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EFFECT OF CHLORIDE AND SULFATE CONCENTRATION ON PROBABLITY BASED CORROSION CONTROL FOR LIQUID WASTE TANKS- PART IV

E.N. Hoffman
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REVIEWS AND APPROVALS

E.N. Hoffman, Co-author, Materials Science and Technology, SRNL — Date

B.L. Garcia-Diaz, Co-author, Materials Science and Technology, SRNL — Date

T.B. Edwards, Co-author, Applied Comp Eng & Statistics, SRNL — Date

B.J. Wiersma, Technical Reviewer, Materials Science and Technology, SRNL — Date

K. E. Zeigler, Manager, Material Performance & Corrosion Technology — Date

M.E. Maryak, Liquid Waste Engineering Programs — Date

1.0 EXECUTIVE SUMMARY

A series of cyclic potentiodynamic polarization tests was performed on samples of A537 carbon steel in support of a probability-based approach to evaluate the effect of chloride and sulfate on corrosion susceptibility. Testing solutions were chosen to build off previous experimental results from FY-07, FY'08, FY'09 and FY'10 to systemically evaluate the influence of the secondary aggressive species, chloride, and sulfate. The FY'11 results suggest that evaluating the combined effect of all aggressive species, nitrate, chloride, and sulfate, provides a consistent response for determining corrosion susceptibility. The results of this work emphasize the importance for not only nitrate concentration limits, but also chloride and sulfate concentration limits as well.

2.0 INTRODUCTION

The chemistry control program, with the aim to reduce the pitting corrosion occurrence on tank walls, has thus far been implemented, in part, by applying engineering judgment safety factors to experimental data. [1] 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 on a log scale of increased aggressive species requiring increased protective species. Primarily supported by experimental data obtained from dilute solutions with nitrate concentrations less than 0.6 M, this linear model was used to produce the current chemistry control program at 1.0 M nitrate or less. Further investigation of the nitrate region of 0.6 M to 1.0 M has a potential for significant inhibitor reduction, while maintaining the same level of corrosion risk associated with the current chemistry control program.

Studies were conducted in FY'07, FY'08, FY'09, FY'10 and FY'11 to evaluate the corrosion controls at the Savannah River Site (SRS) tank farm and to assess the minimum nitrite concentrations to inhibit pitting in ASTM A537 carbon steel at conditions below 1.0 M nitrate. The experimentation from FY'08 suggested a non-linear model known as the mixture/amount model could be used to predict the corrosion probability of ASTM A537 in varying solutions. A probability level of 90% is depicted in Figure 1. [2]

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 inhibit pitting in dilute solutions at a 90% confidence level. [3] The FY'09 results, 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 of no corrosion up to 70%. Additional experimental data were needed to increase the probability to a higher percentage while maintaining a 90% confidence level.

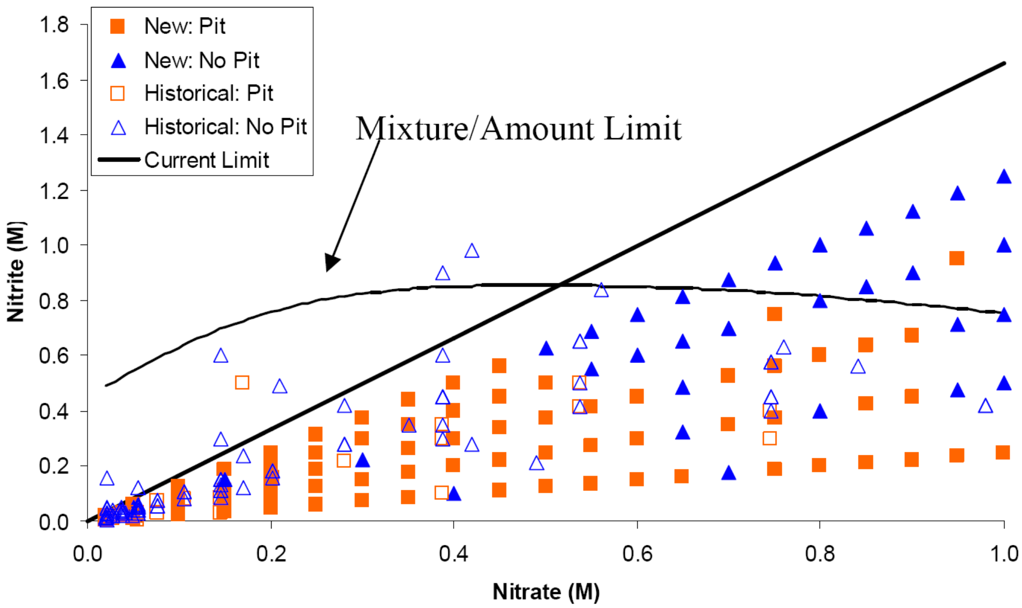

Figure 1 FY'08 results and historical results fitted to the mixture/amount model.

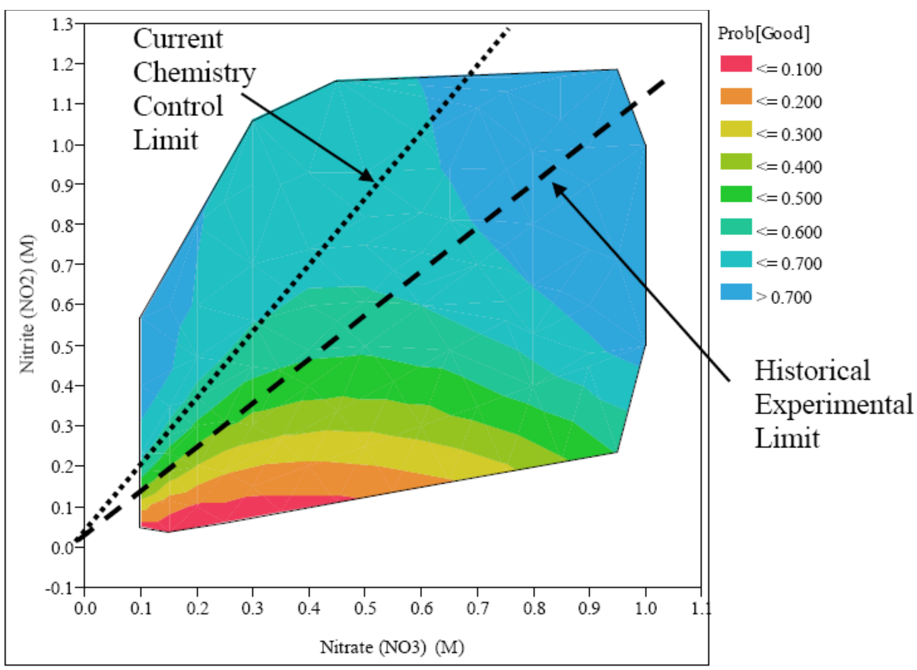

Figure 2 FY'09 results: Regions of probability of no corrosion based on the mixture/amount model.

Cyclic potentiodynamic polarization (CPP) scans have been performed in the past 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 (positive hysteresis) is an indication of pit formation. The scan results are also used to characterize the stability of the oxide coating and to determine the effectiveness of inhibitors.

In FY'10, Figure 3, an additional 63 electrochemical tests were performed to refine the model and to increase the mixture/amount model probability to an acceptable percentage. The results can be seen in Figure 3.

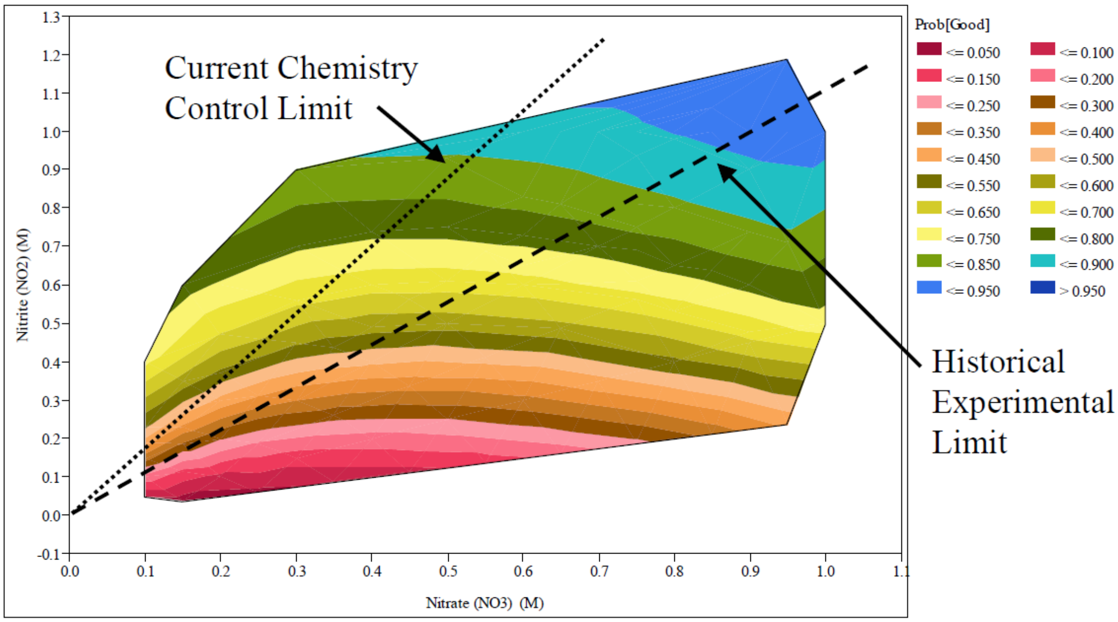

Figure 3 FY'10 results: Contour plot produced in JMP™ statistical analysis software depicting the probability of a no-corrosion outcome for solutions with varying amounts of nitrate and nitrite concentrations. .

A summary of the combined results leading to this work with chloride and sulfate relative to the concentration of nitrite is shown in Figure 4 along with the resulting mixture/amount model derived from the data in Figure 5. While areas of corrosion (solid symbols) and no corrosion (open symbols) are evident, a significant area of the graph is ambiguous with having both corrosion and no corrosion results.

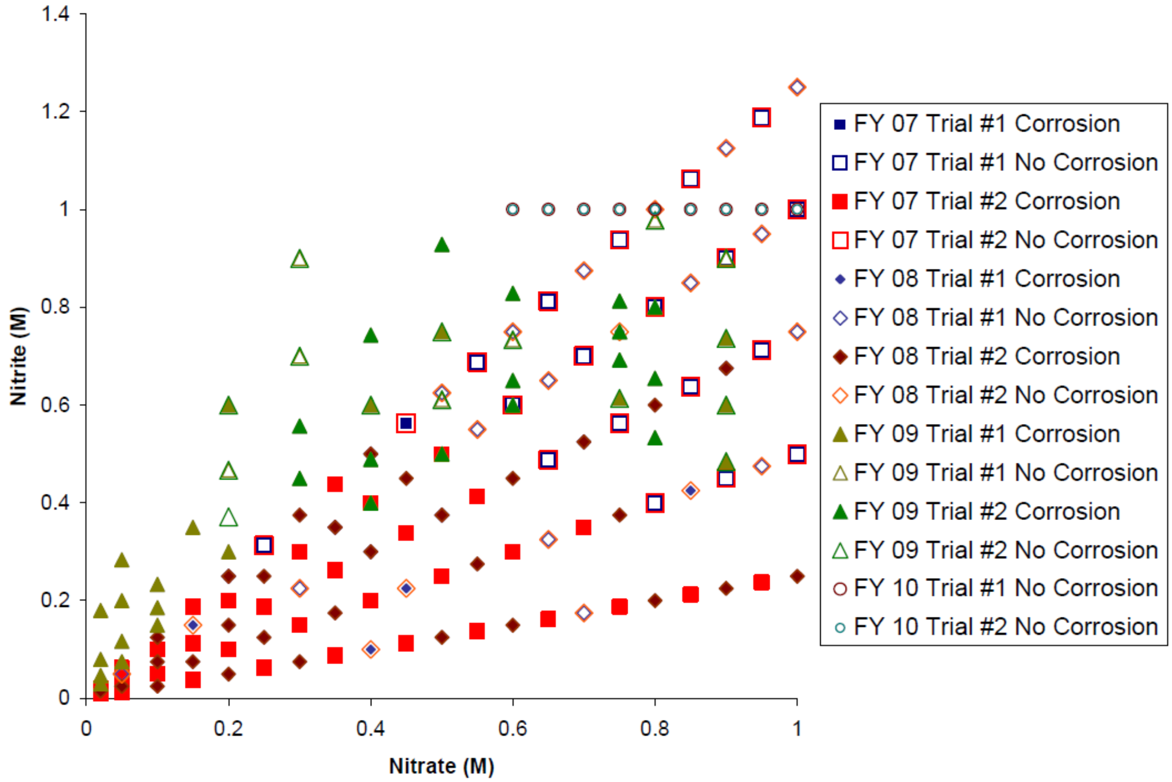

Figure 4 FY'07, FY'08, FY'09, and FY'10 results denoted from which experimental set the data resulted.

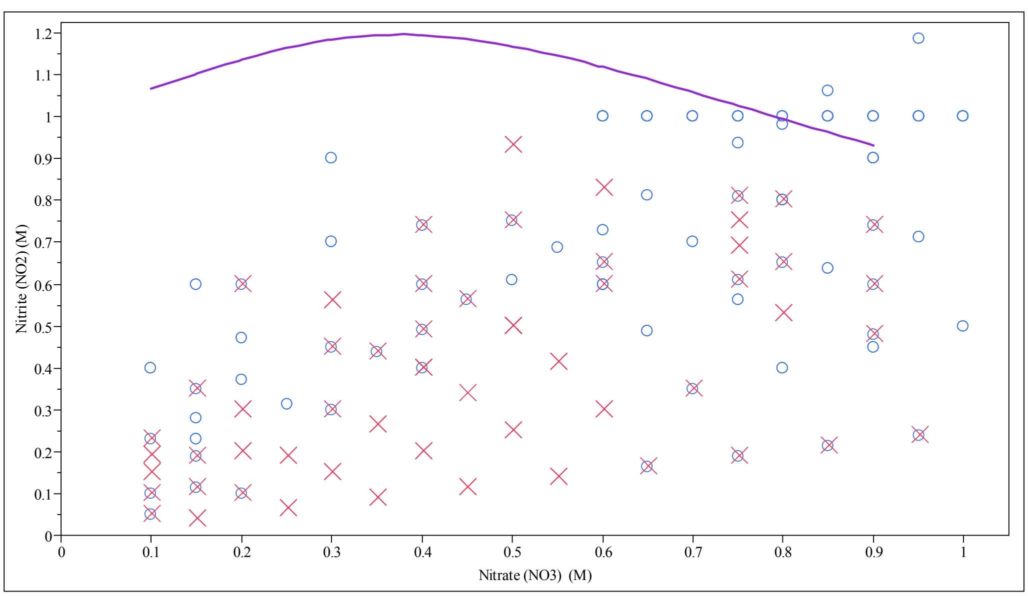

Figure 5 Electrochemical results for FY'07, FY'08, FY'09, and FY'10 plotted with the mixture/amount model curve evaluated for a 90% probability of a no-corrosion outcome limit. A corrosion outcome is represented by "×"; a no-corrosion outcome is represented by "○". Note: To fit the model, data less than 0.1 M nitrate were omitted.

In the latter half of FY'10, a series of experiments was performed to evaluate the effect of chloride and sulfate, thereby allowing the concentration of the species to vary independently compared to the nitrite concentration. The results of the experimentation are shown in Figure 6.

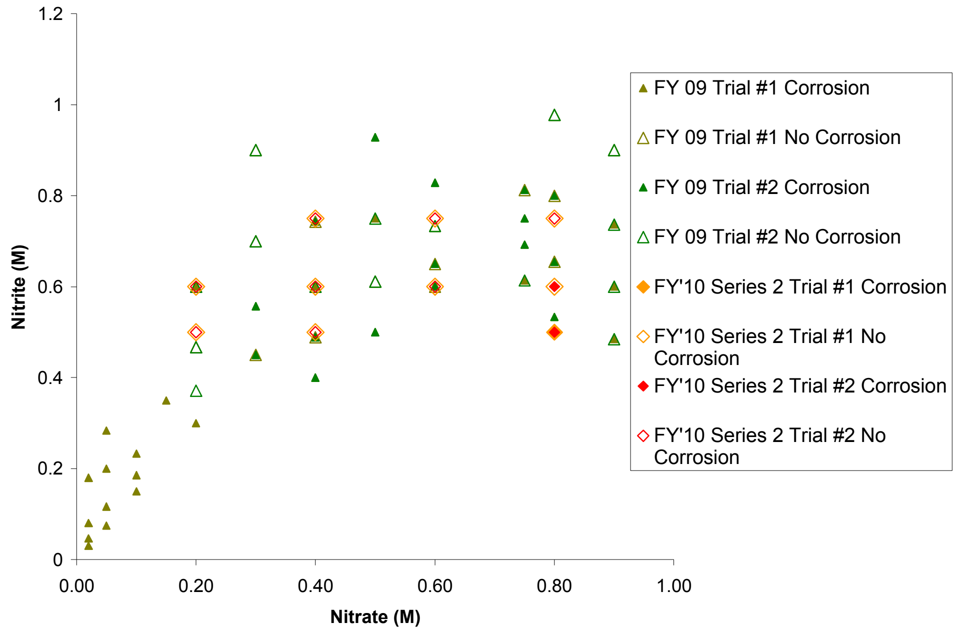

Figure 6 FY'10 Series 2 with constant chloride and sulfate concentrations compared to FY'09 testing in similar nitrate and nitrite concentrations yet chloride and sulfate concentrations that scaled with the nitrite concentration. FY'09 chloride and sulfate concentrations were dependent on the nitrite concentration and were based on chemistry control limits. FY'10 chloride and sulfate concentrations were based on recent washing cycles in Tank 51.

The results of FY'10's Series 2 provided a cleaner break between regions of corrosion and no corrosion potential in the nitrite/nitrate space. This result strongly suggested the need for further evaluation of the effect of chloride and sulfate.

3.0 EXPERIMENTAL

3.1 RISK BASED CORROSION CONTROL

3.1.1 Material

Semi-killed, hot-rolled ASTM A537 Class I carbon steel (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 and the balance being Fe. 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.

3.1.2 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 were 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, carbonate, chloride and sulfate. 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. The matrix is designed to test a series of concentration ratios, or mixtures, of NO_2^- and NO_3^- as well as a series of total concentrations, or amounts, of NO_2^- and NO_3^-. New to FY'11 testing is a systematic evaluation of Cl^- and SO_4^{2-} on the minimum NO_2^- required to inhibit pitting. The planned test matrix focuses on the solution concentration space below the ratios of 0.3 and 0.03 for SO_4^{2-}/NO_3^- and Cl^-/NO_3^-, respectively. The concentrations of NO_3^-, NO_2^-, Cl^- and SO_4^{2-} to be tested are listed in Table 1, as well as the corresponding sums and ratios used to arrive at the prescribed concentrations. Ratios of Cl^-/NO_3^- and SO_4^{2-}/NO_3^- were chosen based off of recommended concentration limits for chloride and sulfates. [5] The ratios of NO_2^-/NO_3^- were chosen to explore the transition region between pitting to no pitting that was determined based off of previous testing, Figure 5. The molar concentrations of Cl^- and SO_4^{2-} (as well as the ratio to the NO_3^- at concentrations of 0.0125 and 0.150 M, respectively) were chosen based on Tank 51 Decants D-I from FY10 washing process [4]. Additional ratios of Cl^-/NO_3^- and SO_4^{2-}/NO_3^- were based on values cited in the Congdon (DPST-87-379) and Zapp (WSRC-TR-94-0250) memos. Critical ratios for Cl^-/NO_3^- and SO_4^{2-}/NO_3^- where cited as 0.03 and 0.3, respectively, when the primary aggressive species was NO_3^-. Values, 0.01 and 0.07 for Cl^-/NO_3^- and 0.1 and 0.5 for SO_4^-/NO_3^-, were selected to bracket these critical percentages.

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 104 solutions were used for electrochemical testing. Solutions were prepared based on a statistically determined experimental design [6].

Table 1 FY'11 test matrix. Each testing solution was run in duplicate totaling 208 tests.

Test	NO_2/NO_3	NO_2+NO_3	Cl/NO_3	SO_4/NO_3	NO_3	NO_2	Cl	SO_4
1	0.50	0.15	0.0050	0.15	0.10	0.05	0.00050	0.01500

Test	NO_2/NO_3	NO_2+NO_3	Cl/NO_3	SO_4/NO_3	NO_3	NO_2	Cl	SO_4
2	0.50	0.38	0.0050	0.15	0.25	0.13	0.00125	0.03750
3	0.50	0.60	0.0050	0.15	0.40	0.20	0.00200	0.06000
4	0.50	0.83	0.0050	0.15	0.55	0.28	0.00275	0.08250
5	0.50	1.05	0.0050	0.15	0.70	0.35	0.00350	0.10500
6	0.50	1.28	0.0050	0.15	0.85	0.43	0.00425	0.12750
7	0.50	1.50	0.0050	0.15	1.00	0.50	0.00500	0.15000
8	0.50	1.80	0.0050	0.15	1.20	0.60	0.00600	0.18000
9	1.00	0.20	0.0050	0.15	0.10	0.10	0.00050	0.01500
10	1.00	0.50	0.0050	0.15	0.25	0.25	0.00125	0.03750
11	1.00	0.80	0.0050	0.15	0.40	0.40	0.00200	0.06000
12	1.00	1.10	0.0050	0.15	0.55	0.55	0.00275	0.08250
13	1.00	1.40	0.0050	0.15	0.70	0.70	0.00350	0.10500
14	1.00	1.70	0.0050	0.15	0.85	0.85	0.00425	0.12750
15	1.00	2.00	0.0050	0.15	1.00	1.00	0.00500	0.15000
16	1.00	2.40	0.0050	0.15	1.20	1.20	0.00600	0.18000
17	1.50	0.25	0.0050	0.15	0.10	0.15	0.00050	0.01500
18	1.50	0.63	0.0050	0.15	0.25	0.38	0.00125	0.03750
19	1.50	1.00	0.0050	0.15	0.40	0.60	0.00200	0.06000
20	1.50	1.38	0.0050	0.15	0.55	0.83	0.00275	0.08250
21	1.50	1.75	0.0050	0.15	0.70	1.05	0.00350	0.10500
22	1.50	2.13	0.0050	0.15	0.85	1.28	0.00425	0.12750
23	1.50	2.50	0.0050	0.15	1.00	1.50	0.00500	0.15000
24	1.50	3.00	0.0050	0.15	1.20	1.80	0.00600	0.18000
25	0.50	0.15	0.0700	0.15	0.10	0.05	0.00700	0.01500
26	0.50	0.38	0.0700	0.15	0.25	0.13	0.01750	0.03750
27	0.50	0.60	0.0700	0.15	0.40	0.20	0.02800	0.06000
28	0.50	0.83	0.0700	0.15	0.55	0.28	0.03850	0.08250
29	0.50	1.05	0.0700	0.15	0.70	0.35	0.04900	0.10500
30	0.50	1.28	0.0700	0.15	0.85	0.43	0.05950	0.12750
31	0.50	1.50	0.0700	0.15	1.00	0.50	0.07000	0.15000
32	0.50	1.80	0.0700	0.15	1.20	0.60	0.08400	0.18000
33	1.00	0.20	0.0700	0.15	0.10	0.10	0.00700	0.01500
34	1.00	0.50	0.0700	0.15	0.25	0.25	0.01750	0.03750
35	1.00	0.80	0.0700	0.15	0.40	0.40	0.02800	0.06000
36	1.00	1.10	0.0700	0.15	0.55	0.55	0.03850	0.08250
37	1.00	1.40	0.0700	0.15	0.70	0.70	0.04900	0.10500
38	1.00	1.70	0.0700	0.15	0.85	0.85	0.05950	0.12750
39	1.00	2.00	0.0700	0.15	1.00	1.00	0.07000	0.15000
40	1.00	2.40	0.0700	0.15	1.20	1.20	0.08400	0.18000
41	1.50	0.25	0.0700	0.15	0.10	0.15	0.00700	0.01500

Test	NO_2/NO_3	NO_2+NO_3	Cl/NO_3	SO_4/NO_3	NO_3	NO_2	Cl	SO_4
42	1.50	0.63	0.0700	0.15	0.25	0.38	0.01750	0.03750
43	1.50	1.00	0.0700	0.15	0.40	0.60	0.02800	0.06000
44	1.50	1.38	0.0700	0.15	0.55	0.83	0.03850	0.08250
45	1.50	1.75	0.0700	0.15	0.70	1.05	0.04900	0.10500
46	1.50	2.13	0.0700	0.15	0.85	1.28	0.05950	0.12750
47	1.50	2.50	0.0700	0.15	1.00	1.50	0.07000	0.15000
48	1.50	3.00	0.0700	0.15	1.20	1.80	0.08400	0.18000
49	0.50	0.15	0.0125	0.05	0.10	0.05	0.00125	0.00500
50	0.50	0.38	0.0125	0.05	0.25	0.13	0.00313	0.01250
51	0.50	0.60	0.0125	0.05	0.40	0.20	0.0050	0.02000
52	0.50	0.83	0.0125	0.05	0.55	0.28	0.00688	0.02750
53	0.50	1.05	0.0125	0.05	0.70	0.35	0.00875	0.03500
54	0.50	1.28	0.0125	0.05	0.85	0.43	0.01063	0.04250
55	0.50	1.50	0.0125	0.05	1.00	0.50	0.01250	0.05000
56	0.50	1.80	0.0125	0.05	1.20	0.60	0.01500	0.06000
57	1.00	0.20	0.0125	0.05	0.10	0.10	0.00125	0.00500
58	1.00	0.50	0.0125	0.05	0.25	0.25	0.00313	0.01250
59	1.00	0.80	0.0125	0.05	0.40	0.40	0.0050	0.02000
60	1.00	1.10	0.0125	0.05	0.55	0.55	0.00688	0.02750
61	1.00	1.40	0.0125	0.05	0.70	0.70	0.00875	0.03500
62	1.00	1.70	0.0125	0.05	0.85	0.85	0.01063	0.04250
63	1.00	2.00	0.0125	0.05	1.00	1.00	0.01250	0.05000
64	1.00	2.40	0.0125	0.05	1.20	1.20	0.01500	0.06000
65	1.50	0.25	0.0125	0.05	0.10	0.15	0.00125	0.00500
66	1.50	0.63	0.0125	0.05	0.25	0.38	0.00313	0.01250
67	1.50	1.00	0.0125	0.05	0.40	0.60	0.0050	0.02000
68	1.50	1.38	0.0125	0.05	0.55	0.83	0.00688	0.02750
69	1.50	1.75	0.0125	0.05	0.70	1.05	0.00875	0.03500
70	1.50	2.13	0.0125	0.05	0.85	1.28	0.01063	0.04250
71	1.50	2.50	0.0125	0.05	1.00	1.50	0.01250	0.05000
72	1.50	3.00	0.0125	0.05	1.20	1.80	0.01500	0.06000
73	0.50	0.15	0.0125	0.50	0.10	0.05	0.00125	0.05000
74	0.50	0.38	0.0125	0.50	0.25	0.13	0.00313	0.12500
75	0.50	0.60	0.0125	0.50	0.40	0.20	0.00500	0.20000
76	0.50	0.83	0.0125	0.50	0.55	0.28	0.00688	0.27500
77	0.50	1.05	0.0125	0.50	0.70	0.35	0.00875	0.35000
78	0.50	1.28	0.0125	0.50	0.85	0.43	0.01063	0.42500
79	0.50	1.50	0.0125	0.50	1.00	0.50	0.01250	0.50000
80	0.50	1.80	0.0125	0.50	1.20	0.60	0.01500	0.60000
81	1.00	0.20	0.0125	0.50	0.10	0.10	0.00125	0.05000

Test	NO_2/NO_3	NO_2+NO_3	Cl/NO_3	SO_4/NO_3	NO_3	NO_2	Cl	SO_4
82	1.00	0.50	0.0125	0.50	0.25	0.25	0.00313	0.12500
83	1.00	0.80	0.0125	0.50	0.40	0.40	0.00500	0.20000
84	1.00	1.10	0.0125	0.50	0.55	0.55	0.00688	0.27500
85	1.00	1.40	0.0125	0.50	0.70	0.70	0.00875	0.35000
86	1.00	1.70	0.0125	0.50	0.85	0.85	0.01063	0.42500
87	1.00	2.00	0.0125	0.50	1.00	1.00	0.01250	0.50000
88	1.00	2.40	0.0125	0.50	1.20	1.20	0.01500	0.60000
89	1.50	0.25	0.0125	0.50	0.10	0.15	0.00125	0.05000
90	1.50	0.63	0.0125	0.50	0.25	0.38	0.00313	0.12500
91	1.50	1.00	0.0125	0.50	0.40	0.60	0.00500	0.20000
92	1.50	1.38	0.0125	0.50	0.55	0.83	0.00688	0.27500
93	1.50	1.75	0.0125	0.50	0.70	1.05	0.00875	0.35000
94	1.50	2.13	0.0125	0.50	0.85	1.28	0.01063	0.42500
95	1.50	2.50	0.0125	0.50	1.00	1.50	0.01250	0.50000
96	1.50	3.00	0.0125	0.50	1.20	1.80	0.01500	0.60000
97	1.50	1.90	0.0700	0.15	0.10	1.80	0.00700	0.01500
98	1.50	2.05	0.0700	0.15	0.25	1.80	0.01750	0.03750
99	4.50	2.20	0.0700	0.15	0.40	1.80	0.02800	0.06000
100	3.27	2.35	0.0700	0.15	0.55	1.80	0.03850	0.08250
101	2.57	2.50	0.0700	0.15	0.70	1.80	0.04900	0.10500
102	2.12	2.65	0.0700	0.15	0.85	1.80	0.05950	0.12750
103	1.80	2.80	0.0700	0.15	1.00	1.80	0.07000	0.15000
104	1.50	3.00	0.0700	0.15	1.20	1.80	0.08400	0.18000

3.1.3 Electrochemical Testing

The electrochemical cell used included A537 samples attached to a conductive wire and mounted in metallographic mount material which was used as the working electrode and two graphite rods used as counter electrodes. The reference electrode was a saturated calomel connected to a Luggin bridge. The cyclic potentiodynamic polarization (CPP) testing was performed using Green cells at 40 ºC. 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 versus 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 or a maximum current of 0.001 Amps. The reverse scan rate of 0.5 mV/sec was used until a final potential of 0 V vs open circuit potential. Each solution was tested in duplicate for a total of 208 electrochemical tests. Digital optical images were taken of the sample surface upon completion of electrochemical testing for visual analysis of pit formation. The visual presence or absence of pits on the sample surface was the basis for the pit/no pit criteria and analysis as the results lent towards a simple binary observation compared to the electrochemical response which yielded several CPP curve shapes spanning a range of current densities and electrical potentials.

4.0 RESULTS

4.1 RISK BASED CORROSION TESTING

Electrochemical CPP curves were evaluated based on a 5 category system as shown below:
Category 1: Negative hysteresis. No pitting susceptibility.
Category 2: Positive hysteresis, but with pitting and protection potentials well above the zero current potential.
Category 3: Positive hysteresis with a noble pitting potential, but with the protection potential relatively near the zero current potential.
Category 4: Positive hysteresis with the protection potential lower than then zero current potential
Category 5: Spontaneous pitting at the zero current potential so that the current increases rapidly upon polarization to potentials above the zero current potential.

The surface of the sample post-electrochemical testing was visually evaluated using a microscope. Ranking for optical results follow:

Category 1: No corrosion
Category 2: Moderate corrosion
Category 3: Significant corrosion.

The optical and electrochemical results of the solutions tested are provided in Table 2.

Table 2 Optical and Electrochemical Results.

Test	NO_3	NO_2	Cl	SO_4	Optic. 1	Optic. 2	Electro. 1	Electro. 2
1	0.1	0.05	0.0005	0.015	2	2	4	4
2	0.25	0.13	0.0013	0.0375	1	1	3	4
3	0.4	0.2	0.002	0.06	2	1	5	4
4	0.55	0.28	0.0028	0.0825	1	1	1	4
5	0.7	0.35	0.0035	0.105	1	1	1	1
6	0.85	0.43	0.0043	0.1275	1	1	1	4
7	1	0.5	0.005	0.15	1	1	1	1
8	1.2	0.6	0.006	0.18	1	1	4	2
9	0.1	0.1	0.0005	0.015	1	1	1	1
10	0.25	0.25	0.0013	0.0375	1	1	4	4
11	0.4	0.4	0.002	0.06	1	1	5	5
12	0.55	0.55	0.0028	0.0825	1	1	4	1
13	0.7	0.7	0.0035	0.105	1	1	4	4
14	0.85	0.85	0.0043	0.1275	1	1	4	1
15	1	1	0.005	0.15	1	1	1	1

Test	NO_3	NO_2	Cl	SO_4	Optic. 1	Optic. 2	Electro. 1	Electro. 2
16	1.2	1.2	0.006	0.18	1	1	4	1
17	0.1	0.15	0.0005	0.015	1	1	1	1
18	0.25	0.38	0.0013	0.0375	1	1	4	1
19	0.4	0.6	0.002	0.06	1	1	1	1
20	0.55	0.83	0.0028	0.0825	1	1	4	1
21	0.7	1.05	0.0035	0.105	1	1	1	1
22	0.85	1.28	0.0043	0.1275	1	1	1	1
23	1	1.5	0.005	0.15	1	1	1	1
24	1.2	1.8	0.006	0.18	1	1	1	1
25	0.1	0.05	0.007	0.015	3	2	5	5
26	0.25	0.13	0.0175	0.0375	3	3	5	4
27	0.4	0.2	0.028	0.06	3	3	5	4
28	0.55	0.28	0.0385	0.0825	3	3	5	4
29	0.7	0.35	0.049	0.105	3	3	5	5
30	0.85	0.43	0.0595	0.1275	3	3	5	5
31	1	0.5	0.07	0.15	2	2	5	5
32	1.2	0.6	0.084	0.18	2	2	5	4
33	0.1	0.1	0.007	0.015	2	2	4	4
34	0.25	0.25	0.0175	0.0375	2	2	4	4
35	0.4	0.4	0.028	0.06	2	2	4	1
36	0.55	0.55	0.0385	0.0825	1	1	1	1
37	0.7	0.7	0.049	0.105	1	1	1	1
38	0.85	0.85	0.0595	0.1275	1	1	1	1
39	1	1	0.07	0.15	1	1	3	3
40	1.2	1.2	0.084	0.18	1	1	1	1
41	0.1	0.15	0.007	0.015	1	1	1	3
42	0.25	0.38	0.0175	0.0375	1	1	3	2
43	0.4	0.6	0.028	0.06	1	1	3	1
44	0.55	0.83	0.0385	0.0825	1	1	1	1
45	0.7	1.05	0.049	0.105	1	1	3	1
46	0.85	1.28	0.0595	0.1275	1	1	3	2
47	1	1.5	0.07	0.15	1	1	1	1
48	1.2	1.8	0.084	0.18	1	1	*	1
49	0.1	0.05	0.0013	0.005	2	2	4	1
50	0.25	0.13	0.0031	0.0125	2	NA	4	1
51	0.4	0.2	0.005	0.02	2	2	2	2
52	0.55	0.28	0.0069	0.0275	2	2	1	2
53	0.7	0.35	0.0088	0.035	2	2	2	3
54	0.85	0.43	0.0106	0.0425	2	2	1	1
55	1	0.5	0.0125	0.05	1	1	1	2

Test	NO_3	NO_2	Cl	SO_4	Optic. 1	Optic. 2	Electro. 1	Electro. 2
56	1.2	0.6	0.015	0.06	1	2	1	1
57	0.1	0.1	0.0013	0.005	2	2	1	1
58	0.25	0.25	0.0031	0.0125	2	1	1	*
59	0.4	0.4	0.005	0.02	2	2	2	1
60	0.55	0.55	0.0069	0.0275	1	1	1	1
61	0.7	0.7	0.0088	0.035	1	1	1	1
62	0.85	0.85	0.0106	0.0425	1	1	1	1
63	1	1	0.0125	0.05	1	1	1	1
64	1.2	1.2	0.015	0.06	1	1	1	1
65	0.1	0.15	0.0013	0.005	1	1	1	1
66	0.25	0.38	0.0031	0.0125	2	2	1	3
67	0.4	0.6	0.005	0.02	1	1	1	1
68	0.55	0.83	0.0069	0.0275	1	1	1	1
69	0.7	1.05	0.0088	0.035	1	1	1	1
70	0.85	1.28	0.0106	0.0425	1	1	1	1
71	1	1.5	0.0125	0.05	1	1	1	1
72	1.2	1.8	0.015	0.06	1	1	1	1
73	0.1	0.05	0.0013	0.05	2	2	5	4
74	0.25	0.13	0.0031	0.125	3	3	4	4
75	0.4	0.2	0.005	0.2	2	2	1	1
76	0.55	0.28	0.0069	0.275	2	2	3	1
77	0.7	0.35	0.0088	0.35	1	1	1	1
78	0.85	0.43	0.0106	0.425	1	1	1	1
79	1	0.5	0.0125	0.5	2	1	1	1
80	1.2	0.6	0.015	0.6	1	1	1	1
81	0.1	0.1	0.0013	0.05	2	1	1	1
82	0.25	0.25	0.0031	0.125	1	1	*	*
83	0.4	0.4	0.005	0.2	1	1	1	1
84	0.55	0.55	0.0069	0.275	1	1	*	*
85	0.7	0.7	0.0088	0.35	1	1	1	1
86	0.85	0.85	0.0106	0.425	1	1	1	1
87	1	1	0.0125	0.5	1	1	1	1
88	1.2	1.2	0.015	0.6	2	1	1	1
89	0.1	0.15	0.0013	0.05	1	1	1	1
90	0.25	0.38	0.0031	0.125	1	1	1	1
91	0.4	0.6	0.005	0.2	1	1	1	1
92	0.55	0.83	0.0069	0.275	1	1	1	1
93	0.7	1.05	0.0088	0.35	1	1	1	1
94	0.85	1.28	0.0106	0.425	1	1	1	1
95	1	1.5	0.0125	0.5	1	1	1	1

Test	NO_3	NO_2	Cl	SO_4	Optic. 1	Optic. 2	Electro. 1	Electro. 2
96	1.2	1.8	0.015	0.6	1	1	1	1
97	0.1	1.8	0.007	0.015	1	1	1	1
98	0.25	1.8	0.0175	0.0375	1	1	1	1
99	0.4	1.8	0.028	0.06	1	1	1	1
100	0.55	1.8	0.0385	0.0825	1	1	1	1
101	0.7	1.8	0.049	0.105	1	1	1	1
102	0.85	1.8	0.0595	0.1275	1	1	1	1
103	1	1.8	0.07	0.15	1	1	1	1
104	1.2	1.8	0.084	0.18	1	1	1	1

* Error occurred during electrochemical run.

Optical results were relied upon for evaluation, however, the electrochemical and optical results agreed for most of the solutions. Duplicate runs for each solution also showed relatively repeatable results. Examples of a cyclic potentiodynamic polarization curve and of the resulting optical image are shown in Figures 7 and 8, respectively.

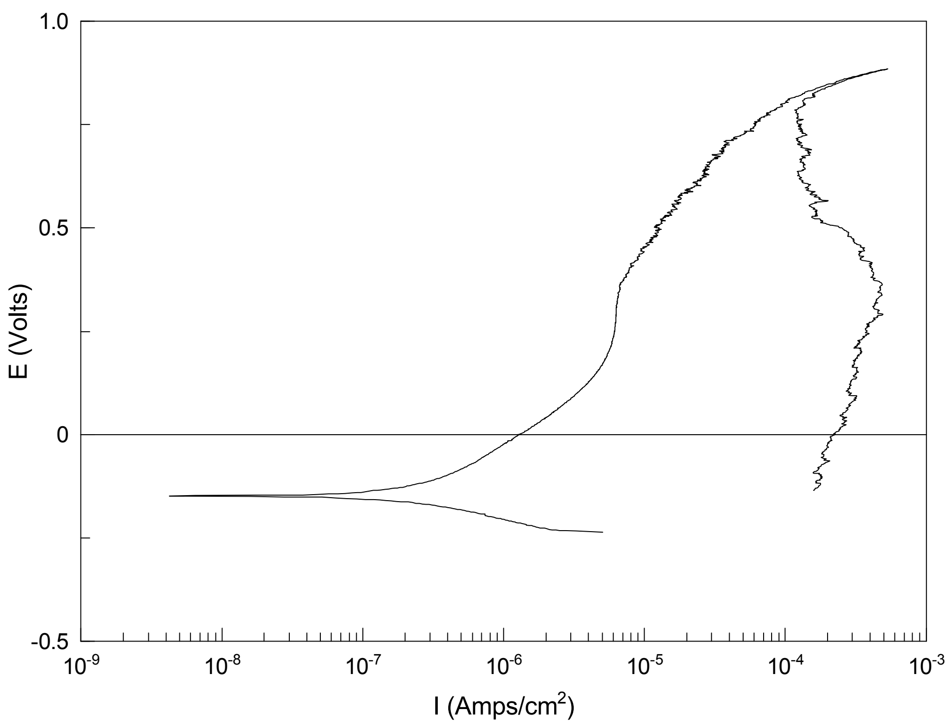

Figure 7 CPP curve for A537 in solution of 0.35 M nitrite, 0.70 M nitrate, 0.049 M chloride, and 0.105 M sulfate.

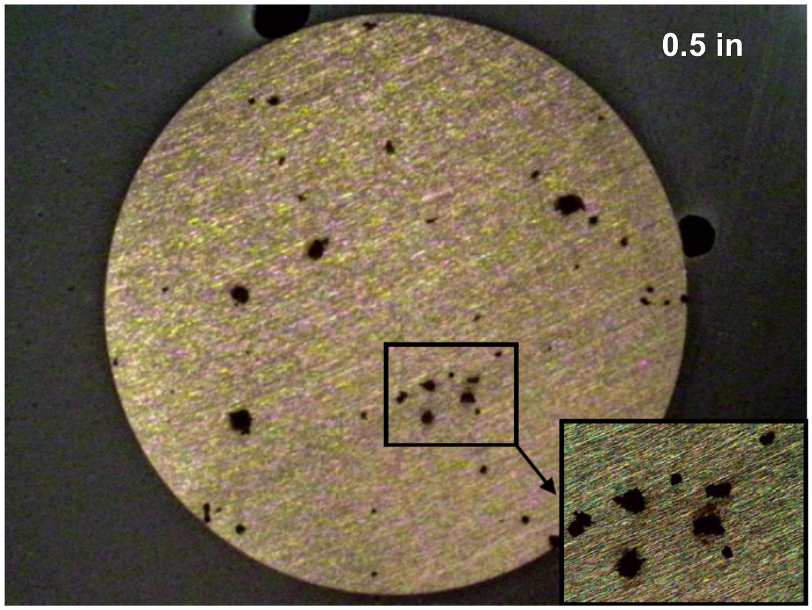

Figure 8 Optical image of A537 after electrochemical test using solution containing 0.35 M nitrite, 0.70 M nitrate, 0.049 M chloride, and 0.105 M sulfate.

The concentration of nitrite is compared to nitrate (Figure 9 and 10), to chloride (Figure 11), to sulfate (Figure 12), and to nitrate + chloride + sulfate (Figure 13). A distinct area of high corrosion susceptibility at low nitrite concentrations is apparent in all of these figures. Figure 9 shows a clear distinction between regions of pitting and no pitting in the nitrite versus nitrate space. The single blue circle at 1.2 M NO_2^- and 1.2 M NO_3^- was found to have a moderate amount of pitting for only one sample. This sample could be considered as "borderline".

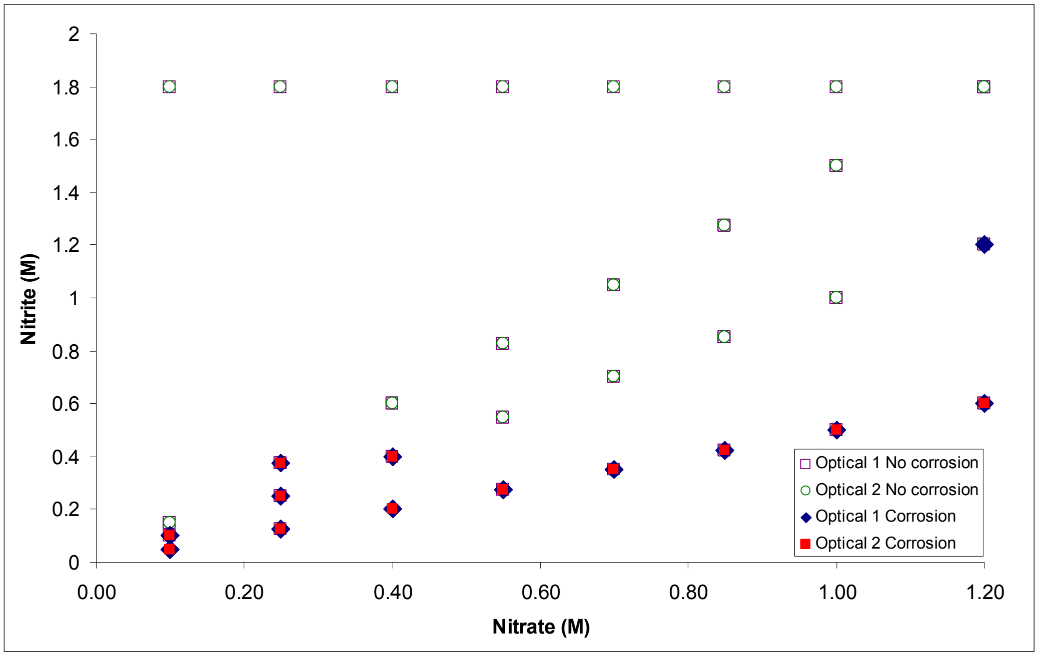

Figure 9 FY'11 results: nitrite versus nitrate concentrations. Note: the data point from optical 1 corrosion set at 1.2 M nitrate and 1.2 M nitrite resulted in two visible pits; however, the electrochemical scan resulted in a negative hysteresis. Due to the conflicting optical and electrochemical results, significant emphasis should not be placed on this outlying data point.

All results from FY-07-FY-11 were combined into the mixture/amount model, which can be seen in Figure 10. The contour plot depicts regions of probability up to >95% of a positive outcome, i.e. no pitting. The region of low nitrate and low nitrite is suggested to result in a corrosion outcome. The resulting contour plot, Figure 10, fits well with the optical results shown in Figure 9.

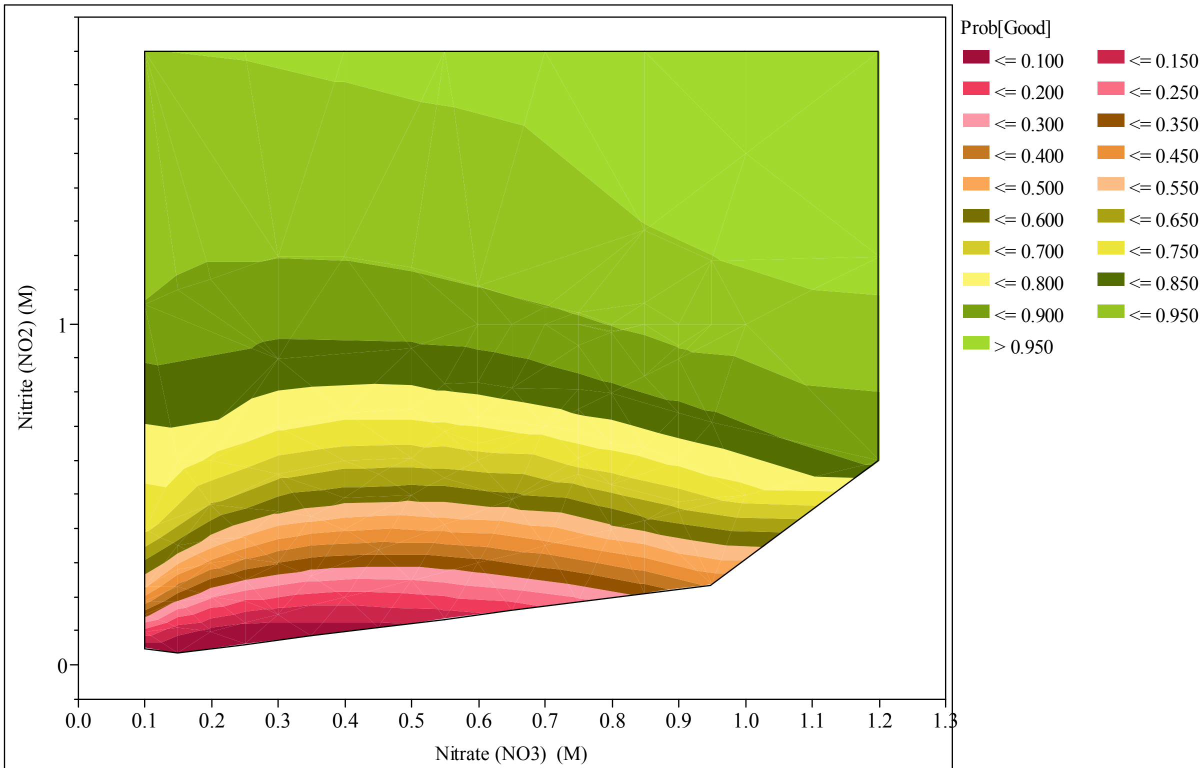

Figure 10 Mixture/amount model applied to the results collected from FY07 to FY11 utilizing JMP™ analysis package [7].

To evaluate the influence of chloride and sulfate ions, the optical results at various nitrite concentrations were plotted against the aggressive species, see Figures 11 and 12.

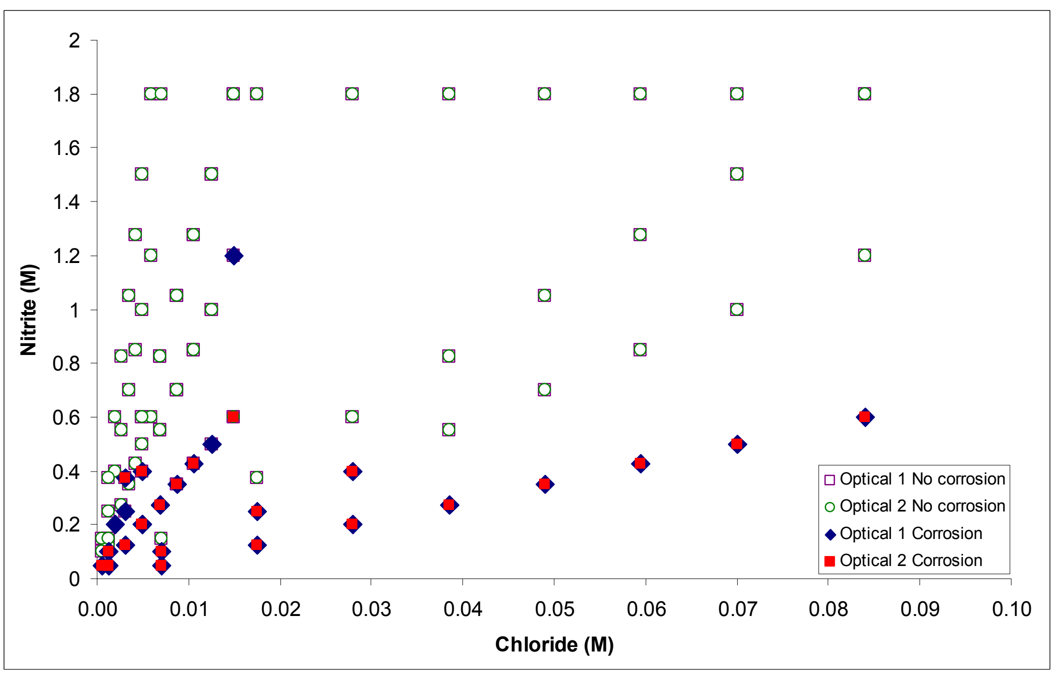

Figure 11 FY'11 results: nitrite versus chloride concentrations.

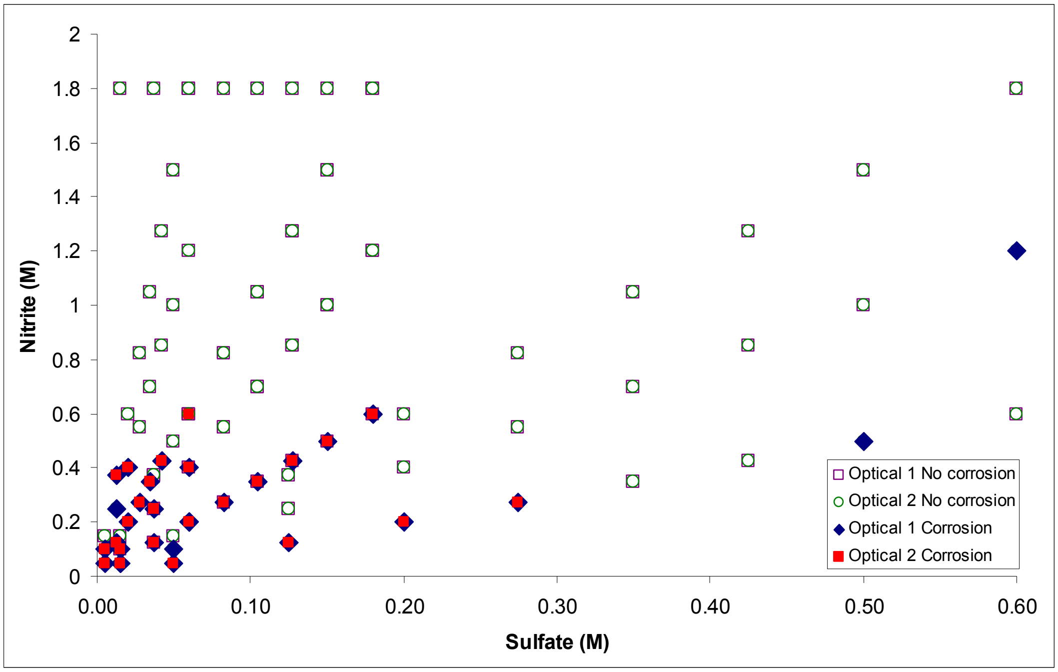

Figure 12 FY'11 results: nitrite versus sulfate concentrations.

Based on Figures 9, and 11-12, increasing the amount of sulfate (Figure 12) does not have as significant of an effect on the probability for pitting corrosion to occur compared to increasing the amount of chloride (Figure 11) or nitrate (Figure 9).

Additionally, nitrate concentrations greater than 1.0 M were evaluated to address the disconnect in concentration limits at 1.0 M nitrate in the chemistry control program. The experimental results do not show an abrupt change in response occurring at 1.0 M nitrate. Therefore, the rapid change in the corrosion control program at this nitrate concentration cannot be justified.

The results can also be viewed in a three-dimensional plot of NO_2^-, Cl^-, and SO_4^-, as seen in Figure 13. The results show that NO_2^- levels can be raised to overcome the influence of Cl^- and SO_4^- concentrations; however, at low levels of NO_2^-, even low levels of Cl^- would result in pitting. For SO_4^-, however, even at high concentrations of SO_4^-, and relatively low levels of NO_2^-, pitting was deterred. This result suggests that Cl^- has a greater contribution to pitting compared to SO_4^-.

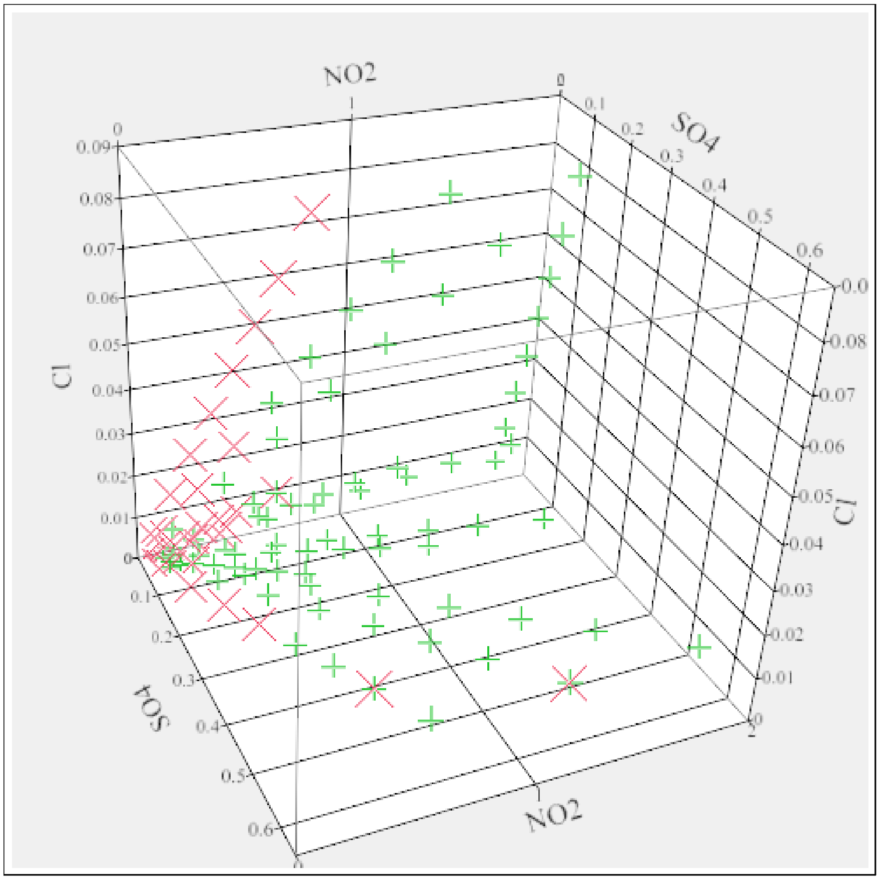

Figure 13 Three-dimensional plot of optical pitting results.

When the results are partitioned based on NO_3^- concentration and the ratios of Cl^- and SO_4^{2-} to the partitioned concentration, it is clear that the pitting probability increases with increasing Cl^-/NO_3^- ratio for a given concentration of inhibitor species, NO_2^-, see Figure.

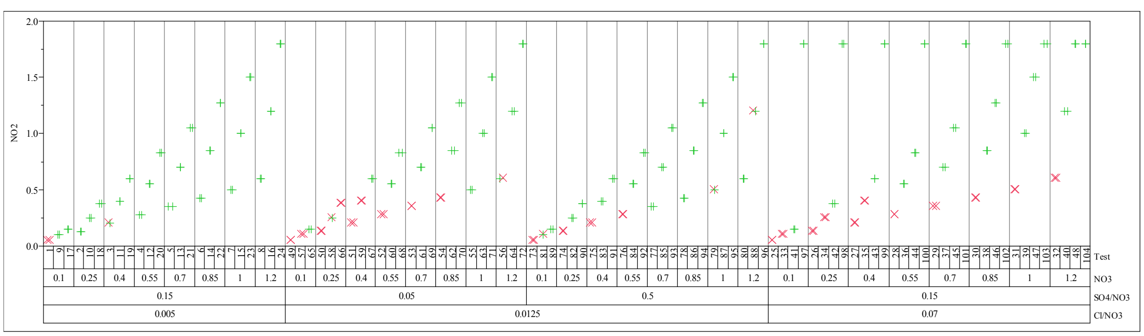

Figure 14 Partitioning of optical results based on NO_3^- concentration, SO_4^-/NO_3^- ratio, and Cl^-/NO_3^- ratio.

Furthermore, when extreme ratios of SO_4^-/NO_3^-, greater than 0.3, and Cl^-/NO_3^-, greater than 0.03, are removed the optical results show further defined clustering in the NO_2 versus NO_3 space, see Figure 15.

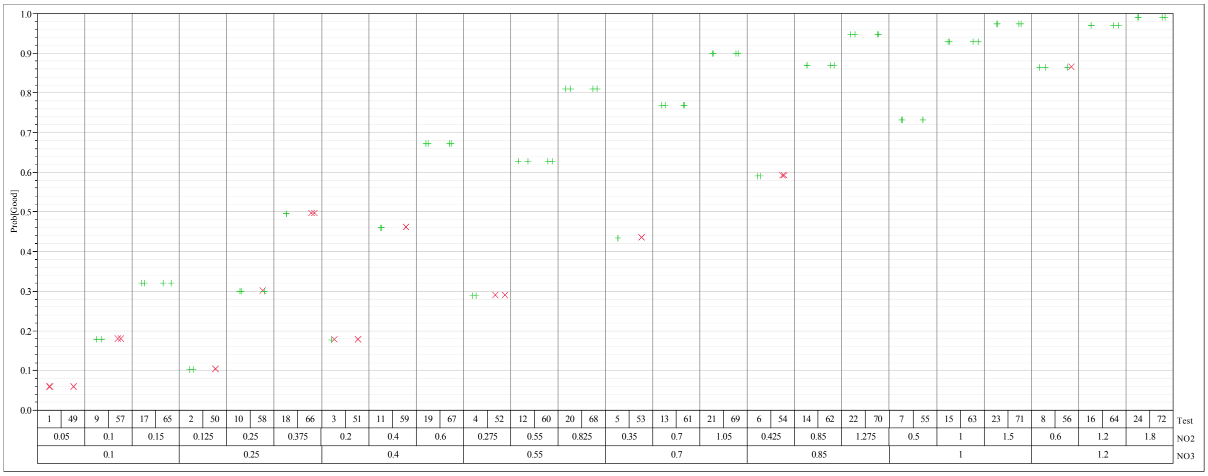

Figure 15 Partitioning of optical results based on NO_3^- and NO_2^- concentrations. Ratios of SO_4^-/NO_3^- > 0.3 and Cl^-/NO_3^- > 0.03 were removed.

The results suggest that the relative concentration of Cl^- and SO_4^{2-} to NO_3^- cannot be overlooked when evaluating the risk of corrosion in solutions containing species NO_2 and NO_3^-.

The combined years' results, evaluated against the current chemistry control limit, are shown in Figure 16. While the region of nitrite > 1.5 M and high nitrate > 0.8 M appears to be consistently safe with no pitting outcomes, the majority of the nitrate/nitrite space is littered with both pitting and no pitting responses. By removing the minor ratios of Cl^-/NO_3^- and SO_4^{2-}/NO_3^-, the region consistently free of pitting becomes significantly larger, see Figure 17.

The experimental results can also be evaluated by plotting the sum of the nitrate and nitrite to the normalized nitrite. Figure 18, which includes all the data, and Figure 19, which omits the extreme minors, further suggests that the current chemistry control limit can be reduced when providing additional restrictions on the chloride and sulfate concentrations.

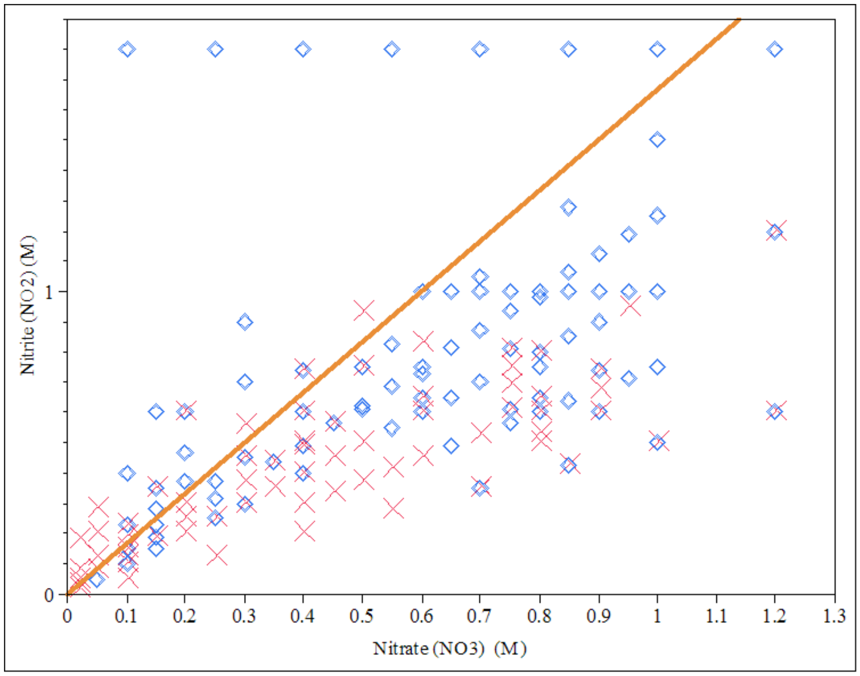

Figure 16 FY'11 results: nitrite versus nitrate concentrations. The solid orange line denotes the current chemistry control limit, red "×" denotes pitting response, blue "◊" denotes non-pitting response.

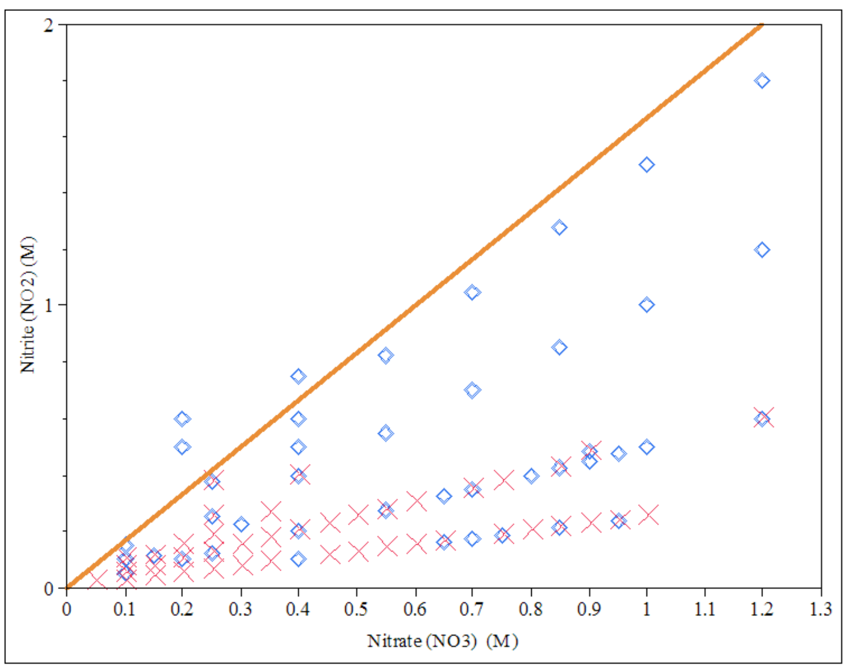

Figure 17 FY'11 results: nitrite versus nitrate concentrations with the exclusion of minor ratios. The solid orange line denotes the current chemistry control limit, red "×" denotes pitting response, blue "◊" denotes non-pitting response.

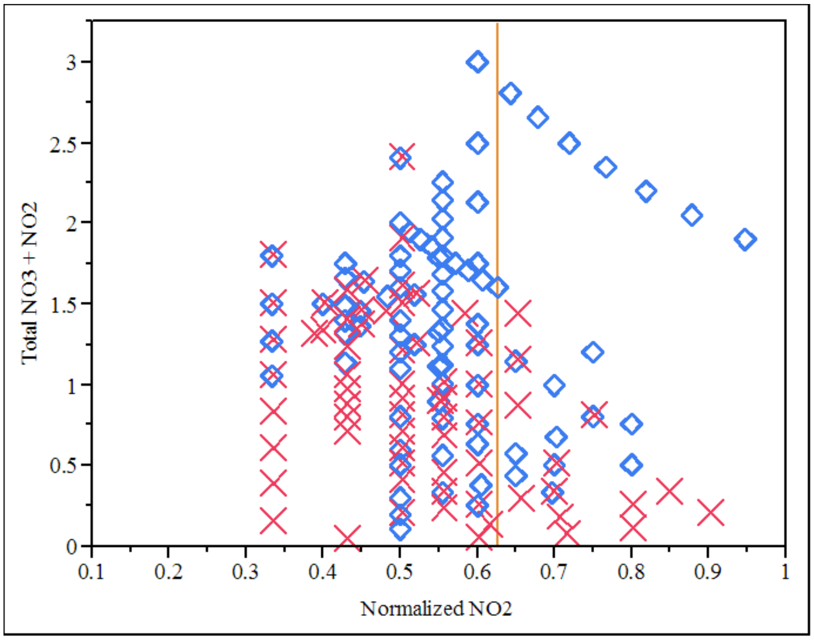

Figure 18 FY'11 results: total nitrite + nitrate versus normalized nitrite concentrations. The solid orange line denotes the current chemistry control limit, red "×" denotes pitting response, blue "◊" denotes non-pitting response.

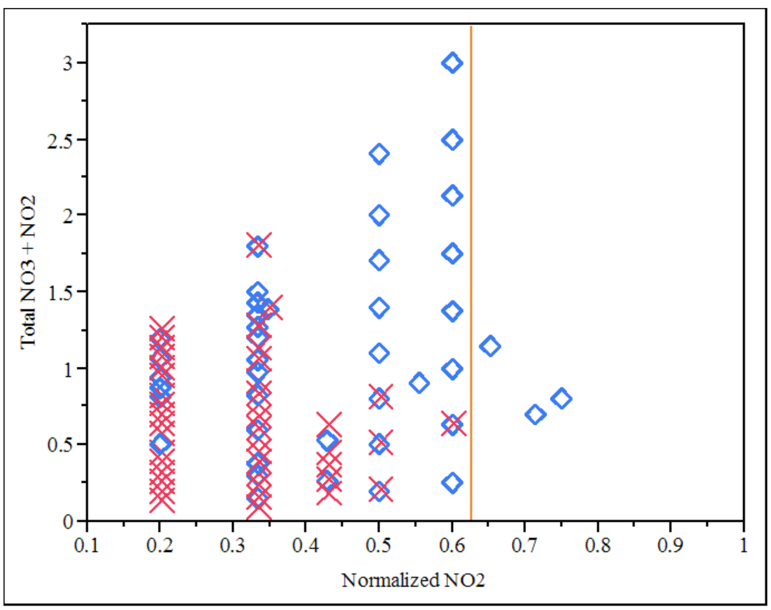

Figure 19 FY'11 results: total nitrite + nitrate versus normalized nitrite concentrations with the exclusion of minor ratios. The solid orange line denotes the current chemistry control limit, red "×" denotes pitting response, blue "◊" denotes non-pitting response.

When theoretical probabilities from the mixture/amount model are applied to the results in Figure 19, agreement can be seen between the experimental results and theoretical predictions. Model predictions for <5% and <10% probability of pitting are shown in Figure 20.

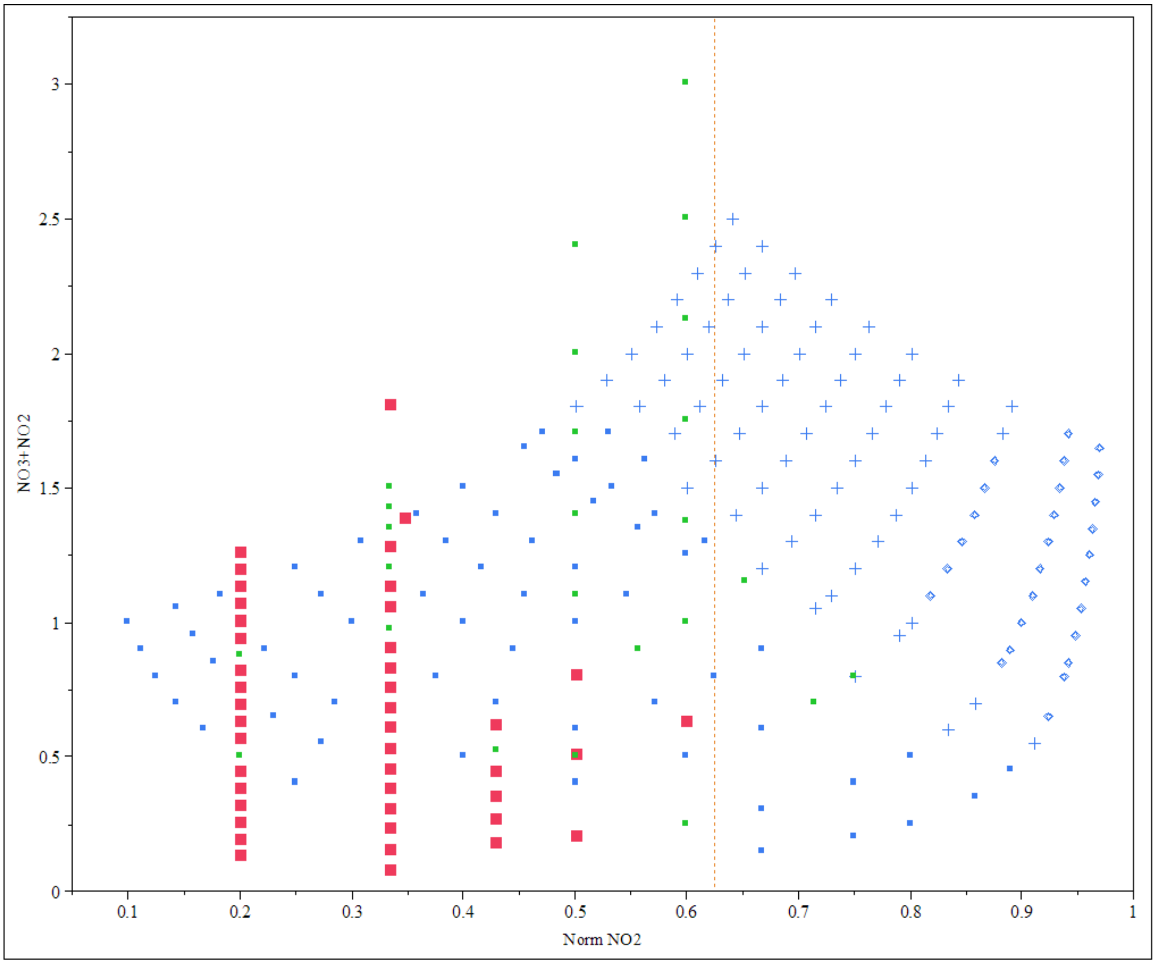

Figure 20 FY'11 results and theoretical mixture/amount model predictions: total nitrite + nitrate versus normalized nitrite concentrations with the exclusion of minor ratios. The dashed orange line denotes the current chemistry control limit, red "■" denotes pitting response, green "■" denotes non-pitting response. Model predicitions are indicated by a blue "+": probability of pitting < 10%, a blue "◊": probability of pitting < 5%.

Another opportunity to assess the performance of the model is provided by Figure 21. In this plot, the optical images of the experimental results with the exclusion of minor ratios are used as labels. A green diamond (◊) is used to represent outcomes whose optical images had no pitting while a red cross (×) is used to represent outcomes with pitting. The probability of pitting for each experimental outcome that is determined from the model is represented on the x-axis with the bound on this probability (at 95% confidence) for the outcome being represented on the y-axis. A 45-degree diagonal line is shown on the plot to highlight the uncertainty (at 95% confidence) of the model's pitting probability as represented by the distance above this diagonal. There are noticeable groupings of no pitting versus pitting results revealed in this plot with no pitting outcomes heavily predominating at probability levels of 0.4 or less. A few experimental outcomes with probability levels less than 0.4 show pitting; the optical images for these results are provided in Figure 22.

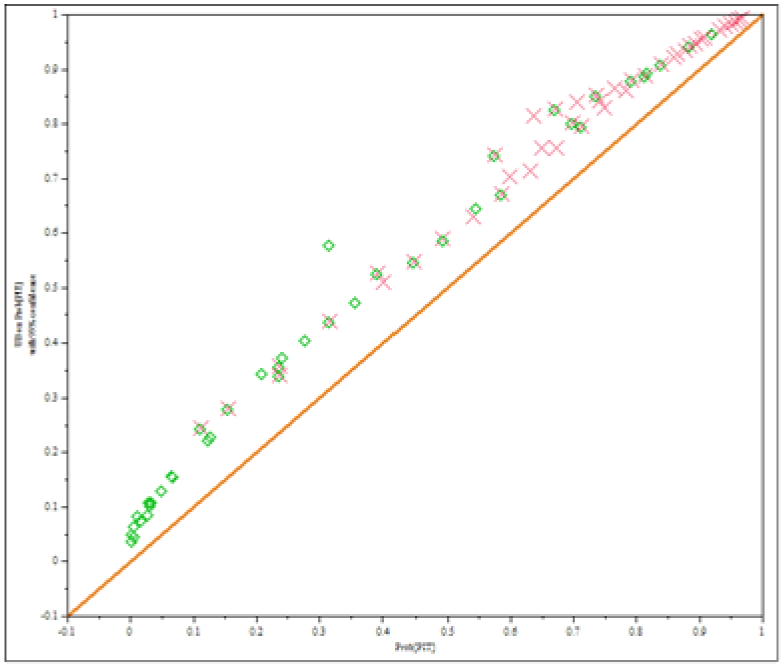

Figure 21 A bivariate fit of upper bound of probability of pitting with a 95% confidence level versus probability of pitting. The orange line is the linear fit. Experimental data: green "◊" denote no pitting, red "×" denote pitting occurrence.

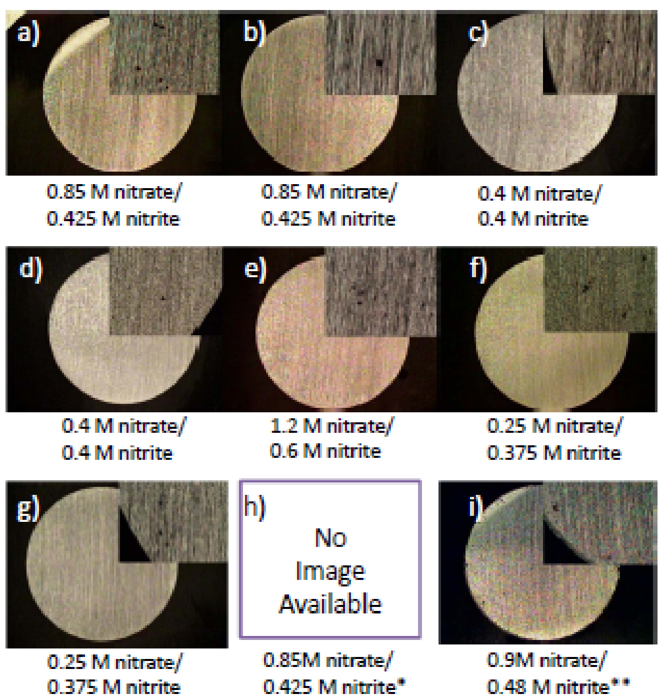

Figure 22 Optical images of electrochemical scans categorized as corroded yet residing in the 0.4 probability or less. Images are from FY11 samples, excluding: * from FY08, ** from FY09.

All of the optical images shown in Figure 22 were classified as moderate corrosion. No clear pits were visible without the aid of increased magnification. The inclusion of the results in the low probability of pitting space highlights the challenge of classifying a sample as a pit versus no pit sample. This result also highlights the potential of a probability based model to predict the severity of pitting in addition to probability.

5.0 CONCLUSIONS

The influence of chloride and sulfate concentration in dilute nitrate solutions was evaluated in FY'11 testing. The results suggest that while nitrate concentrations are the largest of the aggressive species evaluated, chloride and sulfate ions should not be overlooked when evaluating the chemistry control program. In particular, solutions containing $SO_4^-/NO_3^- > 0.3$ or $Cl^-/NO_3^- > 0.03$ have a marked increase in corrosion potential. The current program for tank farm chemistry controls should be modified to reflect the experimental results contained in this report. The net result will be a reduction in inhibitors resulting in fewer additions to the tanks to control corrosion.

6.0 REFERENCES

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[9] DPST-87-379 J.W. Congdon, Inhibition of Washed Sludge with Sodium Nitrite. Inter-Office Memorandum. (April, 1987)

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