for the Hanford corrosion testing protocol.[4] The testing protocol requires a 2-hour rest period before polarizing the electrode at a scan rate of 0.167 mV/second from 50 mV below the measured open circuit potential until a current density of 1 mA/cm^2 is achieved. The scan potential is then stepped down at the same rate until the open circuit potential is reached. All potential measurements are made with respect to a saturated calomel reference electrode.

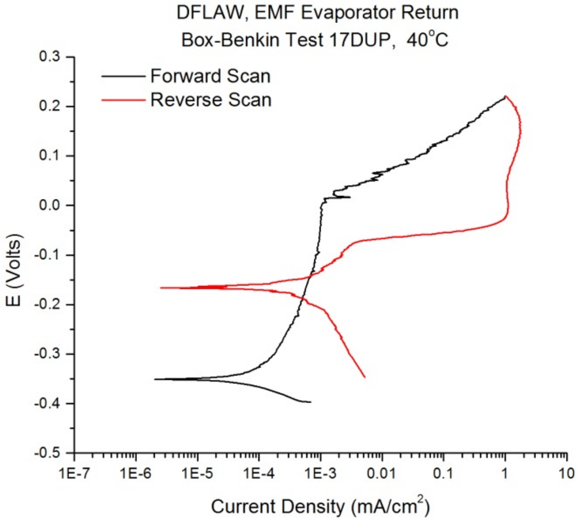
STATISTICAL DESIGN OF TESTS

An experimental test matrix of 19 tests was formulated using a constrained Plackett-Buman statistical design.[5] The results from this test were used to design a second experimental matrix of 28 tests to refine the model and estimate the interaction terms between the variables. The second experimental matrix was designed using a Box-Behnkin statistical design.[6] CPP tests were carried out using the Hanford testing protocol and the results were interpreted using that protocol. The CPP classified based on hysteresis of the curve and the difference between the corrosion potential (E_{corr}) and the repassivation potential (E_{rp}), E_{rp}-E_{corr}, if available. Figure 2 shows the classifications of the CPP curves into by passing, failing, and borderline results. The CPP results in Figure 2a and 2b are considered non-pitting and passing, respectively. Although Figure 2b initially has a higher return current, the repassivation potential is significantly greater than E_{corr}, such that risk of significant pit propagation is minimal by program definitions.[4] Figure 2c is a borderline result and ASTM G 192 test is performed at these test conditions to determine the protection potential.[7] If the ASTM G 192 results in a protection potential that is 200 mV above the corrosion potential (E_{corr}) then test is considered as a passing condition.[8] Figures 2d-f show a pitting or failing condition. The main difference between 2b and 2d is the difference in E_{rp}-E_{corr}. In this case if the difference is less than 200 mV then the curve is considered show a failing condition.

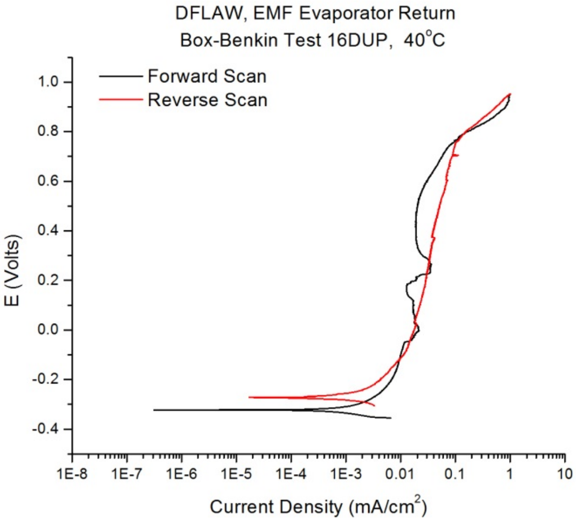
a. Non-pitting



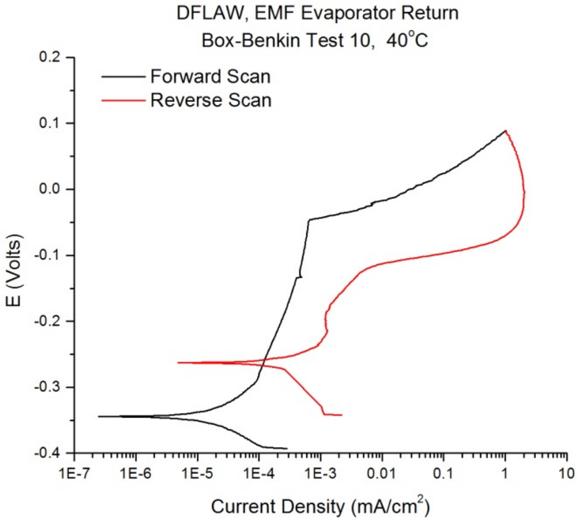
b. Passing



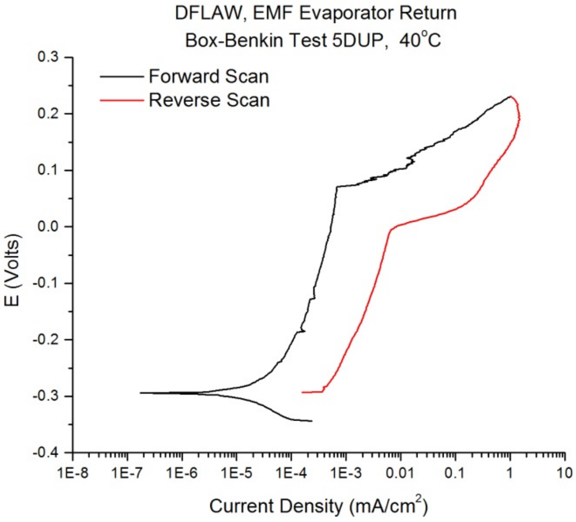
c. Borderline



d. Pitting



e. Pitting



f. Pitting

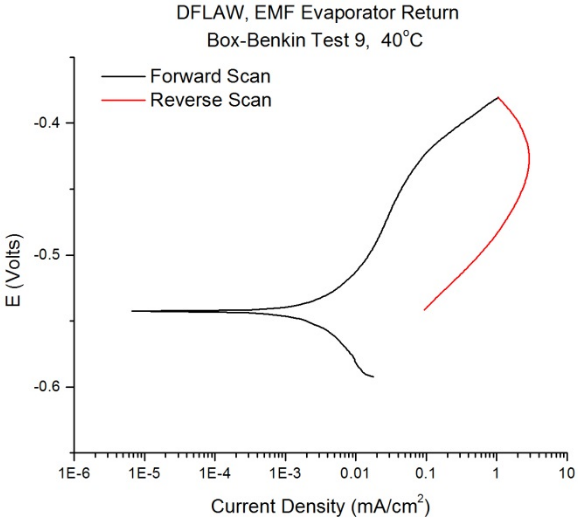


Figure 2. Cyclic Potentiodynamic Polarization Curves showing passing, failing, and borderline results.

For the purposes of the first data analysis, the values determined for E_{rp}-E_{corr} were assumed to have a normal distribution. A second statistical analysis that utilized a logistic distribution was performed on the data collected during tests. In the latter case, the data was treated as either a pass or a fail based on the criteria outlined by the test protocol.[4] The CPP results were used to determine significant linear terms, and interaction terms (cross-product and squared terms) as part of the statistical analysis.

STATISTICAL ANALYSIS OF RESULTS

Two approaches were utilized for statistical data reduction. A multiple regression, least squares analysis was utilized to model the dependent variable, $E_{rp} – E_{corr}$, as a function of the dependent variables. The Plackett-Burman test seriesprovided a linear equation, while the Box-Behnken series provided an equation with cross-product and squared terms.[5,6]

The second approach is referred to as logistic regression.[9] The logistic regression model differs from the multiple regression analysis in that the outcome variable, for logistic regression is binary. Logistic regression is well suited to these corrosion tests where the binary response is the presence or absence of pitting. The method develops a relationship among the dependent variables to calculate the probability of observing pitting during the test.

RESULTS

The Plackett-Burman test matrix, which was used to determine the significance of the variables, predicted that chloride is the most aggressive ion toward carbon steel and nitrite is the most effective corrosion inhibitor within these test compositions and under these test conditions. These results were as expected based on prior experience.[1,10] Equation 1 shows the linear model and the coefficients are shown Table 4. As expected, the coefficients for the inhibitor species are positive, while the coefficients for the aggressive species are negative. The significance of the variable, as determined by the T statistic, is also shown in Table 4. The T statistic is used to conduct hypothesis tests on regression coefficients obtained in simple linear regression. A statistic based on the t distribution is used to test the two-sided hypothesis that the true slope, B1 equals a constant value, B10. Coefficients with T values less than 0.05 are considered statistically significant.

Equation 1

$$Erp - Ecorr\,(V) = A + B[NO_2^-] + C\,[Cl^-] + D\,[NO_3^-] + E\,[F^-] + F\,[PO_4^{3-}] + G\,[SO_4^{2-}] + H\,[TIC]$$

Table 4.
Coefficients for Equation 1 fit to the Plackett-Burman test matrix results

Species	Coefficient (V)	T Statistic
Intercept	0.16	0.26
Nitrite	0.1	0.0027
Chloride	-0.16	0.0278
Nitrate	-0.051	0.22
Fluoride	-0.17	0.41
Phosphate	5.38	0.49
Sulfate	-0.11	0.66
Carbonate	0.59	0.68

The Box-Behnkin test matrix used the results from the Plackett-Burman test to determine the interaction terms among nitrite, chloride, nitrate, and sulfate (i.e., the more statistically significant variables). The carbonate and phosphate species were found to have little significance on the corrosion of carbon steel, so the concentration values for these compounds were held constant at the respective mid-point concentration. Fluoride was excluded from this test matrix for the following reasons:

- Thermodynamic modeling predicted that fluoride would precipitate with sulfate; this was confirmed by laboratory trials. This constraint complicated the statistical design of the test matrix.
- Literature data and the results from the Plackett-Burman testing indicate fluoride is less aggressive than chloride; when compounded with the limited solubility of fluoride in the more concentrated streams, i.e. evaporator bottom streams, the chloride concentration could be used as a total halide limit.
- Fluoride was found to be only moderately significant in the Plackett-Burman tests.
- Sulfate has been shown to be aggressive toward carbon steel and was only found to be moderately significant in the Plackett-Burman tests. However, this may have been due to the presence of and interaction with fluoride.

The results of the Box-Behnkin and Placket Burman testing were combined to yield a model for E_{rp}-E_{corr}. Two equations fit the data reasonably well. Equation 2 accounts for all the CPP data. All four primary variables appear in the equation (i.e., nitrite, chloride, nitrate, and sulfate). The coefficients in red and bold were the most statistically significant. The fit to the data can be improved by removing 2 statistical outliers. These were two cases where the dependent variable was not replicated (i.e., a significant difference between the values existed). Equation 3 represents for all the CPP data except the 2 statistical outliers. In this case, the halide and nitrite were the most significant variables, and the other coefficients were not statistically significant. The most significant coefficients in Equation 2 (in red) are associated with the same dependent variables as Equation 3.

Equation 2

$$E_{rp} - E_{corr}(mV) = 126 + 271[SO_4^{2-}] - \mathbf{606}[Chloride] + \mathbf{287}[NO_2^-] + \mathbf{330}[Chloride]^2 - \mathbf{127}[Chloride][NO_2^-] - 27[NO_2^-]^2 - 193[SO_4^{2-}][NO_3^-]$$

Equation 3

$$Erp - Ecorr\ (mV) = 111 - 459\,[Chloride] + 171\,[NO_2^-] + 249\,[Chloride]^2 - 124\,[Chloride][NO_2^-]$$

Equations 2 and 3 were used to construct a plot of log nitrite concentration versus log chloride concentration.[11] For E_{rp}-E_{corr} of 200 mV, both equations predict pitting and non-pitting conditions well for all testing to date; Equation 3 provides a slightly better fit to the data from the statistical analysis. The solubility limit of solutions, or Na limit, is represented in the plots in Figure 2 and Figure 3 by the green line. Above this total sodium (Na) limit, precipitation of solid species is expected and would therefore change the composition. When historical data in similar solutions was plotted on the same graph, very good agreement with the model was observed (see Figure 3).[9,12,13] There were a few instances in the historical data set that show pitting in the 0.02M to 0.05M chloride range (half shaded boxes), even when the nitrite concentration is above the requirement for pitting inhibition (see Figure 4). These 7 compositions had a higher nitrate concentration relative to the chloride concentration. This suggests there is a limit to the halide to nitrate ratio; from the historic data it is near 0.62. This limit would signify the transition of dominant corrosion species from the chloride ion to the nitrate ion and is important to recognize. The likelihood of this limit being approached will need to be investigated or monitored closely during plant operation or in plant model runs. If there is a wide variability in the halide to nitrate ratio, then further specifications may be required. This ratio will be investigated during confirmatory testing of the corrosion model equations to better understand whether this is a transition in the controlling aggressive species or a synergistic effect observed between nitrate and chloride.

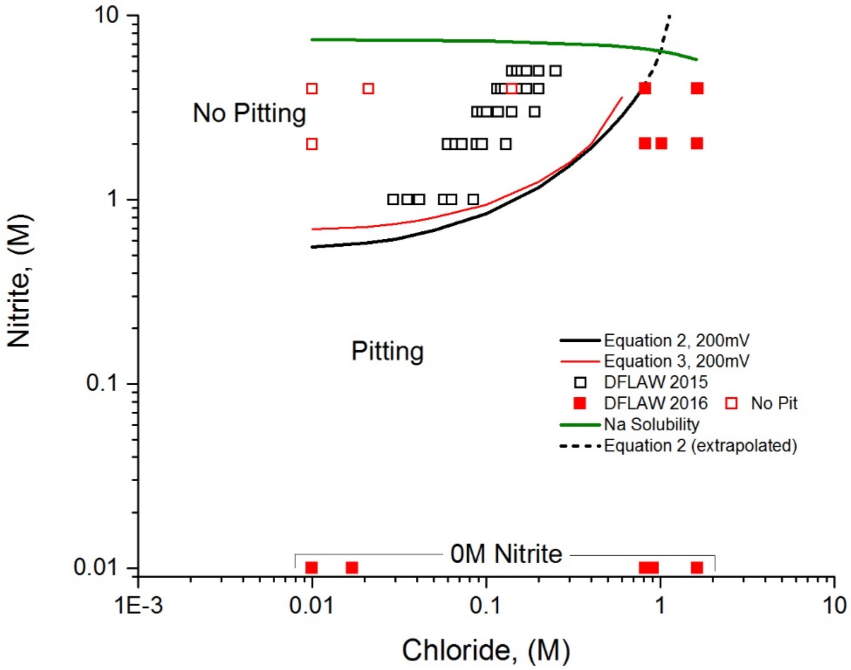


Figure 3. Results of Equations 2 and Equations 3 plotted at 200mV in relation to the DFLAW compositions tested. Open symbols indicate a no pitting condition, while closed symbols indicate a pitting condition.

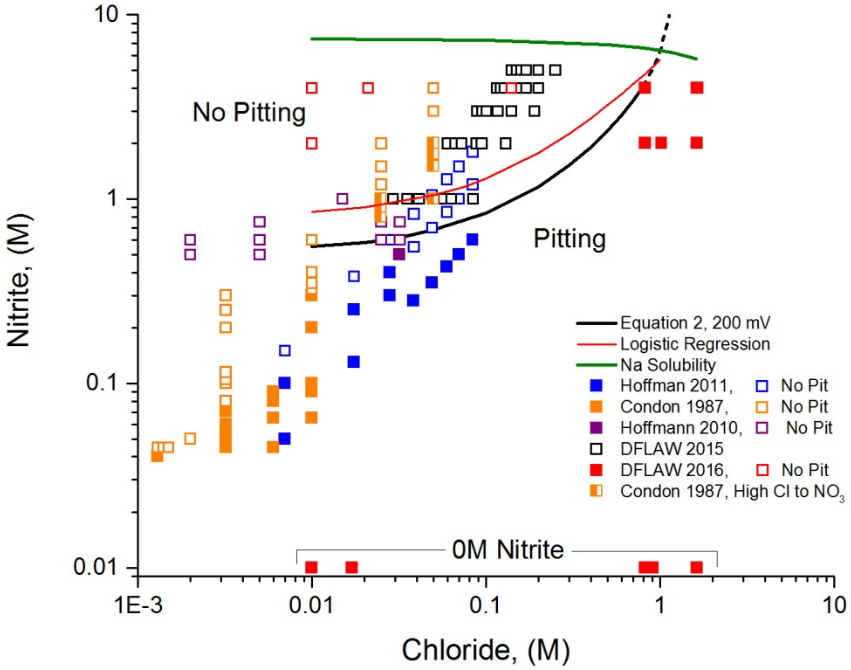


Figure 4. Comparison of historical data with Equation 3 at 200 mV. Open symbols indicate a no pitting condition, while closed symbols indicate a pitting condition.

The logistical regression analysis was applied to the test results. For this testing, the CPP results were considered as either pitting or non-pitting. Regression analysis was only performed on the data points collected from the current tests described in this paper and compared to historical results. As with the previous statistical analysis, chloride and nitrite were the two statistically significant variables in this variable space. The resulting equation is given as Equation 4 at the 0.95 probability for nitrite as a function of halide.

Equation 4

$$[NO_2^-] = 0.805 + 4.868\,[Chloride]$$

The red line plotted in Figure 4 shows the comparison of the logistic model and Equation 2 (black line) that was derived from the Plackett-Burman and Box-Behnkin regression analysis. The logistic regression yields a higher demand for nitrite up to about 1M chloride in comparison to Equation 3 and also predicts some of the results to pit where the testing did not find pitting. Although not defined yet, the confidence limits for each of these models may be rather large and thus overlap between the two models. This model will continue to be refined as testing continues.

CONCLUSIONS

This paper has described the progress of corrosion model development to facilitate the implementation of the DFLAW flowsheet for the Hanford Waste Treatment Plant. A combination of laboratory testing and statistical analysis is being applied to determine the necessary corrosion controls to inhibit corrosion in production waste that may be returned to tank farms from the WTP. Experimental matrices have provided data showing that halide ions are the most aggressive corrosive species in the projected return streams, and nitrite is the most effective inhibitor at pH 10 and 40°C. Statistical regression analysis was utilized to develop an equation that can be used to predict pitting susceptibility. However, additional analysis of the data using logistic regression analysis suggests that alternate methods may provide a more conservative estimate of the corrosion behavior. Future testing is planned to further confirm and refine these models and to investigate optimization of the chemistry controls.

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