RPP-34657-FP
Revision 0

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Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-99RL14047

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Date Published
September 2007

To Be Presented at
Materials Science & Technology 2007 Conference and Exhibition

ACerS; AIST; ASM; TMS
Detroit, Michigan

September 16-20, 2007

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J. D. Aardal 08/21/2007
Release Approval Date

Approved for Public Release;
Further Dissemination Unlimited

Printed in the United States of America

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Keywords: Corrosion, Nuclear Waste, Stress Corrosion Cracking

Abstract

The Hanford reservation Tank Farms in Washington State has 177 underground storage tanks that contain approximately 50 million gallons of liquid legacy radioactive waste from cold war plutonium production. These tanks will continue to store waste until it is treated and disposed.

These nuclear wastes were converted to highly alkaline pH wastes to protect the carbon steel storage tanks from corrosion. However, the carbon steel is still susceptible to localized corrosion and stress corrosion cracking. The waste chemistry varies from tank to tank, and contains various combinations of hydroxide, nitrate, nitrite, chloride, carbonate, aluminate and other species. The effect of each of these species and any synergistic effects on localized corrosion and stress corrosion cracking of carbon steel have been investigated with electrochemical polarization, slow strain rate, and crack growth rate testing. The effect of solution chemistry, pH, temperature and applied potential are all considered and their role in the corrosion behavior will be discussed.

Introduction

The Hanford reservation Tank Farms in Washington State has 177 underground storage tanks that contain approximately 50 million gallons of liquid legacy radioactive waste from Cold War plutonium production. The current disposal plan for the waste is vitrification into glass logs that will ultimately be placed in the Yucca Mountain Repository. Twenty-eight of these tanks have an inner primary tank and a secondary liner and are known as Double-Shelled Tank (DSTs). The waste will continue to be stored in the million-gallon DSTs, until the completion of the construction of the vitrification plant and final waste processing.

Research at Hanford and Savannah River Laboratories (SRL) demonstrated that cracking could be prevented by maintaining a pH above 12 and by stress relieving the welds. Procedures were implemented accordingly to ensure these controls were put in place. As a result, the wastes are all alkaline, with pH typically in the range 11 to 14. Even under these highly alkaline conditions, the presence of certain constituents, such as nitrates and chloride can cause the carbon steels to be susceptible to localized corrosion, such as pitting, and to stress corrosion cracking (SCC).

There is a wide variability of tank chemistry; each tank is unique. Furthermore, the waste chemistry in every tank is changing with time due to the chemical and radiolytic reactions occurring in the tanks. In addition, the chemistries for some tanks have been found to be noncompliant with the original specifications, especially in the interstitial liquid of the condensed solids region (sludge), which can not be readily corrected simply by chemical additions owing to slow mixing kinetics. There is concern within the Department of Energy (DOE) and regulators that tank integrity be maintained through the life of the mission. Consequently, there is a need to better understand the SCC propensity of the carbon steel in the waste chemistries and define mitigation strategies.

Recent research on one of the tank chemistries indicated that elevated pH, long considered the main corrosion inhibitor, and did not have a dominant effect on the susceptibility to SCC in the range 10-13.5 [1, 2]. It was also shown that the nitrite in the waste had a surprisingly strong inhibitory effect. As the waste ages, the future tank chemistry is predicted to be reduced in nitrate and increased in nitrite, indicating that corrosive conditions in the tank will tend to improve with time. If it can be demonstrated that the maintenance of a high pH is not necessary, then there would be a drastically reduced need to add caustic to the tanks. Minimizing or eliminating caustic additions (representing hundreds of thousands of gallons of sodium hydroxide) has the effect of significantly increasing the available DST waste storage capacity, and eliminating the need to install multi-million dollar mixing pumps.

The successes of the previous research in defining the condition for pitting and SCC propensity led to a continuation of the work to study the susceptibility of carbon steels to SCC in the other DSTs with different waste constituents. Some of the species in the highly basic waste, such as nitrate and chloride, are known to contribute to SCC. Others, such as nitrite and aluminate, are considered to be inhibitors. However, the possible synergistic effect of solutions containing multiple species is unknown.

Therefore, the objectives of this work were to study the susceptibility/propensity of carbon steel used in the DST walls to pitting and SCC in the environments of interest. It is expected that a better understanding of susceptibility or propensity of these carbon steel alloys to undergo localized corrosion and SCC can help define and establish effective and efficient corrosion mitigation strategies, and ensure that the integrity of DSTs is maintained for their mission life.

Experimental Approach

This work has focused on wastes contained in DSTs 241-AN107, and 241-AY102 (these are abbreviated to AN107 and AY102, respectively). The AY102 DST contains a supernate transferred from another DST (AP101), but still has its original sludge composition. The material used for the AY102 testing was AAR TC 128 Grade B carbon steel. Samples of this steel were recovered from retired rail tank cars that were known to be of a similar vintage and chemistry to the steels used in the AY Farm DSTs. The material used for the AN107 testing was an ASTM A537 Class 2 steel plate of the same vintage as the tank steel, heat treated to match the tank steel mechanical properties.

Actual tank wastes are highly radioactive, and thus testing in actual wastes can only be accomplished in a hot cell. Because of the cost and complications of using hot waste and because the tank chemistries are predicted to change in known ways over the next 15-20 years of tank operation, non-radioactive waste stimulants were prepared. The AN107 waste chemistry is based on nitrite and nitrate anions. The AY102 sludge waste chemistry is carbonate-based, while the AY102 supernate from AP101 includes nitrite, nitrate, carbonate and aluminate. In the AY102 tank, the wastes from two different tanks have been combined into one tank for logistical reasons. Therefore, the mixture combinations, along with the changing of chemistry with time, show several "end state" chemistries were predicted using thermodynamic speciation modeling. The various combinations of present state and end state chemistries are being studied.

The main constituents of the three base waste chemistries of interest are given below in Table 1. During the course of this work, chemistries were adjusted in order to study the effect on the test steel's susceptibility to SCC. Any changes from these base chemistries are discussed in the text. In some cases, the solutions were purged with nitrogen or oxygen.

Table 1 The main constituents of the three base waste chemistries.

Tank Designation	Nominal pH	Nitrite (M)	Nitrate (M)	Carbonate (M)	Aluminate (M)
AN107	11	1.2	3.7	-	-
AY102 (Sludge)	11	0.001	0.002	1.021	0.002
AY102 (supernate AP101)	14	0.98	2.13	0.47	0.31

Cyclic Potentiodynamic Polarization

To evaluate the electrochemical behavior cyclic potentiodynamic polarization (CPP) tests were performed following the guidelines in ASTM G61 [3]. Prior to CPP testing, the open circuit potential (OCP) was monitored for 18 h. The scan was started from -100 mV vs. OCP at a rate of 0.17 mV/s and reversed at 1 V vs. SCE or a current density of 1 mA/cm^2, whichever was reached first. When pitting corrosion occurred, the pitting potential (E_{pit}) and the repassivation potential (E_{rp}) were determined from the CPP curve.

Tests were run under several conditions. Temperature was maintained at either 50 or 77°C. AN107 and AY102 simulants were typically adjusted to pH 11 and the AP101 simulant was typically adjusted to pH 14. The majority of the tests were performed under nitrogen purging conditions. In one case, an oxygen purge was performed. The chemistry of the solutions was varied, as discussed above. Of particular interest was the effect of various species in the chemistry on the OCP, active to passive transition potential, and pitting potential.

Post-test analysis involved visual examination, stereo-optical microscopy, and sometimes scanning electron microscopy (SEM). Usually, the test samples were examined for general surface condition following the test, and in particular, for the possible presence of pitting.

Slow Strain Rate Testing

To evaluate the propensity for SCC, slow strain rate tests (SSRTs) were performed following the guidelines in ASTM G129 [4]. The test consists of a uniaxial tension test to failure. The strain rate used was nominally 10^{-6} s^{-1}, which generally leads to failure times of between 60 and 75 hours when nominally ductile behavior occurs. To perform the test, a tensile sample is inserted into a Teflon test cell that has sliding seals and then mounted in the load frame. The test solution is then introduced to the test cell just prior to load application.

Tests were run under several conditions. Temperature was maintained at either 50 or 77°C (to bound DST waste temperatures). Tests were run either at OCP or with an applied potential. The selection of applied potential for each of the tests was made based on the electrochemical polarization behavior. Applied potentials varied between +100 and -800 mV vs. SCE. The majority of the slow strain rate tests were performed under quiescent (no gas purging) conditions. The chemistry of the solutions was varied, as discussed above. Of particular interest was the effect of nitrite on SCC susceptibility.

Post-test analysis involved visual examination, stereo-optical microscopy, metallographic cross sectioning, and in some cases SEM. SCC in nitrate, carbonate and caustic solutions is typically characterized by intergranular cracking. In the cases that intergranular cracking was confirmed, the crack growth rate was calculated by dividing the maximum measured crack depth by the total time to failure. This calculation is an estimate only, as it does not take into account the time to initiate cracks and assumes that any observed cracking took place at a constant rate through out the exposure period. Despite these limitations, the estimates provide a simple, semi-quantitative diagnostic to classify the SCC propensity, and compare behavior of the steels in the different environments.

Results and Discussion

Anodic Polarization

Figure 1 summarizes the effect of nitrite concentration on the pitting potential, repassivation potential and OCP in AN107 simulant. Nitrite concentration appeared to have very little effect on the OCP. The more positive OCP value at 2.3M nitrite was likely due to the pH difference of that solution (pH 10 vs. pH 11 in other cases). However, the effect of nitrite concentrations on E_{pit} and E_{rp} is evident. The values of E_{pit} and E_{rp} generally were more positive at higher nitrite concentrations. There appears to be a critical nitrite concentration (~1.2 M) below which the repassivation potentials were more negative than OCP. Therefore, pitting corrosion could initiate at OCP under such conditions, although the initiation could be significantly delayed. It can also be seen from Figure 1 that the repassivation potentials were closer to the pitting potentials at higher nitrite concentrations. This further demonstrates that nitrite appears to be a potent inhibitor for carbon steel in simulated AN107 wastes since the smaller difference between E_{rp} and E_{pit} indicates decreased susceptibility to localized corrosion. However, no extra benefit with respect to improving the pitting and repassivation potentials was gained with further increases in the nitrite concentration above 3.5 M, for a constant nitrate concentration of 3.7 M. Based on the effect of nitrite on the repassivation potential, maintaining the nitrite concentration above a critical value of 1.2 M should be beneficial because the repassivation potential is significantly above OCP above this concentration.

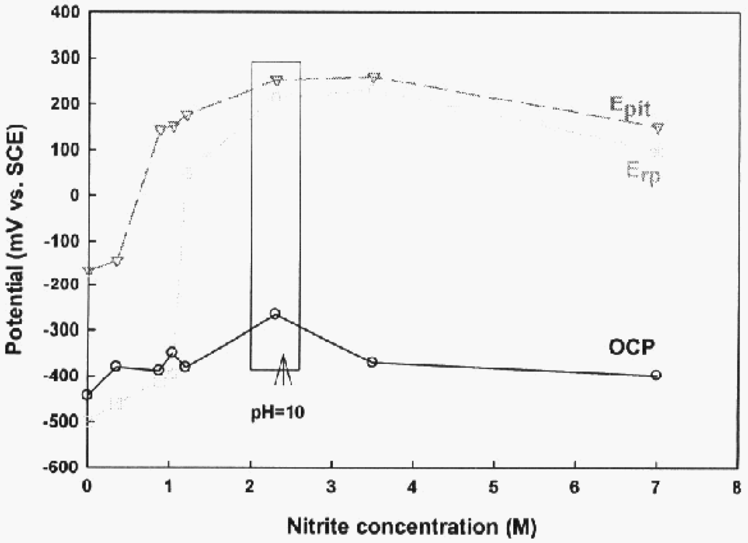
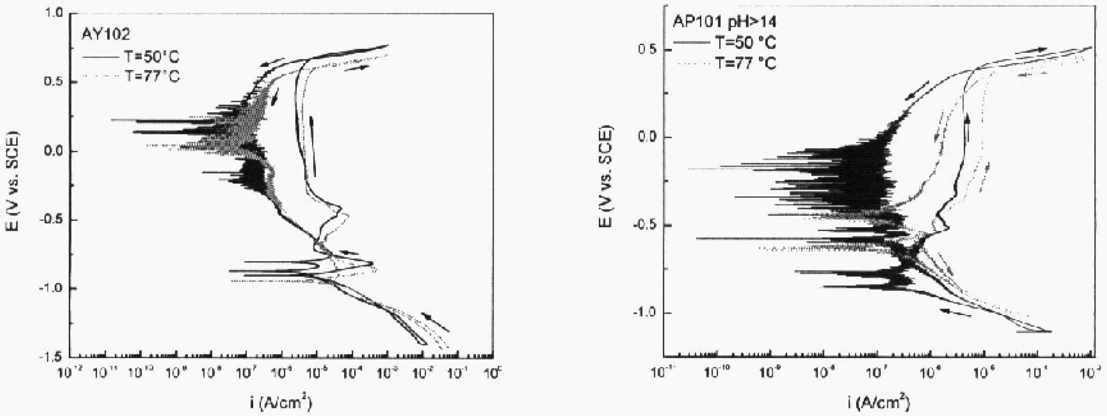


Figure 1. The effect of nitrite concentration on E_{rp}, E_{pit} and OCP in AN107 simulant. The potentials at 2.3M nitrite are from a CPP test in the endpoint solution at pH 10. All others are from CPP tests in solutions with pH 11.

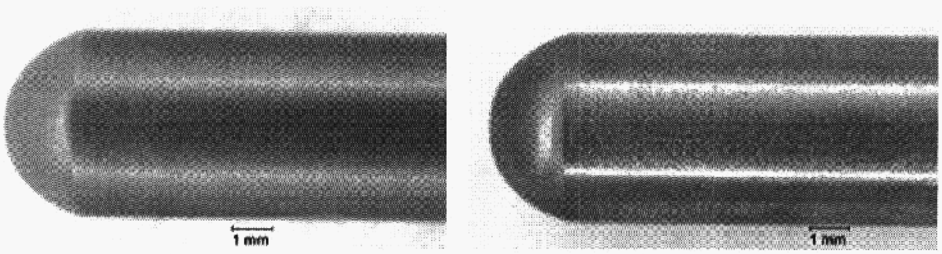
Figure 2 shows typical electrochemical behavior of the test steels in the AY102 and AP101 simulants. Results are given for tests conducted at both 50 and 77°C. The samples initially experienced active dissolution and then reached a pseudo-passive region at both 50°C and 77°C in AY102, Figure 2(a). The passive current densities at both temperatures were almost identical (on the order of 10^{-5} A/cm^2). The cause of an additional anodic nose at around -0.5 V vs. SCE has not been identified as yet. The curves showed a sharp increase in the current at approximately 0.6 V (vs. SCE). This current increase, however, was not associated with pitting corrosion because no pits were observed on any of the samples tested AY102 solution (Figure 3(a)). The sharp increase in the current is likely due to transpassive dissolution, oxidation of a species in the solution (very likely water oxidation given the pH), or a combination of the two. It has been found by others [5] that SCC is possible at potentials near the active-passive transition in carbonate environments. A set of SSR tests performed at this range of potential is discussed in the next section.

The CPP curves in AP101 (pH>14) at both 50 °C and 77 °C are similar to those in AY102 except that no active-passive transition was observed, Figure 2(b). The curves exhibited a fairly wide passive region prior to a current increase at approximately 0.48 V vs. SCE. Again, this current increase is most likely associated with water oxidation with possible concomitant transpassive dissolution. The OCP values at both temperature levels were slightly more positive than those observed in AY102, likely due to a higher nitrate concentration in this solution. The contributions of high nitrate and/or nitrite concentration to the cathodic reactions are discussed below.



(a) (b)

Figure 2 CPP curves from tests run in (a) AY102 (sludge), and (b) AY102 supernate (AP101) simulants.



(a) (b)

Figure 3 Photographs of samples from CPP tests run in (a) AY102 (sludge), and (b) AY102 (supernate from AP101) simulants, both from tests performed at 77°C.

Figure 4 shows a comparison of CPP curves at three different conditions at 77°C: purged with nitrogen, quiescent, and purged with oxygen. The OCP was approximately 700 mV more positive when the solution was under quiescent conditions than when the solution was purged with nitrogen. There was no further change in the OCP when the solution was purged with pure oxygen. The same behavior was observed at 55°C. The effect of oxygen content on the OCP is important as the change in OCP could move the tank into or out of a region with SCC susceptibility.

The shift in the OCP was likely due to the change in the dominant cathodic reaction. In the absence of oxygen, the primary cathodic reaction in AY102 simulant was probably water reduction. However, when oxygen was present, the cathodic reaction likely was dominated by the oxygen reduction reaction, resulting in the expected positive shift in the OCP. It should be noted that oxygen content seemed to have no appreciable effect on OCP in the AN107 solution because the cathodic reaction was dominated by the high concentrations of nitrate and nitrite anions.

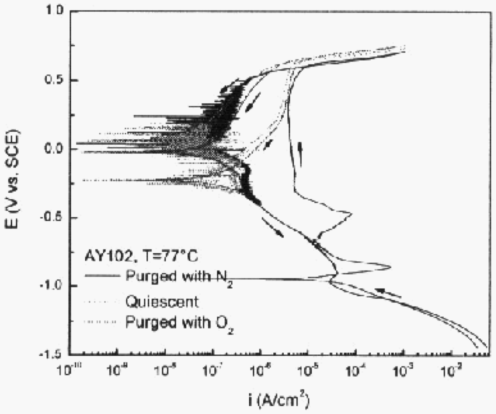


Figure 4 Comparison of CPP curves in AY102 simulants (pH 11) under quiescent condition, purged with nitrogen and with oxygen.

As described previously, the AY102 supernate, from DST AP101, is a nitrate and nitrite based solution, which is similar to AN107 waste although AP101 waste also contains carbonate and aluminate. Thus, one might expect to see an inhibitive effect of nitrite as was observed in AN107 testing. However, experiments in AY102 solutions with varying nitrite concentration did not show any significant impact on the carbon steel corrosion. In these preliminary experiments, nitrite was reduced to half of the original amount while maintaining other concentrations the same.

Slow Strain Rate Testing

Previous work in the AN107 simulant [1, 2] identified a “critical” nitrite/nitrate ratio and applied potential range that could be used to determine susceptibility to SCC. The SCC susceptibility decreased above a critical nitrite/nitrate ratio and below a critical potential. Testing with AY102 and AP101 simulants was performed with this in mind.

Figure 5 is a plot of the stress/strain behavior of samples in the AY102 (carbonate) and AP101 (nitrite, nitrate, carbonate, aluminate) solutions. These tests were performed at 77°C and at open circuit potential. A test in air is shown for comparison. The curves exhibit the typical stress/strain behavior for low carbon steel. They are representative of all of the SSRTs performed in AY102 and AP101 simulants. Failure strains varied between 21 and 25.7%, regardless of whether or not cracking was observed. All samples showed considerable ductility, indicating that high stresses were necessary for cracking to occur.

Stereo-microscopy of the fracture surfaces indicated whether SCC cracking had occurred during the test. Figure 6 gives examples of tests that did not show cracking. These samples were tested in the AY102 and AP101 simulants at 77°C and OCP.

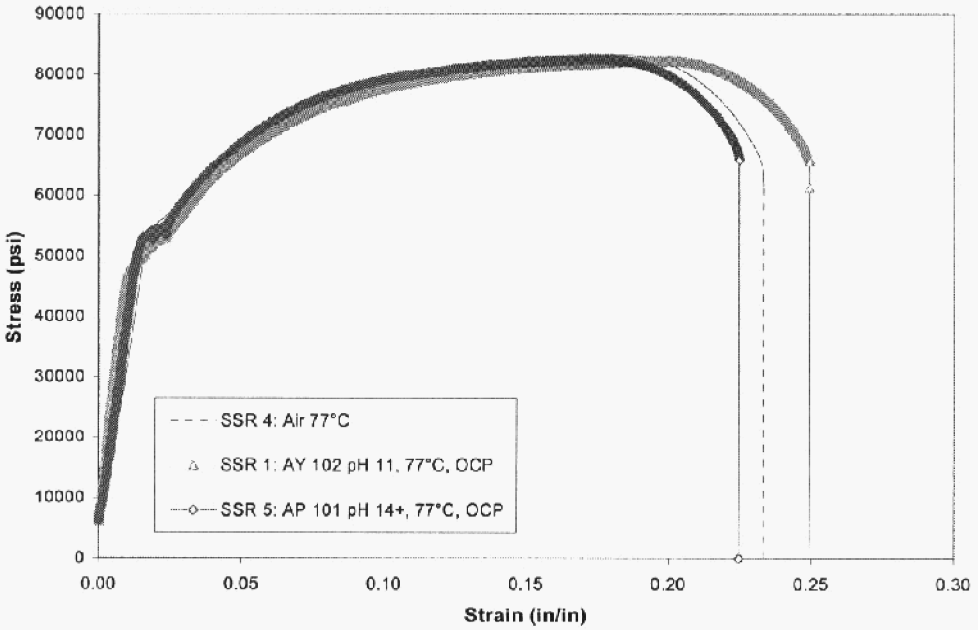
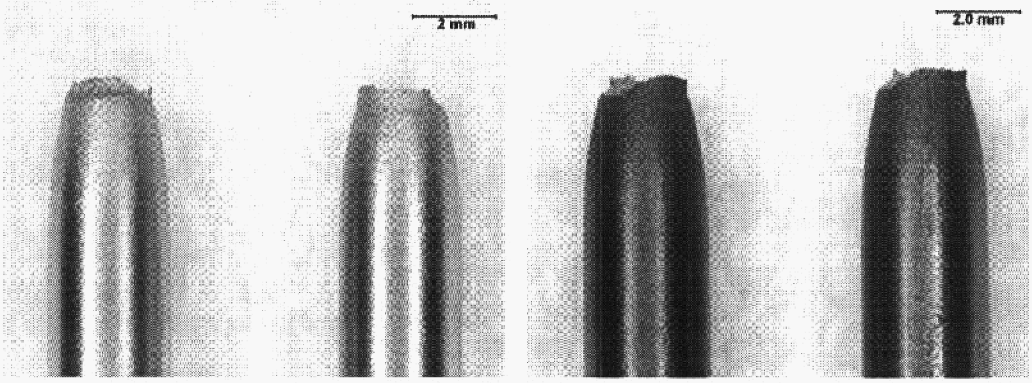


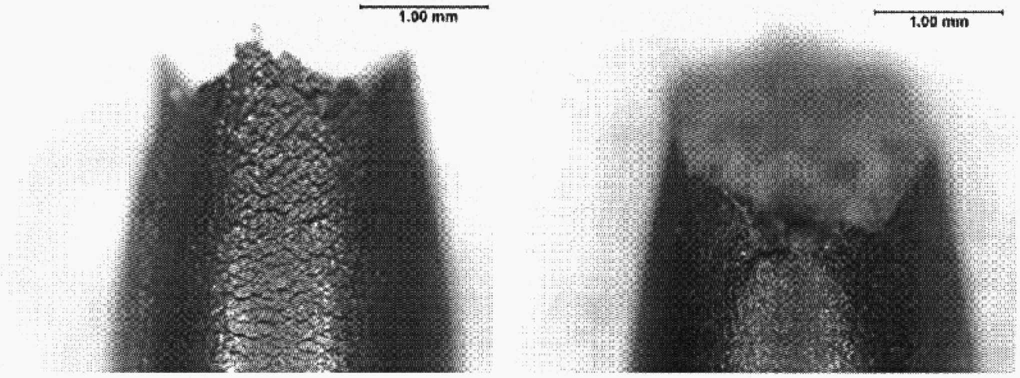
Figure 5 The stress / strain behavior in AY102 (carbonate) and AP101 (nitrite, nitrate, carbonate, aluminate) simulants.

Figure 7 gives examples of tests that did show cracking. One test was performed in AY102 at 77°C, and with an applied potential of -800 mV vs. SCE. The potential was selected based on the active-passive transition between approximately -750 and -800 mV vs. SCE observed in the CPP results as discussed above. SCC of carbon steel is known to occur near this potential range in carbonate based solutions [5]. The other test was performed in AP101 simulant with half the typical nitrite content (i.e. half of 0.98 M) and with a high applied potential of 0 mV vs. SCE. Previous work on AN107 nitrite/nitrate based simulant indicated that nitrite had an inhibitory affect, and this test was designed to see if the SCC behavior is comparable in the AP101 simulant. A reduction in nitrite content would be expected to increase the susceptibility to SCC. The effect of carbonate and aluminate in the AP101 simulant, which are not found in the AN107 simulant, is unknown. Previous work in AN107 simulant with reduced nitrite content showed severe SCC, and failure strains reduced to below 10% due to reduced cross-sectional area. However, in the AP101 simulant with reduced nitrite concentration, the failure strain was 22.0% and Figure 7 indicates only minor cracking. This suggests that there is a beneficial effect of either the carbonate or aluminate in the AP101 simulant, or a difference in the steels that reduced the SCC susceptibility.



(a) (b)

Figure 6 Stereo-optical micrographs of samples that showed no cracking during SSR testing (a) test in AY102 at 77°C and under open circuit potential conditions, and (b) test in AP101 at 77°C and under open circuit potential conditions.

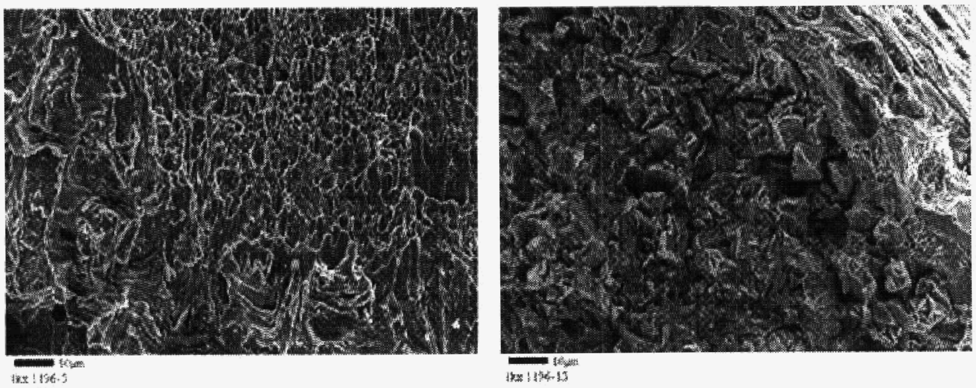


(a) (b)

Figure 7 Stereo-optical micrographs of samples that showed cracking during SSR testing (a)test in AY102 at 77°C and with an applied potential of -800 mV vs. SCE, and (b) test in AP101 with half typical nitrite content at 77°C and with applied potential of 0 mV vs. SCE.

The cracking observed in samples tested in the AY102 and AP101 simulants was minor, and often difficult to identify by simple visual observation in the stereo-optical microscope. SEM examination was performed on all the fracture surfaces of all test samples to confirm that failure had occurred by either ductile overload (no SCC), or intergranular fracture (SCC). In the cases where intergranular cracking was observed, crack length measurements were made and used to estimate pseudo-crack growth rates from the failure times. In all cases, crack growth rates were found to be less than or equal to 1.7×10^{-7} mm/sec.

Figure 8 gives examples of typical micrographs taken during SEM examination. One of the tests was performed in AP101 simulant at 77°C and under open circuit potential conditions. The surface shows a purely ductile overload failure, with no evidence of intergranular fracture. The other test was performed in the AP101 simulant with half the typical nitrite content and with an applied potential of 0 mV vs. SCE. This surface shows evidence of intergranular fracture, indicative of SCC.



(a) (b)

Figure 8 Scanning electron micrographs of samples that showed (a) purely ductile failure during testing AY102 simulant at 77°C and under open circuit potential conditions, and (b)intergranular SCC failure in AP101 with half the typical nitrite content at 77°C and with applied potential of 0 mV vs. SCE.

Tests were run under various conditions. The results can be summarized by discussing the results relating to the key conclusions of the work. No SCC was observed in tests in the AY102 simulant at OCP or with an applied potential of 0 mV vs. SCE. Minor cracking was observed in tests in which the applied potential was either -775 or -800 mV vs. SCE, as shown in the Figure 7(a) above. Despite the presence of cracks, there was no significant change in the stress-strain behavior.

No SCC was observed in tests in the AP101 simulant at OCP or with an applied potential of 0 mV vs. SCE. Minor cracking was observed in tests in which the applied potential was 0 mV vs. SCE, and the nitrite and / or aluminate contents of the simulants had been modified. As discussed above, previous work on AN107 simulants indicated that nitrite had an inhibitory effect on SCC. A series of tests was performed using modified AP101 simulant; two tests with half the typical nitrite, two tests with double the typical nitrite, and two tests with half the typical nitrite and no aluminate. It was expected that increased nitrite would reduce the susceptibility to SCC, especially given the result that the test in the base simulant had shown no cracking with an applied potential of 0 mV vs. SCE. This was not the case. The test run with double the typical nitrite content showed minor cracking, and this was confirmed by SEM examination.

The plot given in the reference [2] is recreated below as Figure 9 and updated to include recent results from the testing in AY102 and AP101 simulants, and modifications. The recent results are generally consistent with the previous results. The notable exceptions are the two tests that showed cracking at -775 and -800 mV vs. SCE. Note that these tests were run in AY102 simulant, which has a different base chemistry than either AP101 or AN107. AY102 simulant is based on carbonate, and contains negligible nitrite or nitrate. Therefore the species responsible for the SCC is likely different in the AY102 simulant. The SCC behavior can also be correlated to the CPP curves given earlier as Figures 2 and 3(a).

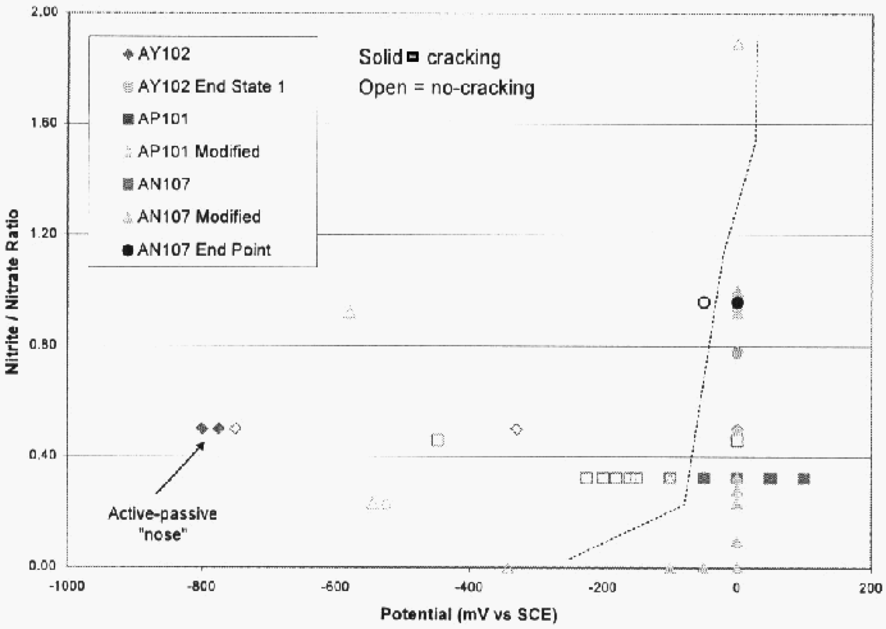


Figure 9 A plot nitrite/nitrate ratio vs. potential indicating two zones of SCC susceptibility Solid symbols represent conditions that lead to cracking. Open symbols represent conditions that lead to no-cracking.

Summary

Experiments were performed on carbon steel samples in simulants for specific Hanford waste storage tanks to investigate the susceptibility to pitting and SCC.

- No pitting corrosion was observed in either AY102 sludge or AY102 supernate (from AP101 simulants). This is in contrast to the results found previously for the AN107 simulant, which showed pitting at high potentials in the CPP testing.
- OCP in these simulants appears to be dependent on oxygen content and the cathodic reaction whereas the AN107 simulants were insensitive to oxygen levels..
- Minor SCC was seen in AY102 simulants at low potentials (-800 mV vs. SCE), and in AP101 simulant at 0 mV vs. SCE, but only with modified nitrite contents. These simulants are benign relative to previously studied AN107 simulant.
- SCC susceptibility in AY102 and AP101 simulant is generally consistent with that found in previously studied AN107 simulant, with respect to nitrite/nitrate ratio and potential.

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