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“CYCLIC POLARIZATION BEHAVIOR OF LOW CARBON STEEL ABOVE SIMULATED HIGH LEVEL
RADIOACTIVE WASTE SOLUTION”

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CYCLIC POLARIZATION BEHAVIOR OF LOW CARBON STEEL ABOVE SIMULATED HIGH LEVEL RADIOACTIVE WASTE SOLUTION

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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 cyclic polarization behavior of ASTM A537 low carbon steel, the materials of construction of the tanks, in the vapor space above simulated waste solution. The results suggest steel in the vapor space is protected provided the bulk solution is sufficiently inhibited.

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.¹

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.

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 vary even if the bulk solution was controlled to prevent nitrate induced pitting, particularly in the vapor space or at the liquid/air interface.

Further 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 steel. 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.³

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.

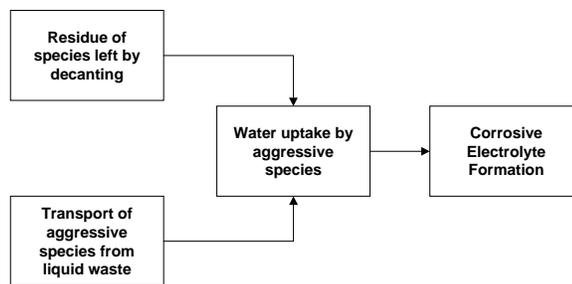


FIGURE 1. Hypothesized VSC Mechanisms

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.

EXPERIMENTAL PROCEDURE

Electrochemical testing was performed on ASTM A537-C1.1 (normalized) steel, the material of construction of the Type III HLW tanks. The nominal composition ASTM A537 is shown in Table 1. The cyclic polarization technique was used to run experiments on variable solution chemistries. The testing was done at a bulk solution temperature of 50°C, representative of the typical waste tank, and to reconcile with the pitting results.

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 |

A three-electrode probe consisting of a carbon steel working electrode, a SS 304-L counter electrode, and a Pt-wire reference electrode, was used for the cyclic polarization testing. The electrodes were embedded in a metallurgical mount useable in the vapor space for testing. The probe is shown in Figure 2.

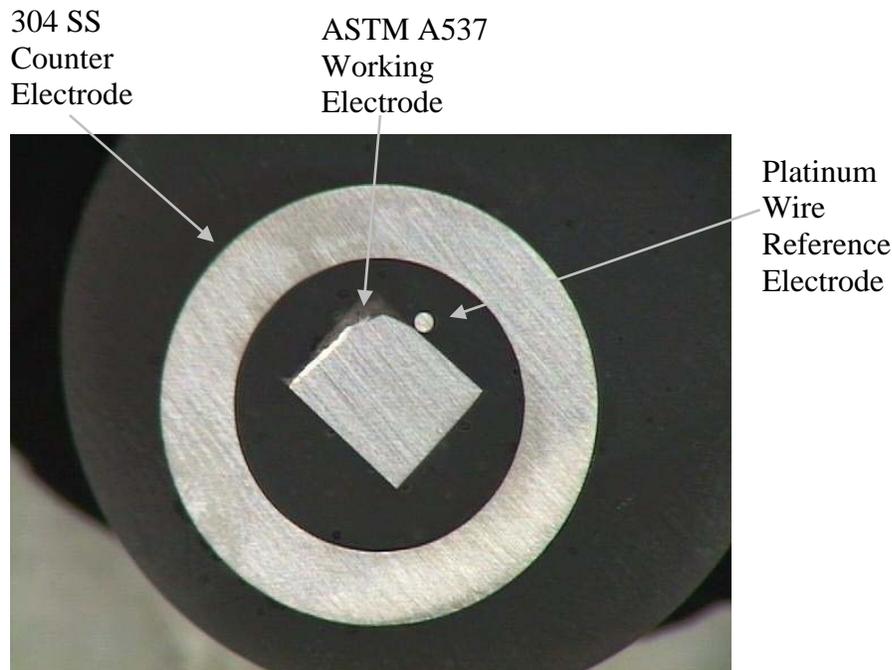


FIGURE 2: PROBE USED FOR ELECTROCHEMICAL TESTING

The probe was tested in both bulk solution and the vapor space to ensure functionality within the vapor space. The bulk solutions used were “uninhibited” and “inhibited”. The inhibited solution is in accordance with chemistry controls currently used within the high level waste tanks. The polarization scans were obtained in accordance with ASTM Standard G61, “Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys”. The tests were performed in a one-liter cell above approximately 750ml of solution. A hot plate was used to control temperature ($\pm 2^\circ\text{C}$).

The testing was done with the metallurgical mount exposed to the vapor space above bulk solution with nominal composition shown in TABLE 2. The bulk solution was maintained at a temperature of 50°C . Cyclic polarization testing was initially performed immediately after exposure, i.e., once a film was visually detected across the sample surface. Testing was then performed after exposures of 24, 48, 72, and 168 hours. The samples were allowed to incubate in the test cell during the exposures.

TABLE 2: TEST MATRIX FOR CYCLIC POLARIZATION TESTING

| Solution # | NaNO ₃ | NaOH |
|------------|-------------------|------|
| 1 | 5M | |
| 2 | | 3M |
| 4 | 5M | 1M |

*Incubation times of 72, 144, and 216 hours were tested

RESULTS AND DISCUSSION

The results for each of the solutions are shown in Figure 3-Figure 5. The data has been refined to provide the best possible representation. However, due to the transient nature and the minimal thickness of the thin film, the data has a significant amount of noise. Nevertheless, key points as to the presence of the hysteresis loop and potential for pitting can be inferred. The key characteristics of the CP scan are summarized in Tables following the figures. The corrosion potential (E_{corr}), pitting potential, and protection potential are reported in the presence of a hysteresis loop.

The cyclic polarization scans performed above 5M NaNO₃ solution are shown in Figure 3. It is seen that the hysteresis

loop was present initially, but disappears with additional incubation time. Passivation of the surface with a stable Fe₂O₃ film appears to protect the surface from pitting.

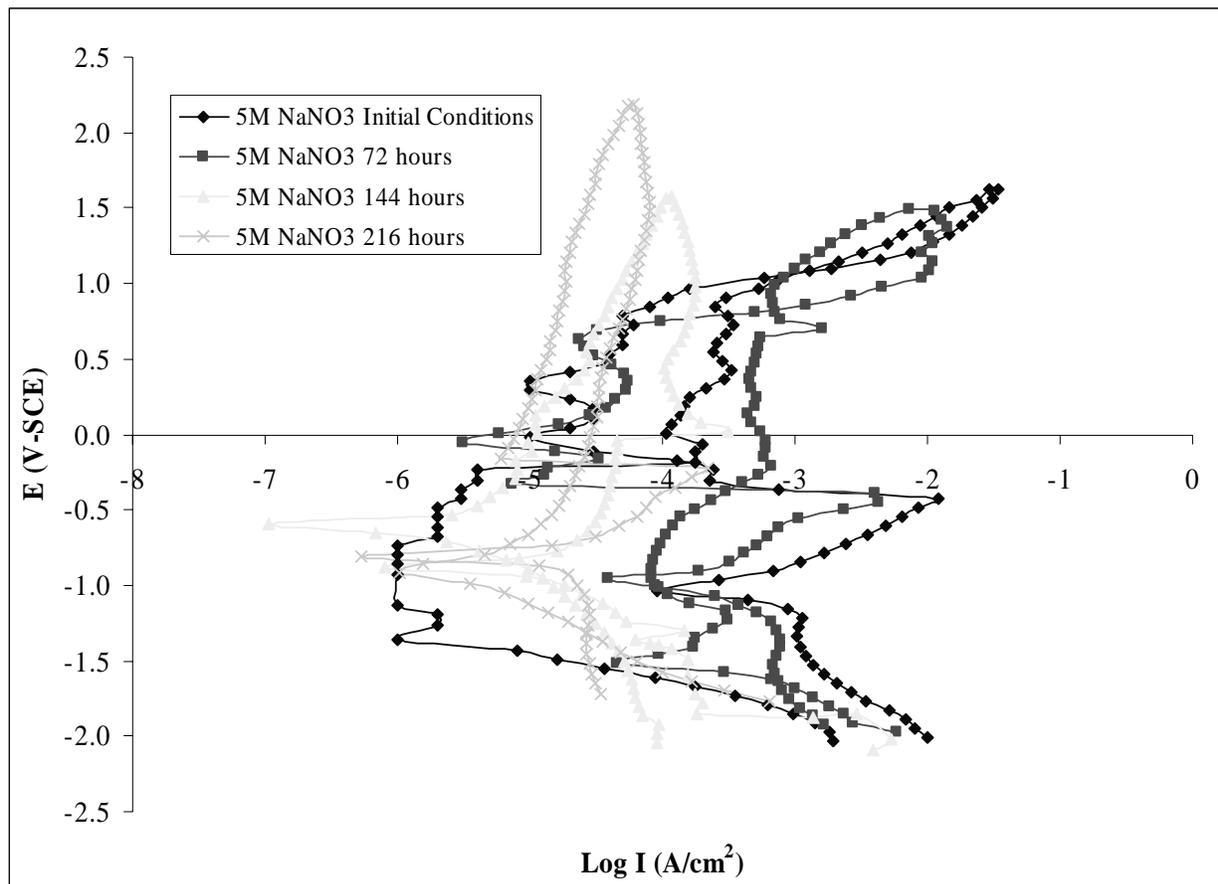


Figure 3: Cyclic Polarization Scans Performed Above 5M NaNO₃ Solution.

The key characteristics are shown in Table 3 and Table 4. It is seen that the initial pitting potential is 0.9V-SCE that is driven to 1.54 V-SCE given time to passivate the surface. The current densities decrease with time indicating the higher stability of the passive oxide film, and hence better protection against pitting. Pitting potentials and E_{corr} have been reported by Zapp and Van Zee for low carbon steel immersed in more dilute solutions of sodium nitrate.⁴ The E_{corr} data in the vapor space are in-line with extrapolation of the Zapp data. However, the pitting potentials are more noble, indicating better protection once a stable oxide film is formed.

Table 3: Key Characteristics of Cyclic Polarization Scans Performed Above 5M NaNO₃ Solution

| Condition | E _{corr} (V-SCE) | Pitting Potential (V-SCE) | Protection Potential (V-SCE) |
|-----------|---------------------------|---------------------------|------------------------------|
| Initial | -1 | 0.9 | 0.9 |
| 72 hrs | -1 | 1.54 | 1.29 |
| 144 hrs | -0.4 | N/A | N/A |
| 216 hrs | -0.9 | N/A | N/A |

In the 3M NaOH solution, no hysteresis loops are present, but there is an increase in passive current density with incubation as shown in Figure 4. This increase in current density may be attributed to the increasing concentration of hydroxide within the thin film present on the surface. Additionally, the increased current density may be the action of the formation of the

Fe₃O₄ layer on the surface with increased concentration of hydroxide.

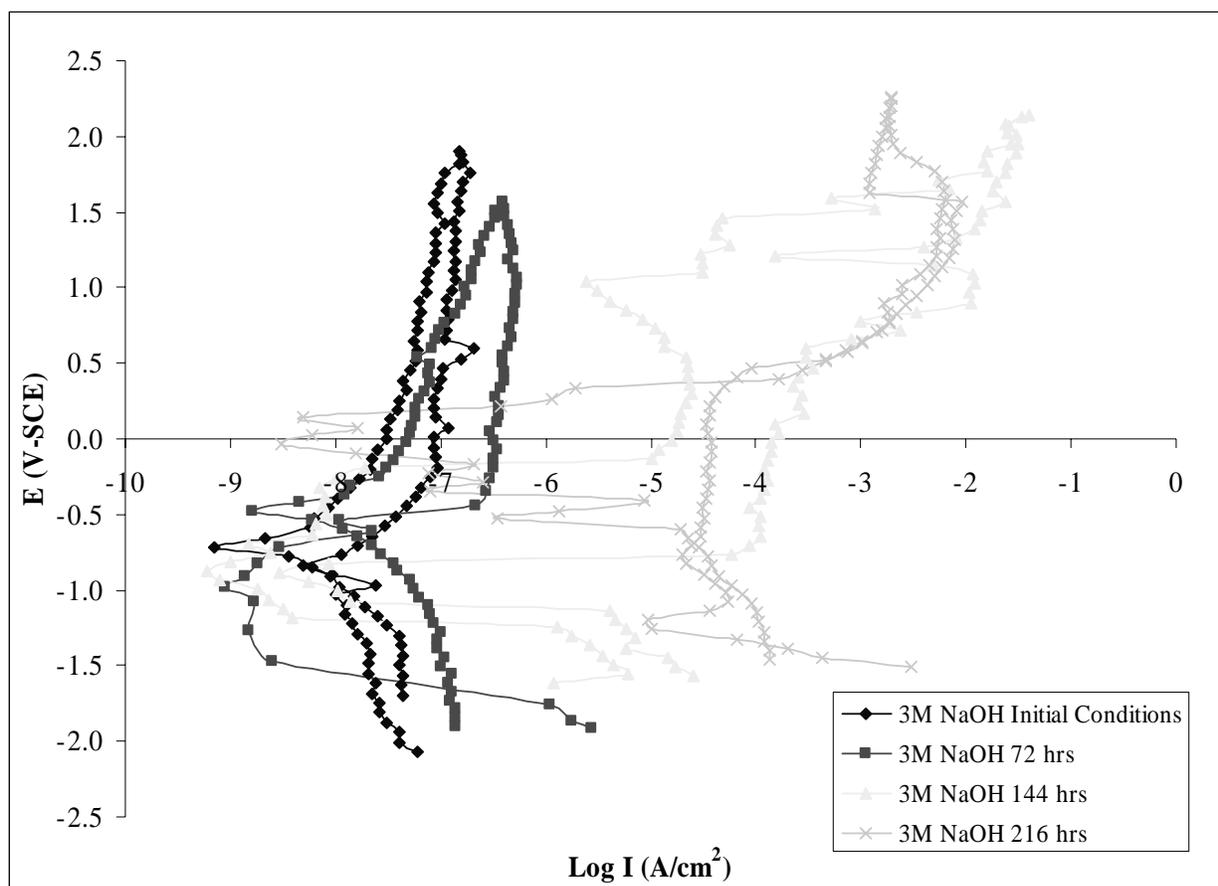


Figure 4: Cyclic Polarization Scans Performed Above 3M NaOH Solution.

The key characteristics are shown in Table 4. It is seen that the E_{corr} remains within experimental error band throughout. The E_{corr} values are similar to those expected when exposed to bulk solution. The E_{corr} does not typically change as a function of hydroxide concentration for low carbon steel.

Table 4: Key Characteristics of Cyclic Polarization Scans Performed Above 3M NaOH Solution

| Condition | E_{corr} (V-SCE) | Pitting Potential (V-SCE) | Protection Potential (V-SCE) |
|-----------|--------------------|---------------------------|------------------------------|
| Initial | -0.9 | N/A | N/A |
| 72 hrs | -1 | N/A | N/A |
| 144 hrs | -1 | N/A | N/A |
| 216 hrs | -1.2 | N/A | N/A |

The cyclic polarization scans performed above 5N NaNO₃/1M NaOH solution are shown in Figure 5. The scans are very stable and do not indicate a hysteresis loop. This indicates the addition of the NaOH drives the transpassive region beyond the scan parameters.

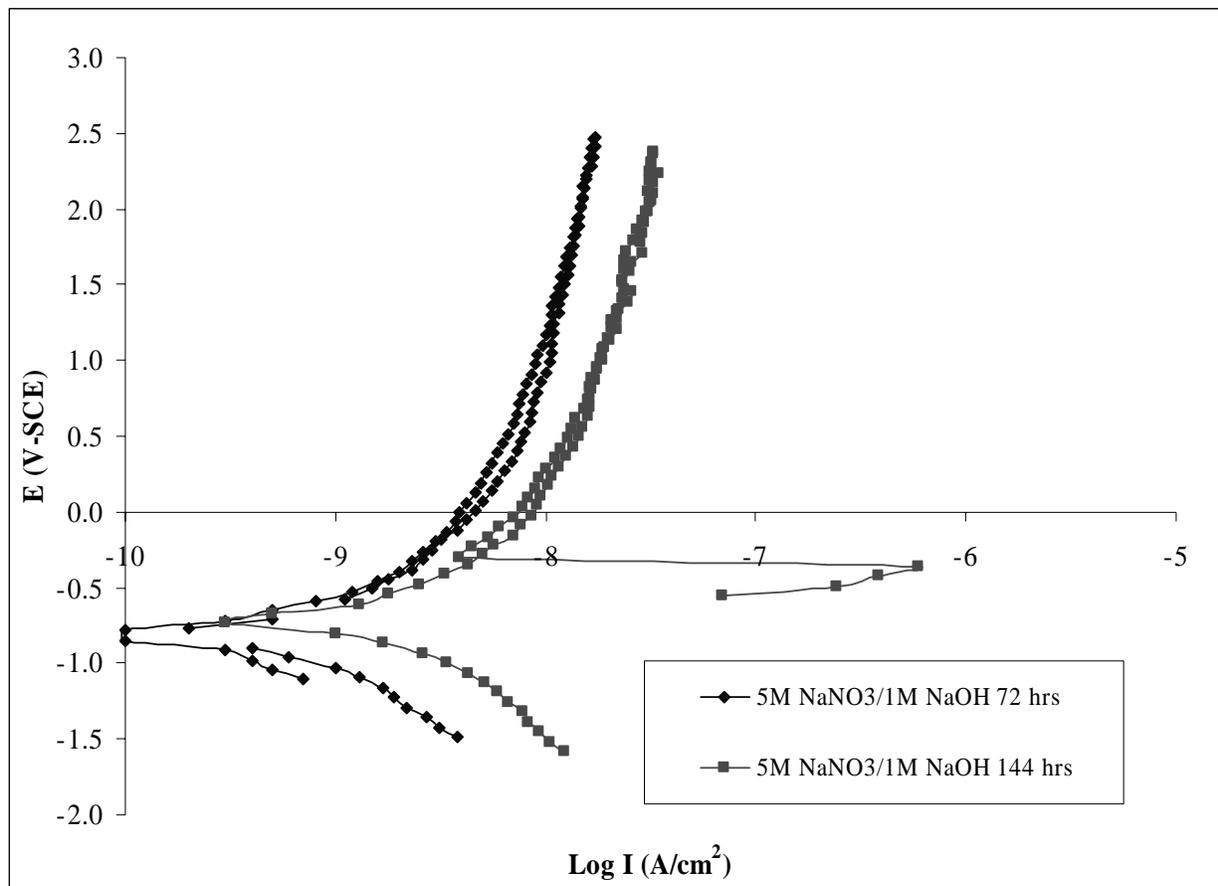


Figure 5: Cyclic Polarization Scans above 5M NaNO₃/1M NaOH Solution.

The characteristics of the passive film on the surface influence the cyclic polarization behavior. Pitting can occur in mild steel under the formation of both the passive γ -Fe₂O₃ and Fe₃O₄ (magnetite) film. The breakdown of this passive film provides the critical access to the underlying base metal for pitting to occur. The samples allowed to incubate and consequently passivate, must develop critical access to base metal through breakdown of the passive film. This may induce a situation where the underlying metal is a small anodic surface to the large cathodic surface of the oxide. As a result, the pitting occurs at these locations.

The breakdown of the oxide also influences the auto-catalytic nature of pitting. The time to failure of the film can be controlled by the nature of the aggressive anions. In this case, nitrate ions are known to destabilize the surface oxide, regardless of oxide type.⁵ However, the time to failure in the presence of the passive hematite (γ -Fe₂O₃) is considerably shorter than the magnetite (Fe₃O₄).⁶ The passive film on samples exposed to nitrate were Fe₂O₃, while hydroxide generally lead to Fe₃O₄ or oxyhydroxides.

CONCLUSIONS

Electrochemical testing was done in the vapor space above various waste simulants containing nitrate/nitrite/hydroxide solutions. The cyclic polarization behavior of low carbon steel in this vapor space was developed to determine the potential for pitting in the Type III Tanks. 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. Further coupon testing and electrochemical testing is planned in more complex solution to determine the effect of the minor constituents

PATH FORWARD

Exposure testing and electrochemical testing will be done in solutions containing minor waste constituents in addition to nitrate and hydroxide. Further experimentation will be done in more representative waste simulants with minor waste constituents. The typical high heat waste constituents (including nitrate, nitrite and hydroxide), their typical concentrations and their corrosive effects on low carbon steel are shown in Table 5.^{7]}

Table 5: Effects of High-Heat Waste Constituents on Steel Corrosion

| Ion | Concentration Range, M | Possible Effect |
|----------------------------------|------------------------|---|
| NO ₃ ⁻ | 1.6 - 4.5 | Cracking |
| NO ₂ ⁻ | 0 - 3 | Inhibition (pitting in very dilute solutions) |
| OH ⁻ | 0 - 5 | Inhibition |
| 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 |

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).

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