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INVESTIGATION OF THE CORROSIVITY OF THE VAPOR PHASE OVER HIGH-LEVEL RADIOACTIVE WASTE

K. H. Subramanian and P. E. Zapp
Westinghouse Savannah River Company
Savannah River Site
Aiken SC 29808

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 a potentially aggressive degradation mechanism. Controls on the solution chemistry are in place to preclude the initiation and propagation of degradation in the tanks within the liquid space. 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 the initiation and propagation of degradation. Experimentation was performed to determine the potential for vapor space corrosion and liquid/air interface corrosion in ASTM A285 and A537 steels, the materials of construction of the Savannah River Site (SRS) HLW storage tanks. Corrosion studies were performed with flat, unstressed coupons in nitrate, nitrite, and hydroxide solutions. The results suggest that the potential for vapor space and liquid/air interface general corrosion and pitting exists even with inhibited solution chemistry. Further experimentation is planned to quantify the magnitude of the corrosion and also to determine the potential for stress corrosion cracking under similar conditions.

Keywords: Pitting, nitrate, carbon steel

INTRODUCTION

Radioactive waste is stored in underground storage tanks at the Department of Energy (DOE) Savannah River Site (SRS). The waste tanks store a combination of salts, consisting primarily of sodium nitrate, nitrite, and hydroxide. An assessment of the potential degradation mechanisms of the 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. Controls on the solution chemistry (minimum nitrite and hydroxide concentrations) are in place to prevent the initiation and propagation of pitting and stress corrosion cracking in the tanks. 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 corrosion, including pitting and stress corrosion cracking. Previous research has also determined that degradation is possible at the liquid-vapor interface due to hydroxide depletion.¹ The results of experiments undertaken to determine the potential for vapor space corrosion (VSC) and liquid/air interface corrosion (LAIC) are presented here.

Vapor Space Corrosion (VSC) Mechanisms

It was 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.

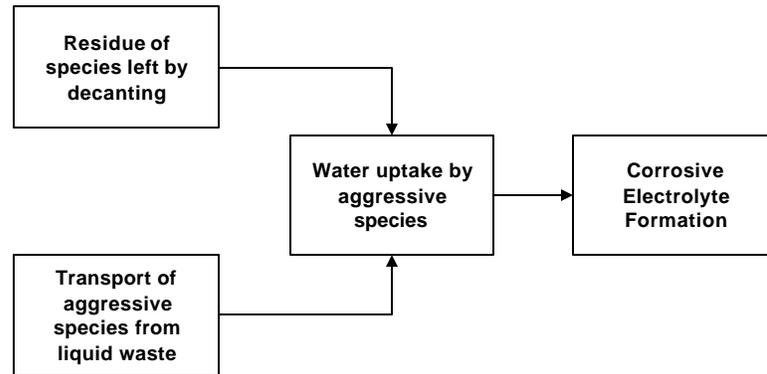


FIGURE 1. Hypothesized VSC Mechanisms

In the first mechanism, it is hypothesized that a corrosive, nitrate-rich liquid electrolyte exists on the tank wall, due to evaporation. These deposits would deplete in hydroxide over time due to reaction with atmospheric carbon dioxide. Under wet conditions the deposits could re-dissolve to create a nitrate-rich electrolyte that could induce degradation.

The alternate hypothesis is that an aqueous solution can lead to the deposition of the salts on the tank wall in the vapor space through an aerosol transport process. The mutual deliquescence relative humidity (MDRH) determines the precipitation sequence of the aerosolized salts as a function of relative humidity. The deliquescence point (relative humidity) of sodium nitrate at room temperature has been reported to be 74%.² However, the MDRH of a mixture of salts is generally lower than the deliquescence point of the single salts indicating the transition to a completely liquid system and the sequential dissolving of the electrolytes. It is known that the eutectic composition of the liquid phase and the MDRH are constant for all ratios of salt. The eutectic point is defined to be the point at which the solution has become saturated with all salts, and the relative humidity is termed the MDRH. As the relative humidity is reduced, the precipitation sequence of the salts may be different depending upon the mixture and thermodynamic properties. In terms of the Gibbs' Phase Rule, at a specific temperature and pressure, there are no degrees of freedom, and the eutectic point is fixed and invariant irrespective of the total amounts of salt present. The relative humidity within the vapor space of a tank is dependent upon ventilation system operation. Since the ventilation air is unconditioned, the natural variation of the humidity may be great enough to cycle the relative humidity around the deliquescence and efflorescence point of the salt mixture. This cycling would lead to a preferential deposition of salts, expected to be nitrate due to its relatively high deliquescence point.

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 and possibly crevice corrosion. Aggressive anion concentration cells may 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 is limited by its solubility in the bulk waste beneath 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, 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 could be a severe source of degradation. Previous research has shown that the inhibitor depletion at the liquid-vapor interface could lead to attack. The experimentation detailed herein would be used to validate and augment those results.

EXPERIMENTAL PROCEDURE

Experimentation to determine the potential for vapor space corrosion (VSC) within the context of the hypothesized mechanisms was performed. In addition, partial immersion tests were done to further characterize liquid/air interface corrosion (LAIC).

Variables

Testing was done using the salt solutions shown in Table 1. Testing was done using aggressive solution W1 containing only 5M NaNO_3^- , which is uninhibited and known to cause stress corrosion cracking of stress carbon steel. The nitrate concentrations in Table 1 are sufficient to permit stress corrosion cracking. The nitrite and hydroxide concentrations in inhibited solution W2 are believed to be sufficient to prevent stress corrosion cracking. It is important to note that the inhibited solution is specified to prevent stress corrosion cracking and not pitting. The general corrosion and pitting response of ASTM A285 and ASTM A537 steel were studied. Experiments were performed within the framework of a test matrix consisting of the variables shown in Table 2. Test solutions were maintained at 50°C.

TABLE 1
MOLAR CONCENTRATIONS OF SALT SOLUTIONS FOR EXPERIMENTATION

Solution Label	$[\text{NO}_3^-]$	$[\text{NO}_2^-]$	$[\text{OH}^-]$
W1	5	-	-
W2	1.5	0.45	0.15

TABLE 2
TEST MATRIX VARIABLES FOR EXPERIMENTATION

Steels	Material Finishes	Relative Humidities
ASTM A285	600 grit (Polished)	50% (low)
ASTM A537	Mill-scale (MS)	>95% (high)

RESULTS

Post-Exposure Macroscopic Observations

Vapor Space. The experiments were intended to determine the potential for vapor space corrosion due to a solution transport process under high and low relative humidity conditions. The results of the macroscopic examination for the high relative humidity testing are summarized in Table 3. It was hypothesized that the salts could be available in the vapor space due to aerosolization. It was expected (and observed) that salts could deposit on coupons in the vapor space in the low relative humidity cells and not in the high humidity cells because the deliquescence point or mutual deliquescence point of the vapor space solution chemistry was not reached. In addition, it was observed that the corrosion of coupons in the low humidity cells was relatively less aggressive than the high humidity cells' coupons, because the deliquescence point for reabsorption of water was not reached in the low humidity cell.

TABLE 3
QUALITATIVE MACROSCOPIC RESULTS OF COUPONS
EXPOSED TO THE VAPOR SPACE IN HIGH RELATIVE HUMIDITY

Steel, Surface	Uninhibited Solution W1	Inhibited Solution W2
A285, MS	Spotty corrosion	No corrosion seen
A285, Polished	Extensive general corrosion	No corrosion seen
A537, MS	Spotty corrosion	Spotty Corrosion
A537, Polished	Extensive general corrosion	No corrosion seen

Extensive general corrosion was seen on the polished surface above the uninhibited solution while no corrosion was seen on the polished surface above the uninhibited solution. This could be due to several reasons. There may have been a lack of wettability on the smooth vertical surface, not allowing for the formation of a corrosive electrolyte. Alternatively there could exist a protective chemistry in the vapor space above the inhibited solution. Hydroxide is expected to be present due to its relatively low deliquescence point. The existence of such a protective chemistry would indicate the potential for aerosolization or suspension of electrolytes in the vapor space.

The results of the low humidity testing are shown in Table 4. Spotty general corrosion was seen on the mill scale surface of the A537 steel even above the inhibited solution, while the A285 steel mill scale remained pristine. Further examination of the mill scale products revealed that the A285 steel had a thicker scale, while the A537 coupons had a thin scale film. In addition, the A537 coupons had inhomogeneities in the mill scale that exposed bare metal.

TABLE 4
RESULTS OF MACROSCOPIC EXAMINATION OF COUPONS
EXPOSED TO THE VAPOR SPACE IN LOW RELATIVE HUMIDITY

Steel, Surface	Uninhibited Solution W1	Inhibited Solution W2
A285, MS	Spotty corrosion	No corrosion, salt deposit
A285, Polished	Patchy general corrosion	No corrosion, salt deposit
A537, MS	Spotty corrosion	Spotty corrosion, salt deposit
A537, Polished	Patchy general corrosion	No corrosion, salt deposit

There were patches of general corrosion seen on coupons suspended in the vapor space above the uninhibited solution. The salt deposits on the coupons above the uninhibited solution protected the surface underneath, while the uncovered portions were left unprotected. The humidity in the chamber remained below the deliquescence point or mutual deliquescence point of the deposited salt. Consequently, the salts were unable to adsorb water to create a corrosive electrolyte. Similar to the high humidity results, spotty corrosion was seen on mill-scale surface of the A537 steel.

It is impossible to differentiate between humid-air corrosion and nitrate-induced corrosion without understanding the surface chemistry. The results suggest, however, that there is a potential for salts to be suspended in the vapor space due to the protective nature of the inhibited solution on the polished surface of the coupons.

Liquid-Air Interface. The results of the macroscopic examination for the testing are summarized in Table 5. Extensive general corrosion was observed throughout the polished surface of the coupons, including the interface, and vapor exposed metal in the uninhibited solution. Spotty corrosion was observed on the polished surface on the inhibited solution at the interface.

TABLE 5
RESULTS OF MACROSCOPIC EXAMINATION OF COUPONS EXPOSED TO THE LIQUID/AIR
INTERFACE

Steel, Surface	Uninhibited Solution W1	Inhibited Solution W2
A285, MS	General corrosion	No corrosion, salt deposit
A285, Polished	Extensive general corrosion	No corrosion, salt deposit
A537, MS	Spotty corrosion	No corrosion, salt deposit
A537, Polished	Extensive general corrosion	Minor spotty corrosion, salt deposit

Several mechanisms are possible for the corrosion at the liquid/air interface and just above the interface in the vapor space: (1) aggressive species transport as an aerosol, (2) development of an oxygen concentration cell, and (3) hydroxide depletion.

The aerosolization of the components in solution is at the greatest concentration at that level. In combination with the high humidity, the conditions may promote aggressive corrosion. Even in the inhibited solution, the potential for corrosion above the solution existed. However, it is not possible to differentiate simple humid-air corrosion and the possibility of a more aggressive nitrate-induced attack. It is an interesting note that corrosion occurred on the polished surface near the liquid/air interface but not on the coupons suspended in the vapor space. An understanding of the surface chemistry would provide insight into the corrosion mechanisms and differentiate between humid-air corrosion and nitrate induced corrosion.

Inhibitor depletion at the liquid-vapor interface could also lead to attack. The alkaline solution pH will drop naturally over a period of time due to chemical reaction of the hydroxide with absorbed atmospheric carbon dioxide. The reduction in pH makes this interface region vulnerable to pitting corrosion and possibly crevice corrosion. Mechanistically, aggressive anion concentration cells may 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 at much lower concentration (<8 ppm) in liquid solution. The concentration gradient anodically polarizes the area of the steel slightly above the surface leading to preferential dissolution of metal 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 can be a severe mode of degradation.

Post-Exposure Microscopic Characterization

Optical microscopy was used to characterize corrosion product morphology and identify and measure pitting. X-ray diffraction (XRD) was used to characterize corrosion products.

Vapor Space. The results of the qualitative analysis are shown in Table 6, only for the high humidity testing. The general corrosion of the polished surface of both steels in the uninhibited solution was too great to observe pitting corrosion. Observation suggests that the mill-scale layer in the A285 steel is more protective than the mill scale layer of the A537 steel because of greater thickness and no inhomogeneities where base metal may be exposed to the environment.

TABLE 6
PITTING IN COUPONS EXPOSED TO THE VAPOR SPACE AT HIGH HUMIDITY

Steel, Surface	Uninhibited Solution W1	Inhibited Solution W2
A285, MS	No pitting observed	No pitting observed
A285, Polished	Underlying pitting observed	No pitting observed
A537, MS	Underlying pitting observed	Underlying pitting observed
A537, Polished	No pitting observed	No pitting observed

Select results of the microstructural analysis and the post-test characterization are presented here for comparison purposes between the uninhibited and inhibited solutions in the vapor space at the high humidity conditions. The testing is compared for A537: (1) coupon number A537-13 – exposed to 5M NaNO₃ solution and (2) coupon number A537-21 exposed to the inhibited solution; and A285: (1) coupon number A285-23 – exposed to 5M NaNO₃ solution and (2) coupon number A285-31 – exposed to the inhibited solution.

ASTM A537 Steel. The A537-13 coupon exhibited extensive tubercle growth typical of low carbon steel corrosion on the polished surface and spotty growth on the mill scale surface, as seen in Figure 2. The A537-21 coupon exhibited no corrosion on the polished surface, but spotty tubercle growth on the mill scale surface, as seen in Figure 3.



Figure 2. Coupon A537-13 (W1, 95% RH, Vapor Space) Tubercle Growth

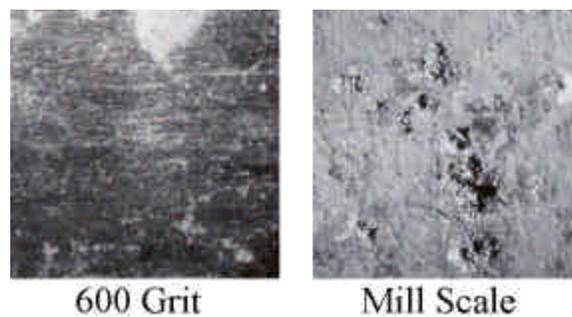


Figure 3. Coupon A537-21 (W2, 95% RH, Vapor Space) Tubercle Growth

The corrosion product was removed layer by layer by scraping and characterized using x-ray diffraction (XRD) analysis. The primary constituents found in A537-13 were oxyhydroxides [FeO(OH)], while the primary constituent found in A537-21 was magnetite (Fe₃O₄).

Underlying pitting was observed on the mill-scale surface of both the coupons, and on the polished surface of coupon A537-13. It is postulated that inhomogeneities in the mill-scale layer allow for the creation of crevices that

could promote more aggressive pitting. The inhibited solution W2 did not induce pitting on the polished surface of the coupon exposed to the vapor space. The pitting on coupon A537-13 is shown in Figure 4. Inclusions determined to be iron copper sulfides were observed in the bottom of some pits. The underlying pitting found in A537-21 on the mill scale surface is shown in Figure 5. The average pit depth was 2.5 mils as determined with optical microscopy at 200X.

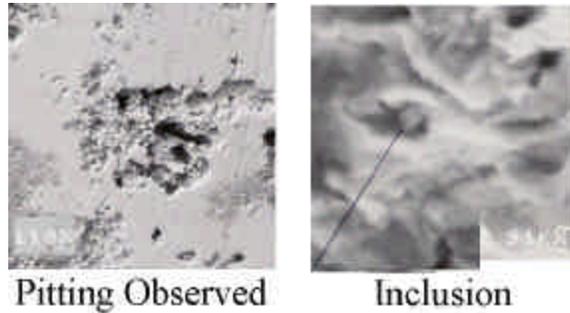


Figure 4. Coupon A537-13 (polished surface) SEM Analysis

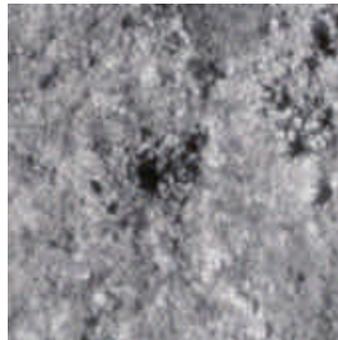


Figure 5. Underlying Pitting found on ASTM A537-21 Mill-scale surface

ASTM A285 Steel. The A285-23 coupon (exposed to W1 solution) also exhibited extensive tubercle growth on the polished surface and no growth on the mill scale surface, as seen in Figure 6. The corrosion products are primarily oxyhydroxides with minor amounts of magnetite. The A285-31 coupon (exposed to W2 inhibited solution) exhibited no corrosion on either surface.



Figure 6. Coupon A285-23 (W1, 95% RH, Vapor Space) Tubercle Growth

Underlying pitting, shown in Figure 7 was observed only on the polished surface of the A285-23 coupons exposed to the uninhibited solution. The average pit depth was 2.5 mils.

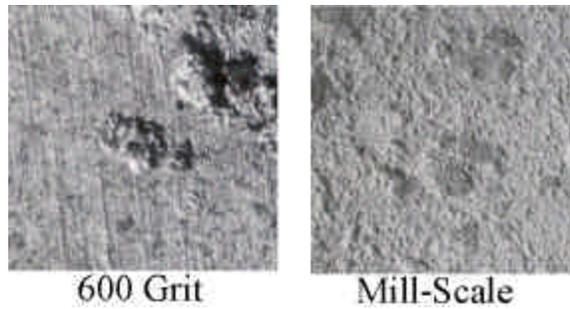


Figure 7: A285-23 SEM Analysis

Liquid/Air Interface. Observations from coupons exposed to the liquid/air interface are summarized in Table 7. The general corrosion on the polished surface of the A537 steel in uninhibited solution was too great and did not allow for pitting. It appears that the mill scale of the A285 sample protected against attack, while the mill-scale of the A537 coupons did not. It was a key observation that shallow pitting was observed on the polished surfaces of both types of steel in the inhibited solution.

TABLE 7
PITTING IN COUPONS EXPOSED TO THE LIQUID/AIR INTERFACE

Steel, Surface	Uninhibited Solution W1	Inhibited Solution W2
A285, MS	No pitting observed	No pitting observed
A285, Polished	Shallow pitting	No pitting observed
A537, MS	Shallow pitting	No pitting observed
A537, Polished	No pitting observed	Shallow pitting

Coupons compared were A537: (1) coupon A537-23 – 5M NaNO₃ and (2) coupon A537-27 – inhibited; and A285: (1) coupon A285-35 – 5M NaNO₃ and (2) coupon A285-37 – inhibited.

ASTM A537 Steel. The A537-23 coupon exhibited extensive tubercle growth in the liquid space typical of low carbon steel corrosion on the polished surface and spotty growth on the mill scale surface, as seen in Figure 8. The A537-27 coupon exhibited no corrosion on the mill scale surface, and shallow pitting on the polished surface. However, there was no distinct tubercle growth.

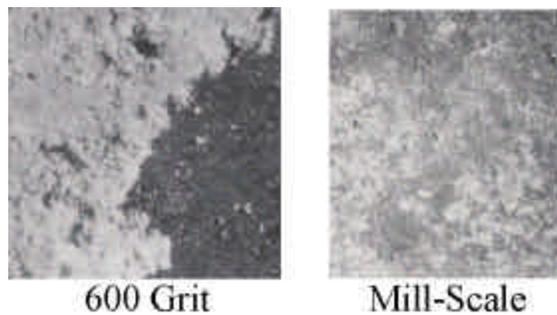


Figure 8: A537-23 Corrosion Product (W1 Solution, Interface)

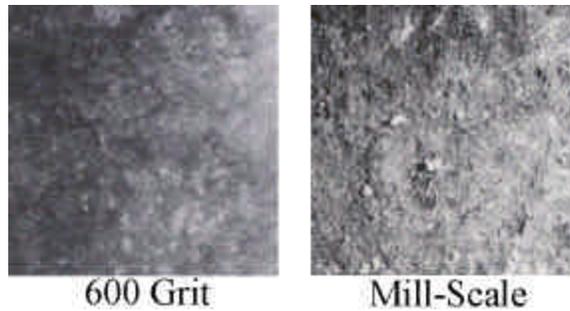


Figure 9: A537-27 Corrosion Products (Inhibited, Interface)

A shallow line of pits was seen along the interface on the A537-23 coupon. The general corrosion occurred throughout the polished surface of the sample, including the vapor space just above the liquid level.

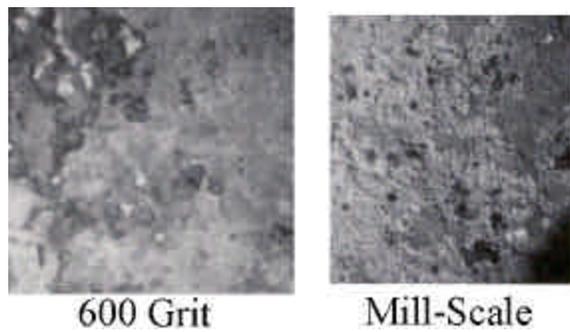


Figure 10: A537-23 SEM Analysis

A shallow line of pitting was evident just above the liquid/air interface of the inhibited solution, particularly on the polished surface. The mill scale surface had minor corrosion product, but underlying pitting was not found. Inclusions were not found at the bottom of the pits in either sample.

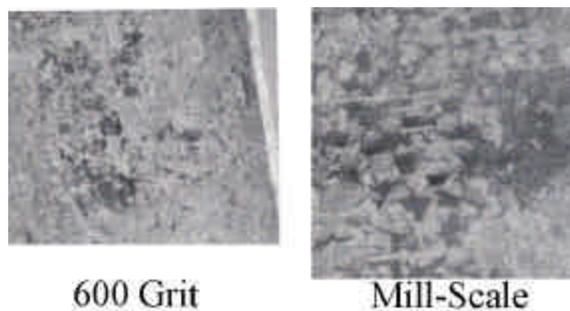


Figure 11: A537-27 SEM Analysis

ASTM A285 Steel. The A285-35 (uninhibited) coupon exhibited extensive tubercle growth in the liquid space typical of low carbon steel corrosion on the polished surface and no growth on the mill scale surface, as seen in Figure 12. The corrosion products are primarily oxyhydroxides with minor amounts of magnetite. The A285-37 (inhibited) coupon exhibited no tubercle growth on the mill scale surface or polished surface. In addition, there was no pitting found on either surface. The micrographs of only the polished surfaces are presented here for comparison purposes.

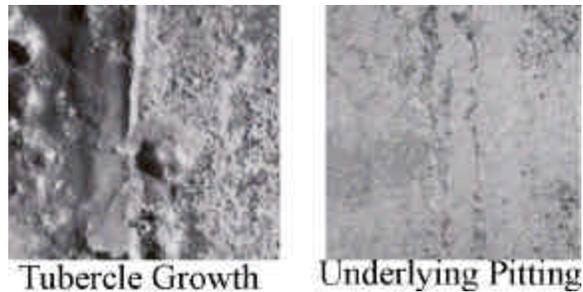


Figure 12. A285-35 (Uninhibited W1, Interface) Polished Surface

The A285-37 sample exhibited no general corrosion or underlying pitting.

CONCLUSIONS

The experimentation provided insight into the potential for vapor space corrosion and liquid/air interface corrosion in ASTM A285 and A537 steels. There were several key observations:

- The polished surfaces in the high humidity vapor space above the inhibited solution showed no corrosion, while the polished surfaces above the uninhibited solution were heavily corroded. It is hypothesized there was a protective vapor space chemistry, most likely consisting of hydroxide. If there was a wettability issue, both surfaces should have remained unattacked.
- The results suggest that the mill scale surface of the ASTM A285 steels were more protective than that of the A537 steels. The oxide scale growth and microstructures on steels are complex and depend on a large number of variables e.g. temperature, time, atmosphere and alloying elements. Further characterization of the oxide scale is necessary to understand the differences.
- The polished surface of the steels pitted at the liquid/air interface even in the inhibited solution. This may be due to hydroxide depletion at the surface due to reaction with the air. However, the nitrite levels are maintained to prevent the depletion of hydroxide inducing nitrate pitting at that interface. In addition, it is possible that the nitrate concentration be very high just above that interface, once again contributing to the aerosol degradation mechanism.
- The mill scale surface of the A537 steel showed a line of pitting at the liquid/air interface, while the A285 steel did not. Once again, further characterization of the oxide scale is necessary to determine the source of this difference.

The experimentation has indicated that the potential for vapor space and liquid/air interface corrosion exists even with inhibited solution chemistry. Further experimentation will be performed to determine the surface chemistry leading to these results. In addition, quantitative measurements will be made to determine pitting rates and general corrosion rates. Long term testing is planned in order to confirm that the corrosion rate decreases as the oxide layer passivates the substrate and provides protection against further degradation. Finally, the potential for stress corrosion cracking will be determined under the same conditions.

ACKNOWLEDGMENTS

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REFERENCES

- 1 P. E. Zapp and D. T. Hobbs, "Inhibiting Pitting Corrosion in Carbon Steel Exposed to Dilute Radioactive Waste Slurries," CORROSION/1992, Paper No. 98, NACE International, Houston TX, 1992.
- 2 Farmer, J. F., McCright, R. D., "General Corrosion and Localized Corrosion of Waste Package Outer Barrier," ANL-EBS-MD-000003, Lawrence Livermore National Laboratory, January 2000.