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Vapor Corrosion Response of Low Carbon Steel Exposed to Simulated High Level Radioactive Waste

K. H. Subramanian

Savannah River National Laboratory
Materials Science and Technology Directorate

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**Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808**

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APPROVALS

Date: 1/17/06
K. H. Subramanian, Author
Materials Performance and Corrosion Technology
Materials Science and Technology Directorate

Date: 1/17/06
B. J. Wiersma, Technical Reviewer
Materials Performance and Corrosion Technology
Materials Science and Technology Directorate

Date: 1/17/06
G. T. Chandler, Manager
Materials Performance and Corrosion Technology
Materials Science and Technology Directorate

Date: 1/26/06
N. C. Iyer, Manager
Materials Science and Technology Directorate
Savannah River National Laboratory

Date: 1/19/2006
G. D. Thaxton, Manager
Structural Integrity
Liquid Waste Process Engineering

Date: 1-24-06
E. J. Freed, Manager
Liquid Waste Process Engineering
Liquid Waste Disposition Projects

Date: 1-25-06
D. B. Little, Manager
LWDP Chief Engineer
Liquid Waste Disposition Projects

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1 EXECUTIVE SUMMARY

A program to resolve the issues associated with potential vapor space corrosion and liquid/air interface corrosion in the Type III high level waste tanks is in place. The objective of the program is to develop understanding of vapor space (VSC) and liquid/air interface (LAIC) corrosion to ensure a defensible technical basis to provide accurate corrosion evaluations with regard to vapor space and liquid/air interface corrosion. The results of the FY05 experiments are presented here. The experiments are an extension of the previous research on the corrosion of tank steel exposed to simple solutions to corrosion of the steel when exposed to complex high level waste simulants.

The testing suggested that decanting and the consequent residual species on the tank wall is the predominant source of surface chemistry on the tank wall. The laboratory testing has shown that at the boundary conditions of the chemistry control program for solutions greater than 1M $NaNO_3$:

- Minor and isolated pitting is possible within crevices in the vapor space of the tanks that contain stagnant dilute solution for an extended period of time, specifically when residues are left on the tank wall during decanting

- Liquid/air interfacial corrosion is possible in dilute stagnant solutions, particularly with high concentrations of chloride.

The experimental results indicate that Tank 50 would be most susceptible to the potential for liquid/air interfacial corrosion or vapor space corrosion, with Tank 49 and 41 following, since these tanks are nearest to the chemistry control boundary conditions. The testing continues to show that the combination of well-inhibited solutions and mill-scale sufficiently protect against pitting in the Type III tanks.

2 INTRODUCTION

An assessment of the potential degradation mechanisms of Types I and II High-Level Waste (HLW) Tanks determined that 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 of non-stress relieved tanks.[1,2] The primary mechanism of concern for the Type III/IIIA is pitting since they have been stress-relieved to prevent SCC. Controls on the solution chemistry have been in place to preclude the initiation and propagation of degradation in the tanks.[3] However, 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 degradation, including pitting and stress corrosion cracking.

A program to resolve the issues associated with potential vapor space corrosion is in place. The objective of the program is to develop understanding of vapor space (VSC) and liquid/air interface (LAIC) corrosion to ensure a defensible technical basis to provide accurate corrosion evaluations with regard to vapor space and liquid/air interface corrosion (similar to current evaluations). There are several needs for a technically defensible basis with sufficient understanding to perform these evaluations. These include understanding of the (1) surface chemistry evolution, (2) corrosion response through coupon testing, and (3) mechanistic understanding through electrochemical studies.

2.1 Proposed Mechanism of Corrosion

It was hypothesized that general or localized corrosion may occur in the vapor space due to conditions created by relative humidity and the deliquescence behavior of aggressive 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 supernate. Alternatively, species may have been deposited on the tank wall by evaporation from the supernate, transport as an aerosol, and then condensation on the tank wall. In sufficiently humid conditions the residue can adsorb atmospheric moisture and dissolve, forming a corrosive electrolyte. A schematic of these mechanisms is shown in Figure 1

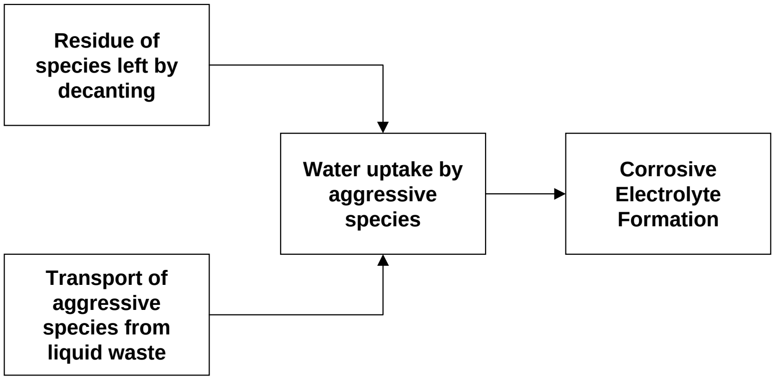


Figure 1: Schematic of Hypothesized VSC Mechanisms

It may be assumed the relative humidity of the vapor space is maintained at atmospheric conditions due to the purge ventilation systems. The HLW tanks are equipped with a purge ventilation system to maintain the tank contents at negative pressure to prevent the release of radioactive material into the environment and also to prevent the buildup of flammable vapor above the critical levels. The humidity in the tank vapor space is hypothesized to reflect the atmospheric variability. Diurnal variation in the relative humidity, similar to daily atmospheric humidity fluctuations, may alternately dissolve and crystallize sodium nitrate, especially in the summer, when morning air is near saturation (100% RH) and afternoon heating lowers the RH below 60%. This cyclic exposure may render the steel more vulnerable than it might be under static conditions, as the cyclic exposure may tend to concentrate aggressive species depending on the precipitation sequence.

2.2 Liquid-Vapor Interface Environment and Degradation

The liquid-vapor interface is a region known to be susceptible to localized corrosion due to (1) inhibitor depletion or (2) concentration cells. Inhibitor (NaOH) depletion may occur when the OH^- ion reacts with atmospheric carbon dioxide creating carbonic acid and thereby depleting the hydroxide inhibitor at the interface.[4] The shift in pH makes this interface region vulnerable to pitting corrosion and possibly crevice corrosion. Alternatively, aggressive anion concentration cells may also develop at stagnant vapor/liquid interfaces to accelerate corrosive attack. This type of attack is also known as waterline or beach-line attack. Oxygen concentration cells may develop as oxygen is readily available at the vapor/liquid interface, but has increasingly restricted access to levels more distant from the surface. The concentration gradient anodically polarizes the area of the tank wall slightly below the surface. This polarization leads to preferential dissolution of tank wall material at this area. Dissolved metal can then react with hydroxide, which is cathodically produced at the liquid/vapor interface, to form corrosion products that precipitate just below the water line. These deposits further retard the diffusion of oxygen and accelerate the dissolution of the tank metal. In tanks with constant waste levels, pitting corrosion may occur.

2.3 Experimental Data to Date

Experimentation performed in FY02 determined the potential for vapor space and liquid/air interface corrosion of ASTM A285-70 and ASTM A537-Cl.1 steels.[5] The material surface characteristics, i.e. mill-scale, polished, were found to play a key role in the pitting response. The experimentation indicated that the potential for limited vapor space and liquid/air interface pitting exists at 1.5M nitrate solution when using chemistry controls designed to prevent stress corrosion cracking.

Experiments performed in FY03 quantified pitting rates as a function of material surface characteristics, including mill-scale and defects within the mill-scale. Testing was performed on ASTM A537-Cl.1 (normalized) steel, the material of construction of the Type III HLW tanks. The pitting rates were approximately 3 mpy for exposure above inhibited solutions, as calculated from the limited exposure times. This translates to a penetration time of 166 years for a 0.5-in tank wall provided that the pitting rate remains constant and the bulk solution chemistry is maintained within the L3 limit.

The FY04 testing consisted of electrochemical testing to potentially lend insight into the surface chemistry and further understand the corrosion mechanism in the vapor space.[6] The cyclic polarization testing confirmed that pitting is electrochemically improbable in the vapor space provided the bulk solution chemistry is sufficiently inhibited, for a bulk solution temperature of 50°C.

The FY05 testing, presented here, consisted of testing in complex simulants. The exposure testing and electrochemical testing was done in more representative waste simulants containing minor waste constituents (e.g. chloride, sulfate) in addition to nitrate, nitrite, and hydroxide. Additional constituents that are to be used include the nitrate salts of the following transition metals: cobalt (II), nickel (II), iron (III), mercury (III), and copper (II).

3 TECHNICAL APPROACH

Coupon exposure testing was performed on ASTM A537-Cl.1 (normalized) steel, the material of construction of the Type III HLW tanks. The coupon testing was done in the vapor space and the liquid/air interface within the framework of a parametric test matrix which included surface conditions as a variable. The bulk solution temperature was maintained at 50°C.

3.1 Coupon Testing

The testing in the vapor space was done on ¼-in. thick round disk samples mounted in epoxy resin. 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 2. The insets give higher magnification of the coupons exposed to the vapor space and the coupons exposed to the liquid/air interface.

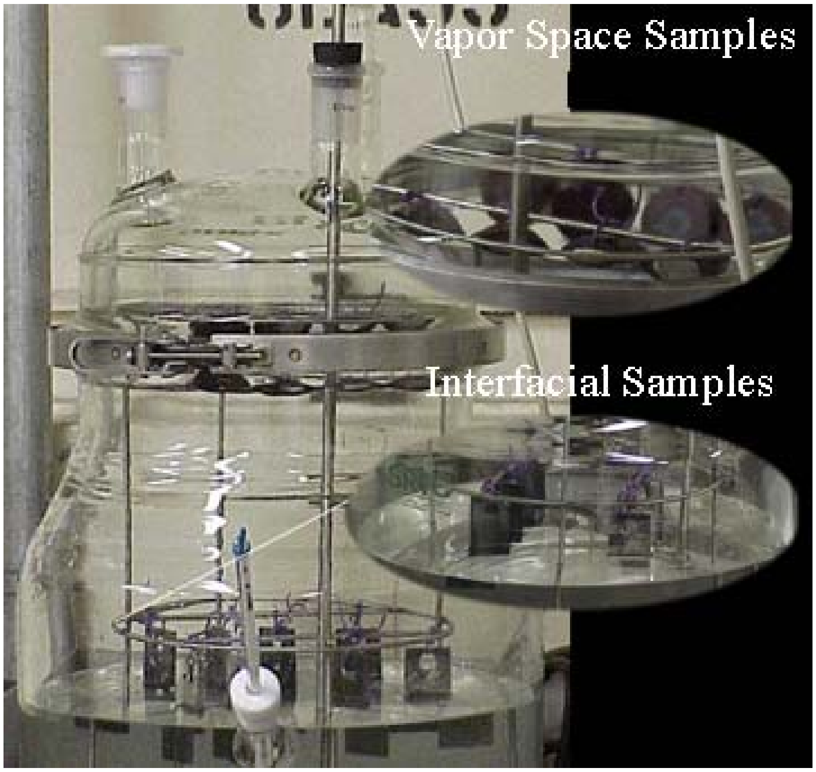


Figure 2: Experimental Test Setup

3.1.1 Surface Characteristics

Testing was performed within the framework of a parametric test matrix consisting of these key variables as summarized in Table 1. The surface was oxidized by heat treatment for 2 hours at 975°C to simulate mill-scale, and defects in the mill scale were introduced utilizing a diamond tip glass drill bit. A representative array of indents is shown in Figure 3. The indents exposed the underlying bare metal, but may have 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.

Table 1: Summary of Variables Tested

Surface	Defects	Chemistry
Mill scale	No indents	No deposit
Polished	Indents	Deposits

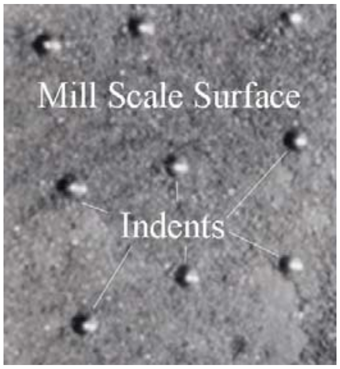


Figure 3: Representative Array of Microindents

3.1.2 Steel Specifications

The tanks were fabricated with semi-killed, hot-rolled A537-Cl.1 plate, with nominal composition shown in Table 2. The A537 steel is a ferritic/pearlitic steel with the microstructure shown in Figure 4. A representative coupon is shown in

Table 2: Steel Specifications

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

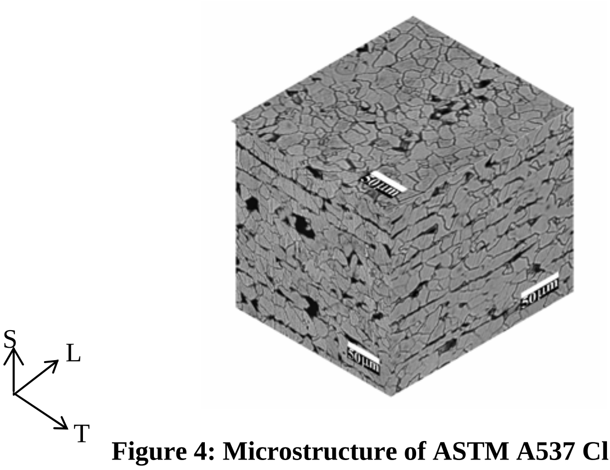


Figure 4: Microstructure of ASTM A537 Cl.1 Steel.

The tanks were made from hot-rolled plate and tend to have manganese sulfide and aluminum oxide inclusions that are oriented parallel to the rolling direction. Previous experiments have shown that pitting on polished coupons above simple waste simulant has initiated in rows suspected to be in line with these inclusions. Other studies revealed that nitrate-induced pitting in these steels typically initiates around manganese sulfide or aluminum oxide inclusions.[7]

3.2 Exposure Solution Chemistry

The solution chemistries tested included minor waste constituents in addition to the $NaNO_3$, $NaNO_2$, and NaOH which comprise the bulk of the high level radioactive waste. The additional constituents were the sodium salts of aluminate, carbonate, sulfate, phosphate, chloride, chromate, and fluoride; and nitrate salts of transition metals, typically found in the high level waste. The typical effect of these constituents on the corrosion of low carbon steel in aqueous conditions is shown in Table 3.[8]

Table 3: Ion Effects on Corrosion of Low Carbon Steel

Ion	Concentration Range, M	Possible Effect
NO_3^-	1.6 - 4.5	Cracking, Pitting, General Corrosion
NO_2^-	0 – 3	Inhibition (pitting in very dilute solutions)
OH^-	0 – 5	Inhibition, Cracking at high temperature
$Al(OH)_4^-$	0.4 – 1.6	Inhibition with the presence of OH-
$(CO_3)^{2-}$	<0.1 – 0.3	Inhibition
SO_4^{2-}	0.02 – 0.2	Pitting
PO_4^{3-}	0.01 – 0.08	Inhibition
Cl^-	0.005 – 0.11	Pitting
CrO_4^{2-}	0.001 – 0.009	Inhibition
F^-	0.001 – 0.004	Pitting

In addition to the unique effects of the anions, there are significant synergistic and temperature effects on the corrosivity of the anions. For example, nitrate is known to cause stress corrosion cracking of steel at intermediate and high temperatures, and significant general corrosion at low temperatures. Hydroxide can cause stress corrosion cracking of steels at high temperatures. However, with control of the solution temperature and nitrate to hydroxide ratios, stress corrosion cracking can be prevented. This complex condition created due to the stability of the surface film on the steel as a function of the cathodic reaction. In the case of nitrate reduction on the surface, cracking is promoted, whereas oxygen reduction reduces the propensity for cracking , but increases general corrosion. However, the addition of hydroxide promotes a stable film that prevents nitrate general corrosion. In high hydroxide conditions, the addition of nitrate at some intermediary level where oxygen reduction is the preferred reaction prevents the electrochemical conditions that can promote caustic stress corrosion cracking.[9] These stress corrosion cracking conditions can be extrapolated to understanding of pitting corrosion in terms of localized corrosion.

Four solutions were chosen for testing. Solutions 1 and 2 were conservatively chosen at the boundary conditions of the current chemistry control program: $NaNO_3 = 1.5M$, $NaNO_2 = 0.45M$, and $NaOH = 0.15$. The pitting studies were conducted within this regime as it is expected to be the most aggressive contributing to pitting in the vapor space and at the interface, particularly at the boundary conditions tested. The limited hydroxide and nitrite availability at the interface may lead to pitting at the interface due to inhibitor depletion during extended periods of waste level stagnancy. Additionally, the limited hydroxide availability may diminish the hypothesized inhibitive effect of hydroxide within the vapor space. The testing was conducted at the boundary conditions to provide a conservative approximation of pitting rates, even though the tanks typically operate at high hydroxide concentrations. In addition, solution 1 had all the aggressive anions at high concentrations, and solution 2 contained aggressive anions at the high concentrations and inhibiting ions at low concentrations. The solutions from Tank 34 and Tank 39 were chosen for several reasons. Tank 39 is an H-Tank farm tank functioning as a fresh waste receiver thereby having the highest temperature. Tank 39 is known to have purge ventilation failures that are consistent with proposed vapor space corrosion mechanisms. [10] A summary of the salt concentrations of the solution chemistries tested is shown in Table 4.

Table 4: Salt Concentrations of Solution Chemistries Tested

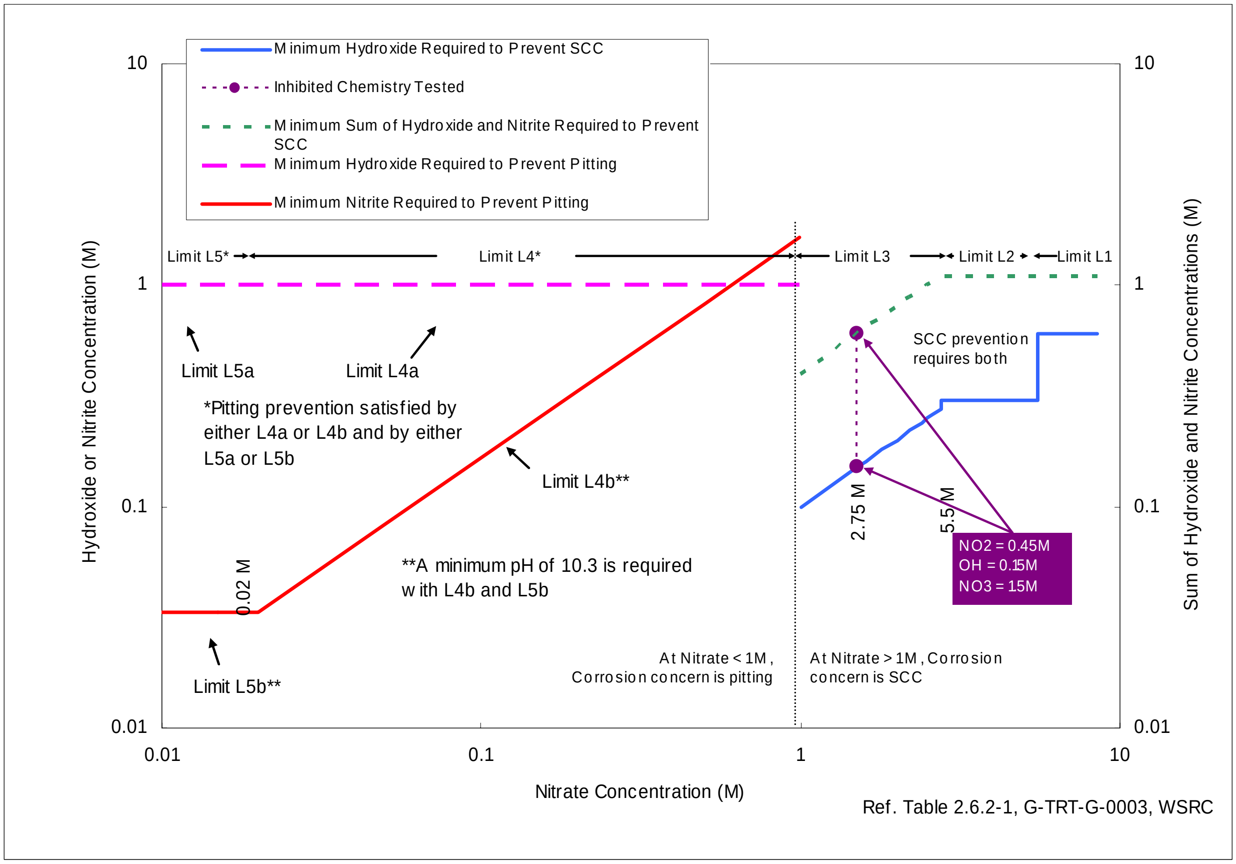
Compound	Formula	Solution 1	Solution 2	Tank 34	Tank 39
Sodium Hydroxide	NaOH	0.15	0.15	6.66	2.6
Sodium Carbonate, Monohydrate	Na_2CO_3•H_20	0.100	0.100	0.120	0.270
Sodium Nitrite	$NaNO_2$	0.450	0.450	1.175	0.641
Sodium Nitrate	$NaNO_3$	1.5	1.5	2.6246	1.8
Aluminum Nitrate	$Al(NO_3)_3$•$9H_20$	0.005	0.005	0.41	0.21
Sodium Chloride	NaCl	0.11	0.11	0.023	0.0066
Sodium Sulfate, Decahydrate	Na_2SO_4•$10H_20$	0.2	0.2	0.027	0.0464
Sodium Fluoride	NaF	0.01	0.01	0.005	0.0059
Sodium Oxalate	$Na_2C_2O_4$	0.002	0.002	0.0057	0.0064
Sodium Chromate, Anyhydrous	Na_2CrO_4		0.001		
Sodium Molybdate, Dihydrate	Na_2MoO_4•$2H_2O$		0.002		
Sodium meta-Silicate, 9 Hydrate	Na_2SiO_3•$9H_2O$				
Sodium Phosphate, Tribasic	Na_3PO_4•$12H_2O$		0.01	0.0097	0.0059

A summary of the transition metal concentrations are shown in Table 5.

Table 5: Transition Metal Concentration in Solution Chemistries Tested

Compound	Chemical Formula	Concentration [M]
Ferric Nitrate	$Fe(NO_3)_3$•$9H_2O$	0.0248
Cupric Sulfate	$CuSO_4$•$5H_2O$	0.0043
Mercuric Nitrate	$Hg(NO_3)_2$•H_2O	0.025
Nickel Nitrate	$Ni(NO_3)_2$•$6H_2O$	0.0015
Cobalt Nitrate	$Co(NO_3)_2$•$6H_2O$	0.003
Chromium Chloride	$CrCl_3$•$6H_2O$	0.00375

A graphical representation of the chemistry control program is shown in Figure 5.[3] The summary indicates the hydroxide and nitrite levels that are to be maintained as a function of nitrate concentration. The inhibited chemistry tested is indicated on the graph. Limit L3, the regime within which the pitting studies were done, addresses the nitrate range that is typical of fresh waste. The limit is specified to prevent nitrate-induced stress corrosion cracking, as SCC is the primary concern at nitrate concentrations above 1M. The limit was based upon a combination of operational experience and the knowledge of the corrosion mechanisms. A minimum hydroxide concentration of 0.1 M was conservatively selected to maintain inhibiting conditions in 1M nitrate waste solutions. The minimum hydroxide concentration and the minimum sum of hydroxide and nitrite in L3 over the range 1 M nitrate to 2.75 M nitrate were selected to transition smoothly to the L2 limit at 2.75 M nitrate. Limit L3 carries a maximum temperature of 70°C, or 105°C if the sum of hydroxide and nitrite concentrations exceeds twice the nitrate concentration.



Ref. Table 2.6.2-1, G-TRT-G-0003, WSRC

Figure 5: Summary of Chemistry Control Program and Tested Solution Chemistry (as reproduced from Reference 3)

Laboratory testing of dilute (hydroxide and nitrate concentrations < 1 molar) simulated radioactive waste solutions has focused on pitting by nitrate. This minimum nitrite concentration was found to vary linearly with the nitrate concentration of the test solution and to depend empirically on the Celsius temperature exponentially.[11] When nitrate, chloride, or sulfate was varied independently of the other waste simulant components, the familiar linear relationship was found between the logarithm of the inhibiting nitrite concentration and the logarithm of the aggressive species concentration.[12] Nitrate controls the minimum nitrite requirement to prevent pitting in certain high-level radioactive waste solutions because it is the most abundant aggressive ion in those solutions.

4 RESULTS

The samples were analyzed for pit location and pit depth, when possible. An average pit depth and a corresponding pitting rate were determined when appropriate. The following section presents the results of the testing for solution 1, solution 2, Tank 34 solution, and Tank 39 solution. Each of the section presents the solution racks as they were removed from exposure, the vapor space coupons, and the liquid-air interface coupons.

4.1 Solution 1 Results

The solution rack as removed from exposure is shown in Figure 6.

Figure 6: Solution 1 Solution Rack as Removed.

The visual analysis of the vapor space coupons, shown in Figure 7 revealed severe corrosion on the polished specimens with the initial deposits, but only spotty corrosion on polished specimens without the initial deposits. The heat treated coupons exhibited severe corrosion only when deposits and indents were both present. The other coupons exhibited spotty corrosion, but were largely protected. It is important to note that the indented sample without the deposit did not exhibit corrosion.

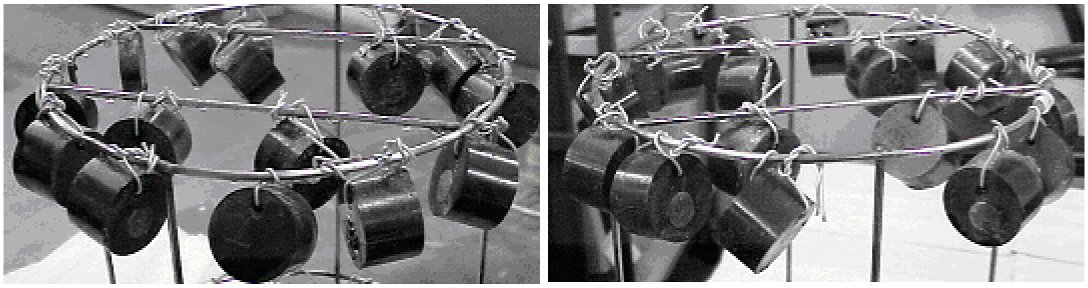


Figure 7: Vapor Space Coupons as Removed from Exposure to Solution 1.

The polished specimens of the liquid air coupons were severely corroded above the line and moderately corroded below the line. The below the line corrosion was limited to the "outer surface" of the sample, while the "inner surface" of the coupons was uncorroded. This may be due to liquid level stagnancy on the outer surface, since the stirring motion within the cell was limited to the center of the cell.

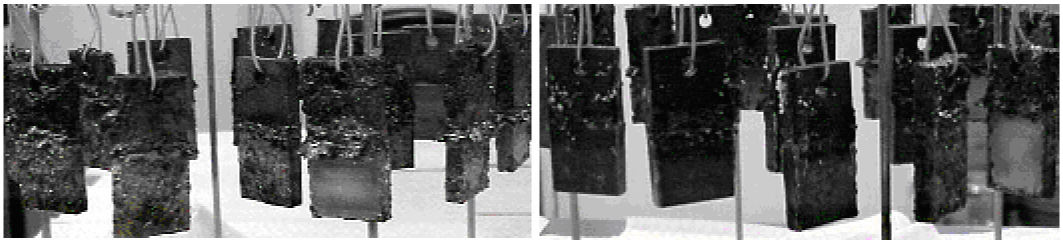
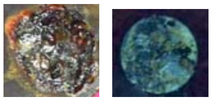
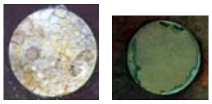
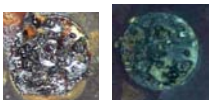
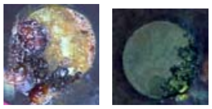


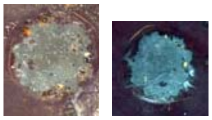
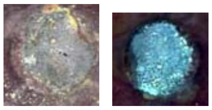
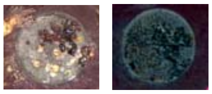
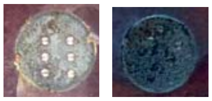
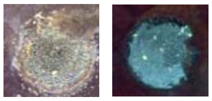
Figure 8: Liquid/Air Interface Coupons as Removed from Exposure to Solution 1.

4.1.1 Solution 1 Vapor Space Results

A summary of the vapor space coupon condition after the exposure is shown in Table 6. The first picture shown is in the as removed state, and the next picture is after cleaning using Clarke's solution which preferentially removes the oxides. The polished specimens with the deposits clearly exhibited the highest amount of corrosion. The heat treated coupons with the deposits also exhibited corrosion, but were primarily protected.

Table 6: Results for Vapor Space Coupons Exposed to Solution 1.

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
1	6 μm			
2	6 μm	x		
3	6 μm		x	
4	6 μm	x	x	
5	6 μm			
6	6 μm	x		
7	6 μm		x	
8	6 μm	x	x	

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
9	Heat Treated			
10	Heat Treated	x		
11	Heat Treated		x	
12	Heat Treated	x	x	
13	Heat Treated			
14	Heat Treated	x		
15	Heat Treated		x	
16	Heat Treated	x	x	

4.1.2 Solution 1 Liquid/Air Interface Results

The results for the liquid/air interface testing are shown in Table 7. The coupons are presented in order with the “inner” surface (i.e. stirred), “outer” surface (stagnant liquid), as exposed and removed. The coupons are then presented after cleaning in Clarke’s solution, once again with the inner surface first, and the outer surface following. The polished samples had a significant amount of corrosion just above the liquid level including growth of the oxide scale approximately ¼” from the surface of the sample. However, corrosion below the level was limited to the outer surface of the coupons where the coupons were exposed to stagnant solution. The heat treated samples exhibited a similar growth of oxide scale and delamination of the heat treatment layer.

Table 7: Results of the Liquid/Air Interface Coupons Exposed to Solution 1.

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
1	6 μm			
2	6 μm	x		
3	6 μm		x	
4	6 μm	x	x	
5	6 μm			
6	6 μm	x		
7	6 μm		x	 N/A 

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
8	6 μm	x	x	
9	Heat Treated			
10	Heat Treated	x		
11	Heat Treated		x	
12	Heat Treated	x	x	
13	Heat Treated			
14	Heat Treated	x		

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
15	Heat Treated		x	
16	Heat Treated	x	x	

4.2 Solution 2 Results

The solution rack as removed from exposure is shown in Figure 9.

Figure 9: Solution 2 Rack as Removed.

The visual analysis of the vapor space coupons revealed severe corrosion on the polished specimens with the initial deposits, but only spotty corrosion on polished specimens without the initial deposits. The heat treated coupons exhibited severe corrosion only when deposits and indents were both present. The other coupons exhibited spotty corrosion, but were largely protected. It is important to note that the indented sample without the deposit did not exhibit corrosion. These observations were consistent with those made on coupons exposed to solution 1.

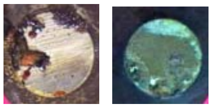
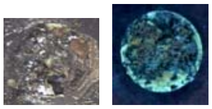
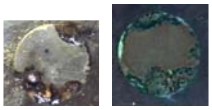
The polished specimens of the liquid air coupons , shown in Figure 10 were severely corroded above the line and moderately corroded below the line. The below the line corrosion was limited to the “outer surface” of the sample, while the “inner surface” of the coupons appeared uncorroded. Consistent with observations on coupons exposed to solution 1, the corrosion was limited to the outer surface where the coupon was exposed to stagnant solution.

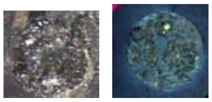
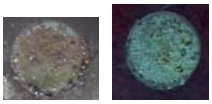
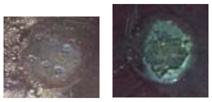
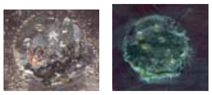
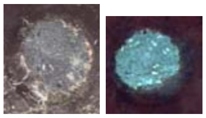
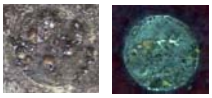
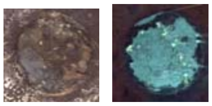
Figure 10: Liquid/Air Interface Coupons as Removed from Exposure to Solution 1.

4.2.1 Solution 2 Vapor Space Results

A summary of the vapor space coupon condition after the exposure is shown in Table 8. The first picture shown is in the as removed state, and the next picture is after cleaning using Clarke's solution which preferentially removes the oxides. The polished specimens with the deposits clearly exhibited the highest amount of corrosion. The heat treated coupons with the deposits exhibited minimal corrosion, but were primarily protected.

Table 8: Results for Vapor Space Coupons Exposed to Solution 1.

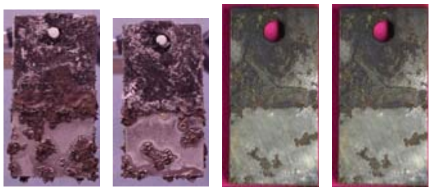
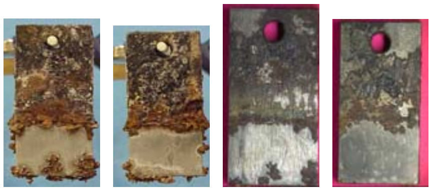
	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
17	6 μm			
18	6 μm	x		
19	6 μm		x	
20	6 μm	x	x	
21	6 μm			
22	6 μm	x		
23	6 μm		x	

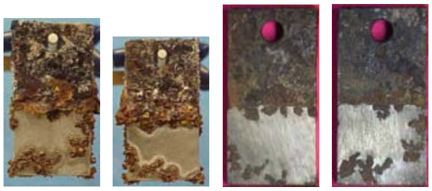
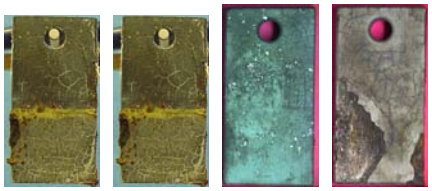
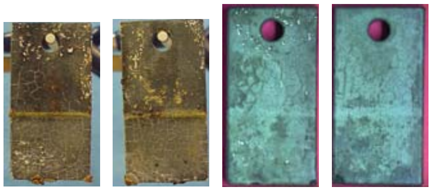
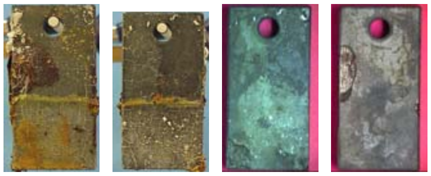
	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
24	6 µm	x	x	
25	Heat Treated			
26	Heat Treated	x		
27	Heat Treated		x	
28	Heat Treated	x	x	
29	Heat Treated			
30	Heat Treated	x		
31	Heat Treated		x	
32	Heat Treated	x	x	

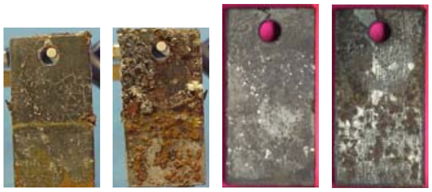
4.2.2 Solution 2 Liquid/Air Interface Results

The results for the liquid/air interface testing are shown in Table 9. The coupons are presented in order with the “inner” surface (i.e. stirred), “outer” surface (stagnant liquid), as exposed and removed. The coupons are then presented after cleaning in Clarke’s solution, once again with the inner surface first, and the outer surface following. The polished samples had a significant amount of corrosion just above the liquid level including growth of the oxide scale approximately ¼” from the surface of the sample. However, corrosion below the level was limited to the outer surface of the sample where liquid was stagnant. The heat treated samples exhibited a similar growth of oxide scale and delamination of the heat treatment layer.

Table 9: Results of the Liquid/Air Interface Coupons Exposed to Solution 1.

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
17	6 μm			
18	6 μm	x		
19	6 μm		x	
20	6 μm	x	x	
21	6 μm			
22	6 μm	x		
23	6 μm		x	

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
24	6 µm	x	x	
25	Heat Treated			
26	Heat Treated	x		
27	Heat Treated		x	
28	Heat Treated	x	x	
29	Heat Treated			
30	Heat Treated	x		

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
31	Heat Treated		x	
32	Heat Treated	x	x	

4.3 Tank 34 Solution Results

The solution rack as removed from exposure is shown in Figure 11.

Figure 11: Tank 34 Solution Rack as Removed.

The vapor space coupons and liquid/air interfacial coupons are shown in Figure 12 and Figure 13 respectively. The coupons exhibit only minor staining and there is no evidence of localized or general corrosion. It is clear that the chemistries within these tanks are sufficiently protecting against vapor space and liquid/air interfacial corrosion.

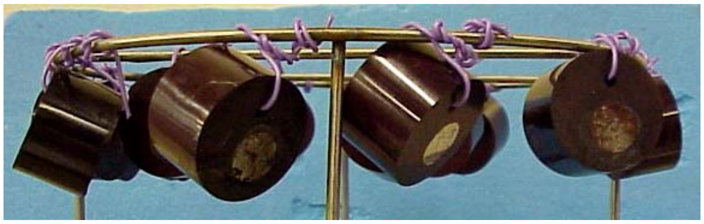


Figure 12: Vapor Space Coupons as Removed from Exposure to Tank 34 Solution.

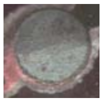
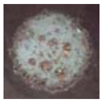
Figure 13: Liquid/Air Interface Coupons as Removed from Exposure to Solution 1.

4.3.1 Tank 34 Solution Vapor Space Results

A summary of the vapor space coupon condition after the exposure is shown in Table 10. The picture shown is in the as removed state, as cleaning in Clarke's solution was determined unnecessary due to the lack of corrosion. The coupons in the vapor space were well protected, and exhibited no corrosion and in some instances only minor staining. The staining, in fact, was limited to coupons with the initial deposits. All heat treated samples, including coupons with indents were well-protected.

Table 10: Results for Vapor Space Coupons Exposed to Solution 1.

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
33	6 μm			
34	6 μm	x		
35	6 μm		x	
36	6 μm	x	x	
37	6 μm			

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
38	6 μm	x		
39	6 μm		x	
40	6 μm	x	x	
41	Heat Treated			
42	Heat Treated	x		
43	Heat Treated		x	
44	Heat Treated	x	x	
45	Heat Treated			
46	Heat Treated	x		
47	Heat Treated		x	
48	Heat Treated	x	x	

4.3.2 Tank 34 Solution Liquid/Air Interface Results

The results for the liquid/air interface testing are shown in Table 11. The coupons are presented in order with the “inner” surface (i.e. stirred), “outer” surface (stagnant liquid), as exposed and removed. The coupons are then presented after cleaning in Clarke’s solution, once again with the inner surface first, and the outer surface following. The coupons exhibited only staining and no corrosion either below the interface, at the interface or just above the interface. A key result was that the heat-treated coupons with indents were protected.

Table 11: Results of the Liquid/Air Interface Coupons Exposed to Solution 1.

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
33	6 µm			
34	6 µm	x		
35	6 µm		x	
36	6 µm	x	x	
37	6 µm			
38	6 µm	x		
39	6 µm		x	

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
40	6 μm	x	x	
41	Heat Treated			
42	Heat Treated	x		
43	Heat Treated		x	
44	Heat Treated	x	x	
45	Heat Treated			
46	Heat Treated	x		

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
47	Heat Treated		x	
48	Heat Treated	x	x	

4.4 Tank 39 Solution Results

The solution rack as removed from exposure is shown in Figure 14.

Figure 14: Tank 39 Solution Rack as Removed.

The vapor space coupons and liquid/air interfacial coupons are shown in Figure 15 and Figure 16 respectively. Consistent with coupons exposed to Tank 34 solution, the coupons exhibit only minor staining and there is no evidence of localized or general corrosion. The results indicate that the chemistries within these tanks are sufficiently protecting against vapor space and liquid/air interfacial corrosion.

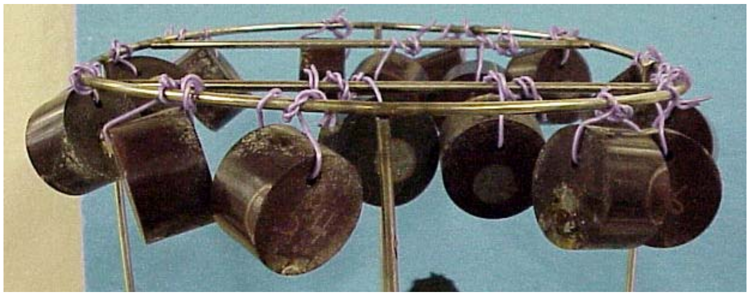


Figure 15: Vapor Space Coupons as Removed from Exposure to Tank 39 Solution.

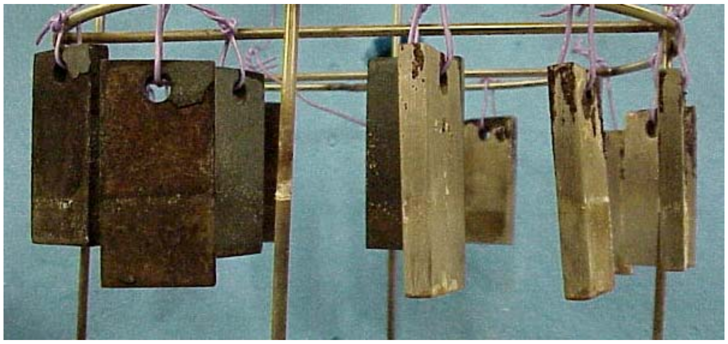


Figure 16: Liquid/Air Interface Coupons as Removed from Exposure to Tank 39 Solution.

4.4.1 Tank 39 Solution Vapor Space Results

A summary of the vapor space coupon condition after the exposure is shown in Table 12. The picture shown is in the as removed state, as cleaning in Clarke's solution was determined unnecessary due to the lack of corrosion. The coupons in the vapor space were well protected, and exhibited no corrosion and in some instances only minor staining. The staining, in fact, was limited to coupons with the initial deposits. All heat treated samples, including coupons with indents were also well-protected.

Table 12: Results for Vapor Space Coupons Exposed to Tank 39 Solution.

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
49	6 μm			
50	6 μm	x		
51	6 μm		x	
52	6 μm	x	x	

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
53	6 μm			
54	6 μm	x		
55	6 μm		x	
56	6 μm	x	x	
57	Heat Treated			
58	Heat Treated	x		
59	Heat Treated		x	
60	Heat Treated	x	x	
61	Heat Treated			
62	Heat Treated	x		
63	Heat Treated		x	
64	Heat Treated	x	x	

4.4.2 Tank 39 Solution Liquid/Air Interface Results

The results for the liquid/air interface testing are shown in Table 13. The coupons are presented in order with the “inner” surface (i.e. stirred), “outer” surface (stagnant liquid), as exposed and removed. The coupons are then presented after cleaning in Clarke’s solution, once again with the inner surface first, and the outer surface following. The coupons exhibited only staining and no corrosion either below the interface, at the interface or just above the interface. A key result was that the heat-treated coupons with indents were protected.

Table 13: Results of the Liquid/Air Interface Coupons Exposed to Tank 39 Solution.

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
49	6 µm			
50	6 µm	x		
51	6 µm		x	
52	6 µm	x	x	
53	6 µm			
54	6 µm	x		
55	6 µm		x	

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
56	6 µm	x	x	
57	Heat Treated			
58	Heat Treated	x		
59	Heat Treated		x	
60	Heat Treated	x	x	
61	Heat Treated			
62	Heat Treated	x		

	Surface Finish			
Condition	Finish	Deposit	Indent	Coupons
63	Heat Treated		x	
64	Heat Treated	x	x	

5 DISCUSSION

The key goal of this testing was to determine the effect of the minor waste constituents on the corrosion response of the tank steel. The minor waste constituents greatly influence the propensity for vapor space and liquid/air interfacial pitting and corrosion response of the steels, specifically at the boundary conditions of the chemistry control program and when the concentration of the proposed aggressive species, for example, chlorides, are high. The vapor space and liquid/air interface coupons exposed to solutions 1 and 2, in which the chlorides are at high concentrations and inhibitors were low, exhibited extensive general corrosion and pitting. However, the coupons exposed to the solutions typical of tank 34/39 exhibited no corrosion.

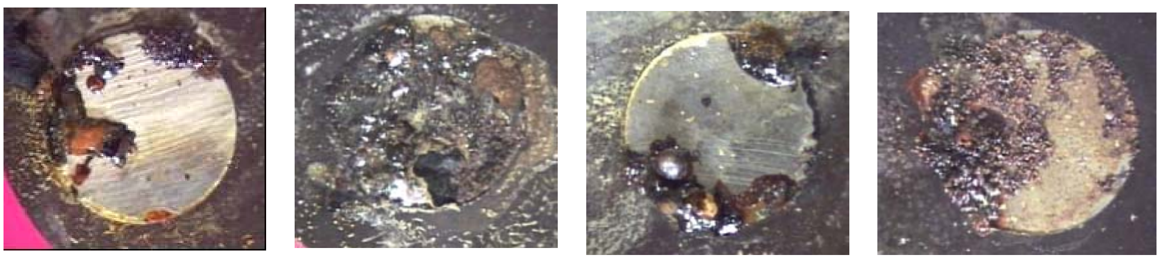
5.1 Coupons Exposed to Solutions 1 & 2

Some general observations were made on the coupons exposed to solutions 1 and 2. The polished vapor space coupons exposed to solution 1 and solution 2 are shown in Figure 17 and Figure 18 respectively. These figures show the coupons with no surface modifications, the coupon with a surface deposit, the coupon with indents, and the coupons with the deposit and the indent (‘D + I’). It is seen that the coupons with the deposits exhibited extensive corrosion, but there didn’t appear to be any significant transport of the salts from the bulk solution to the vapor space during the test period. These results were similar to those of solution 2. The results suggest that decanting of the solution and the consequent residual species may be the primary parameter mechanism by which aggressive species may be available for corrosion in the vapor space. As such, the extent to which the initial solution is inhibited prior to decanting of the solution plays a key role in the corrosion in the vapor space. This is further corroborated by the fact that even a drop in the final solution pH to 9.8 and 9.9 for solution 1 and solution 2 respectively, did not lead to corrosion in the vapor space which would indicate transport of the species into the vapor space. The indented coupons were broadly corroded and the indents did not provide any specific location for extensive corrosion for the polished specimens.

The heat treated coupons for vapor space coupons exposed to solutions 1 and 2 exhibited minor corrosion only in the indented specimens and specifically when surface deposits were present. These results are shown in Figure 19 and Figure 20 for solution 1 and solution 2 respectively.

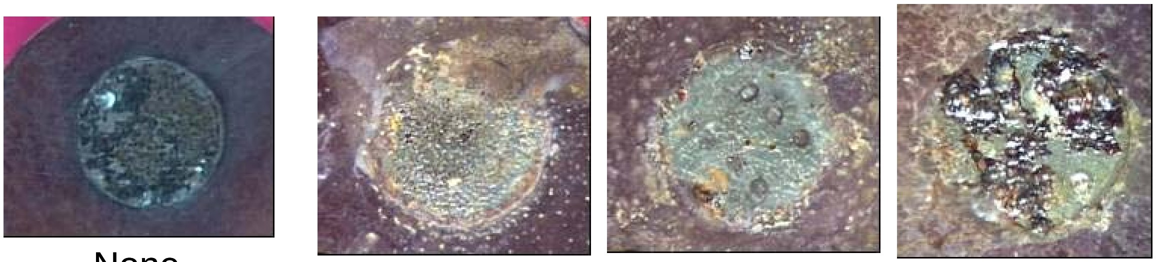
None Deposit Indent D + I

Figure 17: Polished Vapor Space Coupons Exposed to Solution 1.



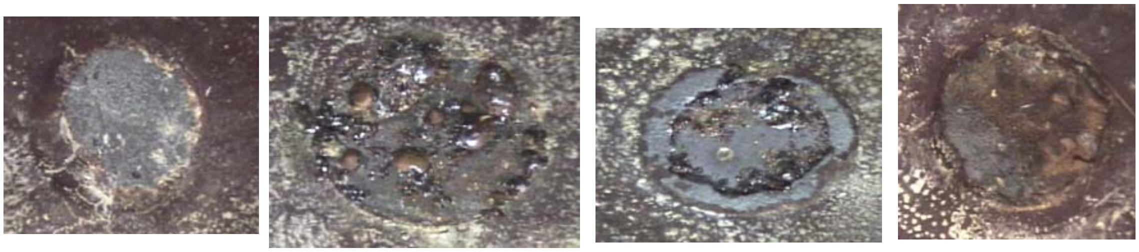
None Deposit Indent D + I

Figure 18: Polished Vapor Space Coupons Exposed to Solution 2



None Deposit Indent D+I

Figure 19: Heat Treated Vapor Space Coupons Exposed to Solution 1.



None Deposit Indent D+I

Figure 20: Heat Treated Vapor Space Coupons Exposed to Solution 2.

The pits in the liquid/air interface coupons exposed to solutions 1 and 2 were measured and corresponding corrosion rates were determined. The pitting rates were calculated below the liquid line, at the liquid line, and just above the liquid line. The results for the polished coupons are shown in Figure 21 and Figure 22 for solutions 1 and 2 respectively. The results indicate that the pitting rates are between 6-16 mpy for solution 1, while 2-13 mpy for solution 2. The pitting rates were higher and sometimes only measurable above the line for solution 2. These results suggest that even small quantities of minor waste constituents known to be corrosion inhibitors, such as chromate and phosphate, reduce the corrosion rate. This is further corroborated by the fact that the heat treated coupons exposed to solution 2 remained protected, while those exposed to solution 1 exhibited pitting as shown in Figure 23.

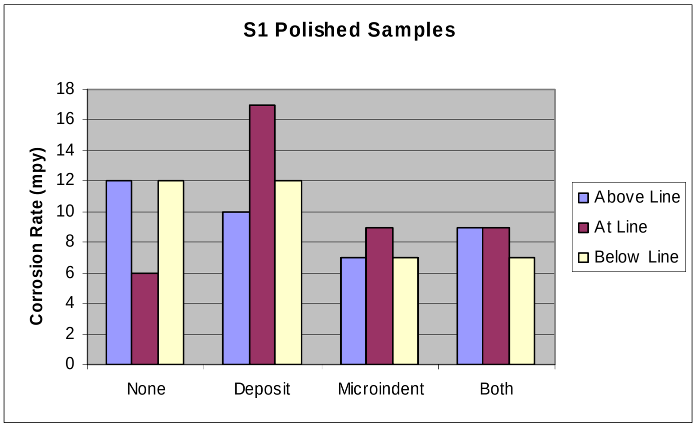


Figure 21: Pitting Rates for Liquid/Air Interface Coupons Polished Exposed to Solution 1.

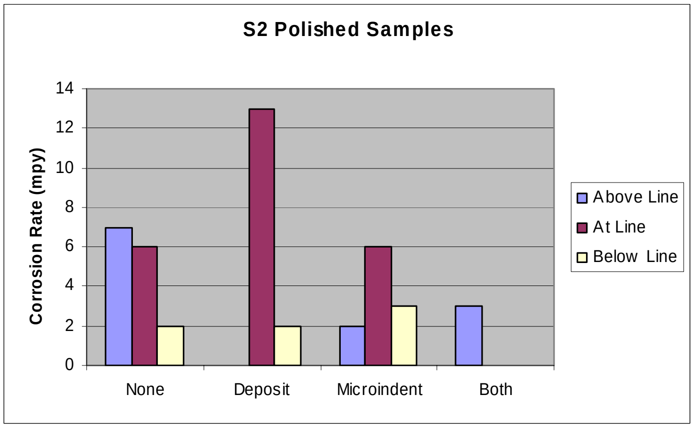


Figure 22: Pitting Rates for Liquid/Air Interface Polished Coupons Exposed to Solution 2.

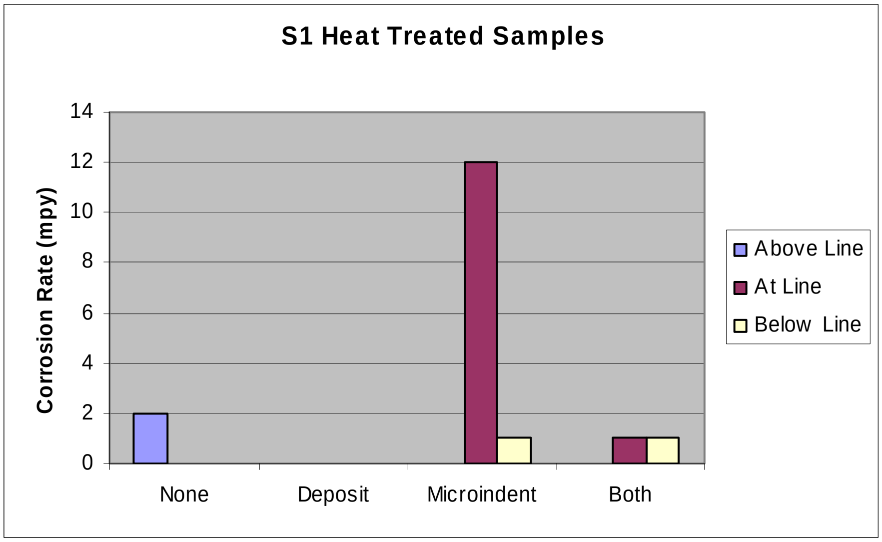


Figure 23: Pitting Rates for Liquid/Air Interface Heat Treated Coupons Exposed to Solution 1.

5.2 Coupons Exposed to Tank 34 & 39 Solutions

The vapor space coupons exposed to solutions typical of Tank 34 and Tank 39 revealed no measurable corrosion on either the polished or heat-treated specimens. In fact, only the coupons with initial deposits in the vapor space showed any staining, as shown in Figure 24. The heat treated coupons exposed to the vapor space above the Tank 34 solution, shown in Figure 25, were also well protected. The coupons exposed to the liquid/air interface showed staining but no corrosion.

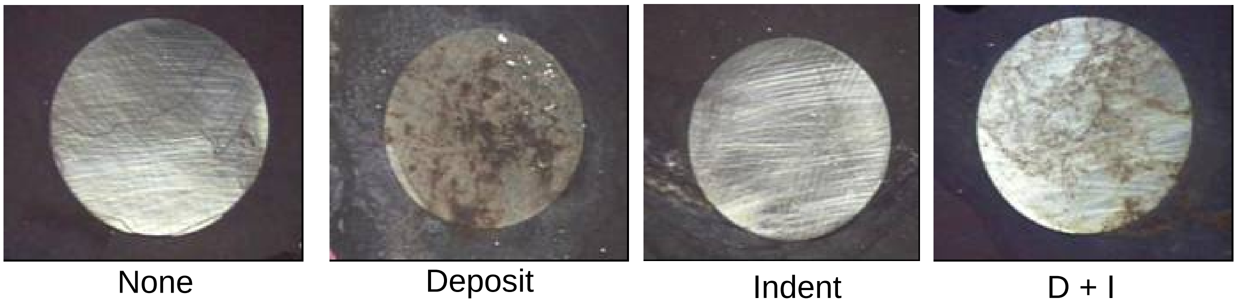
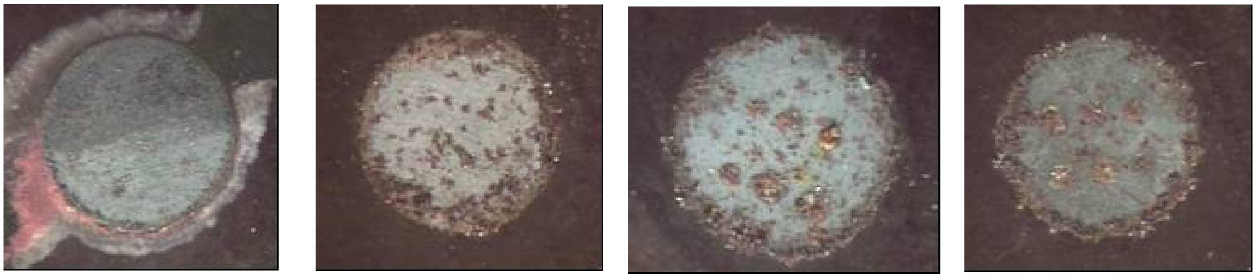


Figure 24: Vapor Space Coupons Exposed to Tank 34 Solution



None Deposit Indent D+I

Figure 25: Heat Treated Vapor Space Coupons Exposed to Tank 34 Solution

6 APPLICATION OF RESULTS

The results of the testing can be qualitatively applied to determining the vulnerability of the tanks to vapor space corrosion or liquid/air interface corrosion. The testing suggested that decanting and the consequent residual species on the tank wall is the predominant source of surface chemistry on the tank wall. The laboratory testing has shown that at the boundary conditions of the chemistry control program for solutions greater than 1M $NaNO_3$:

- Minor and isolated pitting is possible within crevices in the vapor space of the tanks that contain stagnant dilute solution for an extended period of time, specifically when residues are left on the tank wall during decanting,

- Liquid/air interfacial corrosion is possible in dilute stagnant solutions, particularly with high concentrations of chloride.

The experiences of the minor pitting at the liquid/air interface (i.e. Tank 23, Tank 49) have been shallow and are consistent with the experiments. [13,14,15] It was noted that each of these tanks had a relatively quick filling, decanting, and subsequent long period of stagnancy. These indicate that the residues left on the tank wall may have not been well enough inhibited, or the chemistry evolved and depleted inhibitors over many years (i.e. greater than 5 years).

The chemistry analyses from samples taken from the Type III tanks were plotted against the current chemistry control program, as shown in Figure 26, to determine potential vulnerabilities in the tank chemistries in their current state. It is important to note that ultrasonic and visual inspection of the Type III tanks has not found consequential evidence of vapor space or liquid/air interfacial corrosion. The analysis performed here is intended to determine if any tanks are near the boundary conditions of the chemistry control program in which VSC/LAIC may be an issue.

The chemistry of the Type III tanks with greater than 1M $[NO_3^-]$ concentration as taken from recent samples is shown in Figure 26. The chemistry control program is presented in the graph for nitrate concentrations greater than 1M. The chemistry tested in the experiments was 1.5M $NaNO_3$, 0.45M $NaNO_2$, and 0.15M NaOH, which is the boundary condition for the chemistry control program. The red dots on the graph indicate the current nitrite + hydroxide concentrations for the Type III tanks. The analyses showed that the chemistry only in Tank 50 near the boundary conditions for the sum of hydroxide/nitrite in the L2 limit. Tanks 41 and 49 are the only other tanks that are near similar boundary conditions.

However, none of these tanks are currently considered at risk since their hydroxide concentrations are well above the boundary conditions (i.e. 1.18M for Tank 50, 1.8M for Tank 49, and 2.23M for Tank 41) tested in the experiments. Ultrasonic inspection of Tanks 49 and 50 have revealed no reportable pitting in either tank.[16]

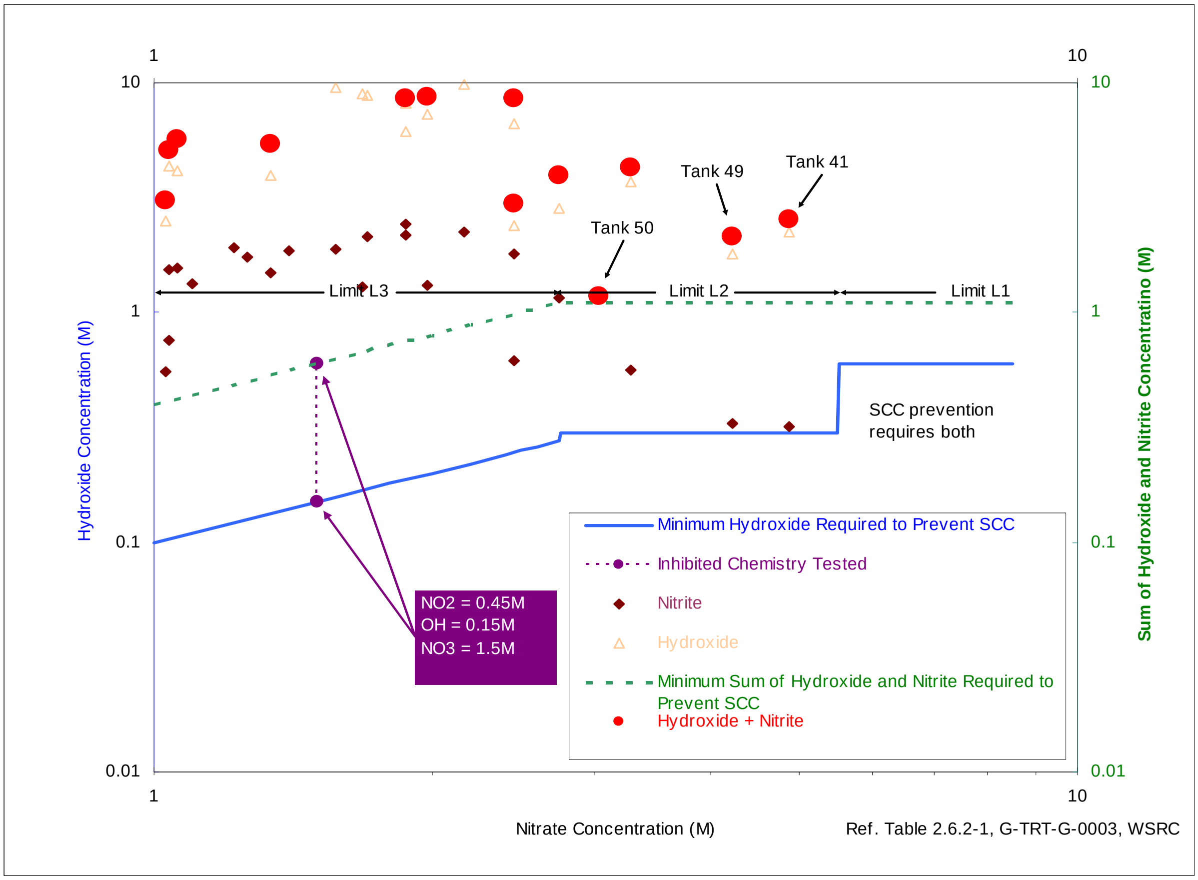


Figure 26: Chemistry of Type III Tanks from Recent Samples

The specific tank chemistries are shown in Table 14, with Tanks 41, 49, and 50 highlighted. Tank 41 and Tank 49 are used as salt dissolution tanks, while Tank 50 is used as an ETF/Saltstone feed tank. The experimental results indicate that Tank 50 would be most susceptible to the potential for liquid/air interfacial corrosion or vapor space corrosion.). It is important to note that the salt dissolution tanks have had a recent change in chemistry and Tank 50 has historically had significantly higher concentrations of inhibitor.

Table 14: Type III Tank Chemistries with Greater than 1M Nitrate Concentration

Tank Number	Nitrate	Nitrite	Hydroxide	Hydroxide + Nitrite
25	1.680	1.290	8.910	10.200
26	2.450	1.790	6.690	8.480
27	1.870	2.180	8.100	10.280
28	2.170	2.260	9.860	12.120
29	1.030	0.550	2.500	3.050
30	1.260	1.740	10.590	12.330
31	1.870	2.440	6.140	8.580
32	1.700	2.140	8.810	10.950
33	1.980	1.320	7.350	8.670

Tank Number	Nitrate	Nitrite	Hydroxide	Hydroxide + Nitrite
34	1.040	0.760	4.310	5.070
35	2.750	1.150	2.820	3.970
36	1.570	1.890	9.540	11.430
37	1.220	1.920	10.610	12.530
38	1.060	1.560	4.130	5.690
39	2.450	0.620	2.380	3.000
41	***4.870***	***0.320***	***2.230***	***2.550***
42	1.340	1.480	3.940	5.420
44	1.100	1.340	12.250	13.590
45	1.400	1.860	13.290	15.150
46	1.040	1.530	13.120	14.650
47	3.280	0.560	3.690	4.250
49	***4.230***	***0.330***	***1.800***	***2.130***
50	***3.030***	***0.005***	***1.180***	***1.185***

7 CONCLUSION

A program to resolve the issues associated with potential vapor space corrosion is in place. The objective of the program is to develop understanding of vapor space (VSC) and liquid/air interface (LAIC) corrosion to ensure a defensible technical basis to provide accurate corrosion evaluations with regard to vapor space and liquid/air interface corrosion (similar to current evaluations). The laboratory testing has developed an understanding of some of the key parameters necessary for chemistry control at the liquid/air interface and vapor space. The results of the laboratory testing can be used to perform corrosion evaluations for the liquid/air interface and vapor space similar to those currently performed for the liquid space. Even though there is no clear quantitative expression for chemistry control in the vapor space, the laboratory testing has developed the understanding necessary for an accurate and defensible technical basis. Focused experiments on tanks that are thought to be at risk may be performed when necessary.

8 ACKNOWLEDGEMENTS

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