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INHIBITING LOCALIZED CORROSION IN MILD CARBON STEEL

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ABSTRACT

Controls on the solution chemistry are in place to prevent the initiation and propagation of pitting and stress corrosion cracking in high level waste (HLW) tanks. These controls are based upon a series of experiments performed using simulated solutions on materials used for construction of the tanks, namely ASTM A537 carbon steel. An experimental program was undertaken to investigate reducing the minimum molar nitrite concentration required to confidently inhibit pitting. The experimental results and conclusions provided herein will support a statistical basis to quantify the probability of pitting for the tank wall, when exposed to various solutions containing dilute concentrations of nitrate and nitrite. Coupon testing was performed within the framework of the statistical test matrix to determine the pitting propensity associated with inhibitor concentrations. The visual observation results indicate a potential for inhibitor reductions without consequence in the solution space. The majority of corrosion occurred at the interface of the solution and vapor space. Only one sample with the dilute concentration of both nitrate and nitrite exhibited visible pitting in the solution space.

Keywords: pitting, carbon steel, high level waste tank

INTRODUCTION

Large underground carbon steel tanks provide storage for high level radioactive waste at the DOE Savannah River Site (SRS). ASTM A537 steel is one of the grades of carbon steel used for tank construction. An assessment of the potential degradation mechanisms of the high level waste (HLW) tanks determined that nitrate-induced pitting corrosion and stress corrosion cracking were the two most significant degradation mechanisms¹. Chemistry controls on the solution chemistry requiring minimum nitrite and hydroxide concentrations are in place to prevent the initiation and propagation of pitting and stress corrosion cracking in the tanks¹. These controls are based upon a series of experiments performed using simulated solutions on carbon steels used in the construction of the tanks.

In dilute waste solutions, nitrate-induced pitting, chloride-induced pitting, and sulfate-induced pitting are the corrosion mechanisms of concern². 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 ≤ 40 °C are:

$$[\text{NO}_2^-] = 1.66 \times [\text{NO}_3^-] \quad (1)$$

$$[\text{NO}_2^-] = 6.11 \times 10^{[1.64+1.34 \times \log[\text{Cl}^-]]} \quad (2)$$

$$[\text{NO}_2^-] = 0.04 \times 10^{[1.64+0.84 \log[\text{SO}_4^{2-}]]} \quad (3)$$

The aforementioned limits are based on the results of electrochemical polarization scans and coupon immersion tests^{3,4}. In the event that the nitrate anion is in low concentration and is not the principal corrosive anion, minimum nitrite levels can be calculated based upon the chloride or sulfate concentrations.

The chemistry control program has thus far been implemented by applying a safety factor based on engineering judgment to the available experimental data. The ideal chemistry control program would add the lowest volume of salts to maintain the solution chemistry at a desired concentration to minimize corrosion vulnerabilities. It was proposed that a probability based approach can be used to quantify the risk associated with the chemistry control envelope. This can lead to an application specific chemistry control program such as broadening the envelope for closure goals, while maintaining current control levels for long-term storage.

An experimental program was undertaken to investigate the potential for relaxing the current chemistry control program without significantly affecting the risk of pitting by reducing the required nitrite concentration. An experimental matrix determined using logistical regression, provided a strategy for experimentation⁵. Figure 1 plots the existing data and the design points where a pitted outcomes from various testing programs are represented by a blue “X” or a red “X” and outcomes that showed no pitting are represented by a solid blue circle “•” or a solid green circle “•”. The design points (□) used for the experimentation described herein shown in Figure 1 were based on 5 constant ratios of nitrate to nitrite. The experimental matrix was designed to provide sufficient data to develop a predictive tool for corrosion vulnerability within the concentration range of 0.02 to 1.00 M nitrite.

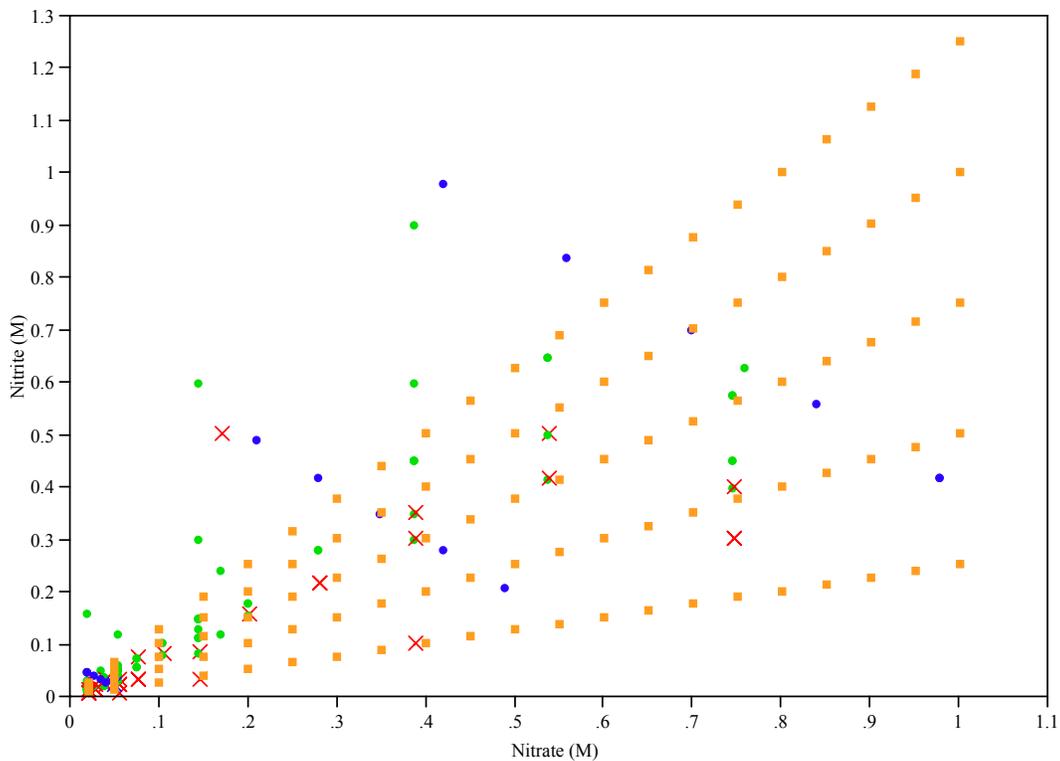


Figure 1. Solution chemistry design matrix compared to previously tested solutions.

EXPERIMENTAL PROCEDURE

The technical approach to develop a probability based chemistry control program was based upon gathering sufficient data to develop a predictive tool for corrosion vulnerability. Coupon exposure testing was performed within the framework of the statistical test matrix. Coupon exposure testing provided insight into the corrosion response in the solution, interface, and vapor space regions based on varying solution chemistries.

Material

ASTM A537 Semi-killed, hot-rolled ASTM A537 plain carbon was used for experimentation. The nominal chemical composition for the alloy is 0.24 wt% C, 0.70-1.60 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. Rectangular coupons of dimension 4” x 1” x 1/8” (Metal Samples,

Munford, AL) were used for coupon testing. A section from each sample set was polished and etched using 2 % nital solution, and viewed for grain size and shape using a Reichert-Jung MeF3 light microscope (Depew, NY). Analysis of inclusions was performed on a Hitachi S3600N scanning electron microscope (Pleasanton, CA) equipped with a Model 7581, Oxford Instruments energy dispersive spectroscopy (EDS) (Abingdon, UK). Two series of coupons from the same manufacturer heat were tested. The first series of coupons was tested with the as-received surface undisturbed. The second series of coupons was tested after a furnace anneal at 700 °C for 20 minutes, followed by a furnace cool to room temperature. Coupons were vertically suspended during heat treatment to provide air circulation on all sides of the sample. Representative materials sections from each heat were polished and etched to evaluate the microstructure. Samples were tested by EDS for chemical analysis.

Simulated Tank Solutions Simulated waste tank solutions were batch 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 molar ratio of 7 to 13 for sodium carbonate to sodium bicarbonate, respectively. The gram amount of carbonate and bicarbonate added was determined based on the nitrite amount. A subset of 24 solutions were prepared based on a statistically determined experimental design⁵, see Figure 2. The design space was defined by molar concentrations of nitrate between 0.02 and 1.00 M with temperature being fixed at 40 °C. Assuming that only nitrate and nitrite would be added to the solutions, the statistical design deliberately contains series of solutions consisting of R-values (molar concentration ratio of inhibitor species to the sum of the aggressive species) to further investigate the value of the ratio in the prediction of corrosion response.

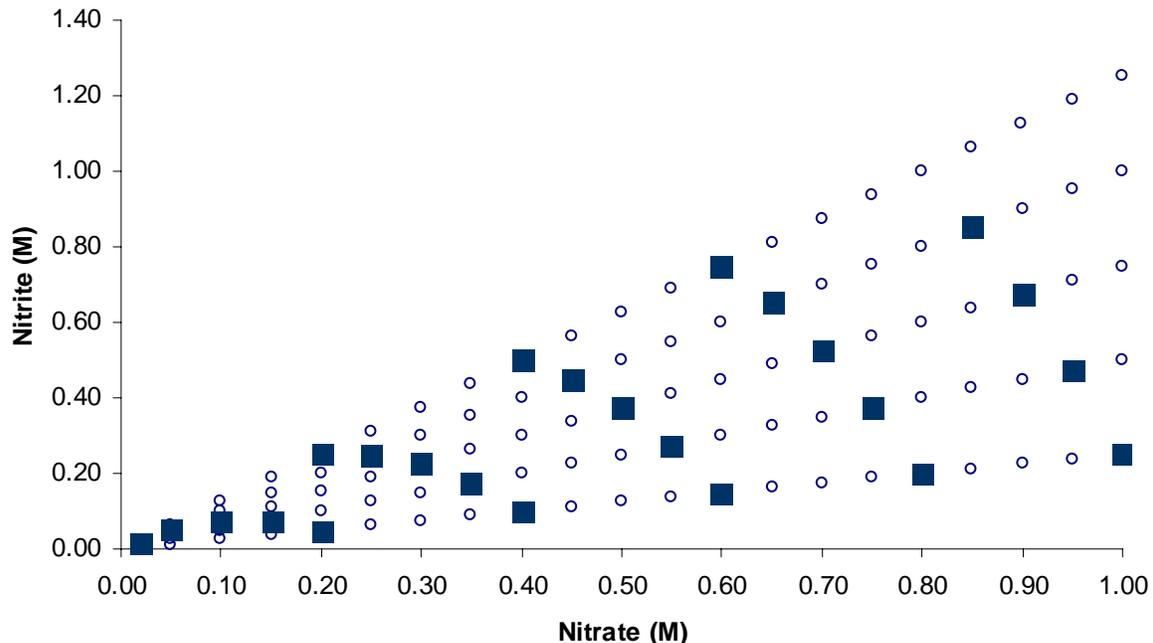


Figure 2. Selection of simulated tank solutions for coupons denoted squares.

Sodium nitrate and sodium nitrite varied based on statistical modeling values. Sodium chloride and sodium sulfate were introduced to promote corrosion. Sodium chloride was added based on maximum amount allowable under current chemistry control limits, see Equation 2. Sodium sulfate was added based on the 84 wt% of the maximum amount allowable under current chemistry control limits, see Equation 3.

Coupon Testing

Coupons were vertically suspended using Teflon® coated wire threaded through the hole at the top of the coupon in simulated waste tank solutions at 40 °C in glass jars. The level of solution was marked on the exterior of each jar to allow for periodic solution replenishing due to evaporation. Once heat treated coupons were annealed, they were added to the respective solution jars. The immersion testing continued for 19 weeks with images taken at 6, 16, and

19 weeks. Formed corrosion product was sampled from the vapor, interface, and solution space areas on the coupon for X-ray diffraction using a Bruker D8 (Madison, WI) equipped with a CuK α source, 45 kV, 40 mA. X-ray diffraction was run from 2 θ from 5-100° with a step size of 0.02 and a dwell time of 3 s. Samples were cleaned using a solution containing hydrochloric acid, antimony trioxide, and stannous chloride in amounts described in ASTM standard G1-03 to remove residual corrosion product. A plastic bristled brush was used to remove majority of product after samples soaked in the acid cleaning solution. Ultrasonic cleaning bath was used to remove stubborn residue. Total time of samples exposed to acid cleaning solution was less than 5 minutes. Weight and dimensional measurements were performed before and after the 19 week immersion period.

Pit Analysis A minimum of 10 pit depths and widths were measured per corroded coupon using a Nikon MM-11 (Melville, NY) optical microscope equipped with a Nikon Digimicro ME-501 digital depth reader and a 200 X objective. The undisturbed surface brought into focus, the depth measurement device was zeroed, then the center of a pit brought into focus, and a depth measurement was taken. It was determined that the accuracy of focusing is +/- 0.0005 in. Pit widths were measured using a Nikon A4-B (Melville, NY) digital X-Y coordinate stage connected to a Nikon SC-112 (Melville, NY) digital readout.

In addition to pit depth, the length of the corroded area was measured using a set of calipers. On most coupons, corrosion appears to have initiated in the interface region and started to creep up the coupon parallel to the suspension direction. It should be noted that the distance of the effected area was around 2" or less. In comparing the result to the actual tanks, this corrosion would be considered in the interface region rather than the vapor space.

Ultrasonic Testing The samples were scanned using a FORCE Technologies (Houston, TX) P-scan automated ultrasonic system and scanner. The coupons were arranged on a magnetic mat to hold them in place. Several samples were placed in a row to allow for the transducer to maintain contact near the edges of the sample. A Panametrics V203-RM (Olympus, Waltham, MA), 0.125" diameter, 10 MHz straight beam longitudinal wave transducer was utilized to scan the coupons. Motor oil was used as a couplant to minimize further corrosion of the coupons during ultrasonic analysis. The setup was set to collect data at 0.010 inch intervals in the X and Y directions and 0.001 in the thickness plane. Since the equipment was not adjusted to account for and accurately measure same surface corrosion, those areas appear to be thicker due to the increased couplant path and difference in velocity.

RESULTS AND DISCUSSION

A537 Microstructure

The microstructure of the A537 coupons revealed a layered ferritic/pearlitic structure with elongated grains on the longitudinal-traverse and short-transverse directions as expected, see Figure 3. The broad plane of the coupons was the section perpendicular to the short direction. This orientation is the plane that faces the interior of the tanks. Therefore, corrosion along this plane was the focus of the coupon study. The average grain size in this plane was 10-15 microns in diameter. The EDS analysis confirmed the presence of Mn-S based inclusions within the microstructure, see Figure 4.

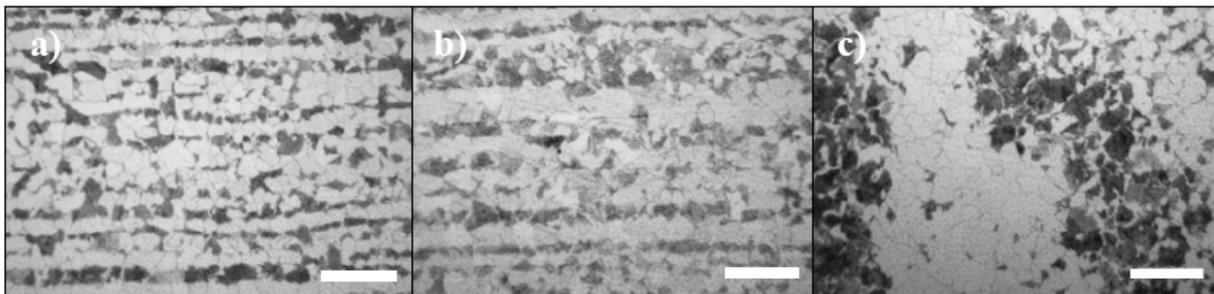


Figure 3. Microstructure of A537 coupons with sections perpendicular to the a) longitudinal b) transverse c) short directions. Scale bar equals 30 microns.

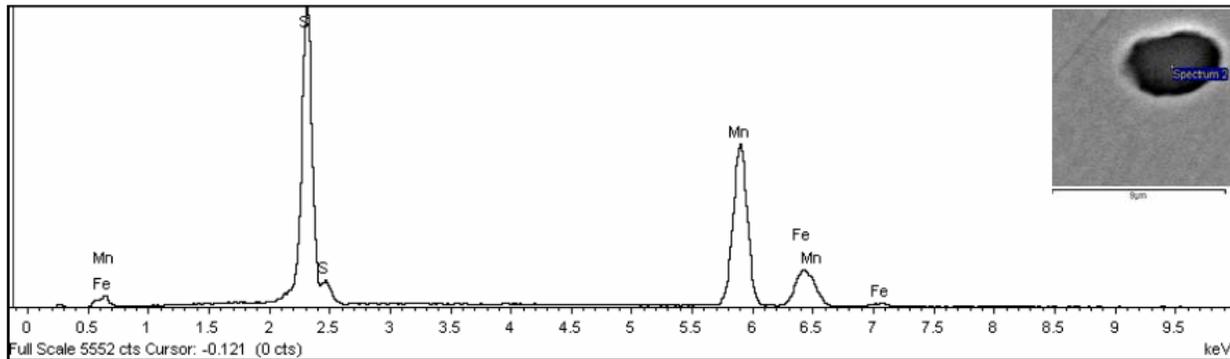


Figure 4. EDS of A537 coupon identifying presence of manganese and sulfur. SEM insert, top right, illustrates location of chemical analysis. Scale bar equals 9 microns.

Coupon Testing

Significant variation in corrosion response occurred after the 19 week immersion testing based on the simulated waste solution used. The solution containing 0.02 M nitrate and 0.015 M nitrite, which is the lowest total sum of nitrate and nitrite used in the solutions exhibited distinctive pitting in the solution space, see Figure 5. Numerous samples within the moderate nitrate and nitrite concentrations exhibited little if any corrosion in the solution space, yet experienced significant uneven localized corrosion in the interface and vapor space, see Figure 6 and Figure 7. The corrosion response in the vapor and interface space seemed to creep from the interface region, see Figure 5. The type of corrosion which occurred in the vapor and interface space on the coupons was generally uneven local corrosion rather than highly localized pitting corrosion. Although less visible damage occurred, the heat treated samples followed a similar trend compared to the as-received samples.



Figure 5. As-received coupon immersed in solution containing 0.02 M nitrate and 0.015 M nitrite at 16 weeks. The sample experienced pitting in the solution space. The corrosion product crept towards the vapor space region vertically from the interface region.



Figure 6. As-received coupons after 19-week exposure to 0.02 M nitrate and 0.015 M nitrite (top), and 0.2 M nitrate and 0.05 M nitrite (bottom). The interface space (center) is flanked by the vapor space (right), and the solution space (left).



Figure 7. Heat treated coupons after 19-week exposure to 0.02 M nitrate and 0.015 M nitrite (top), and 0.2 M nitrate and 0.05 M nitrite (bottom). The interface space (center) is flanked by the vapor space (right), and the solution space (left).

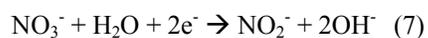
The cathodic reaction responsible for driving the corrosion formation at the interface and vapor space is:



This reaction consumes a significant amount of electrons, thus driving the anodic reactions:



A secondary cathodic reaction responsible for driving corrosion formation is:



X-ray diffraction of corrosion product from vapor, interface, and solution space was analyzed from the as-received coupon used with 0.02 M nitrate and 0.015 M nitrite. The corrosion products were confirmed to be goethite

($\text{Fe}^{+3}\text{O}(\text{OH})$), magnetite ($\text{Fe}^{+2}\text{Fe}_2^{+3}\text{O}_4$), and lepidocrocite ($\text{Fe}^{+3}\text{O}(\text{OH})$). Siderite ($\text{Fe}(\text{CO}_3)$) was confirmed in the interface and vapor space regions. The absence of siderite in the solution space region was confirmed by OLI Stream Analyzer, version 2 (OLI Systems, Inc., Morris Plains, NJ) thermodynamic modeling, in which the carbonate containing siderite does not form in O_2 limited environments.

The heat treatment at $700\text{ }^\circ\text{C}$ formed an oxide scale on the coupons. The weight gain due to scale formation varied from coupon to coupon, see Figure 8. The average weight gain was 0.024 g . The change in thickness averaged $0.002''$ and is not significant. It should not be assumed the scale formation is uniform between or within sample. After the 19 week immersion test, both the as-received and heat treated coupon series lost weight. On average, the drop in weight was larger for the as-received compared to the heat treated coupons with average weight loss for the two series being 1.09 and 0.77 g , respectively, see Figure 9. Variations in the oxide scale should be taken into account when evaluating the weight loss for the heat treated.

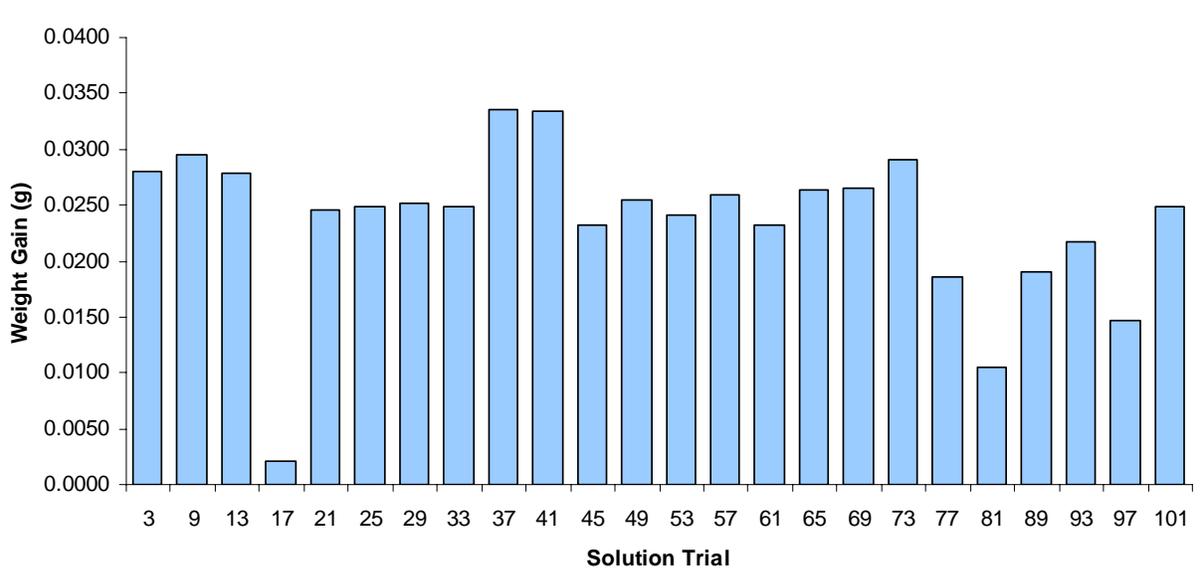


Figure 8. Weight gain due to oxide scale formation resulting from $700\text{ }^\circ\text{C}$ heat treatment.

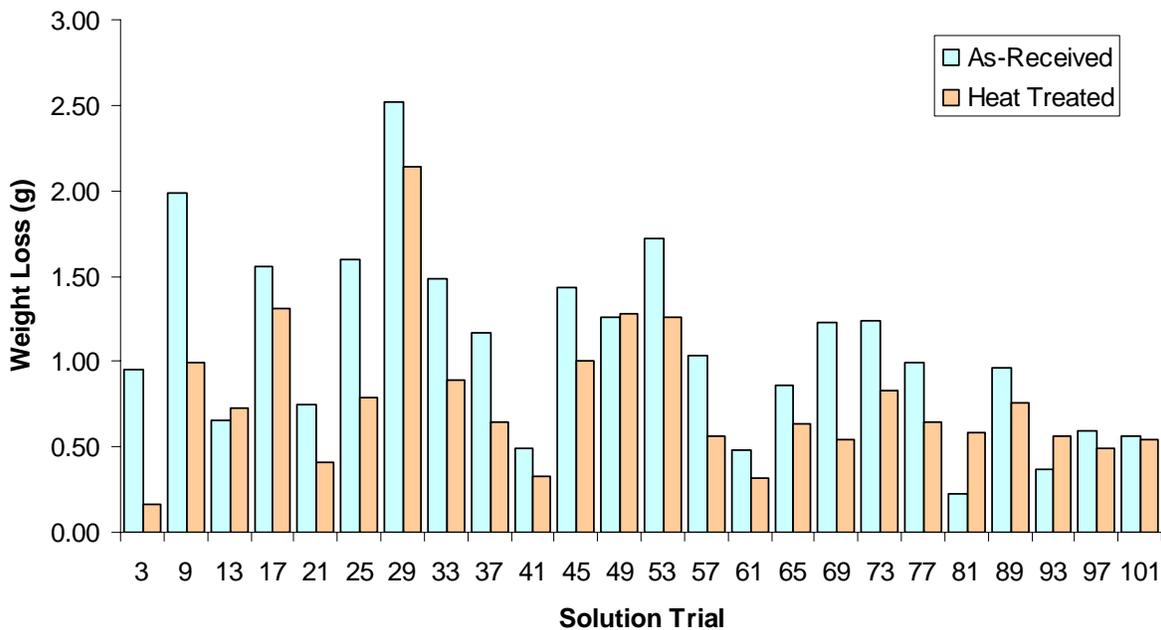


Figure 9. Weight lost after 19 week immersion testing for as-received and heat treated series.

Pit depth results from both the as-received and heat treated coupon series do not show an influence of solution concentration on pit depth. In the as-received series, the maximum pit depth was 0.0183” found on a coupon subjected to 0.1 M nitrate and 0.075 M nitrite. The maximum corroded area was 2.1” long, from a solution of 0.85 M nitrate and 0.85 M nitrite. For the heat treated samples, the maximum pit depth was 0.027” from a solution containing 0.9 M nitrate and 0.675 M nitrite, while the maximum length was 2.092” from a solution containing 0.25 M nitrate and 0.25 M nitrite.

Ultrasonic Testing

The profile of material loss due to corrosion was evaluated using ultrasonic testing. A subset of the coupon samples were measured using ultrasonic testing. As the test method measures the loss of material on both the front and back side of the coupon, it should be noted that measurements are an additive loss of material of both the front and back sides of the coupons. Average and minimum thicknesses of the coupons measured by UT testing are stated in TABLE 1.

TABLE 1
MINIMUM AND AVERAGE COUPON THICKNESS AS MEASURED BY ULTRASONIC TESTING
TECHNIQUE

Solution Chemistry		Heat Treated (Y/N)	Min. Thickness (inches)	Avg. Thickness (inches)
Nitrate (M)	Nitrite (M)			
0.020	0.015	N	0.141	0.150
0.020	0.015	Y	0.143	0.151
0.150	0.075	N	0.136	0.149
0.150	0.075	Y	0.140	0.150
0.600	0.150	N	0.141	0.151
0.600	0.150	Y	0.144	0.150
0.600	0.750	N	0.137	0.150
0.600	0.750	Y	0.138	0.151
0.850	0.850	N	0.143	0.150
0.850	0.850	Y	0.130	0.150
0.950	0.475	N	0.143	0.150
0.950	0.475	Y	0.145	0.150
1.000	0.250	N	0.137	0.150
1.000	0.250	Y	0.140	0.150

The majority of material loss occurred at the interface region, as can be seen in Figure 10-Figure 11. The coupons immersed in the solution containing 0.020 M nitrate and 0.015 M nitrite, pitting in the solution space was visible by eye, however, due to the narrow size of the pits, detailed measurement of pit depth was not possible. As shown in Figure 10, the UT scan suggests general corrosion loss in the solution space. However, this measurement is a result of the testing procedure, as is evident when comparing the corresponding digital image of the surface.

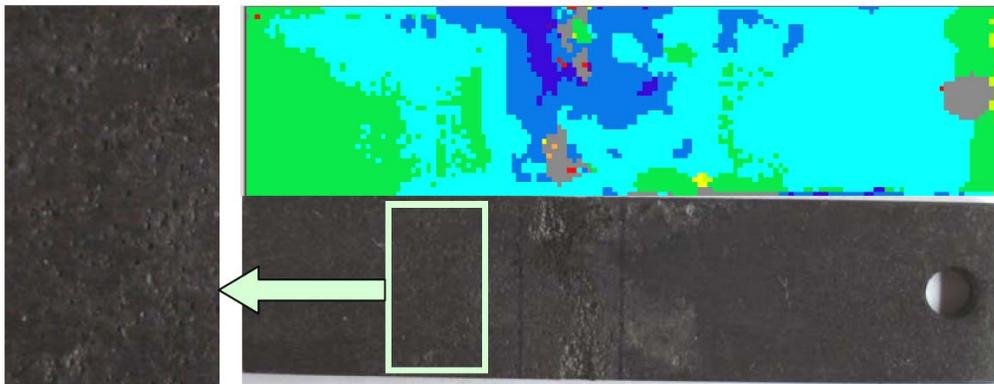


Figure 10. Coupon with as-received surface after 19 week exposure to solution containing 0.020 M nitrate and 0.015 M nitrite. UT scan and corresponding digital image of coupon. Enlarged image of pitting in solution area is shown on the left.

When comparing the as-received coupon corrosion response to the heat treated coupon exposed to the same solution chemistry, less material loss due to corrosion occurred, particularly at the interface region. The majority of the corrosion occurred along the side parallel to the length of the coupon. This corrosion response could be due to the variation in microstructure that occurs on the sides of the coupon, as well as surface tension effects related to the side regions of the coupons. The minimum measured thickness of the heat treated coupon was 0.143" compared to the 0.141" of the as-received sample.

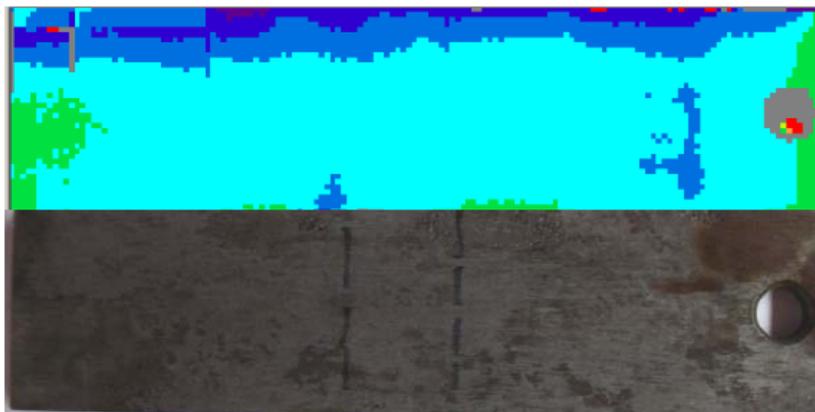


Figure 11. Heat treated coupon after 19 week exposure to solution containing 0.020 M nitrate and 0.015 M nitrite. UT and corresponding digital image are shown.

CONCLUSIONS

Coupon testing provided evidence of localized corrosion in the solution space of ASTM A537 carbon steel at the lowest total concentration amounts of both nitrate and nitrite. Although difficult to draw firm conclusions based on individual solution chemistries due to the limited number of coupons evaluated during testing, it is evident that dilute solutions of nitrate and nitrite encourage localized pitting in the solution space, regardless of steel surface treatment. At higher amounts of nitrate and nitrite, less corrosion occurred within the solution. However, significant corrosion occurred at the interface and vapor space regions.

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