DST Pitting Annual Report

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Abstract: This report provides details of activities during FY 1996 for the double-shell tank pitting kinetics testing task.

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DST PITTING ANNUAL REPORT

September 26, 1996

Prepared By:

R. P. Anantatmula

WESTINGHOUSE HANFORD COMPANY
for the
U.S. Department of Energy
Richland Operations Office

DST PITTING ANNUAL REPORT

This report describes the results from the double-shell tank (DST) pitting kinetics tests performed during FY 1996. Two sets of tests were performed during FY 1996. The first set consisted of utilizing a H-Cell to determine if galvanic corrosion at the waterline is a possibility in the DSTs. The second set of experiments was carried out to verify if vapor phase pitting is a viable degradation mechanism in the DSTs.

The majority of the experiments with the H-Cell indicated that the steel (in contact with the low hydroxide solution) at the waterline is preferentially protected when galvanically coupled with the steel (in contact with the high hydroxide solution) down below the waterline. The few solutions that indicated slight pitting attack of the steel at the waterline had no nitrite present. It should be noted that the DST wastes contain some level of nitrite even near the waste surface.

One-month and three-month vapor phase pitting experiments were completed. The results indicated that pitting was the principal mode of corrosive attack. The measured pit penetration rate was greater than the uniform attack rate. Comparison of the three-month to the one-month test results indicate that the uniform attack rates and pitting rates are decreasing with time.

Ammonia at the 100 ppm concentration is a very effective inhibitor for uniform and pitting corrosive attack on carbon steels in the vapor phase. This is a new and very significant observation since most of the DSTs are ammonia emitters at levels above 100 ppm. This new mechanism may be playing the principal role in protecting the tanks from failure in the vapor phase.

The effect of ammonia on a chloride-containing solution has not been explored in this study but may also have beneficial effects for that case. There are eleven DSTs that have a chloride concentration ≥ 0.1 moles/liter and are also ammonia emitters.

The two types of DST pitting kinetics experiments have been discussed in detail in the attached reports entitled "Final Report - Results on Water-line (Meniscus) Galvanic Corrosion Testing" and "Vapor Phase Pitting Results of ASTM A516 and A537 Carbon Steels Over Three Different Aqueous Solutions After One Month and Three Months of Exposure" in Appendices 1 and 2.

APPENDIX 1

RESULTS ON WATER-LINE (MENISCUS) GALVANIC CORROSION TESTING

September 26, 1996

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1.0 INTRODUCTION

The objective of the Tank Waste Remediation System (TWRS) Life Management/Aging Management (LMAM) Program is to maintain confinement function for all the waste tank systems throughout their desired service life (Shogren 1995). In order to achieve this objective, the LMAM Program has the charter to identify the causes of material degradation, quantify degradation rates, and determine the effect of degradation rates on leak tightness and structural stability. Additionally, the LMAM Program will establish acceptance criteria and establish programs, including testing and surveillance, to ensure that the acceptance criteria are met throughout the desired service life. The work described in this program supports Task 2, "Degradation Mechanisms," Task 4, "Structural Acceptance," and Task 5, "Surveillance," of the TWRS LMAM Plan.

2.0 BACKGROUND

Task 2 of the LMAM Program Plan (Shogren 1995) considers both general and localized corrosion of the Hanford carbon steel waste tanks. Localized corrosion in the form of stress corrosion cracking (SCC) is believed to be the main degradation mechanism causing failure of the single-shell tanks (SSTs) because these tanks were not stress relieved after welding the plate sections together. The degradation mechanisms responsible for SST failures have been discussed in detail in a recent publication (Anantatmula 1994). It is too late to prevent or influence the degradation processes operating on the SSTs, but this is not the case for the double shell tanks.

The Hanford double shell tanks (DSTs) were stress relieved to reduce their propensity for SCC, and the waste chemistry can be adjusted to bring the composition into compliance with Hanford waste tank specifications. One of the proposed degradation mechanisms is localized attack at the waterline region which could act to breach the tank wall (Escalante 1994). The purpose of this testing program is to assess the seriousness of this localized corrosion process and to suggest preventative measures, if necessary.

2.1 Waterline (Meniscus) Attack

Waterline or meniscus attack has been suggested as an important failure mechanism for carbon steel waste tanks (Escalante 1994). The waterline region is characterized as a thin layer of diluted liquid waste at the liquid/vapor surface overlaying a very deep layer of waste with the nominal waste composition. The proposed degradation mechanism is that naturally present gaseous carbon dioxide in the dome air reacts with the hydroxide in the waste at the liquid/vapor (waterline) interphase; thereby, lowering the pH and making the carbon steel

vulnerable to galvanic attack in the waterline. The pH of the hydroxide-containing waste at the surface has been demonstrated (Zapp 1992) to decrease below 10, a value at which carbon steel becomes vulnerable to pitting or galvanic attack. Recent experiments at the Savannah River Laboratory (SRL) (Zapp 1992) indicated that carbon steel will pit in dilute waste solutions of $\text{pH} \leq 10$. SRL personnel periodically adjust the waterline hydroxide concentration in their waste tanks based on this concern.

3.0 EXPERIMENTAL, WATERLINE CORROSION TESTS

The laboratory studies were carried out using an H-cell design (shown in Figure 1-1) similar to that of Escalante (1994). The H-cell design duplicates most of the critical elements of the galvanic cell (in the laboratory environment) that exist at the waste tank waterline (meniscus): One half of the H-cell (right side) duplicates the carbon steel environment located in the waterline region in which the pH is approximately 9.5, while the other half (left side) duplicates the carbon steel located in the more concentrated solution below the waterline. ASTM A-537 carbon steel flags were used for the electrodes to match that used in the construction of the DSTs. A 1010 carbon steel wire (diameter 1.6 mm, 1/16 inch) was TIG-welded to each A-537 flag electrode for electrical contact. The electrode composition is shown in Table 1-1. The left side of the cell (representing the solution below the waterline at the higher hydroxide level) contained three ASTM A-537 electrodes, each with an area of 23.7 cm^2 while the right side of the cell (waterline, generally the more dilute solution) contained a smaller, single ASTM A-537 electrode of 5.4 cm^2 . The actual tank has an area ratio (comparing the steel area below the waterline to that in the waterline) that probably exceeds 100. This experimental apparatus only permitted area ratios of 4.3, 8.7, and 13 to be explored. The electrodes were connected through a zero resistance ammeter (ZRA) which permits the measurement of the galvanic current without adding any electrical resistance to the circuit. Each side of the H-cell also contained a Ag, AgCl reference electrode (0.1 M KCl electrolyte) which was maintained at the same temperature as the cell. Ionic contact was created between the two cells by a 0.3 μ PTFE filter which acted as a solution separator. The PTFE filter and the physical spacing between the electrodes added typically 50 ohms to the cell resistance (measured at 1000 Hz). This cell resistance is the principal error that the H-cell brings to exactly duplicating the waterline galvanic cell in the actual tank. Since the ZRA current was $<100 \mu\text{A}$, this error was negligible for all the tests. Diffusion of hydroxide from the left side of the cell to the right side required a continuous bubbling of carbon dioxide through the right cell to maintain a constant pH of approximately 9.5. A glass pH electrode was used to continuously monitor the pH on the right side. Tests were run at ambient, 60, and 97°C by

installing the H-cell in an air-convection oven. Each side of the H-cell was vented through an air condenser, located outside the oven.

Table 1-1. Material Specifications (Composition in wt%)

Alloy	C	Cr	Fe	Mn	Ni	P	S	Yield Ksi
A537	.15	.05	Bal	1.25	.09	.007	.006	62.0
C1010	.10	---	Bal	0.49	---	.020	.020	---

A major uncertainty in the testing protocol was the composition of the test solutions since tank compositions can vary greatly. The waterline solution simulant in the dilute side of the H-cell (right side) had the pH fixed at ~ 9.5 by a carbonate/bicarbonate buffer to represent the worst case for carbon steel, but the nitrate, nitrite, and chloride concentration ranges for that side required definition. The concentrated side (higher hydroxide conditions, left side) of the H-cell also required the definition of hydroxide, nitrate, nitrite, and chloride concentrations. Since there is believed to be a great variation of composition in the waste tanks, a statistical test design was used to define the sixteen pairs of test solutions. These compositions are shown in Table 1-2 with the concentrations of the anions in g/l. Solutions 1 and 11 acted as blanks to permit the calculation of the experimental error.

The testing protocol was as follows: For each solution test condition, the H-cell was filled with the appropriate solution-pair (approximately one liter per side, the final liquid levels were adjusted to compensate for the different solution densities in order to maintain a constant liquid head pressure between the two sides of the H-cell) and both sides of the H-cell were oxygenated with breathing air (carbon dioxide free) at a rate of about 30 ml/minute. Testing started at ambient temperature, and for the first 24 hours, the electrochemical potential of each electrode was measured relative to a reference electrode installed into each side of the cell. Once the electrode potentials reached a steady state, the two electrodes were

Table 1-2
Table of Solution Compositions in g/l

Solutions below Waterline, g/l					Waterline Solutions*, g/l			
Soln #	OH ⁻	NO ₂ ⁻	NO ₃ ⁻	Cl ⁻	Soln #	NO ₂ ⁻	NO ₃ ⁻	Cl ⁻
1	0.85	0	.002	.02	1a	0	.002	.02
2	39.5	0	.002	.02	2a	147	.002	15.2
3	0.85	147	.002	.02	3a	147	224	.02
4	39.5	147	.002	.02	4a	0	224	15.2
5	0.85	0	224	.02	5a	147	224	.02
6	39.5	0	224	.02	6a	0	224	15.2
7	0.85	147	224	.02	7a	0	.002	15.2
8	39.5	147	224	.02	8a	147	.002	.02
9	0.85	0	.002	15.2	9a	0	224	15.2
10	39.5	0	.002	15.2	10a	147	224	.02
11	0.85	147	.002	15.2	11a	147	.002	15.2
12	0.85	0	224	15.2	12a	147	.002	.02
13	39.5	147	.002	15.2	13a	0	.002	.02
14	39.5	0	224	15.2	14a	0	.002	15.2
15	0.85	147	224	15.2	15a	0	224	.02
16	39.5	147	224	15.2	16a	147	224	15.2

* pH 9.5 to 9.7 fixed by carbonate/bicarbonate buffer, ≈0.5 M

electrically connected by the ZRA. A negative current indicates that the ASTM A-537 specimen in the right side of the cell was anodic (driven to corrode) relative to the left cell. Once a steady state current was achieved, the flow of air to the concentrated solution side (left cell) was switched to nitrogen gas to determine the effects of an oxygenated waterline region on a deoxygenated region below the waterline. After a steady state was achieved, the temperature was increased and the process repeated.

4.0 EXPERIMENTAL RESULTS

The waterline region is characterized as a thin layer of diluted liquid waste overlaying a very deep layer of liquid waste with the nominal (concentrated) tank waste composition. The waterline (dilute, pH ~ 9.5) has been hypothesized to be the vulnerable region for carbon steel corrosion. The region below the waterline has the waste composition which is higher in hydroxide. The experimental results are concerned with the response of carbon steel electrodes in a galvanic cell that duplicates the waterline and deeper regions of a waste tank. Two major issues in the interpretation of the significance of these results are (1) the direction of the ZRA current and (2) the effect of the cathode/anode surface area ratios. If the current direction is positive (+) in the convention chosen here, then the waterline region is cathodically protected and localized corrosion at the waterline becomes unlikely. If the current direction is negative (-), then the waterline region is being anodically driven, a situation that may place this region in danger to accelerated localized corrosive attack. In a real tank, the surface area of the steel below the waterline is huge relative to the area localized at the waterline, and this area ratio may act to increase the severity of the waterline corrosion process. When the waterline region was driven anodically (area fixed at 5.4 cm²), the effect of galvanic cell area was evaluated by increasing the area in the left cell, going from 23.7 to 47.4 to 71.1 cm² (cathode/anode ratio of 4.4, 8.8, and 13.2, respectively), looking for the maximum current (maximum corrosive attack) which became independent of the electrode area. This would then represent the worst case for corrosive attack for the unfavorable cathode to anode ratio which exists in the tank environment.

The ZRA current density data are shown in Figures 1-2 to 1-17, and the general observations on the test results are outlined in Table 1-3. The H-cell data indicate that in most cases, the carbon steel at the waterline region would be cathodically protected by the steel in the lower portion of the tank; thereby, rendering the carbon steel at the waterline immune to localized corrosion attack. The six cases (solution-pairs 1/1a, 4/4a, 6/6a, 7/7a, 14/14a, and 15/15a) where the waterline electrode was driven anodic (and pitting was visually confirmed in two of these

conditions, 4/4a and 14/14a) were conditions in which there was zero nitrite in the solution. Nitrite is a powerful inhibitor for localized-corrosion, but the threshold concentration value where it becomes an inhibitor is presently unknown for these experimental conditions. In only one case (9/9a) was there pitting on carbon steel electrodes in the left side (lower side of the waterline) of the H-cell, and this solution also contained zero nitrite. High levels of hydroxide in the left cell do not always result in cathodic protection of the waterline electrode.

In most cases where the waterline electrode was anodic, the anodic current decreased or became cathodic when the temperature increased. Anodic currents when present were associated with ambient temperature conditions. Realistic testing required the use of both aerated and deaerated conditions for the left cell since it was possible for corrosion reactions or other oxidation reactions to consume the available oxygen at deeper regions in the tank. Aeration of the left side of the H-cell (represents lower tank wall region) always increased the magnitude of the anodic waterline electrode current compared to the anoxic condition. In most cases, the area of the cathodic electrodes did not effect the magnitude of the anodic current (solutions 14/14a were an exception).

The anodic ZRA current density can predict the rate of uniform attack by using the conversion factor of $2 \mu\text{A}/\text{cm}^2$ corresponding to $2.5\text{E-}3 \text{ cm/year}$ (1.0 mil/year) for carbon steel. Test solution 14a would have the highest general corrosion rate for the solutions tested to date of $1.5\text{E-}2 \text{ cm/year}$ (6 mils/year). In general, the anodic ZRA currents are very low ($<2.5\text{E-}3 \text{ cm/year}$ or $<1.0 \text{ mil/year}$), but there is the complication that if all the current is focused on a few pits, could represent a very high penetration rate since the surface area of pits is small.

5.0 CONCLUSIONS

Six of the sixteen solution pairs of the statistically designed test matrix indicated that carbon steel could be anodic in the waterline region of a waste tank. In the other ten cases, the carbon steel was cathodically protected and localized corrosion would be unlikely. Pits were visually observed on the carbon steel in two of those anodic cases. The anodic current decreased as the temperature increased, and in most cases the anodic current densities were insignificant if reported as uniform attack rates. All six waterline solutions contained zero nitrite, an unlikely condition to be found in a waste solution. It is presently unknown what level of nitrite is required for full inhibition.

Table 1-3
Tabulation of Experimental Results

Solutions below Waterline, g/l					Waterline Solutions*, g/l				Observations on the Waterline Electrode (right cell)
Soln #	OH ⁻	NO ₂ ⁻	NO ₃ ⁻	Cl ⁻	Soln #	NO ₂ ⁻	NO ₃ ⁻	Cl ⁻	
1	0.85	0	.002	.02	1a	0	.002	.02	Anodic but current insignificant. No pits observed.
2	39.5	0	.002	.02	2a	147	.002	15.2	Cathodically protected
3	0.85	147	.002	.02	3a	147	224	.02	Cathodically protected
4	39.5	147	.002	.02	4a	0	224	15.2	Anodic @ ambient T. Cathodically protected @ T≥60°C. A few small pits observed on specimen edge; probably formed @ ambient T. Areas effects not studied.
5	0.85	0	224	.02	5a	147	224	.02	Cathodically protected or zero current. No pits observed.
6	39.5	0	224	.02	6a	0	224	15.2	Anodic @ ambient T, 60, and 97°C. No pits observed.
7	0.85	147	224	.02	7a	0	.002	15.2	Anodic but current small (current decreases as T increases). No pits observed.
8	39.5	147	224	.02	8a	147	.002	.02	Cathodically protected
9	0.85	0	.002	15.2	9a	0	224	15.2	Cathodically protected at steady state. No pits observed.
10	39.5	0	.002	15.2	10a	147	224	.02	Cathodically protected. Area Effects Explored.
11	0.85	147	.002	15.2	11a	147	.002	15.2	Current insignificant. No pits observed.**
12	0.85	0	224	15.2	12a	147	.002	.02	Cathodically protected.
13	39.5	147	.002	15.2	13a	0	.002	.02	Cathodically protected. Area Effects Explored.
14	39.5	0	224	15.2	14a	0	.002	15.2	Anodic (current decreases as T increases). Pits observed. Area Effects Explored. Forgot to do N2 test at ambient temperature.
15	0.85	147	224	15.2	15a	0	224	.02	Anodic (current decreases as T increases) but current insignificant. No pits observed.
16	39.5	147	224	15.2	16a	147	224	15.2	Cathodically protected

* pH ~ 9.5 fixed by carbonate/bicarbonate buffer, ≈0.5 M

** Blank test (solutions in right and left side nearly identical) to determine experimental error.

*** Pits observed on electrodes in left cell.

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Waterline Corrosion Test Apparatus

S9508042.1

Figure 1-2

Figure 1-3

Figure 1-4

Figure 1-5

Figure 1-6

Figure 1-7

Figure 1-8

Figure 1-9

Figure 1-10

Sols 10 & 10A

Figure 1-11

Figure 1-12

Figure 1-13

Figure -1-14

Figure 1-15

Figure 1-16

Figure 1-17

Appendix

Escalante Letter to Phil Ohl

NIST

UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Gaithersburg, Maryland 20899

March 15, 1994

Phil Ohl
Waste Tank Corrosion Engineering
Westinghouse Hanford Company
P.O. Box 1970
Richland, WA 99352

Dear Phil,

Attached is a brief summary of our preliminary experiments on the effect of dilution of a simulated HLW on the corrosion of steel, especially at the waterline. The important point of these data is that a decrease in pH of the simulated HLW through dilution causes the normally noncorrosive environment to become corrosive. Local-action corrosion cells that form as a result of differences in concentration of the waste, exacerbate the corrosion problem.

The information provided here is for your information only and is not suitable for reference.

Sincerely,

A handwritten signature in cursive script, appearing to read "Ed", followed by a vertical line.

Edward Escalante
Corrosion Group

Waterline Corrosion of Nuclear Waste Tanks DOE Project

Introduction

Failures of the DOE nuclear waste tanks at Hanford, WA occur through poor tank design and construction or from corrosion of the tank wall. Improper design generally results in an immediate failure of the tank during initial filling (poor corner and weld design). Improper construction often results in short term stress corrosion failures (<5 y) from poor welding procedures or failure to stress relieve after welding. Unlike other forms of failure, corrosion at the waterline is an ongoing process that does not slow down with time.

Our preliminary results indicate that corrosion at the waterline will not occur in the absence of dilution at the air/liquid interface. Conditions for corrosion develop when moisture evaporated from the hot liquid waste condenses on the inner wall of the dome, runs down the wall and reenters liquid at the waterline, diluting the concentration of waste at the point of entry. Our data show that dilution of the waste results in a significant drop in pH, sufficient to allow corrosion to initiate at the steel surface. The electrochemical potentials observed between the concentrated bulk solution and the dilute solutions is of the order of 150 mV, more than sufficient to form a corrosion cell.

The data reported here is measured using A515 pressure plate steel in a simulated waste solution of 3.5 M sodium nitrate and 2.5 M sodium hydroxide. The composition of the simulated waste is made up of the major components found in a "typical" waste tank [1].

Summary of Results & Data

Effect of dilution of simulated waste on pH - Six diluted solutions were made from the simulated waste as listed in Table 1.

Table 1. Concentration of Solutions

Solutions	NaNO ₃ , M	NaOH, M
Sim. Waste	3.53	2.50
Dilution 1	1.76	1.25
Dilution 2	0.88	0.62
Dilution 3	0.44	0.31
Dilution 4	0.22	0.16
Dilution 5	0.11	0.08
Dilution 6	0.06	0.04

The pH of these solutions versus the concentration of sodium hydroxide is shown in Figure 1.

Figure 1. pH vs Conc of Simulated Waste

The effect of localized dilution of the simulated liquid waste on the potential of steel - Two samples of A515 steel were placed in containers of unlike concentrations of waste solution, connected through a fine fritted glass wall. The potentials between the two steel specimens was monitored for 60 minutes when one specimen was in a concentrated waste solution and the second steel specimen was in a dilute solution of simulated waste. This experiment was repeated, using one of the six dilute solutions listed in Table 1 in one container and the concentrated solution in the second container. The difference in potential between the steel specimens was of the order of 150 mV as dilution was increased.

The effect of localized dilution of the simulated liquid waste on the "galvanic" current of steel - Following the potential measurements, the galvanic, or local-action, current between the steel specimens was measured, using a zero resistance ammeter. This current was measured periodically over a 60 minute period, reaching a steady state at approximately $0.35 \mu\text{A}/\text{cm}^2$.

Coupon Tests - Four coupons of AISI 1018 carbon steel were partially immersed in simulated waste solution for periods of up to 60 days. These coupons were periodically examined for evidence of corrosion at the waterline. In the concentrated solution of simulated waste, there was no evidence of any corrosion attack at any time. Similar specimens that were placed in the most dilute solution of simulated waste showed evidence of corrosion attack within a few hours.

Discussion

These preliminary experiments indicate that in the absence of dilution, corrosion of steel will not occur. The pH of the concentrated waste solution is sufficiently high (≈ 13.7) to passivate the steel surface. As the pH decreases through dilution, its ability to passivate the steel decreases. Other work performed in this laboratory, has shown that once corrosion is initiated, repassivation of the steel becomes difficult, because the corrosion process further reduces the pH locally, and the corrosion product that forms acts as a temporary barrier to the bulk, high pH solution [2].

In addition, the electrochemical potential difference that develops between the steel in the bulk solution and the locally dilute solution at the waterline, further exacerbates the corrosion process. The current generated by this corrosion cell is small, but over a period of several years, it may be sufficient to perforate a tank wall.

These data are obtained on a greatly simplified system, and the effects of temperature and oxygen concentration are not addressed. I estimate a minimum of two weeks and a maximum of 30 days to assemble such a report.

References

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APPENDIX 2

**VAPOR PHASE PITTING RESULTS OF ASTM A516 AND A537 CARBON STEELS
OVER THREE DIFFERENT AQUEOUS SOLUTIONS
AFTER ONE MONTH AND THREE MONTHS OF EXPOSURE**

September 26, 1996

Prepared By:

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WESTINGHOUSE HANFORD COMPANY
for the
U.S. Department of Energy
Richland Operations Office

1.0 INTRODUCTION

The objective of the Tank Waste Remediation System (TWRS) Life Management/Aging Management Program (LMAM) is to maintain confinement function of the waste tank systems throughout their desired service life. The LMAM Program is tasked with identifying the causes of material degradation, quantifying degradation rates, and determining the effect of degradation rates on leak tightness and structural stability (Anantamula 1995). A recent assessment of the remaining life of double shell tanks has concluded that vapor phase pitting of the carbon steel tank wall is potentially a major failure mechanism (Abatt 1996). The purpose of this present study is to assess the importance of this proposed mechanism through the use of experimental laboratory tests.

2.0 OBJECTIVE

The objective of these corrosion tests was to quantitatively determine the long term (3 years) vapor phase pitting behavior of A516 and A537 carbon steels in three simulated tank environments. The testing was terminated after the three month exposure because this test environment was discovered to be at a higher relative humidity than presently exists in the double shell tanks. Consequently, these test results are not relevant to predicting the behavior of carbon steels for the present environment.

3.0 DESCRIPTION OF TEST

3.1 Test Materials

The tests were carried out on ASTM A537 and A516 carbon steels. The compositions of the two steels are given in Table 2-1. The flat specimens had the following dimensions: 2.54 cm x 5.1 cm x 0.318 cm (1.0" x 2.0" x 0.125") with a 0.63 cm diameter hole (.25 inch) at one end. The specimens were given a heat treatment of one hour at 1100°F (air) followed by a furnace cool. The surface finish was 200±20 grit alumina.

Table 2-1. Material Specifications (Composition in wt%)

Alloy	C	Cr	Fe	Mn	Ni	P	S	Yield Ksi
A537	.15	.14	Bal	1.31	.10	.011	.003	54.2
A516 Grade 70	.22	--	Bal	1.12	--	.015	.016	52.0

3.2 Test Conditions

Three liquid phases were chosen to represent (1) a control or baseline environment, (2) a chloride-containing environment set to the highest concentration expected in the liquid phase (0.4 M), and (3) an ammonia-containing environment. It was necessary to study chloride because a 1995 carbon steel study at PNNL revealed a serious chloride induced corrosion problem in the vapor phase, adjacent to the waterline (Lund 1996). Ammonia was studied because it is present in a number of the Hanford double shell waste tanks (Anantatmula 1996) and can act to raise the pH in the vapor phase which may be beneficial to inhibiting the pitting attack. The solution compositions are shown below:

Control Environment (Test Container "A")

NaOH	NaNO ₂	NaNO ₃	NaCl
≈0	1.3 M	3.7 M	0 M
Liquid Phase Temperature = 60 °C			

Chloride Effects (Test Container "B")

NaOH	NaNO ₂	NaNO ₃	NaCl
≈0	1.3 M	3.7 M	0.40 M
Liquid Phase Temperature = 60 °C			

Ammonia Effects (Test Container "C")

NaOH	NaNO ₂	NaNO ₃	NaCl
≈0	1.3 M	3.7 M	0 M
Liquid Phase Temperature = 60 °C 100 ppm of ammonia in vapor phase (pH _{liquid phase} ≈ 10)			

3.3 Experimental Test Procedures

The testing was carried out in 114 liter (30 gallon) polypropylene tanks (with cover). A stainless steel specimen rack was constructed to hold 60 specimens (30 of each steel, electrically insulated from the rack and each other) approximately 40 cm (16 inches) above the liquid level. Each tank contained 19 liters of liquid solution (5 gallons) that was heated with an immersion heater and maintained at 60°C using a

temperature controller. The vapor phase temperature at the specimen location was measured by a thermocouple located at the specimen horizon to be 50°C. Air was bubbled through tanks "A and B" at a rate of approximately 20 ml/minute. Breathing air containing 100 ppm of ammonia was bubbled through tank "C" at 20 ml/minute. On a weekly basis, a liquid sample was withdrawn from tank "C" for a pH measurement, and concentrated ammonia solution was added to maintain a 100 ppm ammonia concentration in the solution. The test apparatus (at the start) is shown in Figure 2-1.

The specimens were cleaned at PNNL before starting the testing. The original test protocol was to withdraw 10 specimens (5 of each steel) at intervals of one month, three months, six months, one year, two years, and three years. The testing was terminated after three months of exposure because it was determined that the relative humidity in the actual vapor phase tank environment was considerably lower than the 100% value of these tests. Consequently, this testing did not duplicate the actual tank environmental conditions.

The specimens were examined after one and three months of exposure. Figures 2-2 and 2-3 show the uncleaned specimens for one and three months, respectively. After one month of exposure, the specimens from solutions "A and B" were cleaned of their corrosion product films using CP-9 (10% HCl + formaldehyde inhibitor) and weighed. Specimens from tank "C" were not cleaned after the one month exposure test because they were free of corrosion product and were simply weighed. All specimens were cleaned after the three month exposure tests. The specimens were subjected to a visual examination. ASTM (1990) procedure G46 was used for evaluation of pitting density, diameter, and depth.

4.0 RESULTS

Photographs of the as-removed specimens are shown in Figures 2-2 and 2-3 for one and three months exposures, respectively. Calculated average uniform penetration rates (with one standard deviation) are shown in Table 2-2. Visual observations, maximum pit depths, and calculated maximum pit penetration rates are shown for the one month exposure in Tables 2-3, 2-4, and 2-5 and for the three month exposure in Tables 2-6, 2-7, and 2-8.

The only anomaly is that the uniform corrosion rates in the ammonia environment are greater after three months than one month of exposure. The specimens were not compensated for weight lost due to attack of the stripping solution on the metal. Under most conditions this is an adequate approximation but the corrosion rates from the vapor phase environment are so low that the metal loss during stripping makes an important contribution to the calculated uniform corrosion rate. Even with this error, the calculated corrosion rates are so low as to be unimportant.

Table 2-2. Average Uniform Corrosion Rates
(with One Standard Deviation)

Test	One Month Corrosion Rate, mm/y (mpy)	Three Month Corrosion Rate, mm/y (mpy)
A516, Soln "A"	0.010±.0014 (0.40±.05)	0.0036±.0008 (0.14±.03)
A537, Soln "A"	0.012±.0017 (0.46±.07)	0.0031±.0003 (0.12±.01)
A516, Soln "B"	0.010±.0008 (0.40±.03)	0.0054±.0003 (0.21±.01)
A537, Soln "B"	0.0095±.0014 (0.38±.05)	0.0045±.0006 (0.18±.02)
A516, Soln "C"	0.00067±.00007 (0.026±.003)	0.0013±.0001* (0.052±.006)
A537, Soln "C"	0.00013±.00033 (0.005±.01)	0.00072±.00011* (0.028±.004)

* NOTE: Three month exposure specimens in solution "C" were stripped of their corrosion product, one month exposure specimens were not stripped

mpy = mils/year; mm/y = millimeters/year

Table 2-3. One Month Observations on the Control Test (Test Container "A")

Material	Observation
A537	incipient pitting visible at 5X but below smallest ASTM area criterion ≤20 pits per specimen to unaided eye (specimen area 30.6 cm ²) deepest pit = 0.0017 inch (0.52 mm/y or 20 mpy)
A516	pitting worse than A537, above density: A-4 (1E5 pits/mm ²) Size: B-1 (0.5 mm ²) deepest pit = 0.0054 inch (1.6 mm/y or 65 mpy)

Table 2-4. One Month Observations on Chloride Effects (Test Container "B")

Material	Observation
A537	Rusty Surface with pitting density: A-3 (5E4 pits/mm ²) Size: B-1 (0.5 mm ²) deepest pit = 0.0042 inch (1.3 mm/y or 50 mpy)
A516	Rusty Surface with pitting density: A-2 (1E4 pits/mm ²) Size: B-1 (0.5 mm ²) deepest pit = 0.0043 inch (1.3 mm/y or 50 mpy)

Table 2-5. One Month Observations on Ammonia Effects (Test Container "C")

Material	Observation
A537	Unfilmed surface (did not clean)--little pitting attack 1-5 pits per specimen (specimen area 30.6 cm ²) deepest pit ~ 0.0001 inch (<0.03 mm/y or <1.2 mpy)
A516	Unfilmed surface (did not clean)--little pitting attack 1-3 pits per specimen (specimen area 30.6 cm ²) deepest pit ~ 0.0001 inch (<0.03 mm/y or <1.2 mpy)

Table 2-6. Three Month Observations on the Control Test (Test Container "A")

Material	Observation
A537	pitting visible to naked eye ≤20 pits per specimen to unaided eye (specimen area 30.6 cm ²) deepest pit = 0.0031 inch (0.32 mm/y or 12 mpy)
A516	pitting worse than A537, above density: A-4 (1E5 pits/mm ²) Size: B-1 (0.5 mm ²) deepest pit = 0.0034 inch (0.34 mm/y or 14 mpy)

Table 2-7. Three Month Observations on Chloride Effects (Test Container "B")

Material	Observation
A537	Rusty Surface with pitting density: A-3 (5E4 pits/mm ²) Size: B-2 (2.0 mm ²) deepest pit = 0.0086 inch (0.87 mm/y or 34 mpy)
A516	Rusty Surface with pitting density: A-2 (1E4 pits/mm ²) Size: B-1 (0.5 mm ²) deepest pit = 0.0048 inch (0.49 mm/y or 19.2 mpy)

Table 2-8. Three Month Observations on Ammonia Effects (Test Container "C")

Material	Observation
A537	Shiny surface before and after cleaning. Surface staining indicative of incipient pitting but depth below detection limit. Limit of detection ~ 0.0001 inch (<0.03 mm/y or <1.2 mpy)
A516	Shiny surface before and after cleaning. Surface staining indicative of incipient pitting but depth below detection limit. Limit of detection ~ 0.0001 inch (<0.03 mm/y or <1.2 mpy)

6.0 CONCLUSIONS

- 1) Pitting was the principal mode of corrosive attack. The measured pit penetration rate was greater than the uniform attack rate. Comparison of the three month to the one month test results indicate that the uniform attack rates and pitting rates are decreasing with time.
- 2) Ammonia at the 100 ppm concentration is a very effective inhibitor for uniform and pitting corrosive attack on carbon steels in the vapor phase. This is a new and very significant observation since most of the double shell tanks are ammonia emitters at levels above 100 ppm (Anantatmula, June 1996). This new protective mechanism may be playing the principal role in protecting the tanks from failure in the vapor phase.
- 3) The effect of ammonia on a chloride-containing solution has not been explored in this study but may also have beneficial effects for that case. There are eleven double shell tanks that have a chloride concentration ≈ 0.1 moles/liter and are also ammonia emitters (Anantatmula, June 1996).

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Test A, 60°C

1.3M NaNO₂

3.7 M NaNO₃

Test B, 60°C

1.3 M NaNO₂

3.7 M NaNO₃

0.4 M NaCl

Test C, 60°C

1.3M NaNO₂

3.7 M NaNO₃

100ppm Ammonia

Figure 2-2 Uncleaned Corrosion specimens after 30 days of Exposure.

90 day test

Test A, 60°C

1.3 M NaNO₂3.7 M NaNO₃

Test B, 60°C

1.3 M NaNO₂3.7 M NaNO₃

0.4 M NaCl

Test C, 60°C

1.3 M NaNO₂3.7 M NaNO₃

100ppm Ammonia

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Figure 2-3 Uncleaned Corrosion Specimens after 90 Days of Exposure

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