The Sensitivity of Carbon Steels' Susceptibility to Localized Corrosion to the pH of Nitrate Based Nuclear Wastes

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ABSTRACT

The Hanford tank reservation contains approximately 50 million gallons of liquid legacy radioactive waste from cold war weapons production, which is stored in 177 underground storage tanks. The tanks will be in use until waste processing operations are completed. The wastes tend to be high pH (over 10) and nitrate based. Under these alkaline conditions carbon steels tend to be passive and undergo relatively slow uniform corrosion. However, the presence of nitrate and other aggressive species, can lead to pitting and stress corrosion cracking. This work is a continuation of previous work that investigated the propensity of steels to suffer pitting and stress corrosion cracking in various waste simulants.

The focus of this work is an investigation of the sensitivity of the steels' pitting and stress corrosion cracking susceptibility to simulant pH. Previous work demonstrated that wastes that are high in aggressive nitrate and low in inhibitory nitrite are susceptible to localized corrosion. However, the previous work involved wastes with pH 12 or higher. The current work involves wastes with lower pH of 10 or 11. It is expected that at these lower pHs that a higher nitrite-to-nitrate ratio will be necessary to ensure tank integrity. This experimental work involved both electrochemical testing, and slow strain rate testing at either the free corrosion potential or under anodic polarization. The results of the current work will be discussed, and compared to work previously presented.

Keywords: stress corrosion cracking, carbon steel, nitrate, nitrite, pH, Hanford, nuclear waste

INTRODUCTION AND BACKGROUND

The Hanford tank reservation in Washington State contains approximately 50 million gallons of liquid legacy radioactive waste from cold war weapons production. The waste is stored in 177 underground storage tanks. The current plan is to construct a vitrification plant that will be used to process the waste. The underground storage tanks are expected to continue service until these processing operations are finalized. However, the tanks are approaching their original design lives, and analysis and testing are necessary to ensure that the tanks are fit for continued service and the waste processing operations are complete.

Most of the wastes being stored are highly alkaline (pH > 10). Under these conditions carbon steels tend to remain passive and undergo relatively slow uniform corrosion. However, carbon steels become susceptible to pitting and stress corrosion cracking (SCC) in the presence of certain aggressive species, such as chlorides and nitrates [1]. The original Single Shell Tanks (SSTs) at Hanford experienced some SCC failures due to the high nitrate contents and high residual stresses. Research at both Hanford and Savannah River National Laboratories (SRNL) demonstrated that cracking could be reduced by stress relieving the welds and maintaining a high alkalinity (pH > 13). These practices were incorporated into the construction and operations of the Double Shell Tanks (DSTs) to ensure their structural integrity.

Most of the wastes stored in the DSTs are within their required pH specification, and are expected to remain within these specifications until the waste processing facilities are complete and the wastes can be removed. However, in some cases the waste chemistries will fall out of specification. This is a result of various chemical reactions taking place in the wastes that decrease the pH levels. Wastes falling out of specification could also result from waste transfer and mixing operations. Addition of sodium hydroxide (NaOH) would be necessary to maintain pH specification, which would result in a significant cost and increase in nuclear waste that requires processing. There are concerns within the U.S. Department of Energy (DOE), oversight groups and regulatory bodies that the integrity on the tanks will be compromised if the waste chemistries change. If tank integrity is compromised there is a need to define corrosion mitigation strategies. Additional resources would be required to mitigate potential leaks and to conduct repairs.

Research has been performed with the objective of ensuring the integrity of Tanks 241-AN-107, 241-AN-102, 241-AY-102, 241-AP-101, 241-AY-101, and others [2-8]. These wastes tend to have high nitrite and/or nitrate contents (typically >1 M nitrate). One exception is tank 241-AY-102, which has a high carbonate content (1 M), and is also expected to be susceptible to SCC. Similar work in the oil and gas pipeline industry has demonstrated that steels are susceptible to SCC in high carbonate environments.

The research led to several conclusions that are relevant to tank integrity. Work with simulated Tank 241-AN-107 (AN107) waste, which is high in nitrate (3.7M), demonstrated that susceptibility to localized corrosion is not sensitive to alkalinity provided the pH is maintained above pH 10. The chemical reactions occurring in the AN107 result in a lower pH, and this was originally of concern. By demonstrating the lack of sensitivity to pH, significant costs were avoided. It was known from the previous work that nitrates are aggressive and contributed to SCC in the SSTs. However, the radiochemical reactions in the waste result in a decrease in nitrate and increase in nitrite. This was demonstrated to be beneficial as nitrite inhibits localized corrosion. This also led to confidence that the waste in Tank 241-AN-107 was not likely to cause an integrity concern. It was also demonstrated that the high carbonate waste from Tank 241-AY-102 was only susceptible to SCC at very low potentials (approximately -800 mV vs. SCE), and these potentials are unlikely to be encountered in service.

The continuing work focused on the supernate waste in Tank 241-AP-105 (AP105). The waste has a low nitrite content (0.27 M) and a high nitrate content (3.58 M). This leads to the lowest nitrite-to-nitrate ratio of any of the wastes studied during the program. Previous work demonstrated that the nitrite-to-nitrate ratio may be a key parameter in determining the likelihood of localized corrosion. Work with the AP105 simulant demonstrated that the carbon steel tested has a susceptibility to liquid / vapor interfacial corrosion. Results led to a focused effort to understand the factors contributing to this form of corrosion, which had not been observed during testing in any of the other waste simulants. The work demonstrated the two possible mechanisms exist that explain the liquid / vapor interface corrosion. One possibility is that carbon dioxide in the air is locally acidifying the liquid. This was believed the likely mechanism for tests performed under freely corroding conditions. Another possibility is that the applied potential was oxidizing nitrite to nitrate, thereby locally decreasing the inherent inhibitory property of the simulant. This was believed to be the likely mechanism for test performed under anodically polarizing conditions. The work is continuing and results are reported in a companion paper [9].

The focus of this current work is an investigation of the sensitivity of steels' pitting and stress corrosion cracking susceptibility to simulant pH. Previous work demonstrated that wastes that are high in aggressive nitrate and low in inhibitory nitrite are susceptible to localized corrosion. However, the previous work involved wastes with pH 11 or higher. The current work involves wastes with lower pH of 10. It is expected that at these lower pHs that a higher nitrite-to-nitrate ratio will be necessary to ensure tank integrity. This experimental work involves both electrochemical tests, and slow strain rate tests (SSRTs) at either the free corrosion potential or under anodic polarization. The results of the current work will be discussed, and compared to work previously presented.

EXPERIMENTAL

Test specimens were fabricated from three 3'×2'×1" as-supplied plates of ASTM A537 Class 2 carbon steel material that had been heat-treated to obtain material properties similar to those of the Class 1 carbon steel used for construction of the DSTs. The chemical specification indicates a maximum carbon content of 0.24% and maximum manganese content of 1.6 %. The mechanical specification indicates a 0.2% offset yield strength between 45 and 60 ksi and an ultimate tensile strength between 80 and 100 ksi. A photomicrograph of the microstructure is shown in Figure 1. The microstructure consists of ferrite and pearlite. The ratio of ferrite to pearlite indicates the steel is within specification with respect to carbon content. Slow strain rate testing (SSRT), which will be described later, indicated that the steel was within specification with respect to mechanical properties. No further testing was performed to verify the properties of the steel against the specifications.

Two different specimen geometries were used during the course of this phase of the work. All electrochemical tests used the specimen geometry shown in Figure 2. All SSRTs used the specimen shown in Figure 3. Specimens were machined by the Metal Samples Company in Munford, Alabama. Material close to the flame cuts at the edges of the plates was avoided for fabrication to ensure consistent microstructures. Specimens were machined so that the longitudinal axis was aligned with the plate rolling direction.

This work focuses on nuclear waste simulants with various chemistries, but all of lower pH, less than 11. All testing was done in simulants rather than actual nuclear waste. Main constituents of the waste that are of particular interest to this test program are nitrite, nitrate and hydroxide. Previous testing demonstrated that localized corrosion susceptibility is a strong function of inhibitor nitrite and aggressive nitrate contents. For this work, a variety of compositions of these species and ratios was investigated. In some cases waste simulants were modified in order to investigate specific nitrite-to-

nitrate ratios that are not observed in actual tank wastes. In other cases, test solutions were based on the test simulant performed during previous work by other researchers. Although this testing is not necessarily realistic for tank integrity, it does provide better understanding of the corrosion mechanisms that may be operative. The pH of all of these simulants is less than 13, and therefore out of specification with respect to the guidelines developed following the preliminary work at Hanford and SRNL. The wastes consist of several other species, not considered significant for the purposes of this study; carbonate, chloride, fluoride, aluminate, and others.

Electrochemical testing

The testing performed during this part of the work was cyclic potentiodynamic polarization scanning. Testing was performed following the guidelines in ASTM G61-86e1 [10] unless otherwise noted. Samples were completely immersed in the test solution as is typical for these types of electrochemical tests, unlike some of the previous testing which was performed using partially immersed samples. The partial immersion tests were developed to investigate the phenomenon of liquid / vapor interface corrosion.

Samples were prepared with a 600 grit finish. Immediately prior to testing they were ultrasonically cleaned in isopropanol for five minutes, rinsed with deionized (DI) water and then dried with nitrogen. The test cell was filled with the waste simulant and heated to the desired temperature. All of the tests were performed at temperatures between 40 and 77°C. All scans were deaerated, with the cell purged with nitrogen (99.998% purity) for an hour prior to testing. A SCE reference electrode was used to monitor the potential, maintained at room temperature using a Luggin probe / salt bridge filled with test solution. A platinum flag was used as the counter electrode.

A new sample was inserted into the test cell at the start of each test. The OCP was monitored for 18 hours prior to testing. The start potential was -100 mV relative to OCP. The potential was scanned in the positive direction at a rate of 10 mV /min. The scan was reversed at either 1 V or 1 mA/cm2, whichever was reached first. Potential and current were monitored continuously.

When the tests were complete, the samples were removed from the test cell, rinsed with DI water, and then dried with nitrogen. If corrosion products were visible, the sample was ultrasonically cleaned in acetone. The samples were photographed to document any evidence of corrosion. In some cases the sample was also examined using the stereo-micrograph or SEM. Finally, samples were stored in individual specimen bags in a desiccator for possible further analysis.

Slow strain rate testing

All SSRTs were performed following the guidelines in ASTM G129-00 [11] unless otherwise noted. The specimens were placed through a PTFE test cell and held in place with sliding seals. The specimen and cell were then inserted into the load frame. The solution of interest was introduced and heated to 50°C. Tests for this series were typically performed under freely corroding conditions, but in one case an anodic potential was applied. A saturated calomel electrode (SCE) was used to monitor the potential, maintained at room temperature using a Luggin probe / salt bridge filled with test solution. A platinum flag was used as the counter electrode. Conditions for all tests were quiescent (i.e. open to the air).

The test specimens were all pulled to failure with a strain rate of 10-6 in/in/sec. Following testing the specimens were photographed, cleaned in acetone, examined using the stereographic microscope, and / or examined using the scanning electron microscope (SEM). The fracture surfaces of the samples were examined to identify regions of intergranular fracture that are indicative of high pH or nitrate SCC.

RESULTS AND DISCUSSION

Electrochemical testing

Table 2 is a summary of the electrochemical tests performed in the various waste simulants or modified waste simulants. The tests have been grouped and ordered for comparison purposes, but this does not necessarily reflect the chronological order in which the tests were performed. All tests were performed at a temperature between 40°C and 77°C, and all simulants were of pH 10 or 10.5. The specific objective of each test is listed in the table.

Extensive work on AN107 simulant (nitrite 1.2 M and nitrate 3.7 M) and modified simulants demonstrated that decreased nitrite in solution led to increased susceptibility to stress corrosion cracking. It was decided to continue work by exploring the effects of absolute nitrite and nitrate content, but at a lower pH than in the previous study.

For the initial tests an AN107 based simulant was prepared, but with nitrite 0.35 M, nitrate 3.5 M and balanced to pH 10. CPP testing in the simulant resulted in an open potential-current density curve, and severe pitting was observed on the sample during post-test inspection (Figure 4(a) and Figure 5(a)). This was expected, as the standard simulant had shown pitting when the nitrite content was decreased below 1 M. Performing the same tests with a higher pH of 10.5 or with a lower temperature of 40°C did not have a significant effect, and pitting was also observed.

To investigate the effect of absolute nitrate content, both the nitrite and nitrate contents were decreased, while still maintaining a ratio of 0.1. Even when the nitrate content was decreased to 1.11 M or 0.11 M, pitting corrosion was still observed (Figure 5(b) and (c)), though the low nitrate simulant had a much higher pitting potential (Figure 4(b)). A further test was performed with nitrite 1 M and nitrate 5 M to see if a higher nitrite / nitrate ratio might decrease the susceptibility to pitting. However, an open potential-current density curve was recorded during the CPP scan (Figure 4(b)), and pitting was observed on the sample during post test examination (Figure 5(b)).

Data from the current series of tests in modified AN107 were plotted with those of previous work to look for trends in potential. Figure 6 is a plot of open circuit potential, pitting potential and repassivation potential for various AN107 simulants, both standard (solid symbols) and modified (open symbols). For the standard AN107 simulants the potentials generally track with pH, with values decreasing with increasing pH. The one exception is the repassivation potential at pH 7. In all cases the repassivation potential is lower than the pitting potential, indicating the possibility of pitting corrosion. For the recent modified AN107 simulants, with lower nitrite / nitrate ratios than the standard 0.32 and pH of 10, the repassivation potentials are lower than the open circuit potentials, indicating an increased susceptibility to pitting corrosion.

A further modified simulant (270-LT modified B2), containing a nitrite / nitrate ratio of 0.1 was prepared, using a higher nitrate content of 5.75 M. This represents the bounding nitrate content measured in any of the Hanford nuclear waste storage tanks. As expected, both the CPP scan and post test examination revealed a susceptibility to pitting corrosion (Figure 7 and Figure 8).

CPP tests were also performed in simulated wastes from other tanks, AY101 and AY102. In each case testing was based on an aged interstitial liquid (AIL) composition that was predicted by thermodynamic calculations. The AY101 simulant contained 0.912 M nitrite and 0.017 M nitrate. No corrosion was expected based on the high nitrite / nitrate ratio. The AY102 simulant contained 0.001 M nitrite and 0.002 M nitrate. This simulant has very low nitrate content and high nitrite / nitrate ratio, so corrosion would not be expected based on previous testing. However, the test was performed at higher

temperature 77°C and lower pH than previous tests, which may lead to a problem. Post test examination indicated no pitting, though there was some staining observed on the test sample from the test performed in the AY102 simulant.

Slow strain rate testing

Table 3 is a summary of the slow strain rate tests performed in the various waste simulants or modified waste simulants. The tests have been grouped and ordered for comparison purposes, but this does not necessarily reflect the chronological order in which the tests were performed. All tests were performed at a temperature between 25°C and 77°C, and all simulants were of pH 10 or 10.5. One test was performed with an applied anodic potential, but all others were performed under freely corroding conditions.

SSRTs performed in the modified AN107 simulants with nitrite / nitrate ratio 0.1 or 0.2, and pH 10 or 10.5, showed no evidence of SCC. Minor corrosion was observed in one case, but all fracture surfaces examined showed purely ductile features (see sample micrographs Figure 10 and Figure 11). An SSRT performed in the 270-LT modified B2 simulant with the limiting nitrate content also did not show any evidence of SCC. However, a milky white scale was observed on the sample surface during post test examination (Figure 12).

SSRTs were also performed in the tank AY101 and AY102 simulants. No pitting was observed during the CPP testing, and no corrosion was expected based on previous experience in working with these simulants. No evidence of SCC was observed during post test examination (Figure 13 and Figure 14). However, a test performed in the AY102 simulant at a pH 10.5 showed evidence of liquid-air-interface corrosion (Figure 15). This form of corrosion was observed in the AP105 tank simulant, which has a low nitrite-to-nitrate ratio, and resulted in a focused and continuing effort to understand the phenomenon.

Previous test programs have demonstrated relationship amongst nitrite / nitrate ratio, test potential and susceptibility to SCC. Figure 16 is an illustration of SCC susceptibility as a function of nitrite / nitrate ratio and applied potential. Data from previous work and the current test program are included. Various test conditions are represented, and in most cases pH, temperature, and secondary species are different from test to test. The plot demonstrates the general trend that high nitrite / nitrate ratio and/or low potential decrease susceptibility to SCC, and vice versa. It should be noted that the solid cracking symbols at ratio 0.5 and potential -800 mV (SCE) represent tests in simulants with high carbonate contents and applied cathodic currents. The mechanism behind their cracking is different from that of the other tests and conditions are not expected to be observed in tank service.

SUMMARY

A series of electrochemical and mechanical testing was performed to investigate the susceptibility of a plain carbon steel to pitting and stress corrosion cracking in various nuclear waste simulants and modified simulants. The focus of this work was to investigate if a decrease of pH to 10 would lead to enhanced susceptibility to localized corrosion, as well as further study of the role of nitrite / nitrate ratio on cracking behavior. Pitting was observed in nearly all cases in which the nitrite / nitrate ratio was at 0.1. This indicates that to decrease the susceptibility of localized corrosion the nitrite/nitrate ratios must be greater than it is for simulants that are of pH 12 or greater. It should be noted that the majority of testing during the current program was performed at open-circuit potentials, as opposed to much of the previous work performed at applied potentials. While the results of the current test program are good from the perspective of tank integrity, it is acknowledged that further testing is required to determine both the critical potentials for cracking in each of the simulants, and to gain confidence in electrochemical potential measurements being made in the waste tanks. Work is continuing in this direction.

REFERENCES

1. R. N. Parkins, and R. Usher, "The Effect of Nitrate Solutions in Producing Stress Corrosion Cracking in Mild Steel", Proceedings First International Congress on Metallic Corrosion. London, U.K..: Butterworths (1962): 296-302
2. "Hanford Tanks 241-AN-107 and 241-AN-102: Effect of Chemistry and Other Variables on Corrosion and Stress Corrosion Cracking", CC Technologies Inc, September 8, 2006.
3. "Hanford Tanks AY102 and AP101: Effect of Chemistry and Other Variable on Corrosion and Stress Corrosion Cracking", CC Technologies Inc, September 2007.
4. "Hanford Tank AY101: Effect of Chemistry and Other variables on Corrosion and Stress Corrosion Cracking", CC Technologies Inc, January 2008.
5. C. S. Brossia, C. Scott, J. A. Beavers, M.P.H. Brongers, G. L. Edgemon, H. Berman, G. S. Frankel, L. Stock and B. Wiersma, "Inhibition of Stress Corrosion Cracking of Carbon Steel Storage Tanks at Hanford", Corrosion 2007, Paper 07606, Houston 2007.
6. F. Gui, C. S. Brossia, J. A. Beavers, G. S. Frankel, G. L. Edgemon, H. Berman, and L. Stock, "A Study on Localized Corrosion of Carbon Steel in Hanford Nuclear Wastes", Corrosion 2008 Paper 08589, Houston 2008.
7. C. S. Brossia, C. S. Scott, J. A. Beavers, G. L. Edgemon, H. Berman, G. S. Frankel and K. Boomer, "Stress Corrosion Cracking of Carbon Steel in Nitrate and Carbonate Wastes at Hanford". Corrosion 2008 Paper 08599, Houston 2008.
8. C. S. Scott, F. Gui, C. S. Brossia, J. A. Beavers, G. L. Edgemon, K.D. Boomer, G.S. Frankel, B. J. Wiersma and L. Stock, "A Study of Stress Corrosion Cracking and Localized Corrosion of Carbon Steel in Nitrate Based Nuclear Waste", Corrosion 2009, Paper 06465, Houston 2009.
9. Work to be presented NACE San Antonio 2010.
10. ASTM G61-86e1, 2003, *Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys*, American Society for Testing and Materials, ASTM International, West Conshohocken, PA.
11. ASTM G129-00, 2006, *Standard Practice for Slow Strain Rate Testing to Evaluate the Susceptibility of Metallic Materials to Environmentally Assisted Cracking*, American Society for Testing and Materials, ASTM International, West Conshohocken, PA.

TABLES

Table 1. A listing of the waste simulants using for testing during the course of this work.

Simulant	Nitrite	Nitrate	Ratio	pH
AN107 modified 1	0.35	3.50	0.10	10
AN107 modified 2	0.11	1.11	0.10	10
AN107 modified 3	0.011	0.11	0.1	10
AN107 modified 4	1.00	5.00	0.2	10
AY101-AIL	0.912	0.017	54	10
AY102-AIL	0.001	0.002	0.5	10.5
270-LT modified B2	0.575	5.75	0.1	10
AN102-AIL	1.8	3.2	0.56	10
AN107	1.2	3.7	0.32	11

Table 2. A summary of the electrochemical tests performed in the waste simulants with low pH.

Simulant	Nitrite (M)	Nitrate (M)	Ratio	pH	Temp (°C)	Objective	Result
AN107 modified 1	0.35	3.5	0.1	10	50	Explore low nitrite/nitrate ratio at pH10	Pitting
AN107 modified 1	0.35	3.5	0.1	10.5	50	pH effect	Pitting
AN107 modified 1	0.35	3.5	0.1	10.5	40	Temperature effect	Pitting
AN107 modified 2	0.11	1.11	0.1	10	50	Explore low nitrite/nitrate ratio at pH10	Pitting
AN107 modified 3	0.011	0.11	0.1	10	50	Explore low nitrite/nitrate ratio at pH10	Pitting
AN107 modified 4	1	5	0.2	10	50	Explore low nitrite/nitrate ratio at pH10	Pitting
270-LT (modified) B2	0.575	5.75	0.1	10	50	Bounding nitrate at low pH	Pitting
AY101-AIL	0.912	0.017	54	10	50	pH effect	No pitting
AY102-AIL	0.001	0.002	0.5	10	77	pH effect	No pitting
AY102-AIL	0.001	0.002	0.5	10.5	77	pH effect	No pitting

Table 3. A summary of slow strain rate tests performed in the waste simulants with low pH.

Simulant	Nitrite	Nitrate	Ratio	pH	Temp (°C)	Pot (mV)	Failure Time (hrs)	Failure Strain (%)	Result
AN107	1.2	3.7	0.32	11	25	-50	81.6	29.4	No cracking
AN107 modified 1	0.35	3.5	0.1	10	50	-254 (OCP)	71.8	25.9	No cracking
AN107 modified 2	0.11	1.11	0.1	10	50	-172 (OCP)	71.7	25.8	No cracking
AN107 modified 3	0.011	0.11	0.1	10	50	-239 (OCP)	74.6	26.8	No cracking
AN107 modified 4	1	5	0.2	10	50	-109 (OCP)	71.3	25.7	No cracking
270-LT (modified) B2	0.575	5.75	0.1	10	50	-212 (OCP)	74.7	26.9	No Cracking
AY101-AIL	0.912	0.017	54	10	50	-114 (OCP)	61.7	22.2	No Cracking
AY102-AIL	0.001	0.002	0.5	10	77	-337 (OCP)	66.1	23.8	No Cracking
AY102-AIL	0.001	0.002	0.5	10.5	77	-321 (OCP)	64.9	23.4	No cracking LAI

FIGURES
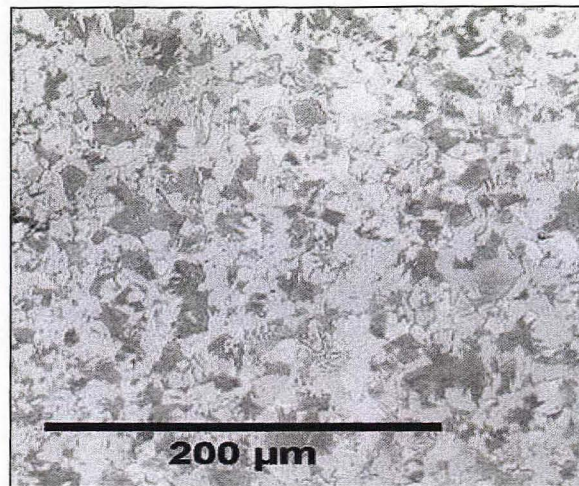
Figure 1. A photomicrograph of the microstructure of the A537 Class 2 steel used for the current work.
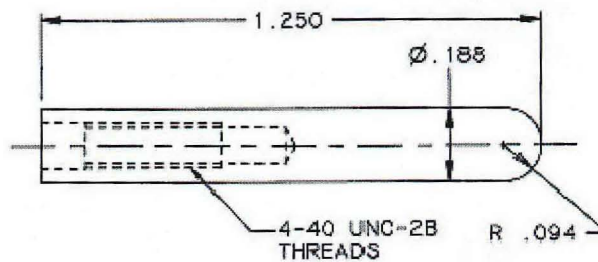
Figure 2. An engineering drawing of the standard electrochemical test specimen (units are in inches).
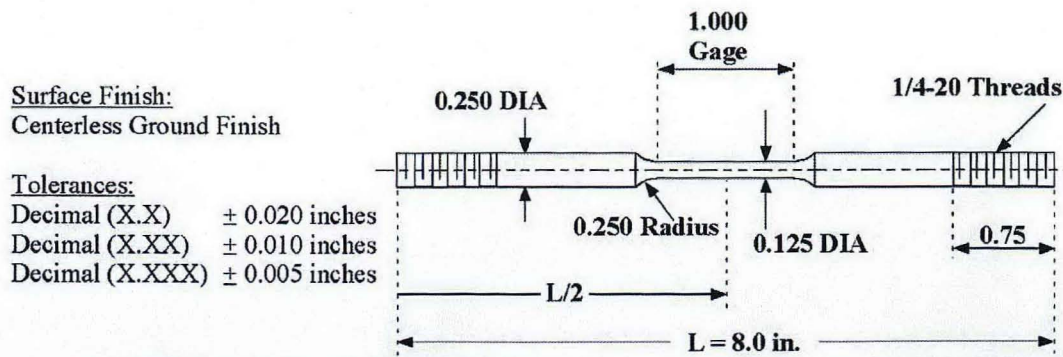
Figure 3. An engineering drawing of the standard slow strain rate test specimen (units are in inches).
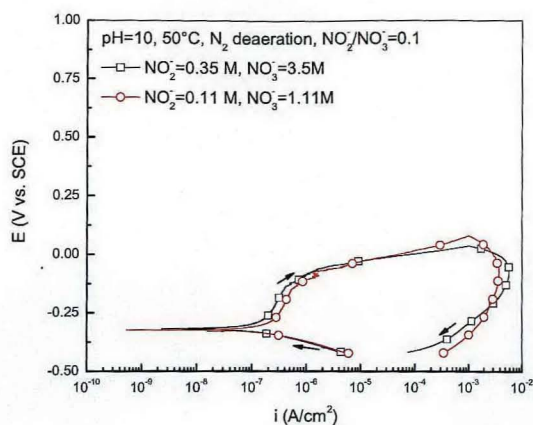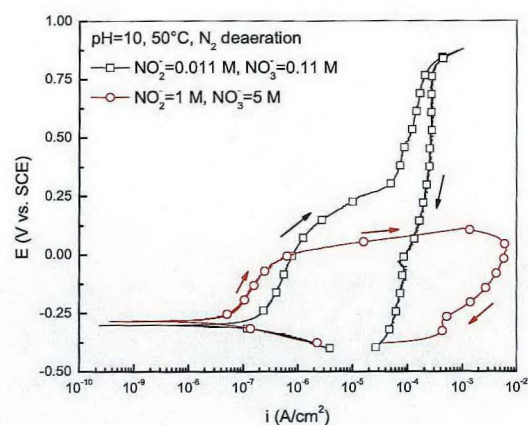
(a)　　　　　　　　　　　　　　　　　　(b)

Figure 4. A CPP curve from the test performed in deaerated AN107 simulant at 50°C and pH 10 with different nitrite and nitrate concentrations.
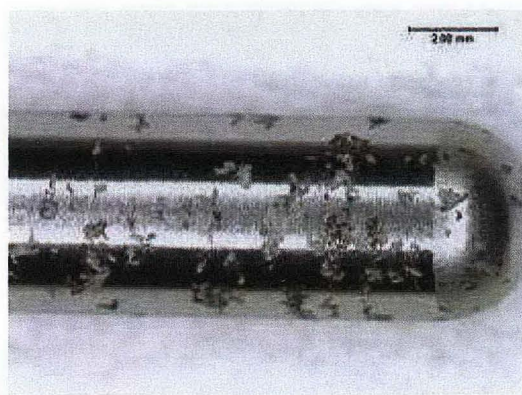
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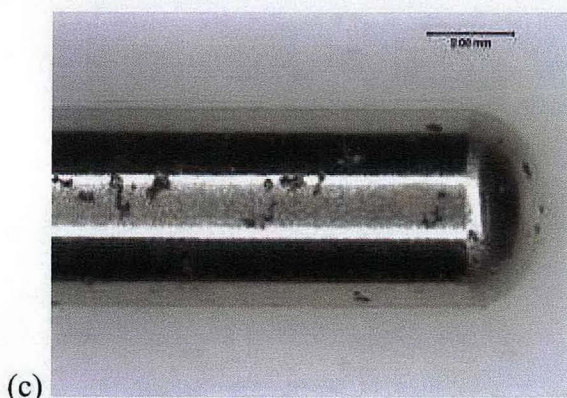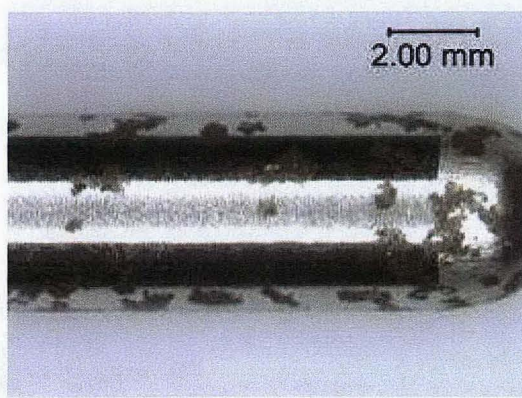
(c)　　　　　　　　　　　　　　　　　　(d)

Figure 5. The appearance of the sample after CPP testing in deaerated AN107 simulant at 50°C and pH 10. (a) Nitrite/Nitrate=0.1, Nitrite=0.35M, Nitrate=3.5M; (b) Nitrite/Nitrate=0.1, Nitrite=0.11M, Nitrate=1.11M; (c) Nitrite/Nitrate=0.1, Nitrite=0.011M, Nitrate= 0.11M; (d) Nitrite/Nitrate=0.2, Nitrite=1M, Nitrate=5M.

11
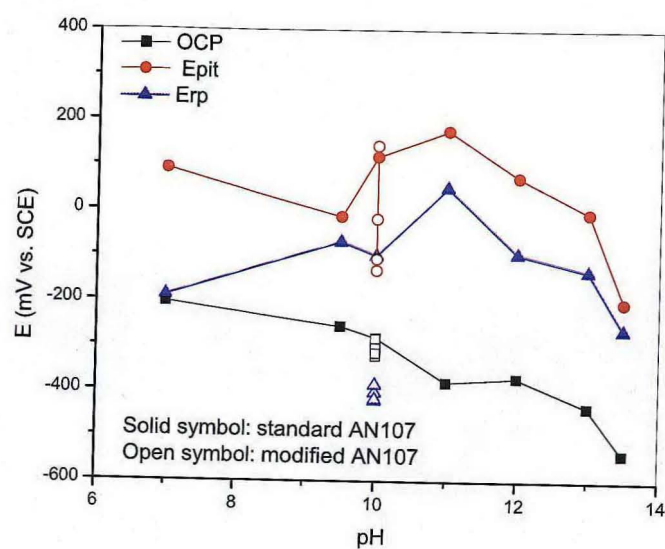
Figure 6. The changes in the pitting potential, OCP and repassivation potential as a function of pH in both standard AN107 and modified AN107 simulants.
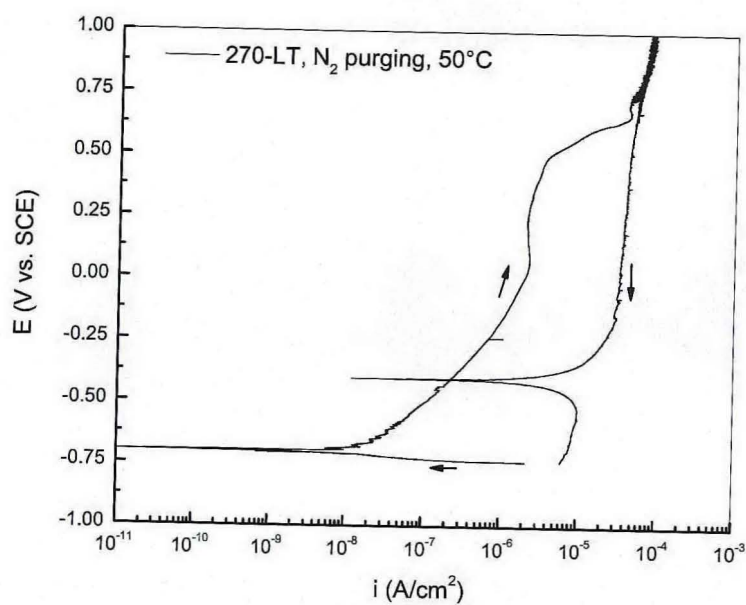
Figure 7. A CPP curve from the test performed in deaerated 270-LT simulant at 50°C.

Figure 8. The appearance of the sample after CPP testing in deaerated 270-LT simulant at 50°C
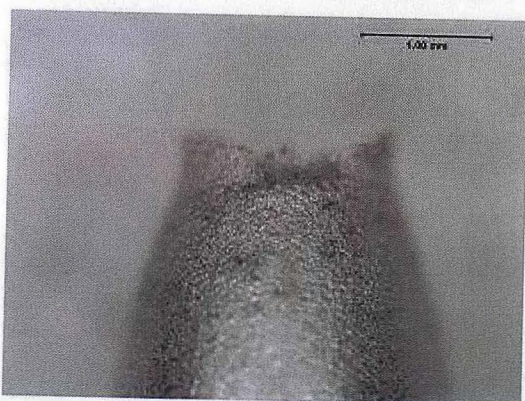

(a)
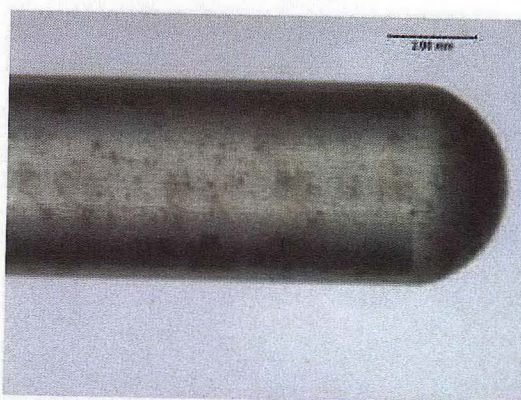
(b)

Figure 9. The appearance of the sample after CPP testing in (a) deaerated AY101-AIL at pH 10 and 50°C, and (b) deaerated AY102-AIL at pH 10.5 and 77°C.
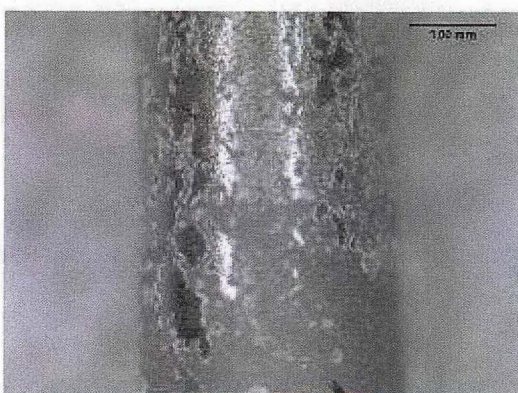

(a)

(b)

Figure 10. A stereo micrograph of the sample from the test performed in modified AN107 (0.35 M nitrite, 3.5 M nitrate) at 50°C and at OCP (-254 mV vs. SCE).
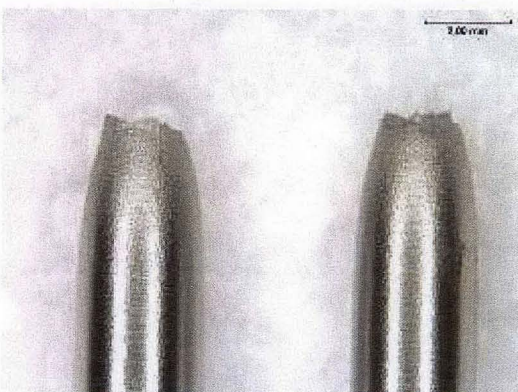
13
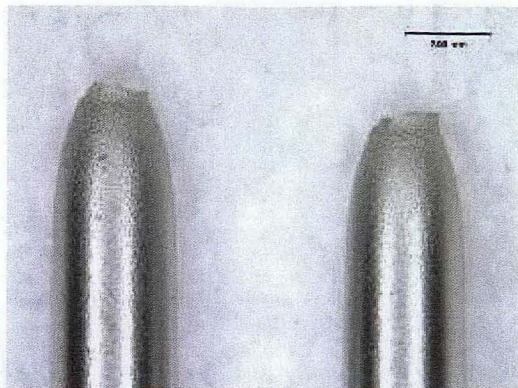
Figure 11. A stereo micrograph of the sample from the test performed in modified AN107 (1 M nitrite, 5M nitrate) at 50°C and at OCP (-109 mV vs. SCE)
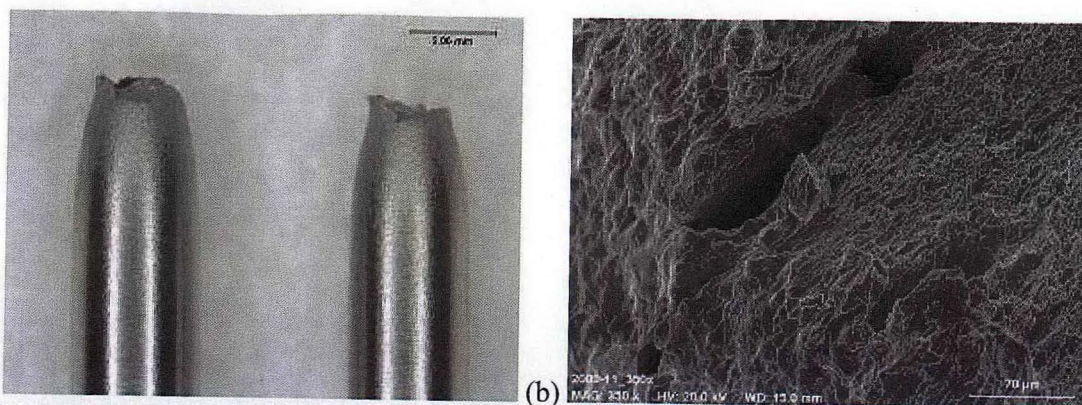

Figure 12. A stereo micrograph of the shaft of the sample from the test performed in 270-LT simulant at 50°C and at OCP (-359 mV vs. SCE).
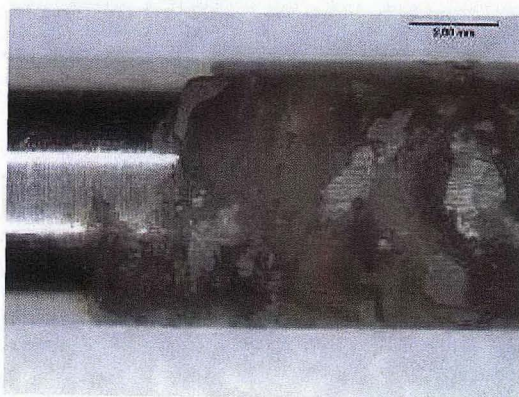

Figure 13. A stereo micrograph of the sample from the test performed in AY101-AIL pH 10 at 50°C and at OCP (-114 mV vs. SCE).

(a)   (b)

Figure 14. A stereo micrograph of the sample from the test performed in AY102-AIL pH 10.5 at 77°C and at OCP (-321 mV vs. SCE).

Figure 15. A stereo micrograph of the shaft of the sample from the test performed in AY102-AIL pH 10.5 at 77°C and at OCP (-321 mV vs. SCE).
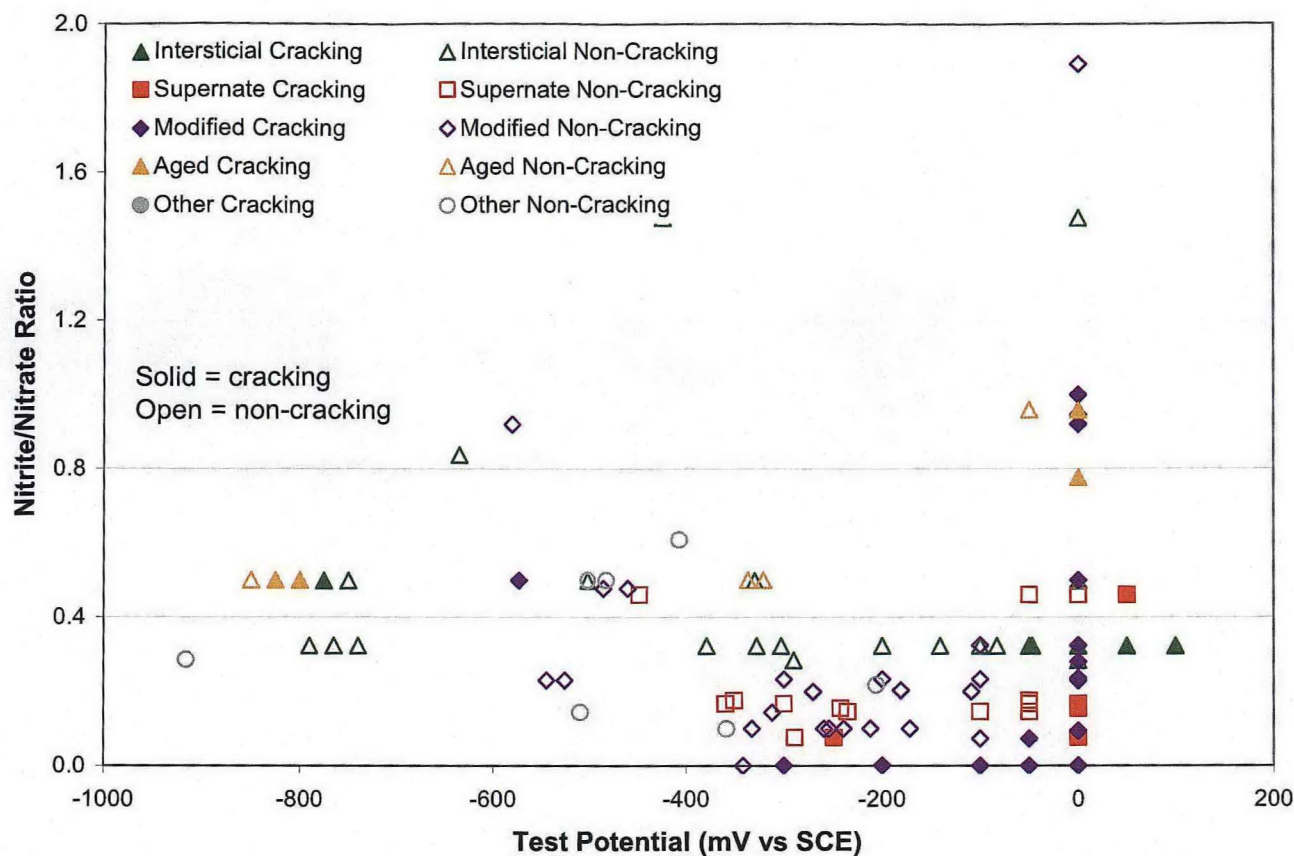
Figure 16. A plot of nitrite / nitrate ratio as a function of test potential for various simulant investigated during the course of this program. Solid symbols represent cracking behavior and open symbols represent non-cracking behavior.