**Contract No:**

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

**Disclaimer:**

This work was prepared under an agreement with and funded by the U.S. Government. Neither the U. S. Government or its employees, nor any of its contractors, subcontractors or their employees, makes any express or implied: 1. warranty or assumes any legal liability for the accuracy, completeness, or for the use or results of such use of any information, product, or process disclosed; or 2. representation that such use or results of such use would not infringe privately owned rights; or 3. endorsement or recommendation of any specifically identified commercial product, process, or service. Any views and opinions of authors expressed in this work do not necessarily state or reflect those of the United States Government, or its contractors, or subcontractors.
Laboratory Testing to Simulate Vapor Space Corrosion in Radioactive Waste Storage Tanks

Joshua R. Gray, Brenda L. Garcia-Diaz, Bruce J. Wiersma
Savannah River National Laboratory
Aiken, SC 29808
USA

Kayle D. Boomer
Washington River Protection Solutions
Richland WA,
USA

ABSTRACT

Radioactive liquid waste has been stored in underground carbon steel tanks for nearly 70 years at the Hanford nuclear facility. Vapor space corrosion of the tank walls has emerged as an ongoing challenge to overcome in maintaining the structural integrity of these tanks. The interaction between corrosive and inhibitor species in condensates/supernates on the tank wall above the liquid level, and their interaction with vapor phase constituents as the liquid evaporates from the tank wall influences the formation of corrosion products and the corrosion of the carbon steel. An effort is underway to gain an understanding of the mechanism of vapor space corrosion. Localized corrosion, in the form of pitting, is of particular interest in the vapor space. CPP testing was utilized to determine the susceptibility of the steel in a simulated vapor space environment. The tests also investigated the impact of ammonia gas in the vapor space area on the corrosion of the steel. Vapor space coupon tests were also performed to investigate the evolution of the corrosion products during longer term exposures. These tests were also conducted at vapor space ammonia levels of 50 and 550 ppm NH₃ (0.005, and 0.055 vol.%) in air. Ammonia was shown to mitigate vapor space corrosion.

Key words: radioactive waste, carbon steel, vapor space corrosion, inhibition.

INTRODUCTION

Weapons, space and medical research programs led by the U. S. Department of Energy have created a legacy of nuclear waste. The waste is being stored on an interim basis in large, underground carbon steel waste tanks at the Hanford and Savannah River Site (SRS). The corrosion processes affecting these tanks below the liquid level are generally well understood and are being managed by chemistry control
programs. However, vapor space corrosion of the tank walls is an ongoing challenge to overcome in demonstrating the structural integrity of the Double Shell Tanks (DST). Experience to-date indicates that there have been no consequential incidences of uniform or localized corrosion on the tanks at Hanford or SRS. There have however, been incidences of unexplained corrosion discovered in equipment suspended in tanks or in the tank ventilation systems. For example, both sites have experienced varying levels of ventilation exhaust duct failures, some attributed to stress corrosion cracking [1].

The interaction between corrosive and inhibitor species in condensates/supernates on the tank wall above the liquid level, and their interaction with vapor phase constituents as the liquid evaporates from the tank wall influences the formation of corrosion products and the corrosion of the carbon steel. An effort is underway to gain an understanding of the mechanism of vapor space corrosion. Three areas have been or are being explored: 1) The evolution of the chemistry of the liquid that condenses on the steel in the vapor space, 2) The type and degree of corrosion that occurs in the vapor space, and 3) The evolution of the corrosion products as they are exposed to various vapor space chemistries. Each of these areas is reviewed briefly below.

**Evolution of Vapor Space Chemistry**

Thermodynamic models were utilized to predict the chemistry of adsorbed surface condensates based on the equilibrium between key vapor space constituents and the condensate and changes that occur in the condensate chemistry due to evaporation of water [2]. These models were verified with experimental studies. Six representative Hanford DST supernates were targeted for the study. Some of the key findings from the studies include:

- Carbon dioxide (CO₂) and ammonia (NH₃) are the dominant species in the vapor space. The ratio of CO₂/NH₃ has a strong influence on the equilibrium pH of the liquid phase that adsorbs on the steel surface.
- The primary species in the condensate that forms on the tank walls include ammonia, nitrate, and possibly carbonate/bicarbonate.
- Aerosol transport is not significant as observed by the low concentrations of NO₂ and Na observed in the vapor condensates.
- The pH remains relatively stable (i.e., > 9) until the solutions are nearly evaporated and solids precipitation occurs. The pH changes during the final stage were a function of the initial condensate pH and the formation of carbamates and other solids.
- The experimental studies showed that the final pH for the evaporated wastes was higher than that predicted for the model. This result may have occurred due to low humidity which would cause the evaporation rate of the water to be faster than the reaction of hydroxide with CO₂ from the air [2]. As a result, the equilibrium conditions predicted by the model were not met and some aluminum-containing solid phases, which would deplete hydroxide, did not form.
- The condensates produced by evaporation of water become increasingly rich in nitrite ion.

Corrosion testing was performed in solutions predicted from these models. For each of the six supernate simulants, 3 levels of evaporation were selected for further testing: No evaporation (0%), Mid-level evaporation (25%-35%), and High Evaporation (55%-76%).
Corrosion Testing in Evaporated Condensates

Cyclic potentiodynamic polarization (CPP) testing was utilized to investigate the corrosion response of carbon steel to the six DST simulants at three levels of evaporation [3]. The tests were conducted on carbon steel samples that were completely immersed in a bulk simulant. CPP tests with and without ammonium salts present in the simulant were performed. Four different levels of response were observed from the CPP tests.

- No pitting at any level of evaporation;
- Pitting at the 0% evaporation level, but increasing resistance at higher levels of evaporation;
- Minor pitting at the 0% evaporation level, but decreasing resistance to pitting at higher evaporation levels;
- Heavy pitting at all levels of evaporation.

The addition of small amounts of ammonium nitrate (0.001 M) to the solutions had a small effect on the corrosion response. An increase in the ammonium nitrate concentration to 0.5 M resulted in a significant increase in the pitting resistance. This result suggested further studies are needed to evaluate the effect of ammonium nitrate concentration on corrosion.

Electrochemical and coupon exposure tests were utilized to examine the benefits of ammonia in the vapor space. Cyclic potentiodynamic polarization (CPP) were performed on three most aggressive condensates, at various levels of evaporation, to evaluate the susceptibility of pitting corrosion in bulk solutions simulating vapor space condensates with varying quantities of ammonium nitrate. Coupon exposure tests above the most aggressive condensate, in a vapor space with varying ammonia quantities, were also performed to understand the protective ability of corrosion product or salt that form on the surface of the steel.

**EXPERIMENTAL PROCEDURE**

**Simulant Compositions**

The compositions of the 3 aggressive condensates predicted from the thermodynamic models are shown in Table 1. The letter designations with the solution number represent the evaporation level: A is none, B is mid-level, and C is high-level. A high-level evaporation condition for solution 3 was not possible as the solution became saturated. The electrochemical tests were performed in these 8 solutions at ammonia concentrations of 0, 50 ppm, and 550 ppm. The concentration levels approximate the range of anticipated ammonia concentrations in the vapor space of the DST. Ammonium nitrate was added to the test solution such that the ammonia concentration in the test solutions met the required values.

The most aggressive condensate was solution 3B. Two solutions with this composition were used for the coupon tests. One solution contained ammonia the 50 ppm level, while the other solution contained ammonia at the 550 ppm level. A cover gas, at the same ammonia level as the test solution, was utilized for each test with a balance of air in the gas stream.

**Test Materials**
Test samples were fabricated from A537 carbon steel, class I, which is a low carbon normalized steel. The composition of the material is shown in Table 2 with the balance being iron. The samples were ground and polished to a 600 grit finish for both the electrochemical and coupon tests.

<table>
<thead>
<tr>
<th>Species</th>
<th>1A</th>
<th>1B</th>
<th>1C</th>
<th>2A</th>
<th>2B</th>
<th>2C</th>
<th>3A</th>
<th>3B</th>
</tr>
</thead>
<tbody>
<tr>
<td>KNO₃</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.040</td>
<td>0.053</td>
<td>0.105</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>NaBr</td>
<td>0.005</td>
<td>0.007</td>
<td>0.017</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.064</td>
<td>0.088</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.013</td>
<td>0.020</td>
<td>0.048</td>
<td>0.086</td>
<td>0.110</td>
<td>0.180</td>
<td>0.011</td>
<td>0.015</td>
</tr>
<tr>
<td>NaF</td>
<td>0.011</td>
<td>0.016</td>
<td>0.038</td>
<td>0.010</td>
<td>0.013</td>
<td>0.026</td>
<td>0.003</td>
<td>0.004</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>1.010</td>
<td>1.490</td>
<td>3.590</td>
<td>1.540</td>
<td>2.027</td>
<td>4.045</td>
<td>3.639</td>
<td>5.019</td>
</tr>
<tr>
<td>NaNO₂</td>
<td>0.167</td>
<td>0.248</td>
<td>0.600</td>
<td>0.972</td>
<td>1.280</td>
<td>2.550</td>
<td>0.097</td>
<td>0.130</td>
</tr>
<tr>
<td>Na₃PO₄</td>
<td>0.040</td>
<td>0.060</td>
<td>0.144</td>
<td>0.043</td>
<td>0.057</td>
<td>0.110</td>
<td>0.024</td>
<td>0.033</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.015</td>
<td>0.023</td>
<td>0.055</td>
<td>0.033</td>
<td>0.044</td>
<td>0.087</td>
<td>0.047</td>
<td>0.064</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.089</td>
<td>0.087</td>
<td>0.082</td>
<td>0.092</td>
<td>0.093</td>
<td>0.042</td>
<td>0.030</td>
<td>0.045</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>0.446</td>
<td>0.695</td>
<td>1.070</td>
<td>0.828</td>
<td>1.117</td>
<td>0.466</td>
<td>0.265</td>
<td>0.360</td>
</tr>
<tr>
<td>pH</td>
<td>10.15</td>
<td>10.23</td>
<td>10.43</td>
<td>10.29</td>
<td>10.39</td>
<td>10.32</td>
<td>10.01</td>
<td>10.16</td>
</tr>
</tbody>
</table>

Table 1. Compositions of Vapor Condensate Solutions at Different Levels of Evaporation

Table 2. Chemical Composition (Wt %) of A537 Carbon Steel, Class I

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Ni</th>
<th>Cr</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.14</td>
<td>1.44</td>
<td>0.008</td>
<td>0.003</td>
<td>0.14</td>
<td>0.11</td>
<td>0.09</td>
<td>0.29</td>
</tr>
</tbody>
</table>

Cyclic Potentiodynamic Polarization Test Procedure

Cyclic Potentiodynamic Polarization (CPP) is utilized to investigate the susceptibility of a material to localized corrosion in a given environment. The test set-up is shown in Figure 1. Approximately 600 ml of solution was placed in a flat-bottomed, spherical vessel for each test. The test temperature was maintained by a hot plate that had a temperature controller. Evaporation of the solution during the test was minimized with the use of a condenser. The test set-up consisted of a working electrode, a counter-electrode and a reference electrode. The carbon steel working electrode was a disk with an area of approximately 2 cm² that was anchored in a cold mount epoxy. Graphite rods were utilized for the counter electrodes. A saturated silver-silver chloride (Ag/AgCl) electrode was utilized as the reference electrode.

The tests were performed utilizing a programmable potentiostat. Prior to initiating the test, the sample was exposed to the solution for 2 hours. Open circuit potential (OCP) measurements were made during this time. This test is initiated at a potential 50 mV less than the OCP. The potential was increased at a scan
rate of 0.167 mV/second to a vertex potential of 0.5 V vs. the reference electrode. The potential was then scanned in the reverse direction back to the OCP. At the conclusion of the test, the sample was also visually inspected for evidence of corrosion. Duplicate tests were performed on separate samples.

Figure 1. CPP Test Set-up to Run Simultaneous Duplicate Experiments

**Coupon Test Procedure**

Coupon exposure tests are conducted to determine the long-term extent and mechanism of corrosion attack on the alloy being tested in the absence of accelerated electrochemical driving force. The set-up for these tests are shown below in Figure 2. Each test cell consists of a thermocouple controlled hotplate set to 40°C and a test solution volume of approximately 1.5L. Ammonia gas of the desired concentration is metered into each test vessel using digitally controlled flow controllers. Each coupon exposure test vessel has a bubbler attached on the hotplate with the test solution in it, through which the ammonia gas is passed to pre-humidify the gas before entering the test vessel.

Coupons are loaded into the test vessel and hung in the vapor space above the test solution in the vessel. These coupons are suspended on glass sample holders attached through a 3/16” hole drilled in the sample. There are 8 total samples in each test vessel, such that the vapor space corrosion samples are removed once per month in duplicate for a total 4 month exposure test. The samples are removed from the test vessel and gently rinsed with distilled water and dried in air, then wrapped in protective tissue and placed within a desiccator. The samples are removed from the desiccator and photographed. The general morphology is noted and any distinguishing characteristics are noted. After this, the sample mass is noted. If there is enough corrosion product to gather, it is scraped off for XRD analysis. Samples are subsequently cleaned using a combination of distilled water and Clark’s solution if necessary to remove corrosion product and the mass is measured again. From this weight loss can be
calculated. The sample surface is inspected under optical microscopy and any localized corrosion morphology such as pit depth and size are noted.

Figure 2. Coupon Test Set-up.

RESULTS AND DISCUSSION

CPP results

CPP results for representative experiments are shown in Figure 3. The plots in Figure 3 group results with four separate base solutions that have three different concentrations of dissolved NH₃. Figure 3a) has results from solution 1B, which has less than half the nitrate concentration of solutions in 2C, 3A, or 3B. Solution 1B also has a nitrite concentration more than 10 times lower than 2C. The passive layer breakdown and repassivation for the solution with 550 ppm of NH₃ shows behavior significantly different from the behavior of other solutions. The passive film requires going to higher potentials to break down the film to the point where an equivalent pitting current density is produced. This means that the passive film is generally more stable. However, after the passive film is broken down, the sample in solution with 550 ppm of dissolved NH₃ had a current on the reverse scan due to localized corrosion that was approximately 5 times the current in samples with 0 ppm and 50 ppm of dissolved NH₃. This indicates that the presence of dissolved ammonia tends to make repassivation of the sample more difficult. Nitrate/nitrite solutions have a complex passivation behavior [3, 4] where nitrate can act as an aggressive species at low concentrations, but as a passivating species at high concentrations. Therefore, the solutions that are more dilute solutions can tend to show more aggressive localized corrosion than concentrated solution, but this behavior is also significantly affected by addition of other passivating agents like nitrite ions. Therefore, relative concentrations of these ions can matter significantly. The addition of ammonia at low concentrations might be theorized to act as a reducing agent during both the forward and reverse scans which gets oxidized and delays breakdown of the passive film.
forward scan, but which continues to be reduced during the reverse scan and delays repassivation of the sample. Therefore, the NH$_3$ can have both positive and negative effects on localized corrosion depending on the condition of the passive oxide film.

Figure 3b) presents results for solution 2C, which has the second highest nitrate concentration, but the highest concentration of the nitrite ion as a corrosion inhibitor. The solutions with 0 ppm and 50 ppm of NH$_3$ show positive hysteresis indicating localized corrosion even with the high concentration of the nitrite inhibitor, but addition of 550 ppm of NH$_3$ eliminates positive hysteresis in this solution and therefore significantly reduces localized corrosion. This indicates that the NH$_3$ at 550 ppm is helping to make the corrosion inhibitors more effective and is helping to control localized corrosion after the passive film is disrupted.

Figures 3c) and 3d) show CPP results in solutions 3A and 3B. Both of these solutions have high nitrate concentrations with very low concentrations of nitrite corrosion inhibitors. Both solutions show very large positive hysteresis loops indicating high localized corrosion susceptibility. The presence of NH$_3$ appears in both cases to reduce the maximum currents during the reverse scan due to pitting by at least a factor of 2. The much higher presence of nitrate ions in these solutions indicates that ammonia at a concentration of 550 ppm is improving localized corrosion inhibition in these solutions. The lack of nitrite initially present in these solutions may indicate that the NH$_3$ may be converting some of this nitrate into more protective nitrite species.
Equation 1 is an electrochemical reaction for the reduction of nitrate to nitrite by ammonium hydroxide which is in equilibrium with the dissolved ammonia. This reaction has a relatively high standard reduction potential of 0.41 V vs. SCE and with the dissolved NH₃ gas a similar the reduction reaction becomes even more favorable with a standard reduction potential of 0.65 vs. SCE.

\[
NH_4OH + 3NO_3^- + H_2O + 6e^- \leftrightarrow 2NO_2^- + 7OH^- + N_2
\]  

(1)

This reaction provides a mechanism by which the nitrate can be converted into a more protective nitrite species in the presence of ammonia and potentially help to reduce corrosion as seen in Figures 3c) and 3d). This equilibrium potential would be significantly affected by Nernstian corrections for the concentration of the individual species which may be a reason for complex trends in the data with varying nitrate, nitrite and ammonia concentrations. More investigation would be needed to confirm this as a possible corrosion reduction mechanism and compare corrosion results with thermodynamic predictions for this system.

**Coupon Test Results**

Coupon tests are an ongoing activity for this project, with only one month samples having been collected. At this stage of coupon testing, it is clearly evident that the 50 ppm samples are corroding much more
aggressively than the 550 ppm samples. This is apparent in the general appearance of the two cells shown in Figure 4 below where the 50 ppm solution on the left is seen to have aggressive corrosion on the test samples suspended above the solution to sufficient extent that the corrosion product in the test solution has discolored it reddish-brown. In comparison, very little corrosion can be seen in the 550 ppm test solution on the right, and the test solution is still clear.

Figure 4. 1 Week Comparison Between 50ppm NH₃ exposure and 550 ppm NH₃ Exposure on A537 Test Coupons

Samples were removed after 1 months testing and visually inspected. A visual inspection reveals that observed corrosion attack is generally observed on the sides and edges, with increasing penetration into the interior regions of the flat exposed coupon faces. The corrosion attack in the 50 ppm NH₃ tests is observed to be much more severe than that in 550 ppm NH₃, consistent with the observations after 1 week. This can be seen below in Figure 5. The corrosion product is generally a reddish-brown. The mass loss of the samples was calculated after 1 month exposure time, and then losses are less than fractions of 1 percent at this short exposure time.

Figure 5. Observed Coupon Surfaces After Exposure to 50ppm NH₃ and 550 ppm NH₃ for 1 Month Exposure Time.
It was also noted that a salt product tends to precipitate on samples which are being held partially immersed in the test solutions (note: Liquid-Air Interface tests not reported in this paper). These salt deposits are shown below in Figure 6 and will be collected for analysis. It is possible that similar salts are present in the samples in the vapor space, and information about their composition could be useful in understanding corrosion mechanisms or critical concentrations for corrosion attack in these conditions.

![Figure 6. Salt Precipitation Deposits for Test Solutions of 50 ppm NH₃ and 550 ppm NH₃](image)

CONCLUSIONS

The inhibition and initiation of localized corrosion on carbon steel A537 samples in this study are a complex function of the concentrations and concentration ratios of the dominant species in the electrolyte solutions. Of the solutions studied here, solutions high in nitrate and with a high nitrate/nitrate ratio were found to be the most aggressive for localized corrosion attack, with concentrations of NH₃ in the vapor space having a mitigating effect on the severity of corrosion attack. For more dilute solutions, the role of NH₃ seems to have a dual role based on preliminary observations, where the NH₃ in the vapor space seems to donate stability to the protective oxide layer and delaying the oxide breakdown. This is possibly related to the NH₃ forming NH₄OH in solution, which can act as a reducing agent and provide inhibiting agents to strengthen the oxide film. However, once oxide film breakdown is achieved, NH₃ gas appears to prevent reformation of the oxide film as evidenced by increased reverse scan currents during CPP testing. Coupon tests currently confirm that the 550 ppm NH₃ exposure condition seems to hinder the development of corrosion on the A537 samples, whereas the 50 ppm NH₃ exposure seems much less effective after 1 month of exposure time. Mass loss measurements show fractional percentages of mass loss for the preliminary month long exposures.

ACKNOWLEDGEMENTS

The authors wish to gratefully acknowledge Washington River Protection Solutions for the funding and support for the work presented herein. We would like to thank Tracy Murphy and Karen Hicks for performing laboratory experiments for this work, and John Mickalonis for input and guidance in the development of the experiments. The authors also acknowledge consultation with Dr. Leon Stock, retired, and Dr. Donald Camaioni, Pacific Northwest National Laboratory, with regard to vapor space chemistry.

REFERENCES


