

**PROBABILITY BASED CORROSION CONTROL FOR LIQUID WASTE
TANKS- PART III**

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SEPTEMBER 2010

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**Prepared for the U.S. Department of Energy Under
Contract Number DE-AC09-08SR22470**



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Printed in the United States of America

**Prepared for
U.S. Department of Energy**

Key Words:

Pitting
Corrosion
Inhibitor

Retention:

Permanent

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1.0 EXECUTIVE SUMMARY

A series of cyclic potentiodynamic polarization tests were performed on samples of A537 carbon steel in support of a probability-based approach to quantify the risk associated with the chemistry control program for liquid waste tanks. Testing solutions were chosen to build off previous experimental results from FY'07, FY'08 and FY'09 to increase the confidence level in the proposed mixture/amount model. When combining FY'10 results with previous data, the mixture/amount model is capable of predicting up to a 95% confidence level that no corrosion will occur when proper concentrations of nitrate and nitrite are present. The results concur with results of FY'08 and FY'09 in that in the nitrate region of 0.6 M to 1.0 M, the amount of nitrite required to inhibit corrosion decreases with increasing amounts of nitrate. This result, consistent in all three years of risk-based testing, is of importance for the chemistry control program particularly for tanks in which nitrate concentrations cross the 1.0 M threshold.

An additional experimental series was performed to investigate the influence of chloride and sulfate concentrations. The result suggest that chloride and sulfate play a significant role in the corrosion response of A537 carbon steel in the nitrate region of 1.0 M or less.

2.0 INTRODUCTION

The liquid waste chemistry control program is designed to reduce the pitting corrosion occurrence on tank walls. The chemistry control program has been implemented, in part, by applying engineering judgment safety factors to experimental data. [1] However, the simple application of a general safety factor can result in use of excessive corrosion inhibiting agents. The required use of excess corrosion inhibitors can be costly for tank maintenance, waste processing, and in future tank closure. It is proposed that a probability-based approach can be used to quantify the risk associated with the chemistry control program. This approach can lead to the application of tank-specific chemistry control programs reducing overall costs associated with overly conservative use of inhibitor. Furthermore, when using nitrite as an inhibitor, the current chemistry control program is based on a linear model of increased aggressive species requiring increased protective species. This linear model was primarily supported by experimental data obtained from dilute solutions with nitrate concentrations less than 0.6 M, but is used to produce the current chemistry control program up to 1.0 M nitrate. Therefore, in the nitrate space between 0.6 and 1.0 M, the current control limit is based on assumptions that the linear model developed from data in the <0.6 M region is applicable in the 0.6-1.0 M region. Due to this assumption, further investigation of the nitrate region of 0.6 M to 1.0 M has potential for significant inhibitor reduction, while maintaining the same level of corrosion risk associated with the current chemistry control program.

Ongoing studies have been conducted in FY'07, FY'08, FY'09 and FY'10 to evaluate the corrosion controls at the SRS tank farm and to assess the minimum nitrite concentrations to inhibit pitting in ASTM A537 carbon steel below 1.0 molar nitrate. The experimentation from FY'08 suggested a non-linear model known as the mixture/amount model could be used

to predict the probability of corrosion in ASTM A537 in varying solutions as shown in Figure 1. [2]

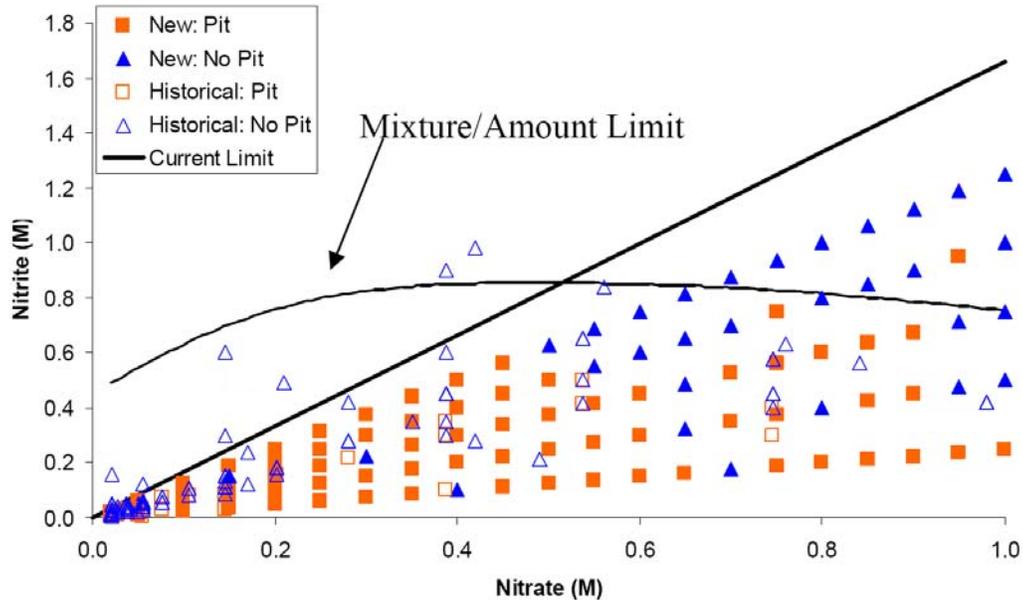


Figure 1 FY'08 results and historical results fitted to the mixture/amount model.

The mixture/amount model takes into account not only the ratio (or mixture) of inhibitors and aggressive species, but also the total concentration (or amount) of species in a solution. Historically, the ratio was the only factor taken into consideration in the development of the current chemistry control program. During FY'09, an experimental program was undertaken to refine the mixture/amount model by further investigating the risk associated with reducing the minimum molar nitrite concentration required to confidently inhibit pitting in dilute solutions. [3] The results of FY'09, as shown in Figure 2, quantified the probability for a corrosion free outcome for combinations of nitrate and nitrite. The FY '09 data predict probabilities up to 70%. Additional experimental data are needed to increase the probability to an acceptable percentage.

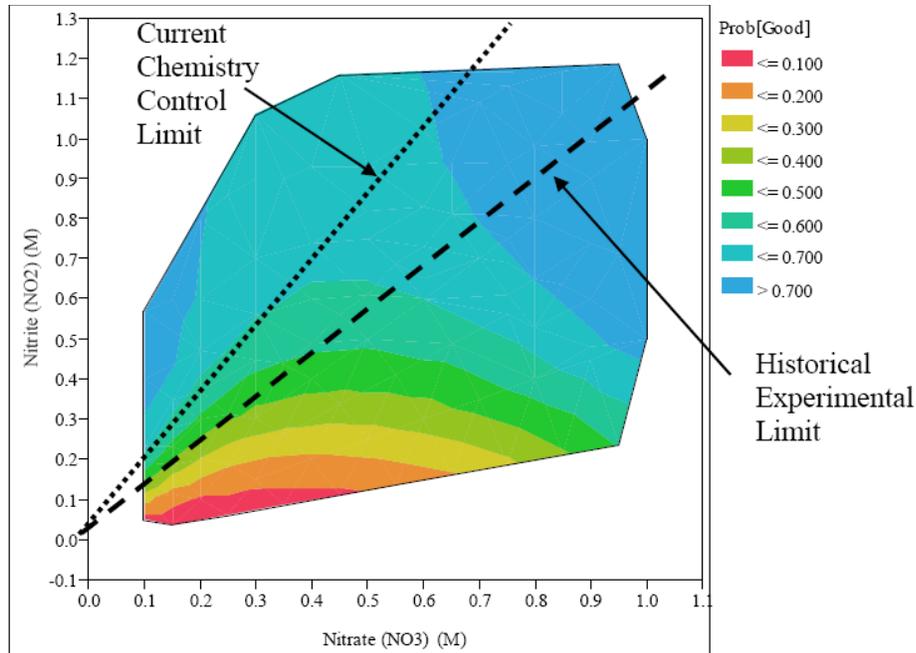


Figure 2 FY'09 results: Regions of probability of no corrosion based on the mixture/amount model.

3.0 EXPERIMENTAL

3.1 MATERIAL

Semi-killed, hot-rolled A537 was used for experimentation. The nominal chemical composition for the alloy is 0.24 wt% C, 0.7-1.60 wt% Mn, 0.040 wt% S, 0.035 wt% P, and 0.15-0/5 wt% Si with small amounts of Cu, Cr, and Ni. The electrochemical tests were conducted on disc samples of A537 that were nominally 5/8" diameter (Metal Samples, Munford, Al). Samples were ground using 800 grit SiC grinding sheets to remove the native oxide layer and provide a flat surface.

3.2 SIMULATED TANK SOLUTIONS

The aqueous phase of radioactive waste is a complex solution containing numerous ionic species. Corrosive nitrate anions are in relatively high concentration. Other corrosive ions, chloride, sulfate, and fluoride, are present in relatively low concentrations. Protective anions are predominantly nitrite and hydroxide. Protective anions such as phosphate, chromate, and molybdate are also present, but have relatively low concentrations compared to nitrite. Cost-effective, non-radioactive laboratory test solutions are used as simulant waste solutions. Corrosion testing experience in SRNL has shown that non-radioactive laboratory simulants of waste yield similar results to those of actual waste solutions [1].

A simplified non-radioactive simulant of waste was chosen for the testing reported here. The major constituents were nitrate, nitrite, bicarbonate, and carbonate. Chloride and sulfate were added for conservatism to ensure that the most potentially corrosive solution would be

tested. Sodium nitrate and sodium nitrite were varied based on statistical modeling values with sodium nitrite at deliberately high concentrations, providing experimental data to increase the confidence level in the mixture/amount model as shown in Table 1. Sodium chloride and sodium sulfate were introduced to have a solution more representative of waste, which contains chloride and sulfate ions. Sodium chloride was added based on the maximum amount allowable under current chemistry control limits. The sodium sulfate concentration was 84 wt% of the maximum amount allowable under current chemistry control limits. For all of the FY'10 tests, the chloride and sulfate anions were both present at high concentration. Previous studies used solutions with either chloride or sulfate, but both were included in the current study so that testing represents the most conservative condition.

Table 1 Series 1 FY'10 test matrix. Each concentration was run 7 times for a total of 63 tests.

Nitrate (M)	Nitrite (M)	Chloride (M)	Sulfate (M)
0.60	1.0	0.015	0.430
0.65	1.0	0.015	0.430
0.70	1.0	0.015	0.430
0.75	1.0	0.015	0.430
0.80	1.0	0.015	0.430
0.85	1.0	0.015	0.430
0.90	1.0	0.015	0.430
0.95	1.0	0.015	0.430
1.0	1.0	0.015	0.430

Upon completion of Series 1, it was determined that the chloride and sulfate limits should also be based not only on nitrate concentration, as in Series 1, but alternatively, on nitrite concentration. The chloride and sulfate limits were chosen based on recent Tank 51 washing cycles opposed to the maximum chemistry control limit [4]. Series 2, listed in Table 2, was then tested.

Table 2 Series 2 FY'10 test matrix. Each concentration was run 2 times for a total of 20 tests.

Test #	Nitrate (M)	Nitrite (M)	Chloride (M)	Sulfate (M)	Tank 51 Washing Cycle Basis
1	0.2	0.5	0.002	0.025	After Decant G
2	0.2	0.6	0.002	0.025	After Decant G
3	0.4	0.5	0.005	0.055	After Decant D
4	0.4	0.6	0.005	0.055	After Decant D
5	0.4	0.75	0.005	0.055	After Decant D
6	0.6	0.6	0.025	0.09	After Decant C
7	0.6	0.75	0.025	0.09	After Decant C
8	0.8	0.5	0.032	0.121	After Decant B
9	0.8	0.6	0.032	0.121	After Decant B
10	0.8	0.75	0.032	0.121	After Decant B

Simulated waste tank solutions were prepared using distilled water and reagent-grade chemicals: sodium chloride, sodium sulfate anhydrous, sodium carbonate, sodium bicarbonate, sodium nitrite, and sodium nitrate. The pH was maintained to 10.0 using a

constant carbonate/bicarbonate molar ratio of 7 to 13. The gram amount of carbonate and bicarbonate added was determined based on the nitrite amount. A total of 63 solutions were used for electrochemical testing. Solutions were prepared based on a statistically determined experimental design [5].

3.3 ELECTROCHEMICAL TESTING

Cyclic potentiodynamic polarization (CPP) scans were also performed to experimentally determine the pitting propensity. The CPP technique qualitatively evaluates the pitting propensity based on a slow linear sweep of the electrochemical potential of a metal. Potential scans are applied beginning slightly below the corrosion potential, E_{corr} , and continuing in the positive direction at a constant rate. The current is recorded during the voltage scan to measure the corrosion rate at each potential. After the scan reaches a set potential value, the applied potential is scanned back to the corrosion potential. The scan is analyzed to determine pitting and crevice corrosion susceptibility. Significant hysteresis with higher currents generated on the reverse scan is an indication of pit formation. The scan results are also used to characterize the stability of oxide coating and to determine the effectiveness of inhibitors.

In FY'10, an additional 63 electrochemical tests have been performed to increase the mixture/amount model probability to an acceptable percentage.

The electrochemical cell used included A537 samples attached to a conductive wire and mounted in metallographic mount material as the working electrode and two graphite rods used as counter electrodes. The reference electrode was a saturated potassium chloride (KCl) connected to a Luggin bridge. The cyclic potentiodynamic polarization (CPP) testing was performed using Green cells at 40 °C. Prior to each CPP test, the samples were allowed to equilibrate for 2.5 hours at 40°C to determine the corrosion potential. The CPP curve started at an initial potential of -0.1 V vs the open circuit potential. The potential was increased at a rate of 0.5 mV/sec to a vertex potential of 1.2 V vs reference. The reverse scan rate of 0.5 mV/sec was used until a final potential of 0.0 V vs open circuit potential.

4.0 RESULTS

All solutions tested in Series 1 provided a no-corrosive response on the A537 samples. This result was expected due to the large amount of inhibitor used in the solutions. A representative CPP and sample surface after testing is shown in Figures 3 and 4. Minimal or negative hysteresis occurred in the CPP curves, signifying that the passive layer did not break down during the potential rise.

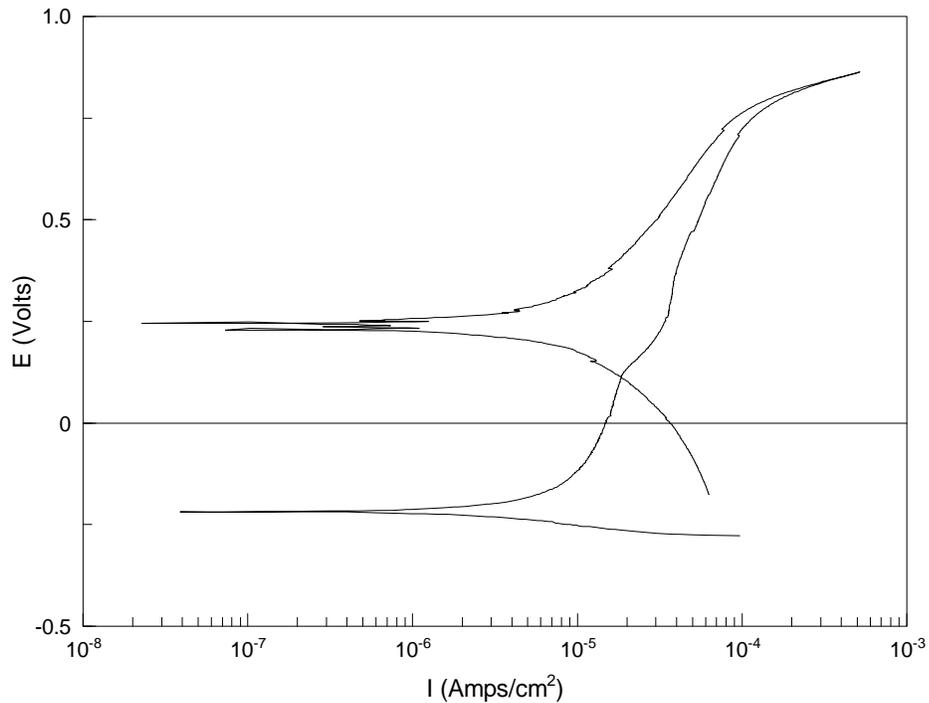


Figure 3 CPP curve for A537 in solution of 1.0 M nitrite and 0.70 M nitrate showing a negative hysteresis.

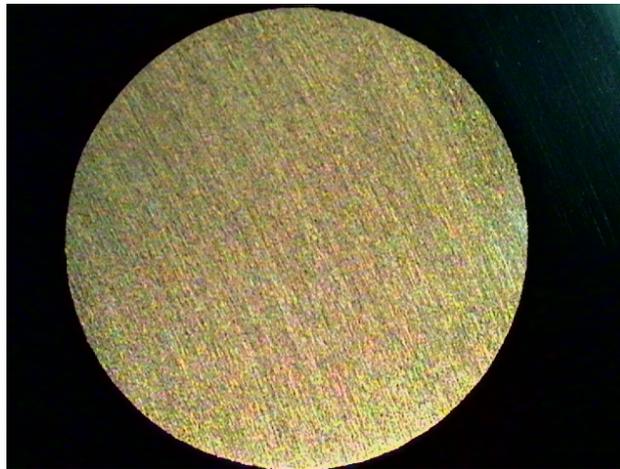


Figure 4 Optical image of A537 after electrochemical test using solution containing 1.0 M nitrite and 0.70 M nitrate.

FY'10 results were incorporated with FY'07, FY'08 and FY'09 (see Figure 5) and the mixture/amount model theory was applied using a 90% confidence level. The nitrite limit increases with increasing nitrate up to 0.38 M, at which point, the concentration limit of nitrite decreases with increasing nitrate, see Figure 6.

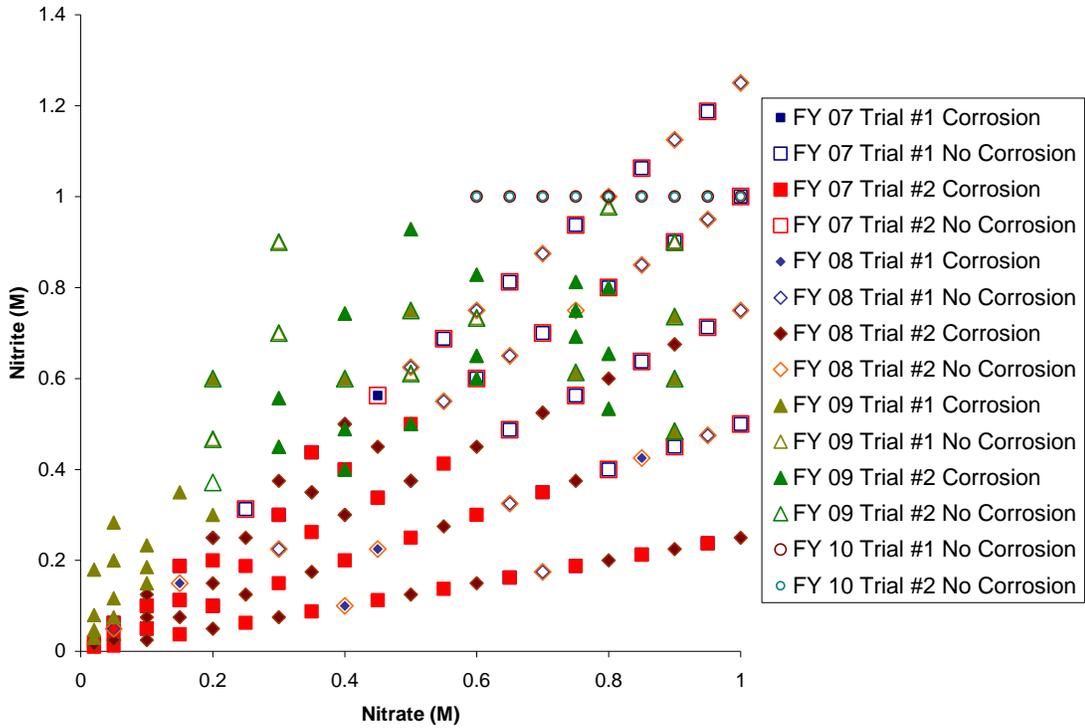


Figure 5 FY'07, FY'08, FY'09, and FY'10 results with a breakdown showing from which experimental set the data resulted. Note, Series 2 from FY'10 was omitted due to the change in the chloride and sulfate concentration dependency on nitrite instead of nitrate.

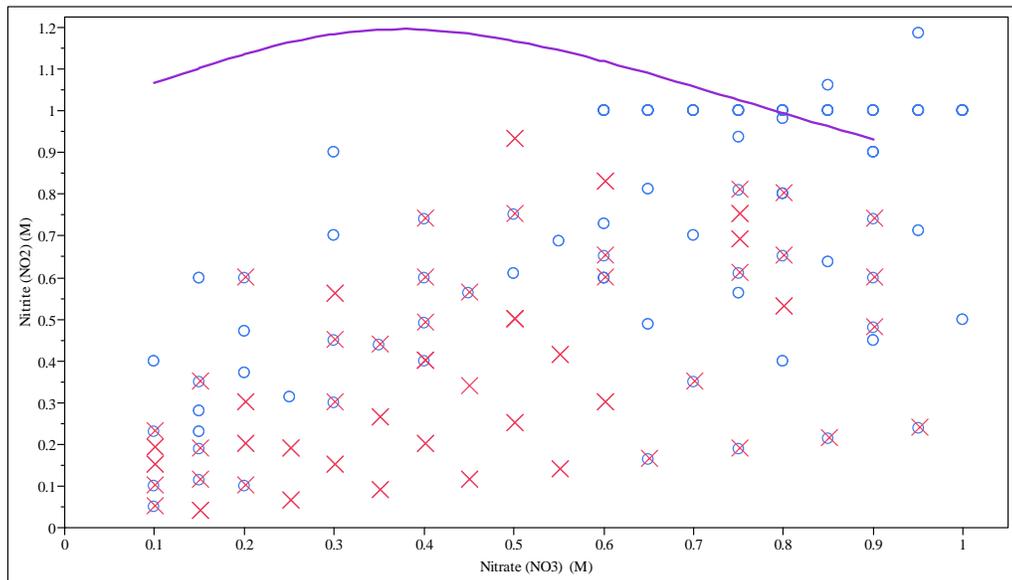


Figure 6 Electrochemical results for FY'07, FY'08, FY'09, and FY'10 plotted with the mixture/amount model curve evaluated for a 90% probability of a no-corrosion outcome limit. A corrosion outcome is represented by an "x", a no-corrosion outcome represented by an "o". Note: To fit the model, data less than 0.1 M nitrate was omitted. Also, Series 2 from FY'10 was omitted.

When the results were applied to the JMP version 7.0.2 statistical analysis software and evaluated based on the mixture/amount model, a contour plot was produced representing regions of confidence percentile regarding a corrosion or no-corrosion outcome, see Figure 7.

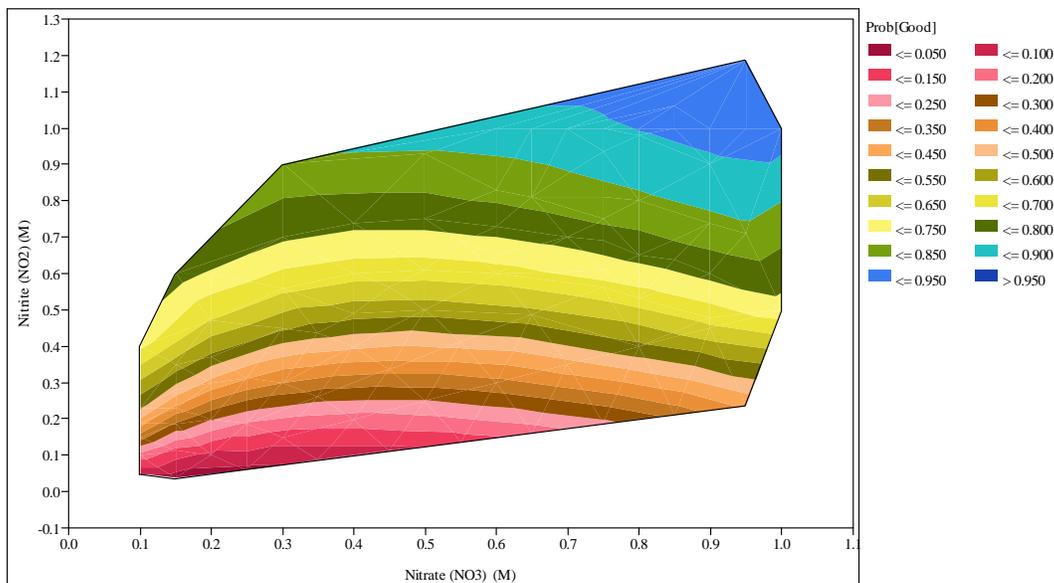


Figure 7 Contour plot produced in JMP statistical analysis software depicting the probability of a no-corrosion outcome for solutions with varying amounts of nitrate and nitrite concentrations. Series 2 of FY'10 was omitted.

The JMP software is capable of modeling high confidence levels of a no-corrosion response in the high nitrate region due to the increased number of testing data available at the high nitrate/high nitrite region. The mixture amount model is capable of predicting >90% confidence level of a no-corrosion response in the low nitrate regions of 0.4 M nitrate or less, however, for the JMP software to predict the 90% level of confidence, further data would be required at the high nitrite/low nitrate region.

Series 2, formulated with a varying concentration of chlorides and sulfates based on nitrate concentrations, resulted in corrosion for two of the solutions. Solution 8 with a nitrate concentration of 0.8 M, nitrite concentration of 0.50 M, chloride concentration of 0.032 M and sulfate concentration of 0.121 M resulted in corrosion for both trials tested. The cyclic potentiodynamic polarization curves and corresponding optical images are shown in Figures 8 and 9.

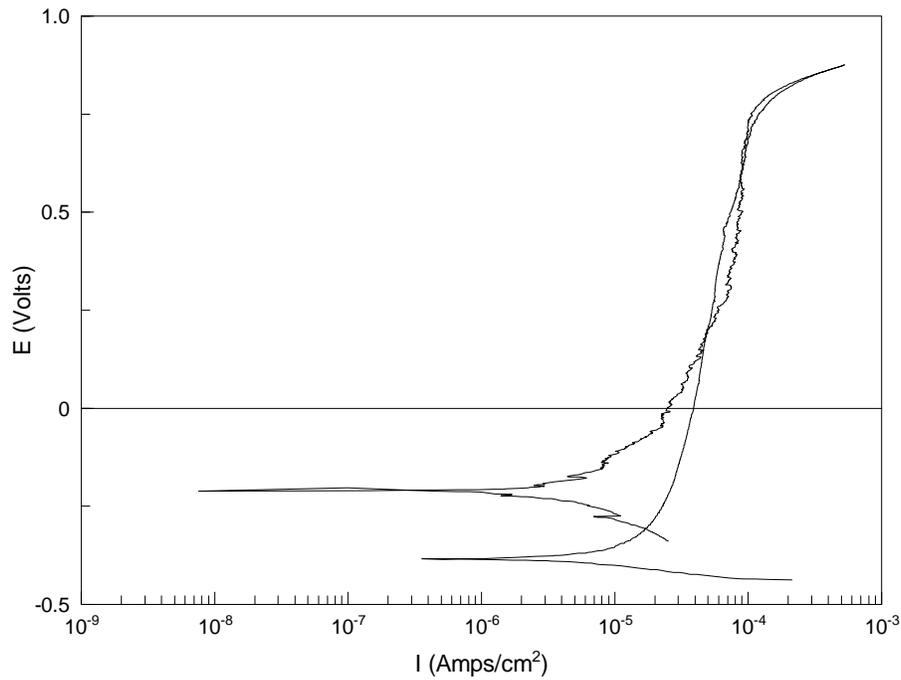


Figure 8 Cyclic potentiodynamic polarization curve for solution 8 of Series 2. The sample resulted in a corrosion outcome.

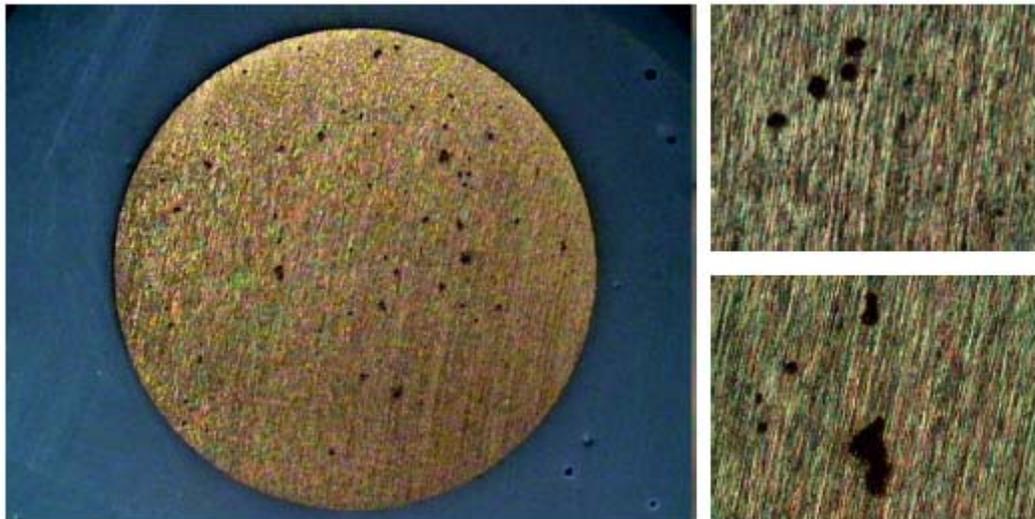


Figure 9 Optical images after cyclic potentiodynamic testing of A537 carbon steel in solution containing 0.8 M nitrate, 0.50 M nitrite, 0.032 M chloride and 0.121 M sulfate.

Solution 9, with a slightly higher concentration of the inhibitor nitrite (0.60 M) corroded in one trial tested. The other trial resulted in a non-corrosion result. The difference between

solution 8, 9, and 10 indicates that for a constant aggressive species concentration, which includes nitrate, chloride, and sulfate, by increasing the nitrite concentration, the potential for corrosion to occur will decrease. Figure 10 compares Series 2 testing to previous testing where the chlorides and sulfates were based on nitrite concentration instead of nitrate. By comparing the results between the two different years, it is clear that chlorides and sulfates play a significant role in the corrosion response of A537. Due to the high concentration of sulfate in particular, tests run in FY'09 resulted in a corrosion response, while a similar nitrate and nitrite concentration in FY'10 did not due to the lower sulfate concentration.

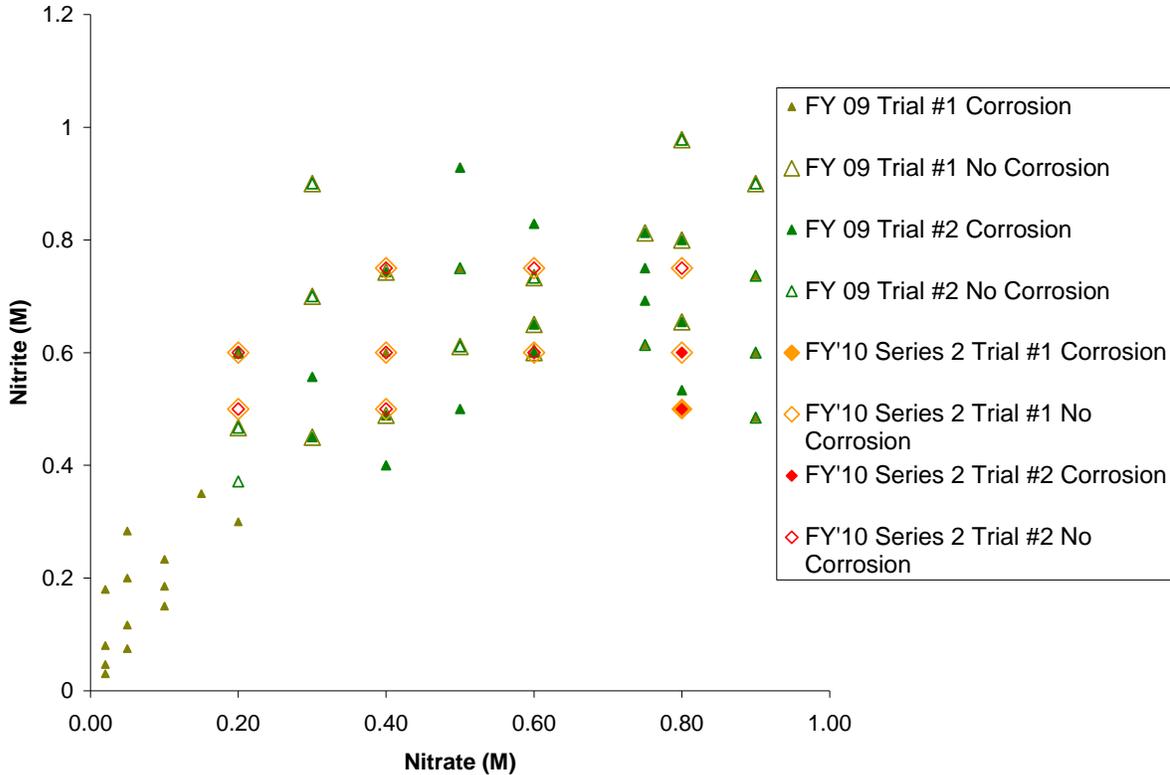


Figure 10 FY'10 Series 2 testing compared to FY'09 testing in similar nitrate and nitrite concentrations. FY'09 chloride and sulfate concentrations were dependent on the nitrite concentration and were based on chemistry control limits. FY'10 chloride and sulfate concentrations were based on recent washing cycles in Tank 51.

5.0 CONCLUSIONS

The confidence level in the mixture/amount model was further strengthened through FY'10 testing. A >95% region of confidence of a no-corrosion result is predicted through the mixture/amount theory and has been confirmed through electrochemical experimentation. The model supports the reduction of nitrite inhibitor concentration with increasing nitrate concentration in the region of 0.4 M to 1.0 M nitrate. This result is based on a series of electrochemical tests using solutions with extreme, yet within the chemistry control limits, amounts of aggressive chlorides and sulfate ions. Further testing using solutions with lesser

concentrations of chloride and sulfate ions would provide further insight into the potential for nitrite reductions in the nitrate concentration region between 0.02 M and 1.0 M.

The results from Series 2 suggest that chloride and sulfate concentrations have a critical effect on the corrosion response of A537.

6.0 REFERENCES

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[4] Per conversation with J. Gillam.

[5] E.N. Hoffman, B.L. Garcia-Diaz, T.B. Edwards, "Task Technical Plan for Risk Based Corrosion Analysis-Part III", SRNL-TR-2009-00463, January 2010.

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