Radioactive High Level Waste Tank Pitting Predictions: An Investigation into Critical Solution Concentrations

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Abstract

A series of cyclic potentiodynamic polarization tests was performed on samples of ASTM A537 carbon steel in support of a probability-based approach to evaluate the effect of chloride and sulfate on corrosion the steel's susceptibility to pitting corrosion. Testing solutions were chosen to systemically evaluate the influence of the secondary aggressive species, chloride, and sulfate, in the nitrate based, high-level wastes. The 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.

INTRODUCTION

Underground carbon steel tanks are located at the Savannah River Site (SRS) purposed to store radioactive liquid waste. A waste tank chemistry control program, with the goal of reducing the susceptibility of the tank wall to pitting corrosion, 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 the overly conservative use of inhibitor. Furthermore, when using nitrite as an inhibitor, the amount of inhibitor required by the current chemistry control program is based on a linear model of a log scale relationship between aggressive and protective species. Primarily supported by experimental data obtained from dilute solutions with nitrate concentrations less than 0.4 M, this linear model was used to produce the current chemistry control program at 1.0 M nitrate or less. Based on the current chemistry control program, the minimum molar concentrations of nitrite species required to prevent pitting in the 0.02 to 1.00 M nitrate concentration range at $T \leq 40$ ˚C depends on the concentration of chloride and sulfate and are:

$$[NO_2^-] = 1.66 \text{ x } [NO_3^-]$$
$$[NO_2^-] = 6.11 \text{ x } 10^{[1.64+1.34 \text{ x } \log[Cl-]]}$$
$$[NO_2^-] = 0.04 \text{ x } 10^{[1.64+0.84 \text{ x } \log[SO_4 2-]]}$$

The control program limits are based on the results of electrochemical polarization scans and coupon immersion tests.

Studies were conducted 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 when the nitrate concentration is below 1.0 M.

A summary of the combined results that illustrate the potential importance of chloride and sulfate ions as well as the nitrite content in the high-level waste is shown in Figure 1. While areas of corrosion (solid symbols) and no corrosion (open symbols) are evident, significant areas of the graph are ambiguous, having both corrosion and no corrosion results.

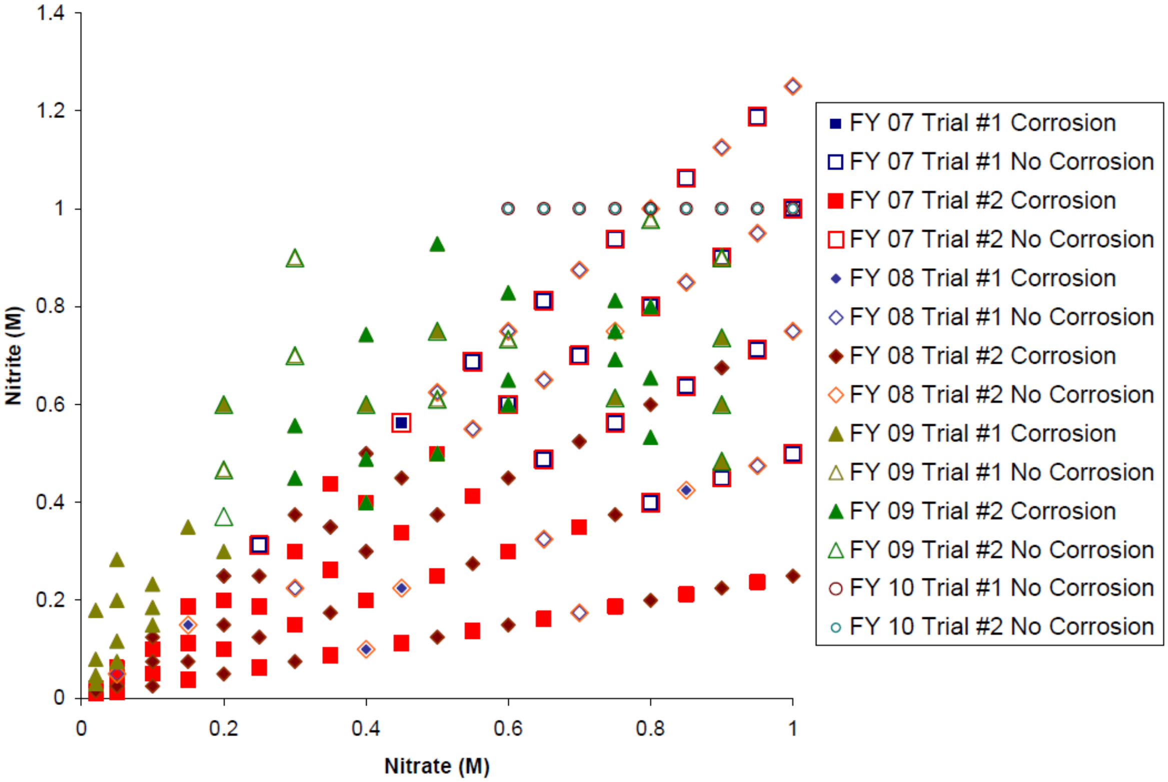

Figure 1 Optical results of electrochemical testing.

Logistical regression was utilized to design a statistically based experimental matrix to develop a tool for predicting corrosion vulnerability and realistically determining the required inhibitor concentrations as a function of aggressive ion content. This paper presents the experimental program, provides the test results and develops the data/analyses to show how chloride and sulfate concentrations should be included in the waste tank chemistry control program to minimize both the susceptibility to corrosion and the addition of nitrite to inhibit the waste solution. The data package is included in the paper to provide the reader the opportunity to further evaluate the assessments.

EXPERIMENTAL METHOD

Cyclic potentiodynamic polarization (CPP) scans have been performed routinely to experimentally determine the pitting propensity of various alloys exposed to aqueous environments. 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 of the alloy. Significant hysteresis in the potential vs current plots with higher currents generated on the reverse scan (positive hysteresis) provide an indication of pit formation. The scan results are also used to characterize the stability of the surface oxide and to determine the effectiveness of inhibitors.

MATERIALS

Material

Semi-killed, hot-rolled ASTM A537 Class I carbon steel 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 600 grit SiC grinding sheets to remove the native oxide layer and provide a flat surface.

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, corrosion inhibiting, anions in the solution 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 high-level 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, as shown in Table 1. The chloride and sulfate limits were chosen based on Tank 51 washing cycles rather than using the maximum chemistry control limits.

Table 1 Test matrix #1. Each testing solution was run in duplicate totaling 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

A second matrix, Table 2, was 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^-. The testing is a systematic evaluation of Cl^- and SO_4^{2-} on the minimum NO_2^- required to inhibit pitting. The test matrix focuses on the solution concentration space below the maximum critical 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-} tested are listed in Table 2, 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. 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^- were 0.03 and 0.3, respectively, when the primary aggressive species in the test solution 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 the critical ratios.

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 at 10.0 using a constant carbonate/bicarbonate molar ratio of 7 to 13. The gram amount of carbonate and bicarbonate added was based on the nitrite concentration in the solution. A total of 104 solutions were used for electrochemical testing. Solutions were prepared based on a statistically determined experimental design [6].

Table 2 Test matrix #2. 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
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

Test	NO_2/NO_3	NO_2+NO_3	Cl/NO_3	SO_4/NO_3	NO_3	NO_2	Cl	SO_4
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
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

Test	NO_2/NO_3	NO_2+NO_3	Cl/NO_3	SO_4/NO_3	NO_3	NO_2	Cl	SO_4
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
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

Electrochemical Testing

The electrochemical cell used had the A537 test samples attached to a conductive wire and mounted in metallographic mount material which was used as the working electrode and two graphite rods were 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 until either a vertex potential of 1.2 V vs the saturated calomel reference electrode or to a maximum current of 0.001 Amps was reached. The reverse scan rate of 0.5 mV/sec was used until a final potential of 0 V vs open circuit potential was reached. Steel samples in each solution were 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 because the optical/visual results lent towards a simple binary observation compared to the much more complex electrochemical response which yielded several CPP curve shapes spanning a range of current densities and electrical potentials.

Post-Electrochemical Evaluation

The surface of samples post-electrochemical testing was visually evaluated using a microscope, see Figure 2. Ranking for optical results were categorized as follows:

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

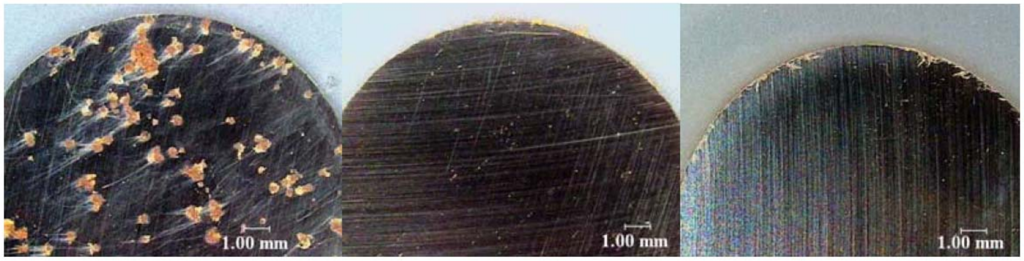

Figure 2 Degrees of corrosion: (left) significant, (center) moderate, (right) no corrosion. Note: crevice corrosion was not taken into account.

RESULTS

1.1 RISK BASED CORROSION TESTING

Test matrix #1 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 3.

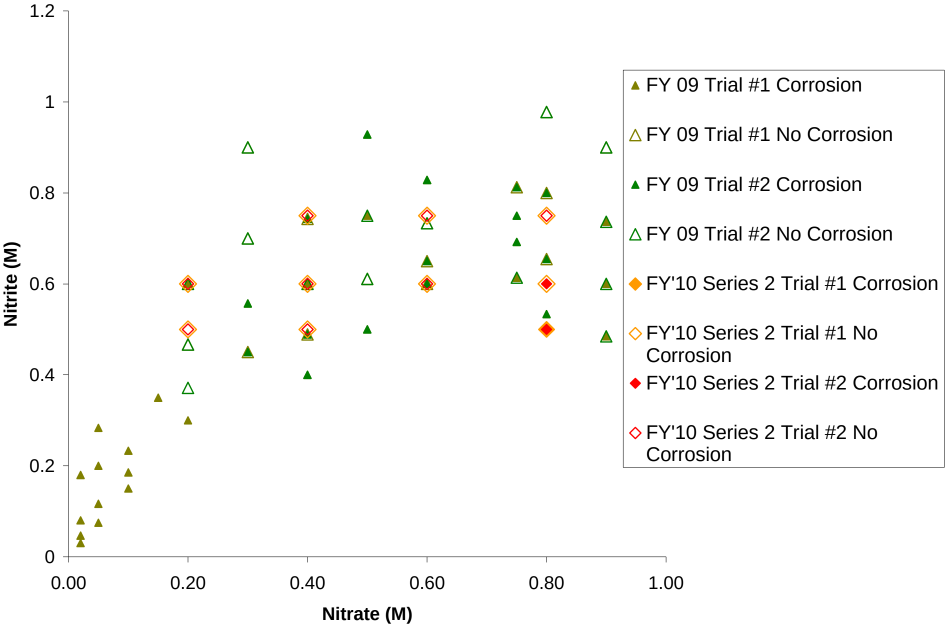

Figure 3 Test matrix #1 with constant chloride and sulfate concentrations compared to testing in similar nitrate and nitrite concentrations with chloride and sulfate concentrations that scaled with the nitrite concentration. Chloride and sulfate concentrations were dependent on the nitrite concentration and were based on chemistry control limits for FY09 data. Chloride and sulfate concentrations were constant and based on recent washing cycles in Tank 51 in FY10 data.

The results test matrix #1 provided a semi-clean break between regions of corrosion and no corrosion in the nitrite/nitrate space, especially when the chloride and sulfate concentrations were constant. This result strongly suggested the need for further evaluation of the effect of chloride and sulfate.

The optical results of the test matrix #2 solutions tested are provided in Table 3.

Table 3 Test matrix #2 optical results.

Test	NO_3	NO_2	Cl	SO_4	Optic. 1	Optic. 2
1	0.1	0.05	0.0005	0.015	2	2
2	0.25	0.13	0.0013	0.0375	1	1
3	0.4	0.2	0.002	0.06	2	1
4	0.55	0.28	0.0028	0.0825	1	1
5	0.7	0.35	0.0035	0.105	1	1
6	0.85	0.43	0.0043	0.1275	1	1
7	1	0.5	0.005	0.15	1	1
8	1.2	0.6	0.006	0.18	1	1
9	0.1	0.1	0.0005	0.015	1	1
10	0.25	0.25	0.0013	0.0375	1	1
11	0.4	0.4	0.002	0.06	1	1
12	0.55	0.55	0.0028	0.0825	1	1
13	0.7	0.7	0.0035	0.105	1	1
14	0.85	0.85	0.0043	0.1275	1	1
15	1	1	0.005	0.15	1	1
16	1.2	1.2	0.006	0.18	1	1
17	0.1	0.15	0.0005	0.015	1	1
18	0.25	0.38	0.0013	0.0375	1	1
19	0.4	0.6	0.002	0.06	1	1
20	0.55	0.83	0.0028	0.0825	1	1
21	0.7	1.05	0.0035	0.105	1	1
22	0.85	1.28	0.0043	0.1275	1	1
23	1	1.5	0.005	0.15	1	1
24	1.2	1.8	0.006	0.18	1	1
25	0.1	0.05	0.007	0.015	3	2
26	0.25	0.13	0.0175	0.0375	3	3
27	0.4	0.2	0.028	0.06	3	3
28	0.55	0.28	0.0385	0.0825	3	3
29	0.7	0.35	0.049	0.105	3	3
30	0.85	0.43	0.0595	0.1275	3	3
31	1	0.5	0.07	0.15	2	2
32	1.2	0.6	0.084	0.18	2	2
33	0.1	0.1	0.007	0.015	2	2
34	0.25	0.25	0.0175	0.0375	2	2

Test	NO_3	NO_2	Cl	SO_4	Optic. 1	Optic. 2
35	0.4	0.4	0.028	0.06	2	2
36	0.55	0.55	0.0385	0.0825	1	1
37	0.7	0.7	0.049	0.105	1	1
38	0.85	0.85	0.0595	0.1275	1	1
39	1	1	0.07	0.15	1	1
40	1.2	1.2	0.084	0.18	1	1
41	0.1	0.15	0.007	0.015	1	1
42	0.25	0.38	0.0175	0.0375	1	1
43	0.4	0.6	0.028	0.06	1	1
44	0.55	0.83	0.0385	0.0825	1	1
45	0.7	1.05	0.049	0.105	1	1
46	0.85	1.28	0.0595	0.1275	1	1
47	1	1.5	0.07	0.15	1	1
48	1.2	1.8	0.084	0.18	1	1
49	0.1	0.05	0.0013	0.005	2	2
50	0.25	0.13	0.0031	0.0125	2	NA
51	0.4	0.2	0.005	0.02	2	2
52	0.55	0.28	0.0069	0.0275	2	2
53	0.7	0.35	0.0088	0.035	2	2
54	0.85	0.43	0.0106	0.0425	2	2
55	1	0.5	0.0125	0.05	1	1
56	1.2	0.6	0.015	0.06	1	2
57	0.1	0.1	0.0013	0.005	2	2
58	0.25	0.25	0.0031	0.0125	2	1
59	0.4	0.4	0.005	0.02	2	2
60	0.55	0.55	0.0069	0.0275	1	1
61	0.7	0.7	0.0088	0.035	1	1
62	0.85	0.85	0.0106	0.0425	1	1
63	1	1	0.0125	0.05	1	1
64	1.2	1.2	0.015	0.06	1	1
65	0.1	0.15	0.0013	0.005	1	1
66	0.25	0.38	0.0031	0.0125	2	2
67	0.4	0.6	0.005	0.02	1	1
68	0.55	0.83	0.0069	0.0275	1	1
69	0.7	1.05	0.0088	0.035	1	1
70	0.85	1.28	0.0106	0.0425	1	1
71	1	1.5	0.0125	0.05	1	1
72	1.2	1.8	0.015	0.06	1	1
73	0.1	0.05	0.0013	0.05	2	2
74	0.25	0.13	0.0031	0.125	3	3

Test	NO_3	NO_2	Cl	SO_4	Optic. 1	Optic. 2
75	0.4	0.2	0.005	0.2	2	2
76	0.55	0.28	0.0069	0.275	2	2
77	0.7	0.35	0.0088	0.35	1	1
78	0.85	0.43	0.0106	0.425	1	1
79	1	0.5	0.0125	0.5	2	1
80	1.2	0.6	0.015	0.6	1	1
81	0.1	0.1	0.0013	0.05	2	1
82	0.25	0.25	0.0031	0.125	1	1
83	0.4	0.4	0.005	0.2	1	1
84	0.55	0.55	0.0069	0.275	1	1
85	0.7	0.7	0.0088	0.35	1	1
86	0.85	0.85	0.0106	0.425	1	1
87	1	1	0.0125	0.5	1	1
88	1.2	1.2	0.015	0.6	2	1
89	0.1	0.15	0.0013	0.05	1	1
90	0.25	0.38	0.0031	0.125	1	1
91	0.4	0.6	0.005	0.2	1	1
92	0.55	0.83	0.0069	0.275	1	1
93	0.7	1.05	0.0088	0.35	1	1
94	0.85	1.28	0.0106	0.425	1	1
95	1	1.5	0.0125	0.5	1	1
96	1.2	1.8	0.015	0.6	1	1
97	0.1	1.8	0.007	0.015	1	1
98	0.25	1.8	0.0175	0.0375	1	1
99	0.4	1.8	0.028	0.06	1	1
100	0.55	1.8	0.0385	0.0825	1	1
101	0.7	1.8	0.049	0.105	1	1
102	0.85	1.8	0.0595	0.1275	1	1
103	1	1.8	0.07	0.15	1	1
104	1.2	1.8	0.084	0.18	1	1

Duplicate runs for each solution showed relatively repeatable results. The concentration of nitrite is compared to nitrate (Figure 4), to chloride (Figure 5), and to sulfate (Figure 6). A distinct area of high corrosion susceptibility at low nitrite concentrations is apparent in all of the figures. Figure 6 shows a clear distinction between regions of pitting and no pitting in the nitrite versus nitrate space. The single blue data point at 1.2 M NO_2^- and 1.2 M NO_3^- in Figure 4 is considered a "borderline" result because a moderate amount of pitting was found in one sample and no pitting was found in the duplicate sample.

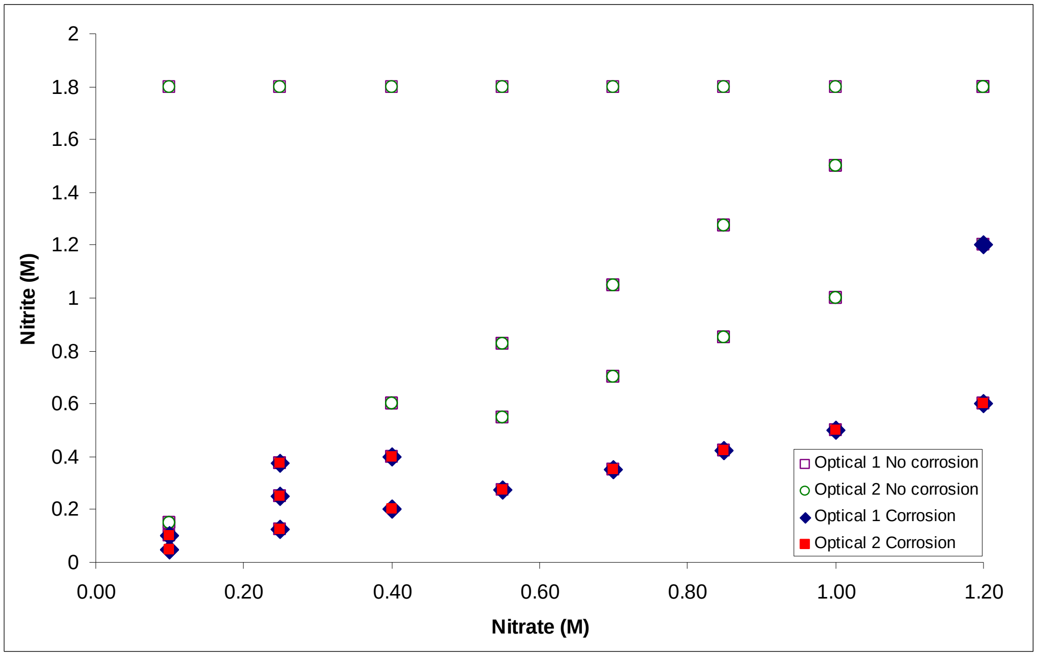

Figure 4 Nitrite versus nitrate concentrations. Note: the data point from optical 1 corrosion set at 1.2 M nitrate and 1.2 M nitrite resulted in two visible pits; however, the electrochemical scan resulted in a negative hysteresis. Due to the conflicting optical and electrochemical results, significant emphasis should not be placed on this outlying data point.

To further evaluate the influence of chloride and sulfate ions, the optical results at various nitrite concentrations were plotted against the aggressive species, see Figures 5 and 6.

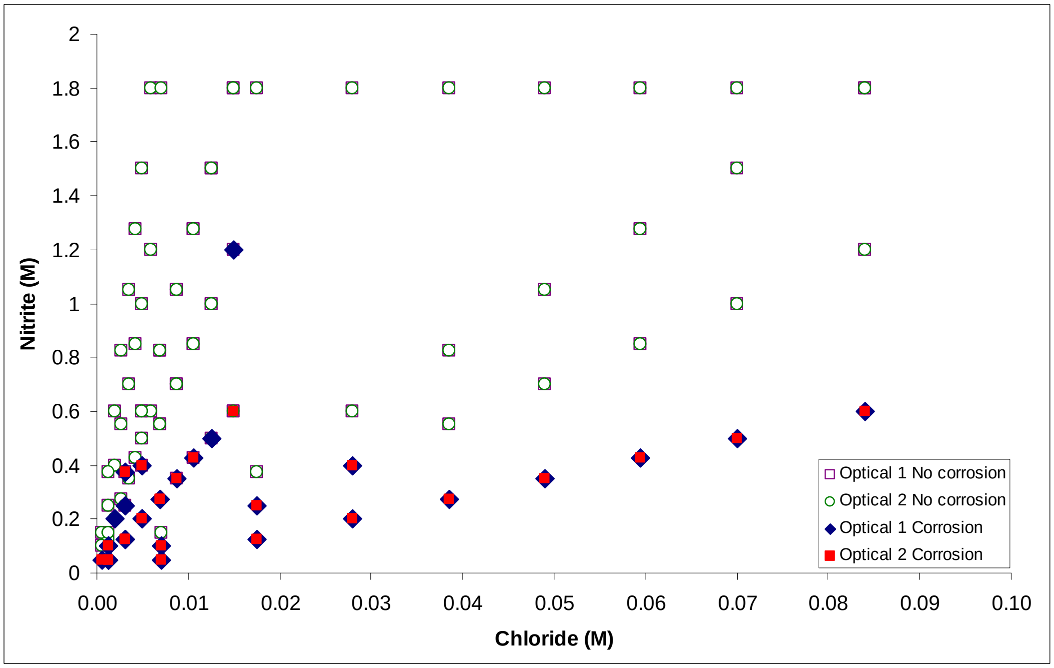

Figure 5 Nitrite versus chloride concentrations.

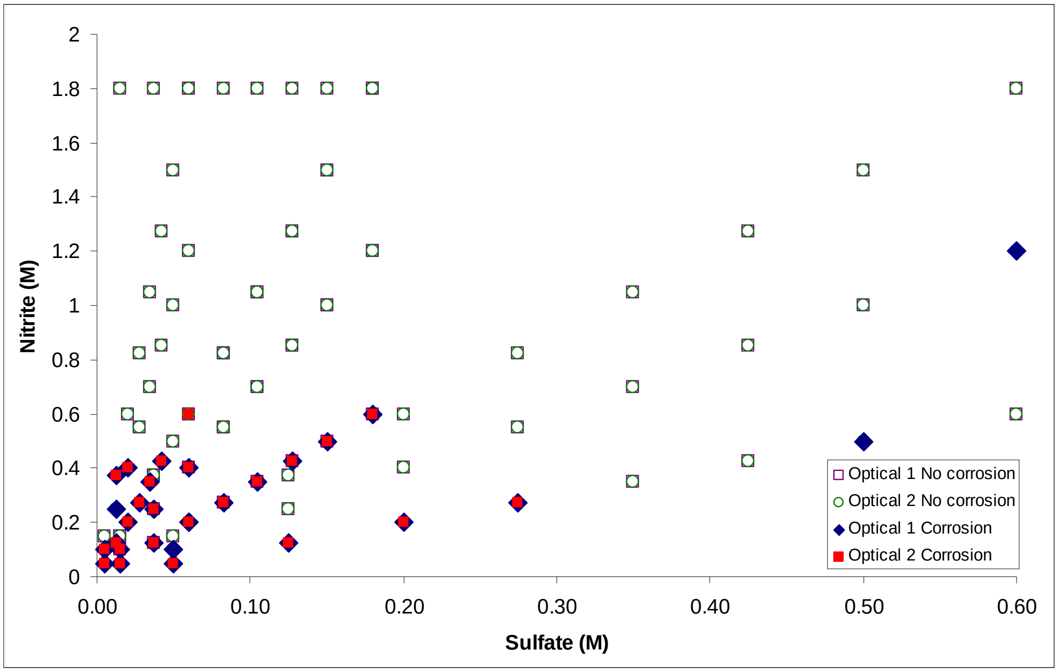

Figure 6 Nitrite versus sulfate concentrations.

Based on Figures 4-6, increasing the amount of sulfate (6) does not have as significant effect on the probability for pitting corrosion as increasing the amount of chloride (5) or nitrate (4).

Additionally, nitrate concentrations greater than 1.0 M were evaluated to address the abrupt change in concentration limits that currently exists in the chemistry control program at 1.0 M nitrate. 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 7. 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^-.

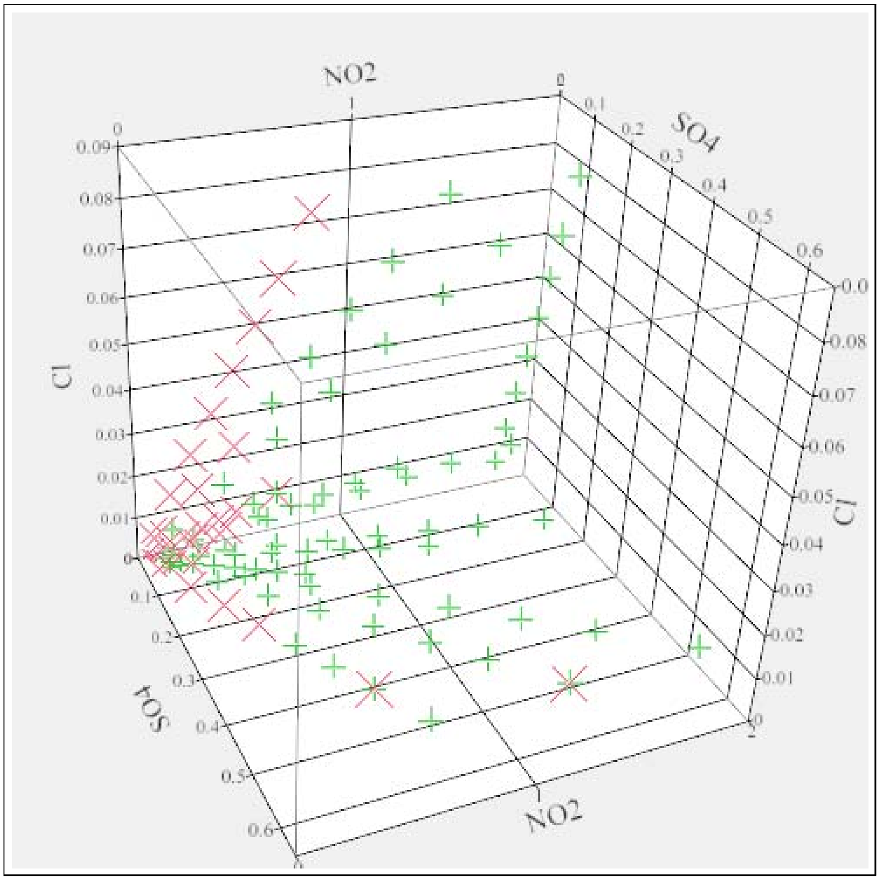

Figure 7 Three-dimensional plot of optical pitting results.

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 8.

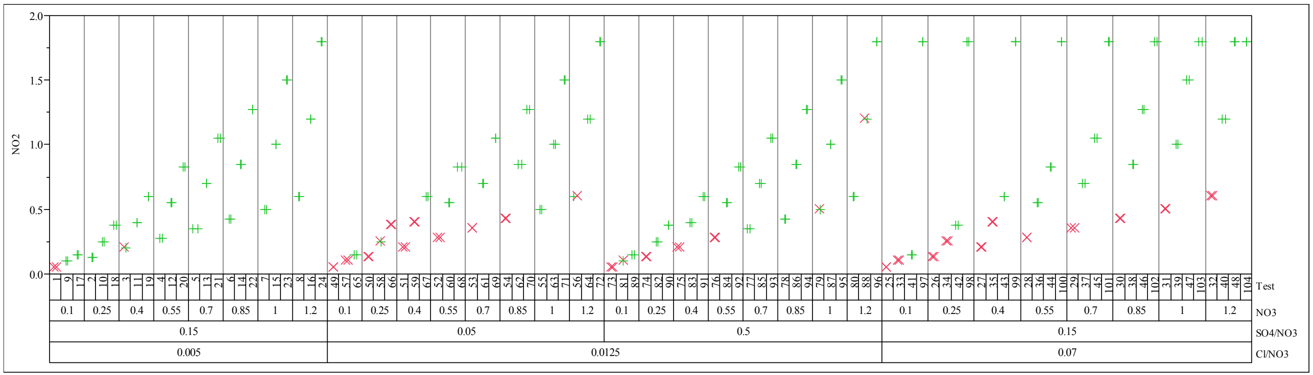

Figure 8 Partitioning of test matrix #2 optical results based on NO_3^- concentration, SO_4^-/NO_3^- ratio, and Cl^-/NO_3^- ratio. Liz – Figure 8 is hard to read and understand – please rework the figure.

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 9.

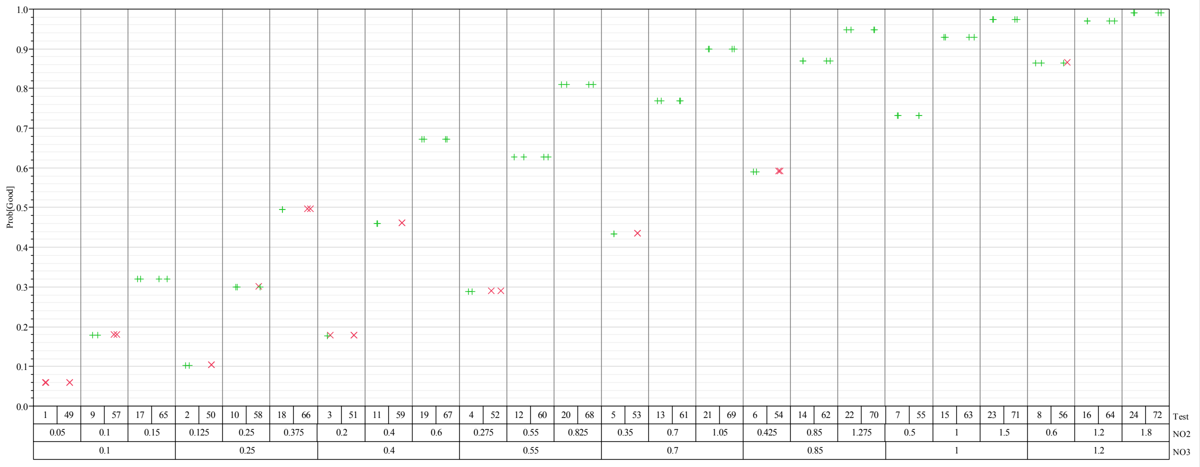

Figure 9 Partitioning of test matrix #2 optical results based on NO_3^- and NO_2^- concentrations. Ratios of SO_4^-/NO_3^- > 0.3 and Cl^-/NO_3^- > 0.03 were removed. Please rework.

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

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.

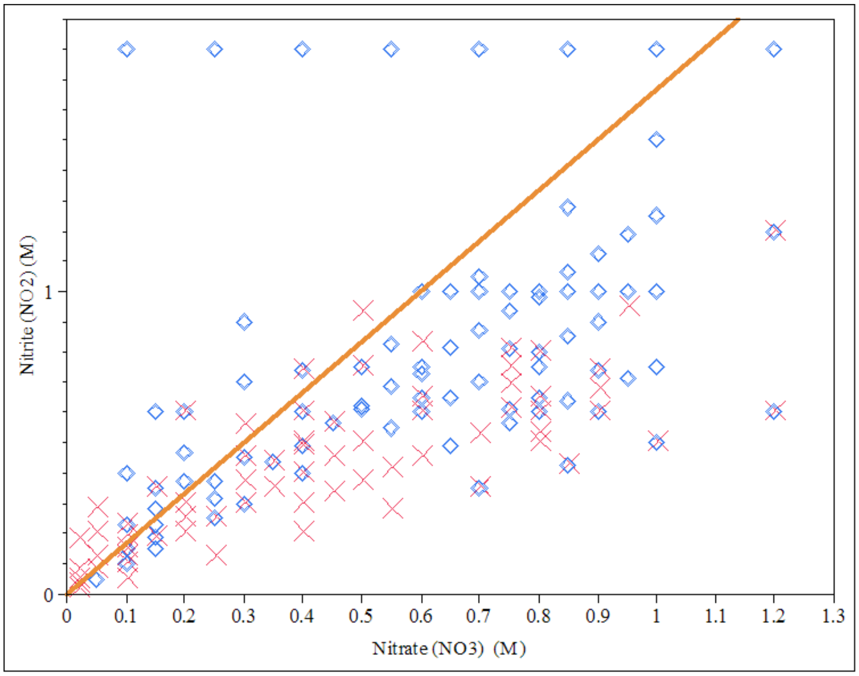

Figure 10 **Nitrite versus nitrate concentrations with inclusion of minor ratios. The solid orange line denotes the current chemistry control limit, red "×" denotes pitting response, blue "◊" denotes non-pitting response.**

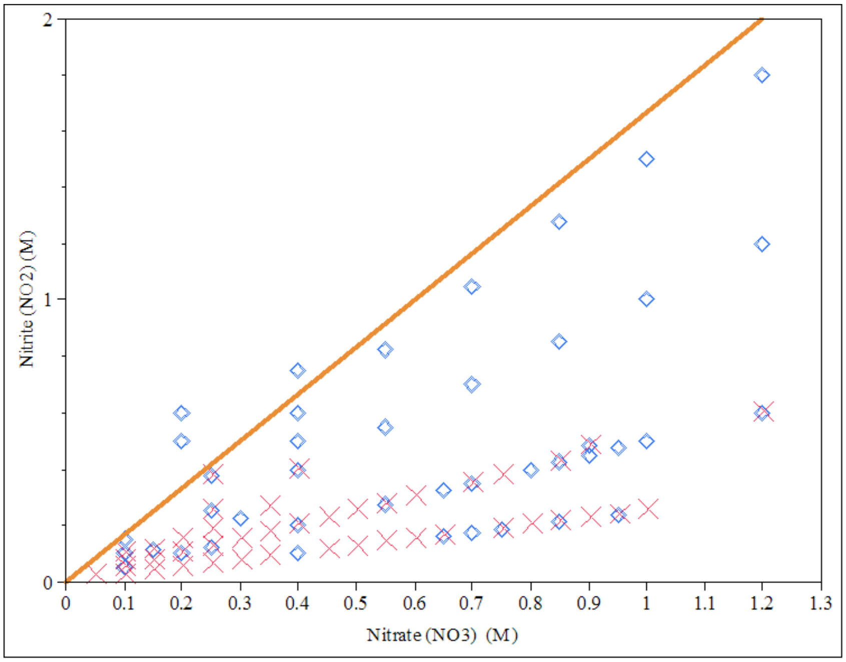

Figure 11 **Nitrite versus nitrate concentrations with the exclusion of minor ratios. The solid orange line denotes the current chemistry control limit, red "×" denotes pitting response, blue "◊" denotes non-pitting response.**

CONCLUSIONS

The influence of chloride and sulfate concentration in dilute nitrate solutions was evaluated. The results suggest that, of the aggressive species evaluated, nitrate concentrations have the largest effects on corrosion but the effects of 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 inhibitor additions to the tanks to control corrosion.

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