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Laboratory Simulation of Vapor Space Corrosion in Radioactive Waste Storage Tanks

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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. Ammonia inhibition of vapor space corrosion has been observed on an anecdotal basis and through limited laboratory testing. Ammonia is produced predominantly in the liquid waste through thermal and radiolytically induced reactions between organic waste components and nitrate and nitrite anions. The demonstration of corrosion inhibition by ammonia may provide a technical basis for the observed lack of propensity of corrosion in the vapor space of the waste tanks. New corrosion chemistry limits for the waste have been recommended to minimize the threat of stress corrosion cracking (SCC) of the carbon steel. Previous testing demonstrated that the new SCC inhibitor requirements for the waste were not sufficient for mitigation of pitting in the vapor space for the anticipated waste chemistry envelope. Coupon tests demonstrated that ammonia concentrations typically observed in the tank vapor space (i.e., between 50 and 550 ppm) are sufficient to mitigate vapor space corrosion.

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

INTRODUCTION

Weapons, space and medical research programs led by the U. S. Department of Energy have created a legacy of nuclear waste over the past 70 years. The waste is currently being stored on an interim basis in large, underground carbon steel waste tanks at the Hanford Site in Washington state and at the Savannah River Site (SRS) in South Carolina. Combined both sites store approximately 90,000 million gallons of waste in more than 200 waste tanks.

The disposition of the liquid waste into a solid form, either vitrified glass or a grout formulation, will likely take several more decades. Understanding potential degradation mechanisms are a key to preserving the structural integrity of the waste tanks until final disposition of the waste. The corrosion processes (e.g., pitting, stress corrosion cracking, general) that affect these tanks below the liquid waste level are generally well understood and are being managed by a chemistry control program. However, assessing the degree to which vapor space corrosion of the tank walls occurs is an ongoing challenge to overcome in demonstrating the structural integrity of the waste tanks.

An effort is underway to assess the likelihood of significant vapor space corrosion in the waste tanks. 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.

Previous laboratory coupon exposure testing above waste simulants has demonstrated that if the supernate chemistry is compliant with the corrosion chemistry control program vapor space corrosion is limited. However, new corrosion chemistry limits have been recommended for the minimization of the threat of stress corrosion cracking in the waste tanks.[1] These limits are summarized in Table 1. The specific limit of interest for the current testing is the minimum nitrite/nitrate ion ratio (R) of 0.15 with a minimum nitrite concentration of 0.05M. The new minimum R value of 0.15 was found to be insufficient to prevent pitting corrosion in the vapor space for nitrate concentrations of 0.4, 2, and 4.5 M.[2] The pitting that occurred, however, did not progress extensively over the four-month test.

Table 1
Proposed Specifications for the Control of SCC in Nitrate Ion Wastes in DSTs

Maximum Temperature:	50 °C
Maximum Concentration of Nitrate Ion	6.0 M
Maximum Concentration of Hydroxide Ion	6.0 M
Minimum pH	11
Minimum Concentration of Nitrite Ion	0.05 M
Minimum Nitrite Ion/Nitrate Ion Ratio	0.15

Ammonia inhibition of vapor space corrosion has been observed on an antidotal basis and through limited laboratory testing.[3, 4] Ammonia in the waste tank environments is produced predominantly in the supernate through thermal and radiolytically induced reactions between organic waste components and nitrate and nitrite anions. The vapor space concentration of ammonia in the Hanford waste tanks varies, but is as high as 550 ppm. Previous vapor space testing in a worst-case waste simulant was performed to determine the minimum ammonia concentration necessary to mitigate vapor space corrosion. The findings from this study showed that the presence of ammonia gas (550 ppm) in the vapor space was sufficient to reduce corrosion for the test period (i.e. four months).[2]

The purpose of this testing was to demonstrate the efficacy of ammonia for inhibition of vapor space corrosion above solutions that are inhibited to the minimum inhibitor requires for stress corrosion cracking. Long-term exposure testing in ammonia environments was performed to accomplish this objective.

EXPERIMENTAL PROCEDURE

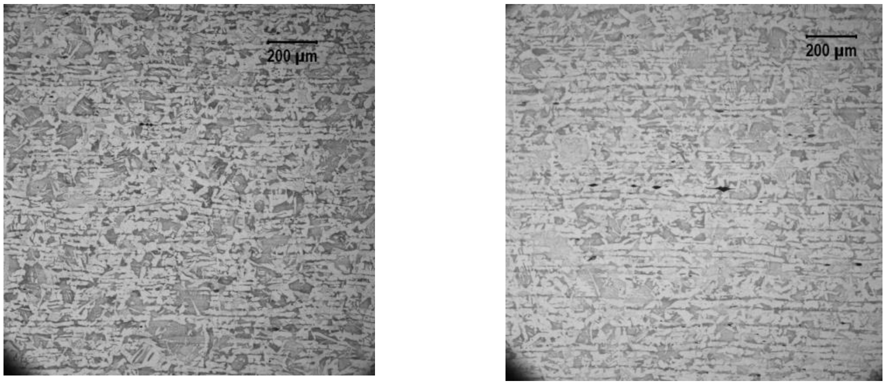
Materials Tested

The coupons were fabricated from Association of American Railroads (1) Tank Car (AAR TC) 128 Steel. This steel was selected for testing since it approximates the chemistry and microstructure of UNS K03101 (i.e., American Society for Testing and Materials (2) (ASTM) A515 Grade, Grade 60 carbon steel), the steel from which the tanks were fabricated.[5] The AARTC 128 steel was also selected because it was of the same vintage as the tank steel. The chemical composition of the steel is shown in Table 2. The yield strength for the material was greater than 380 MPa and the ultimate tensile strength was greater than 550 MPa. All elemental compositions except for Mn and Si meet the ASTM specification. The Mn is greater than the maximum allowed of 0.9 wt.%, while the Si is less than the required range. The higher Mn could explain the higher than specified tensile properties as well (e.g., ultimate strength between 410 MPa to 500 MPa required).

Table 2
Chemical Composition of AAR TC 128 Steel (wt.%).

	C	Mn	P	S	Si	Fe
Specification	0.24 (max.)	0.9 (max.)	0.035 (max.)	0.04 (max.)	0.13 to 0.33	Balance
Measured	0.212	1.029	0.012	0.013	0.061	Balance

Figure1 shows the microstructure of the rail car steel as exhibited in the longitudinal and transverse orientation. A banded, ferrite/pearlite matrix was observed. The transverse orientation also exhibited several inclusions, likely manganese sulfide inclusions. These could be sites for pit initiation.[7]



(a) (b)

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(1) American Association of Railroads, 425 3rd Street SW, Washington, DC 20024

(2) ASTM International, 100 Barr Harbor Dr., West Conshohocken, Pa 19428-2959

Figure 1: Microstructure of AAR TC Steel (a) longitudinal, (b) transverse.

Solutions Tested

Vapor space coupon tests were conducted above simulants that have the composition shown in Table 3. The nitrate concentrations were selected to represent a range of possible supernate concentrations in the Hanford waste tanks. The nitrite concentrations were calculated from the nitrate concentrations so that the nitrite/nitrate ratio was 0.15, which is the minimum requirement for the new corrosion chemistry standards. The pH of the waste was selected to be slightly above the minimum requirement. In the actual tanks, the pH is much greater than 12, however, with time, the pH will decrease due to reaction with the carbon dioxide in air.[6] The composition of the minor constituents in the simulant is consistent with values from samples of the waste supernates and that utilized during previous testing.[3] The tests were conducted at vapor space ammonia levels of 0.005, and 0.055 vol.% in air (50 and 550 ppm) for a total of six tests. The simulant test temperature was 40 °C.

Table 2
Proposed Supernate Chemistry for Vapor Space Corrosion Tests

Solution Number	Initial pH	$NaNO_2$	$NaNO_3$	NaCl	NaF	Na_2SO_4	Na_2CO_3	Na_3PO_4	$Na_2OAl_2O_3$ $3H_2O$
1	12	0.06	0.4	0.01	0.003	0.005	0.1	0.0005	0.0002
2	12	0.3	2	0.04	0.01	0.05	0.5	0.01	0.002
3	12	0.675	4.5	0.1	0.02	0.1	1	0.05	0.0033

Sample Mounting

The test material was fabricated into a disk that was approximately 1.6 cm in diameter and 0.6 cm thick. The disk was mounted in a cold mount epoxy such that only one face of the coupon was exposed (See Figure 2). Finger nail polish was utilized around the edges of the disk to minimize crevices. At the same time the disk was place in the cold mount, a wire tie was embedded as well. The wire tie was then attached to one of the rings located on the movable ring stand that is shown below in Figure 3. This configuration allows for several light weight coupons to be tested at the same time.

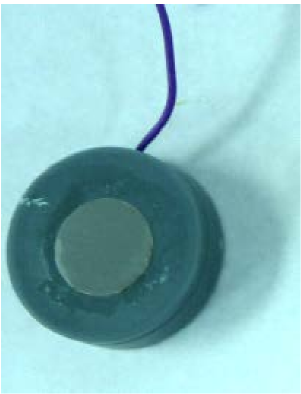


Figure 2: Mounted Coupon

Test Apparatus

The apparatus that was used for these tests is shown in Figure 3. The chamber for these tests is a 1 meter by 15 cm diameter glass cylinder. Inside the cylinder is a movable ring stand with the rings located at three different levels. At the bottom of the cylinder is a glass bowl that contains approximately 1.5 liters of the test solution of interest. The gas, in this case ammonia, passes through a bubbler that contains the solution of interest, enters the near the bottom of the cylinder just above the solution, and exits the top of the cylinder. The flow rate for the gas was adjusted to 5 cc/min. The temperature of the solution in the bowl was controlled to 40 °C utilizing a water circulator.

For the tests, the coupons were positioned at three different levels above the liquid simulant. The wire tie on the sample was wrapped around rings that were fixed at these levels.

Level 1: Prior to the test, the coupons were dipped in the simulant and then dried to form a salt film on the surface. The coupons were then suspended approximately 3 cm above the liquid level. Once every two weeks, the coupons were dipped into the simulant for approximately 5 minutes, then removed and allowed to dry above the simulant. This level is representative of a vapor space region of the tank that experiences periodic wetting/drying. This sequence could occur due to: a) waste transfers into and out of the tank, b) splashing due to flushing operations, and/or c) solution “creep” above the liquid air interface.

Level 2: Prior to the test, the coupons were dipped in the simulant and then dried to form a salt film on the surface. The coupons were then suspended approximately 8 cm above the liquid. This level is representative of a vapor space region of the tank that at one time was exposed to waste, but now has infrequent or no contact with the waste. However, this region is exposed to the humidified air and the ammonia gas.

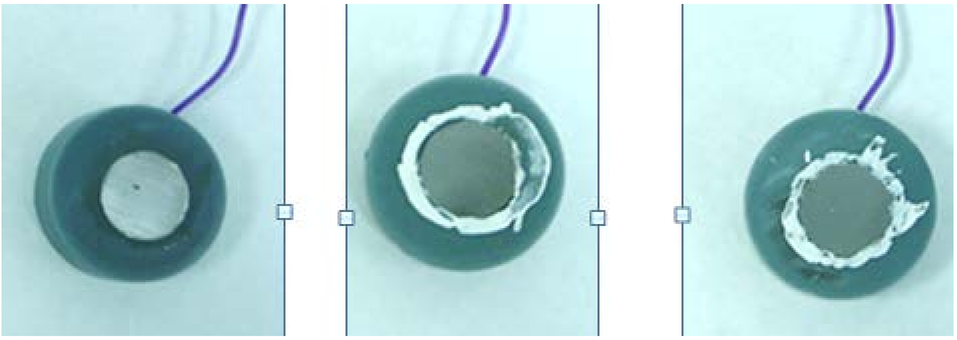
Level 3: This set of coupons was not exposed to the solution prior to testing. The coupons were suspended approximately 1 meter above the liquid. This level is representative of a vapor space region that is only exposed to the humidified air the ammonia, and any vapors from the solution.

The tests were conducted for 4 months. The coupons were removed on a monthly frequency and examined for corrosion. Degree of attack (i.e., percentage of surface corroded) and pit depths were measured.

Figure 3: Vapor Space Corrosion Test Apparatus.

RESULTS

Figure 4 shows coupons that were exposed to a 50 ppm ammonia environment above solution 1 after 1 month of exposure. A small pit was observed in the center of the coupon along with a few indications of crevice attack at the edge on the sample that was exposed to Level 1. No attack was observed on samples exposed on Level 2 or Level 3. This degree of attack was observed on all the coupons in both the 50 and 550 ppm ammonia environments for all three test solutions. For comparison Figure 5 shows a coupon that was exposed to a Level 2 location, above the same solution, for the same exposure time, without ammonia. Clearly, as little as 50 ppm ammonia is sufficient to prevent significant vapor space corrosion above wastes that are inhibited to the new chemistry control requirements.



Level 1 Level 2 Level 3

Figure 4: Coupons removed after 1 month exposure to 50 ppm ammonia above Solution 1 at

40 °C.

Figure 5: Coupon removed from Level 2 after 1 month exposure above Solution 1at 40 °C with no ammonia in vapor space. [7]

These results are consistent with previous vapor space corrosion testing performed in ammonia environments.[2] Solutions high in nitrate with a high nitrate/nitrite ratio were found to be the most aggressive for localized corrosion attack, with concentrations of NH_3 in the vapor space having a mitigating effect on the severity of corrosion attack. For more dilute nitrate solutions, the role of NH_3 seems to have a dual role, where the NH_3 in the vapor space seems to donate stability to the protective oxide layer and delaying the oxide breakdown. This is possibly related to the NH_3 forming NH_4OH in solution, which can act as a reducing agent and provide inhibiting agents to strengthen the oxide film. However, once the oxide film breakdown is achieved, NH_3 gas may prevent the reformation of the oxide film.

The waste tank operator relies on the natural generation of ammonia for the inhibition of vapor space corrosion. Therefore, this data will be used as an assessment tool for the likelihood of vapor space corrosion given the amount of ammonia generation determined from vapor space sampling of the tanks. Tanks that contain less than 50 ppm ammonia in the vapor space should be required to have higher inhibitor levels (i.e., the current corrosion chemistry controls) than the new specifications allow.

CONCLUSIONS

Coupon exposure tests were performed to assess the likelihood of vapor space corrosion above waste chemistry that is at new, lower inhibitor requirements. The tests demonstrated that the presence of ammonia in the vapor space at levels of as little as 50 ppm effectively mitigates significant vapor space corrosion. It was recommended that results from vapor space sampling of the waste tanks be utilized to assess the vulnerability of a tank to vapor space corrosion. Tanks that contain less than 50 ppm ammonia in the vapor space should be required to have higher inhibitor levels (i.e., the current corrosion chemistry controls) than the new specifications allow.

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