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PITTING CORROSION IN THE VAPOR SPACE AND LIQUID/AIR INTERFACE OF HIGH LEVEL RADIOACTIVE WASTE TANK

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ABSTRACT

Corrosion in the vapor space and at the liquid/air interface of the Department of Energy (DOE) high level waste (HLW) tanks have emerged as potentially active corrosion mechanisms. Controls on the solution chemistry are in place to preclude the initiation and propagation of further nitrate induced pitting and stress corrosion cracking. However, recent experience has shown that steel not in contact with the bulk waste solution but exposed to the “vapor space” above the bulk waste and the liquid/air interface may be vulnerable to pitting or stress corrosion cracking. Experimentation was performed to determine the influence of steel surface characteristics and solution chemistry on pitting rates within the vapor space and at the liquid/air interface on ASTM A537 steels, the materials of construction of the tanks. The results suggest that inhibited bulk solution chemistry does not ensure pitting protection within the vapor space when there are surface inhomogeneities. However, the characteristic residual salts on the steel play a key role in the pitting characteristics.

Keywords: pitting, carbon steel, high level waste tank

INTRODUCTION

Radioactive waste is stored in underground storage tanks at the Department of Energy (DOE) Savannah River Site (SRS). The waste tanks, made of ASTM A537 steel, store a combination of salts, consisting primarily of sodium nitrate, sodium nitrite, and sodium hydroxide. An assessment of the potential degradation mechanisms of the high level waste (HLW) tanks determined that nitrate-induced pitting corrosion and stress corrosion cracking were the two most significant degradation mechanisms. Specifically, nitrate-induced stress corrosion cracking was determined to be the principal degradation mechanism for the primary tank steel. Sodium hydroxide and nitrite are used to inhibit nitrate-induced stress corrosion cracking and nitrate-induced pitting corrosion in the liquid phase of the waste tanks. General corrosion is also prevented by the inhibitor levels specified for these two localized corrosion modes. The corrosion control program is based upon empirical data used to determine vulnerability to stress corrosion cracking and pitting at typical compositions of waste.

Recent experience has shown that steel not in contact with the bulk waste solution or slurry, but exposed to the “vapor space” above the bulk waste, may be vulnerable to the initiation and propagation of corrosion, including pitting and stress corrosion cracking. Degradation is also possible at the liquid-vapor interface due to hydroxide depletion, particularly when the interface has remained stagnant for long periods of time.¹

The potential for vapor space and liquid/air interfacial corrosion was established through previously performed scoping experimentation. The experimentation provided insight into the potential for vapor space corrosion and liquid/air interface corrosion in A537 steels.² Testing was done on samples with polished surface vs. surfaces that had oxide layers. The key observation was that the mill scale surface with inhomogeneities could provide crevices in which the local solution chemistry could be variant even if the bulk solution was controlled to prevent nitrate induced pitting, particularly in the vapor space or at the liquid/air interface.

Proposed Vapor Space Corrosion (VSC) Mechanism

It is hypothesized that nitrate-induced degradation may occur in the vapor space environment of a waste tank in the special conditions created by relative humidity and the deliquescence behavior of aggressive nitrate species. Several mechanisms have been proposed for the deposition of aggressive species on the tank wall within the vapor space. In dry environments, the salt may exist as a solid residue on the steel tank, left by evaporation or decanting of the waste. Alternatively, sodium nitrate may have been deposited on the tank wall by evaporation from the supernate, transport as an aerosol, condensation, and deposition on the tank wall. In sufficiently humid conditions, the nitrate residue can adsorb atmospheric moisture and dissolve, forming a corrosive electrolyte. A schematic of these mechanisms is shown in Figure 1.

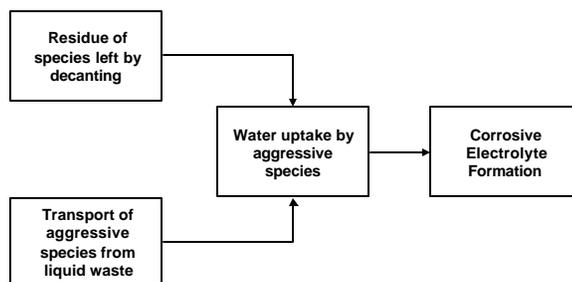


FIGURE 1. Hypothesized VSC Mechanisms

Both mechanisms depend upon the residual species of salts on the tank wall. An understanding of the residual species is key in determining the impact of pitting and/or stress corrosion cracking on the structural integrity of these tanks.

Proposed Liquid-Vapor Interface Corrosion (LAIC) Mechanism

The LAIC mechanism is dependent upon the extent of inhibitor depletion at the interface. At the vapor-liquid interface, the pH of waste solutions drops naturally over a period of a few months from greater than 12 to pH 10 due to chemical reaction of the hydroxide with absorbed atmospheric carbon dioxide. The shift in pH makes this interface region vulnerable to pitting corrosion.

EXPERIMENTAL PROCEDURE

Experimentation to determine the pitting rates for vapor space corrosion (VSC) and liquid/air interfacial corrosion (LAIC) within the context of the hypothesized mechanisms was performed. Testing was performed on ASTM A537-C1.1 (normalized) steel, the material of construction of the HLW tanks. The tanks were fabricated with semi-killed, hot-rolled A537-C1.1 plate, with nominal composition shown in Table 1.

TABLE 1: STEEL COMPOSITION

Steel Specification	C _{max} (wt%)	Mn (wt%)	P _{max} (wt%)	S _{max} (wt%)
ASTM A537	0.24	0.7-1.35	0.035	0.035

Pitting rates in the vapor space and liquid/air interface were determined as a function of solution chemistry and surface characteristics on the steel. Exposures were performed using the salt solutions shown in Table 2. Waste solution W1, containing 5M NaNO₃, is an aggressive solution known to cause pitting of low carbon steel. Waste solution W2, containing nitrite and hydroxide as inhibitors, is believed to be sufficient to prevent stress corrosion cracking, as per current chemistry controls used. A review of the chemistry controls for DOE-HLW tanks and their evolution is being concurrently published.³ Test solutions were maintained at 50°C.

TABLE 2: MOLAR CONCENTRATIONS OF SALT SOLUTIONS FOR EXPERIMENTATION

Solution Label	[NO ₃ ⁻]	[NO ₂ ⁻]	[OH ⁻]
W1	5	-	-
W2	1.5	0.45	0.15

The surface characteristics of the steel were varied in terms of surface oxidation and solution deposits. The surface was oxidized by heat treatment at 975°C to simulate mill-scale, and defects in the mill scale were induced utilizing a Rockwell hardness tester. A representative array of indents is shown in Figure 2. The indents exposed the underlying bare metal and crushed the oxidized layer into the indent. The surface area of the exposed bare metal was not quantified.

Deposits of the bulk solution were made on the sample surface to simulate the mechanism of salt deposition through decanting. Testing was performed within the framework of a parametric test matrix consisting of these key variables as summarized in Table 3. Testing was done for a total of 16 conditions, with exposures for 60 days and 120 days for the vapor space and 60 days for the interfacial samples. A summary of the surface characteristic variables is shown in Table 3.

TABLE 3: SUMMARY OF VARIABLES TESTED

<u>Surface</u>	<u>Defects</u>	<u>Chemistry</u>
Mill scale	No indents	No deposit
Polished	Indents	Deposits

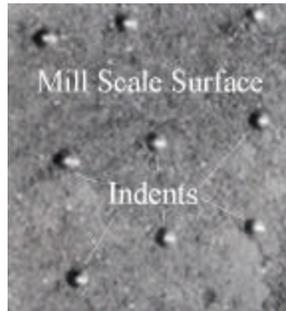


FIGURE 2: Example Mill-Scale Surface With Indents

The testing in the vapor space was done on ¼-in. thick round disk samples that were metallurgically mounted. All heat treatments were done prior to mounting. Polishing, indenting, and deposition of bulk salts were performed after mounting. The liquid air interfacial testing was done on 2-in x 1-in x 0.125 in. standard pitting coupons. A photograph of the experimental test setup is shown in Figure 3. The insets give higher magnification of the coupons exposed to the vapor space and the coupons exposed to the liquid/air interface.

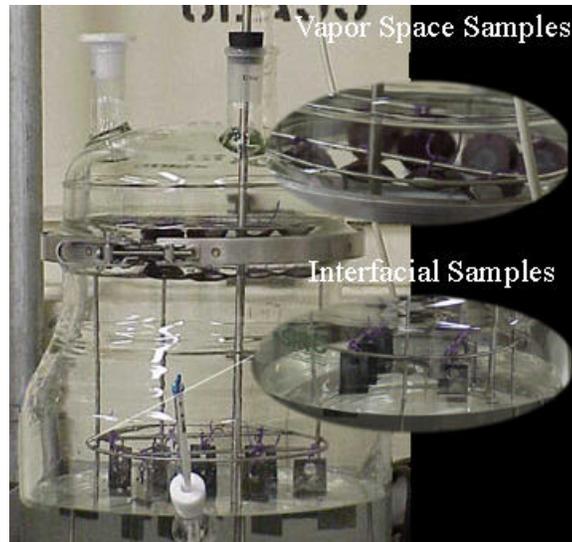


FIGURE 3: Experimental Test Setup

The liquid level was maintained with 2 rows of indents immersed, and 2 rows exposed to the vapor just above the solution. An additional row of indents was at the interface.

RESULTS AND DISCUSSION

The samples were analyzed for pit location and pit depth. An average pit depth and a corresponding pitting rate were determined when appropriate. The next section details the results of the vapor space testing, with the following section detailing the results of the interfacial testing.

Results of Vapor Space Testing

A summary of the results of the pitting studies on vapor space coupons is presented in Tables 4-7. The results show that there is extensive corrosion on the polished coupons exposed to the vapor space above waste solution W1. The results are summarized in Table 4. Pitting was revealed underneath the corrosion product with pitting rates up to 0.399 in/year. The pits were not limited to the indent locations, and pitting was higher in the samples with deposited salt, as would be expected. The pitting rates did not diminish with time suggesting that the pitting may be autocatalytic in nature for the times tested. A decrease in pitting rate with time would indicate alternatively that the passivated layer is effective in preventing further pitting. A representative sample with corrosion is shown in Figure 4.

TABLE 4: RESULTS OF VAPOR SPACE PITTING TESTING FOR W1, POLISHED SURFACE

Condition	Chemistry	Surface			Days	Avg. Pit Depth (in.)	Pit Rate (in./yr)
		Finish	Deposit	Indent			
1	W1	6 μm			60	0.0109	0.0663
2	W1	6 μm	x		60	0.0219	0.1332
3	W1	6 μm		x	60	0.0256	0.1557
4	W1	6 μm	x	x	60	0.0085	0.0517
5	W1	6 μm			120	0.0412	0.2505
6	W1	6 μm	x		120	0.0622	0.3784
7	W1	6 μm		x	120	0.0600	0.3650
8	W1	6 μm	x	x	120	0.0655	0.3985



FIGURE 4: Corrosion on Vapor Space Sample Exposed to W1 (Condition 2)

There was no corrosion evident on any of the polished samples exposed to the vapor space above the inhibited solution, as summarized in Table 5. The indents and deposits did not affect the corrosion properties, suggesting that the vapor space chemistry was inhibitive. It is surmised the relative greater activity and the relatively low deliquescence (~6%RH) point of the hydroxide contributes to the vapor space inhibition. In addition, the smooth polished surface does not allow crevices within which the local solution chemistry can be changed, dependent upon condensate deposition.

TABLE 5: RESULTS OF VAPOR SPACE PITTING TESTING FOR W2, POLISHED SURFACE

Condition	Chemistry	Surface			Days	Avg. Pit Depth (in.)	Pit Rate (in./yr)
		Finish	Deposit	Indent			
9	W2	6 μm			60	No Pitting	No Pitting
10	W2	6 μm	x		60	No Pitting	No Pitting
11	W2	6 μm		x	60	No Pitting	No Pitting
13	W2	6 μm	x	x	60	No Pitting	No Pitting
12	W2	6 μm			120	No Pitting	No Pitting
14	W2	6 μm	x		120	No Pitting	No Pitting
15	W2	6 μm		x	120	No Pitting	No Pitting
16	W2	6 μm	x	x	120	No Pitting	No Pitting

The results show that there is pitting corrosion on the heat-treated coupons exposed to the vapor space above waste solution W1 when there are defects on the surface. The pitting rates are summarized in Table 6. Pitting was detectable to 0.005-in. translating to a 0.003 in/year pitting rate. The samples with defects and deposits had an average pit rate of 0.1 – 0.12 in/year.

TABLE 6: RESULTS OF VAPOR SPACE PITTING TESTING FOR W1, HEAT TREATED SURFACE

Condition	Chemistry	Surface			Days	Avg. Pit Depth (in.)	Pit Rate (in./yr)
		Finish	Deposit	Indent			
17	W1	HT			60	No Pitting	No Pitting
18	W1	HT	x		60	No Pitting	No Pitting
19	W1	HT		x	60	0.0005	0.0030
20	W1	HT	x	x	60	0.018	0.1095
21	W1	HT			120	No Pitting	No Pitting
22	W1	HT	x		120	No Pitting	No Pitting
23	W1	HT		x	120	0.001	0.0030
24	W1	HT	x	x	120	0.02	0.1217

A composite photograph of the heat-treated samples exposed to the vapor space above waste solution W1 is shown in Figure 5. It is seen that the samples with the deposit and the indents have the experienced the worst degradation, while the samples with no defects see no corrosion. The deliquescence point of sodium nitrate is known to be approximately 74% at room temperature, and the sample with the salt deposit shows that the corrosion is much worse when an uninhibited salt is present on the tank wall. The defects shown in condition 23 indicate corrosion in and around the indents. However, it is unknown whether this is due to nitrate-induced pitting or simply humid-air corrosion.

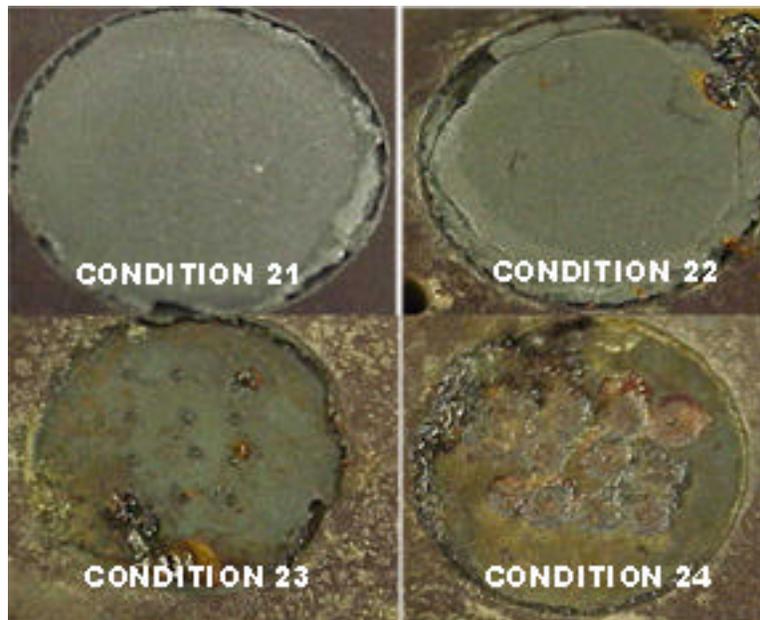


FIGURE 5: Photographs of Mill-Scale Coupons Exposed to Vapor Space Above Waste W1

The pitting rates for the mill-scale surface coupons exposed to the vapor space above inhibited waste solution W2 are shown in Table 7. The pitting rates indicate that deposition of bulk inhibited solution salts is protective in nature, even with defects in the mill scale. This suggests that decanting of inhibited solution depositing residual salts which include inhibitors is protective. Shallow pitting was found in the samples with defects and plain heat treated surface. However, post-test characterization revealed that the heat treated surfaces had inherent defects that could have contributed to the pitting.

TABLE 7: RESULTS OF VAPOR SPACE PITTING TESTING FOR W2, HEAT TREATED SURFACE

Condition	Chemistry	Surface			Days	Avg. Pit Depth (in.)	Pit Rate (in./yr)
		Finish	Deposit	Indent			
25	W2	HT			60	0.0005	0.003
26	W2	HT	x		60	No Pitting	No pitting
27	W2	HT		x	60	0.0005	0.0030
28	W2	HT	x	x	60	No Pitting	No pitting
29	W2	HT			120	0.0005	n/a
30	W2	HT	x		120	No Pitting	No pitting
31	W2	HT		x	120	0.0005	No Pitting
32	W2	HT	x	x	120	No Pitting	No pitting

Results of Liquid/Air Interfacial Testing

Testing of coupons exposed to the liquid/air interface was performed at the same conditions as in the vapor space, however, only exposures of 60 days were completed. Pit depths, pitting rates, and locations were determined as appropriate.

The results of the liquid/air interfacial testing for waste solution W1 with a polished surface are given in Table 8. The general corrosion rates were from 0.41-0.66in/yr, with the samples with deposited salts exhibiting higher corrosion rates. Three thickness measurements were taken on the samples : (1) completely immersed, (2) interface, and (3) just above the interface. These corrosion rates were similar for all three measurements for the conditions shown in TABLE 8.

TABLE 8: RESULTS OF LIQUID/AIR INTERFACIAL TESTING FOR W1, POLISHED SURFACE

Condition	Chemistry	Surface			Days	General Corrosion Rate (in./yr)
		Finish	Deposit	Indent		
1	W1	6 μm			60	0.48
2	W1	6 μm	x		60	0.66
3	W1	6 μm		x	60	0.41
4	W1	6 μm	x	x	60	0.57

The results of the liquid/air interfacial testing for waste solution W2 for polished specimens are summarized in Table 9. Similar to the results for vapor space exposures, there was no corrosion for these conditions. The indents and deposits did not affect the corrosion properties suggesting that the chemistry was inhibitive. Once again, the activity of the hydroxide solution and the relatively low deliquescence point contributes to the inhibitive characteristics.

TABLE 9: RESULTS OF LIQUID/AIR INTERFACIAL TESTING FOR W2, POLISHED SURFACE

Condition	Chemistry	Surface			Days	Corrosion
		Finish	Deposit	Indent		
9	W2	6 μm			60	None
10	W2	6 μm	x		60	None
11	W2	6 μm		X	60	None
12	W2	6 μm	x	X	60	None

The results of the liquid/air interfacial testing for waste solution W1, for samples with a heat treated surface are shown in Table 10. The general corrosion and pitting rates were not quantifiable for the samples without indents. It seems that the mill-scale layer is protective and does not allow for extensive general corrosion.

TABLE 10: RESULTS OF LIQUID/AIR INTERFACIAL TESTING FOR W1, HEAT-TREATED SURFACE

Condition	Chemistry	Surface			Days	Observations
		Finish	Deposit	Indent		
17	W1	HT			60	No pitting, general corrosion
18	W1	HT	x		60	No pitting, general corrosion
19	W1	HT		x	60	Bands across rows of indents
20	W1	HT	x	x	60	Bands across rows of indents

A composite picture of samples exposed to conditions 19/20 is shown in Figure 6. The interface lies in the center of the picture represents the interface with the indents above and below the interface controlling the corrosion features. Bands of corrosion were revealed just below the interface along the rows of indents. The pitting above the interface was limited to the indents.

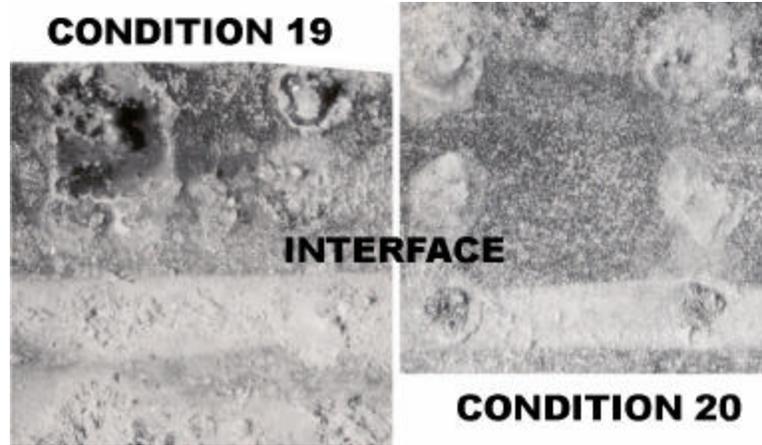


FIGURE 6: Optical Microscopy of Samples Exposed to Conditions 19/20

The results of the liquid/air interfacial testing in waste solution W2 for samples with heat-treated surfaces are summarized in Table 11. The results suggest that the indents in the mill scale do not allow for chemistry variances when immersed in the bulk solution, unlike the vapor space exposures.

TABLE 11: RESULTS OF LIQUID/AIR INTERFACIAL TESTING IN W2, HEAT-TREATED SURFACE

Condition	Chemistry	Surface			Days	Observations
		Finish	Deposit	Indent		
25	W2	HT			60	No corrosion
26	W2	HT	x		60	No corrosion
27	W2	HT		x	60	Few indents corroded
28	W2	HT	x	x	60	Few indents corroded

CONCLUSIONS

Experimentation has been completed to determine pitting characteristics and rates where appropriate in the vapor space and the liquid/air interface of high level radioactive waste tanks. Hydroxide and nitrite levels are maintained to prevent further nitrate induced stress corrosion cracking and pitting within these tanks. The current testing focused on possible corrosion within the vapor space and liquid/air interface when the bulk solution is inhibited. The effect of surface characteristics on the pitting characteristics and rates were measured. The surface characteristic variables were (1) polished surface vs. mill-scale surface, (2) solution deposits vs. no deposits, and (3) defected mill-scale vs. homogeneous mill-scale.

The key results were whether the inhibitors within the bulk solution would be sufficient to protect the vapor space and the liquid/air interface, particularly where mill-scale defects provide crevices within which the local solution chemistry could be change. The results suggest the following:

- Polished samples exposed to the vapor space above inhibited solution are not subject to degradation.
- Mill-scale samples exposed to the vapor space above inhibited solution with defects in the passive layer are protected by inhibited salt deposits, but are not protected when inhibited salt deposits are not present. If the salt deposits are inhibited however, the pitting rates are much higher.
- Polished samples expose to the liquid/air interface with inhibited solution are not subject to pitting.
- Mill-scale samples with defects and/or deposits exposed to the liquid/air interface of inhibited samples are not subject to pitting due to the influence of the bulk solution.

The results suggest that the combination of mill-scale surface and the deliquescence behavior of hydroxide provides sufficient protection at the liquid/air interface, while crevices particularly on initially oxidized surfaces provide possible points of pit initiation within the vapor space. The role of oxide films have been found to play a role in the local chemistry evolution in stress corrosion cracking, which can be applied to the pitting studies here. Pitting can occur in mild steel under the formation of both the passive $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 (magnetite) film. However, the time to failure in the presence of the passive $\gamma\text{-Fe}_2\text{O}_3$ is considerably shorter than the magnetite.⁴ The oxide film on the samples within this study were primarily magnetite and may have a greater resistance to film breakdown.

PATH FORWARD

The pitting rate studies have been completed for application to the vapor space and the liquid/air interface for the current chemistry control program. Electrochemical testing within the vapor space is to be performed to lend further understanding to the corrosion kinetics as well as corroborate pitting rates with the various waste solutions

ACKNOWLEDGMENTS

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