Research in Management of Corrosion in High Level Waste Tanks - 10367

Elizabeth N. Hoffman, Thomas B. Edwards, and Philip E. Zapp
Savannah River National Laboratory, Aiken, South Carolina 29808

ABSTRACT

High level waste tanks fabricated from carbon steel are susceptible to corrosion of tank walls. Tanks contain layers of crystalline salts, sludge, and liquid supernate. Historically, significant corrosion occurred in the supernate solution space of waste tanks. A chemistry control program, based on experimental results from bulk solutions, was implemented to minimize corrosion in the solution space of the tanks. The program relies on the hydroxide and nitrite ions as inhibitors, and continues to successfully control corrosion. A statistical test matrix was developed to refine and solidify the application of a statistical mixture/amount model to the corrosion of ASTM A537 steel, the waste tank material of construction. A mixture/amount model was identified based on a statistical analysis of recent and historically collected electrochemical data. This model provides a more complex relationship between the nitrate and nitrite concentrations and the probability of pitting than is represented by the model underlying the current chemistry control program, and its use may provide a technical basis for the utilization of less nitrite to inhibit pitting at concentrations below 1.0 molar nitrate. FY09 results fit within the mixture/amount model, and further refine the nitrate regime in which the model is applicable. The combination of visual observations and cyclic potentiodynamic polarization scans indicates a potential for significant inhibitor reductions at nitrate concentrations near 1.0 M without a significant increase in corrosion risk.

INTRODUCTION

Nuclear reprocessing operations at U. S. Department of Energy plants resulted in the generation of millions of gallons of high-level (that is, fission product) radioactive waste. Figure 1 depicts the system of radioactive liquid waste movement at the Department of Energy's Savannah River Site (SRS) in South Carolina, from the dissolution of nuclear reactor fuel and target elements to liquid storage to the solidification of the waste in either borosilicate glass or concrete. The acidic liquid waste from the fuel and target dissolution was neutralized and made highly alkaline with sodium hydroxide in the reprocessing plants before the transfer of the waste to carbon steel storage. Under high pH conditions the waste consists of precipitated transition metal oxides and hydroxides including the insoluble radioisotopes, an aqueous liquid solution containing high concentrations of hydroxide, nitrate, and nitrite ions along with soluble cesium and strontium radioisotopes, and a solid phase of sodium salts crystallized concentration of the liquid solution by evaporation. The waste tanks were constructed from the 1950s to the 1980s, with later tanks having improved designs and grades of steel. Of the total of 51 tanks constructed at SRS, the 27 most recently constructed tanks (termed Type III or IIIA tanks) were fabricated from ASTM A537 class 1 carbon steel (Figure 1), incorporated full secondary containment and heat treated after construction to relieve weld residual stresses.

Carbon steel is essentially immune from general corrosion under normal waste storage conditions due the waste's high hydroxide concentration, typically > 1.0 M. However, nitrate-induced localized corrosion in the forms of stress-corrosion cracking and pitting has occurred. Extensive research has been carried out to understand and mitigate these forms of corrosion. As the Department of Energy has undertaken to immobilize liquid radioactive waste in a solid borosilicate glass and to close non-compliant, older waste tanks that lack full secondary containment, new operating conditions have presented the need to develop new and more cost-effective corrosion mitigation controls.

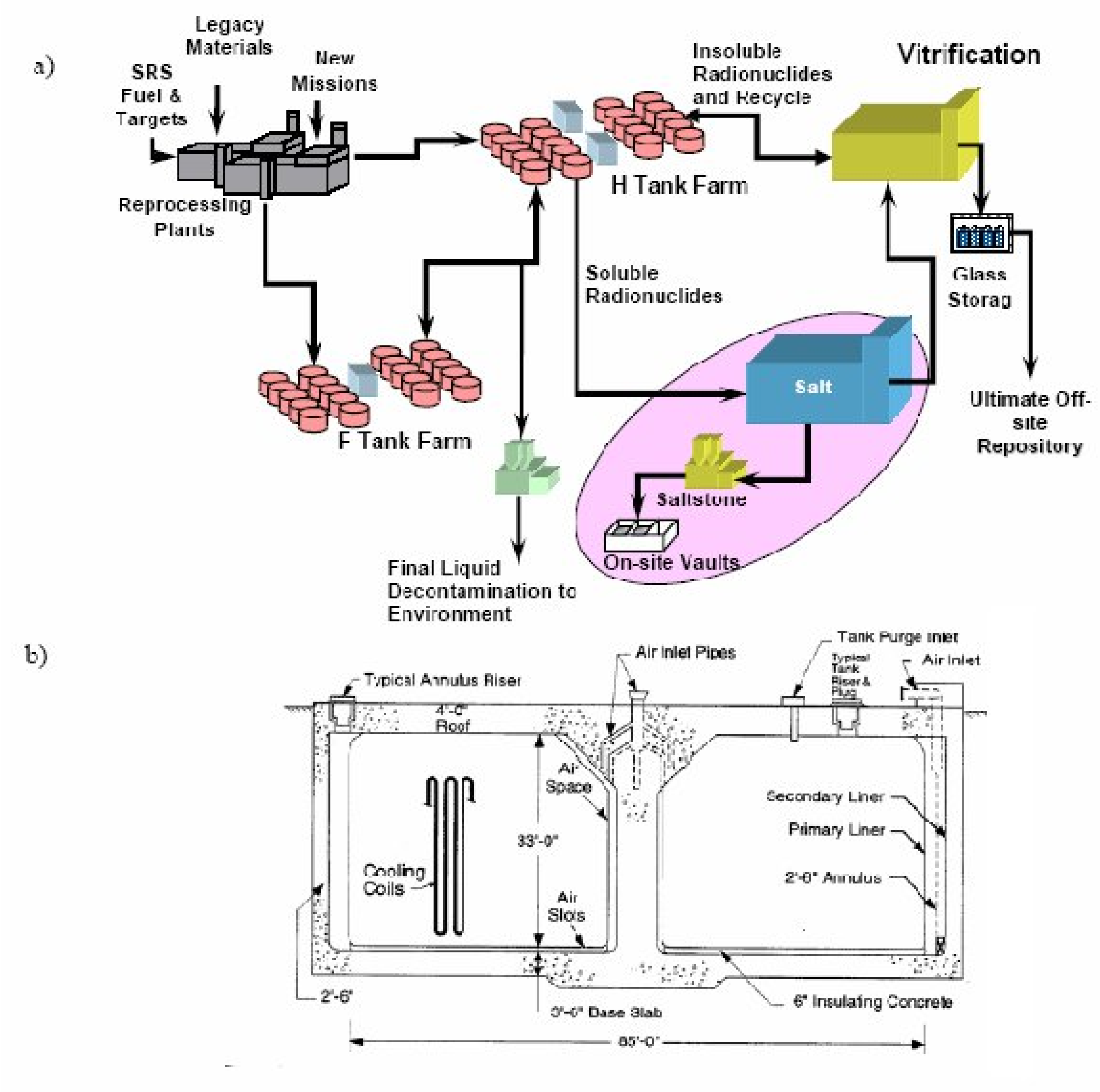


Fig. 1 Illustration of U.S. Department of Energy Savannah River Site liquid waste system: (a) overall components and (b) Savannah River Site Type III/IIIA radioactive waste tank of 1.3-million-gallon capacity.

Historically the corrosion modes of concern have been, first, stress corrosion cracking (SCC) initiating in steel in contact with high-nitrate (≥ 1.0 M concentration) bulk waste and, second, pitting in steel in contact with the interface between low-nitrate (< 1.0 M concentration) bulk waste and the vapor space above the waste. Nitrate-induced SCC was discovered in many 1950s-vintage waste tanks, which were constructed without post-fabrication heat treatment to relieve the corrosion-driving weld residual stresses. SCC has never been observed in the stress-relieved tanks. Through-wall pitting was discovered in a cooling coil of a tank whose waste was highly diluted with well water used in that instance to slurry the waste for transfer out of the tank [2]. Pitting has been particularly associated with the metal exposed to the liquid-air interface because of the depletion of hydroxide by reaction with absorbed atmospheric carbon dioxide to form bicarbonate and carbonate. These reactions in the interface solution and in a thin aqueous layer or film that is believed to form on the steel wall immediately above the interface are thought to proceed more rapidly than the diffusion rate of hydroxide from the bulk waste, resulting in orders of magnitude decrease in the hydroxide concentration in the thin film [3]. An assessment of the potential degradation modes of the waste tanks determined that nitrate-induced stress corrosion cracking and pitting were the two most significant degradation modes. [4]

Additions of concentrated solutions of sodium hydroxide and sodium nitrite are used to inhibit both nitrate-induced stress corrosion cracking and nitrate-induced pitting corrosion of steel in contact with the waste liquid phase. Protective concentrations of the inhibiting species have been determined through many years of research using non-radioactive simulants of the liquid phase of the waste as well as actual radioactive waste solutions. The research established minimum inhibitor concentrations as functions usually of the nitrate concentration, but also, for pitting prevention, as functions of the chloride and sulfate concentrations. Chloride and sulfate may become significant corrosion initiators under the unusual condition of very low nitrate concentrations caused by the radiolytic reduction of nitrate. The inhibitor concentrations have been codified and tabulated in a formal corrosion control program. The program is based upon empirical data used to determine vulnerability to stress corrosion cracking and pitting at typical compositions of waste. A summary of the corrosion controls and a technical basis for each limit are presented below.

The hydroxide and nitrite concentration limits address nitrate-induced corrosion in the concentration range 0.02 M to 8.5 M nitrate in five steps. Steps 1 through 3 cover the nitrate range 1.0 M to 8.5 M and specify the minimum hydroxide concentration and the minimum sum of the hydroxide and nitrite concentrations that are required to prevent stress corrosion cracking. Steps 4 and 5 cover waste solutions with nitrate concentrations below 1.0 M. These steps were developed subsequently to steps 1 through 3 in order to control the initiation of pitting, as new waste processing operations to prepare radioactive liquid waste for vitrification produced solutions in the dilute nitrate concentration range. The chemistry control program relates the hydroxide and nitrite inhibitor concentrations to the concentration of the principal corrosive species, nitrate. A discontinuity exists in the nitrite concentration at 1.0 M nitrate due to the merging of results of two experimental programs dealing with the corrosion modes of SCC and pitting.

The discontinuity presents tank operational challenges as waste processing yields nitrate concentration changes that rise above or fall below 1.0 M. Therefore, new corrosion control research for the waste tanks has focused on a reexamination of the nature of nitrite inhibition for pitting. The approach in this reexamination has been to undertaken a statistically designed investigation of the probability of pitting as function of the nitrate and nitrite concentration.

Statistically Design Testing

Statistically driven testing was initiated in FY08 with 104 test solutions. Based on visual observations of samples that had undergone CPP testing, a model based on the mixture/amount theory [8] was developed, see Figure 2. This model, while creating a good fit with the higher (0.5-1.0 M) concentrated nitrate, did not provide credible guidance at the lower concentration of nitrate (0.0-0.5 M). A second set of statistically determined solution sets was developed and analyzed in FY09. The intent of the second set is to provide increased confidence in and validity of the mixture/amount model by evaluating corrosion response in the solution space around the proposed limit.

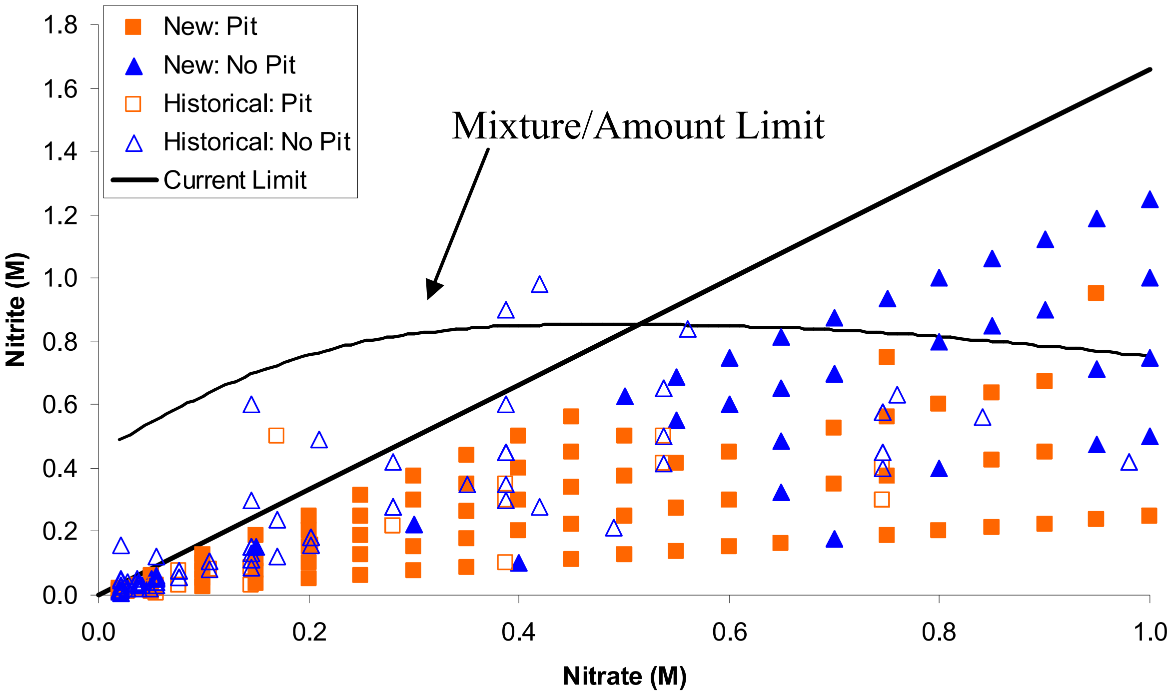


Fig. 2 Results from Part 1 (FY 08) risk-based corrosion results.

The mixture/amount model allowed for the investigation of a more complex relationship between the nitrate and nitrite concentrations and the probability of pitting than is represented by the model underlying the current chemistry control program as represented by equation (1). The model of equation (1) indicates that only controlling the ratio of nitrite to nitrate is sufficient to control the probability of pitting over the range of nitrate concentration of interest. For the mixture/amount, the probability of pitting is linked to a more complex function of the concentrations of nitrite and nitrate. The use of the mixture/amount model may provide a technical basis for the utilization of less nitrite to confidently inhibit pitting at concentrations below 1 molar nitrate as discussed below.

EXPERIMENTAL

Cyclic potentiodynamic polarization (CPP) testing was performed within the framework of the statistical test matrix to refine the current control limits. The CPP testing can be used to determine the electrochemical potential regimes in which low carbon steel is susceptible to pitting [9]. The material used for the CPP testing was semi-killed, hot-rolled A537. The nominal chemical composition for the alloy is 0.24 wt% C, 0.70-1.60 wt% Mn, 0.040 wt% S, 0.035 wt% P, and 0.15-0.5 wt% Si with small amounts of Cu, Cr, and Ni. The tests were conducted on disc samples of A537 that were nominally 1.5 cm diameter (Metal Samples, Munford, AL). Samples were ground using 800 grit grinding sheets to remove the native oxide layer and provide a flat surface. Grain size and shape were analyzed during previous testing [1].

Simulated Tank Solutions

The aqueous phase of radioactive waste is a complex solution containing numerous ionic species. These include the corrosive anion nitrate, in relatively high concentration and the corrosive anions chloride, sulfate, and fluoride, in relatively lower concentration. The protective anions are predominantly nitrite and hydroxide, but the waste also includes such protective anions as phosphate, chromate and molybdate in relatively low concentrations compared to the nitrite. Cost-effective, non-radioactive laboratory test solutions are simplifications of actual waste solutions. Corrosion testing experience in SRNL has shown that non-radioactive laboratory simulants of waste yield similar results to those of actual waste solutions [7,10]. It has also been shown that nitrate is the dominant corrosive anion. Chloride and sulfate have been shown not to require increased nitrite inhibitor concentration when they were individually increased over their typical waste concentrations. Sufficiently high concentrations of chloride and sulfate do eventually require higher nitrite concentrations to prevent pitting, and these higher nitrite concentrations have been quantified and incorporated into the waste tank corrosion control program.

A relatively simple non-radioactive simulant of waste was chosen for the testing reported herein. The major constituents were nitrate, nitrite, bicarbonate and carbonate. Chloride and sulfate were added for conservatism to ensure that the most potentially corrosive solution would be tested. Sodium nitrate and sodium nitrite were varied based on statistical modeling values. Sodium chloride and sodium sulfate were introduced to have a solution more representative of waste, which contains chloride and sulfate ions. Sodium chloride was added based on the maximum amount allowable under current chemistry control limits. Sodium sulfate was added based on the 84 wt% of the maximum amount allowable under current chemistry control limits.

Simulated waste tank solutions were prepared using distilled water and reagent-grade chemicals: sodium chloride, sodium sulfate anhydrous, sodium carbonate, sodium bicarbonate, sodium nitrite, and sodium nitrate. The pH was maintained to 10.0 using a constant carbonate/bi-carbonate molar ratio of 7 to 13. The gram amounts of carbonate and bicarbonate added were determined based on the nitrite amount. Solutions were prepared based on a statistically determined experimental design [2]. The design space was defined by molar concentrations of nitrate between 0.02 and 1.0 M at a fixed temperature of 40 °C. The objective was to investigate the molar nitrite concentration required to confidently inhibit pitting and provide further confidence in the mixture/amount model fit.

Electrochemical Testing

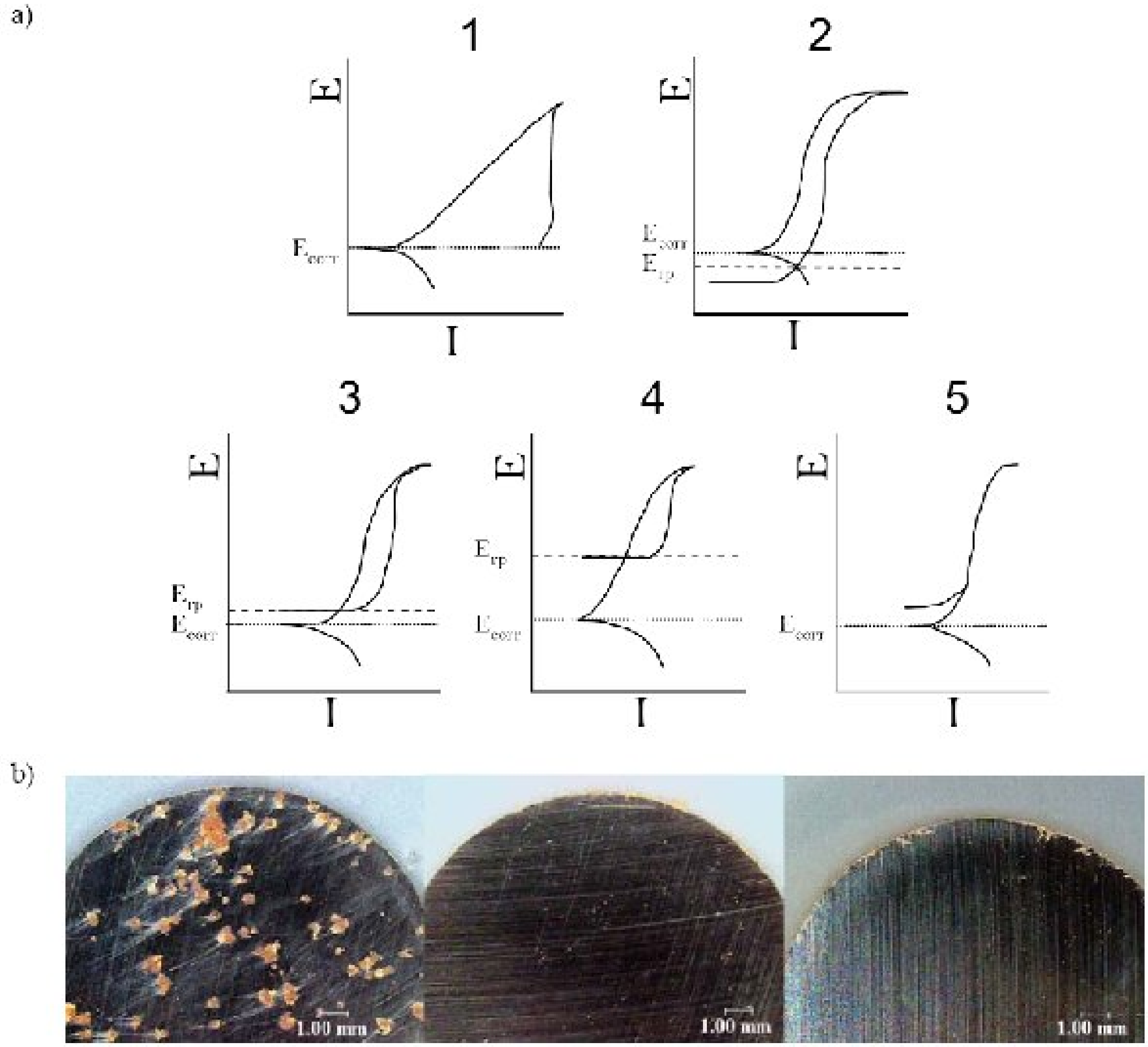
The electrochemical cell was setup with A537 samples attached to a conductive wire and mounted in metallographic mount material as the working electrode and two graphite rods were used as counter electrodes. The reference electrode was a saturated calomel electrode (SCE) connected to a Luggin bridge. The SCE in conjunction with a Luggin bridge was used to minimize noise/interference in the scans, as well as reduce the IR-drop which can form when large distances separate the working electrode and reference electrode [11]. Two scans were performed simultaneously on samples submerged in simulated solution and heated to 40 ºC with heating tape and a hot plate. Aluminum foil was used to create Faraday cages around each electrochemical cell to minimize electrical interference. Samples were held at the open circuit potential (E_{OC}) for 2 hours prior to CPP testing.

Immediately following the open circuit potential hold, the CPP scan was performed on the sample. The cyclic polarization scans were performed by anodic polarization from -0.1 V vs. E_{OC} to 1.2 V vs. E_{OC} using a scan rate of 0.5 mV/sec. Immediately following the forward scan, a reverse scan was started at 1.2 V vs. E_{OC} and stopped once the potential returned to 0 V vs. E_{OC}.

After testing, the CPP scans were evaluated based on the shape of the CPP curve and the appearance of the sample after testing. The shape of the CPP curve was evaluated against a five category system to provide a method for assessing the degree of pitting. The categories, in order of decreasing susceptibility, are:

1 Spontaneous pitting, significantly sloped forward scan, reverse scan never re-crosses;
2 Small hysteresis with E_{rp} returning at a lower potential compared to E_{corr};
3 E_{rp}-E_{corr} < 300 mV;
4 E_{rp}-E_{corr} > 300 mV;
5 Reverse scan retraces forward scan -OR- negative hysteresis (i.e., reverse scan occurs at lower current densities than forward scan)

E_{corr} represents the open-circuit potential, also known as the corrosion potential and E_{rp} is the repassivation potential, which is the potential at which the polarization re-crosses the passive portion of the cyclic polarization scan, indicating repassivation and the cessation of pitting.



Heavy Pitting, Test 81

Moderate Pitting, Test 83

No Pitting, Test 85

Fig. 3 Category systems for (a) cyclic polarization categories and (b) visual analysis of electrochemical samples.

While the electrochemical scans were rated by a five category system (Figure 3a), the visual results of the samples run in the electrochemical test were rated on a three category scale. Visually, the samples were rated on a three category scale: (1) heavy pitting, (2) moderate pitting, and (3) no pitting. To view the three categories see Figure 3b.

RESULTS AND DISCUSSION

CPP Testing

There were two criteria utilized to evaluate the results from the electrochemical tests. First, the potential-current plot was analyzed to determine critical potentials indicating breakdown (i.e., pitting potential) and/or repair (i.e., repassivation potential) of the passive film. Once these potentials were identified, they were then categorized on a scale from 1 to 5 as previously described. Secondly, at the completion of the test, each sample was evaluated visually for pitting and rated on a scale from 1 to 3 as previously described. The results are described below.

CPP Curves

A summary of the cyclic potentiodynamic polarization testing results based on the five category system of analyzing the cyclic potentiodynamic curves is shown in Figure 3a**Error! Reference source not found.**. The results indicate that the ratio of nitrite to nitrate must be greater at low nitrate concentrations (< 0.5 M) than at high nitrate concentrations (~ 0.7-1.0 M). This result implies that the minimum nitrite required by the corrosion control program may be overly conservative in the vicinity of 1.0 M hydroxide.

The open-circuit potential for each solution was analyzed to determine the effect of the solution chemistry on the E_{corr}. No significant correlation was identified.

Visual Observations of CPP Samples

Electrochemical testing resulted in a range of corrosion responses from heavily corroded to unaffected metal surfaces. Overall, samples exhibiting significant amounts of corrosion were from solutions with low levels of nitrite. Note several samples showed evidence of crevice corrosion on the interface between the mounting material and the metal sample. Crevice corrosion was discounted during visual examination of samples.

Results also indicated that the ratio of nitrite to nitrate must be greater at low nitrate concentrations (< 0.5 M) than at high nitrate concentrations (~ 0.7-1.0 M). However, some discrepancy occurred between the electrochemical and visual observations in terms of degree of corrosion for a given experimental condition. Since visual observation is a more direct corrosion evaluation method as compared to evaluation of electrochemical curves, the electrochemical statistical analysis was based on the visual results summary. Visual evaluation provided a better fit for the overall electrochemical data and allowed for discrimination between pitting and crevice corrosion.

Statistical Analysis of Results

Both CPP and visual observation results were evaluated. The corrosion results were treated as a binary function, leading to either a pit or no-pit outcome. CPP results with category values less than or equal to 4 were classified as corroded; visual observation results any amount of corrosion, either significant or moderate, were classified as corroded. Statistical models based on logistic regression were employed to analyze the results. [8]

The advantage of using the model is that the amount of nitrite needed to inhibit corrosion can be predicted based on percentage probability, allowing the facility to make quantifiable risk-based decisions.

When the optical result from FY09 were combined with the even solution trials from FY08, the mixture/amount model still applied and indicated that a lower concentration of inhibitor is needed at 0.8-1.0 M nitrate compared to the 0.4-0.8 M nitrate regime. The additional experimental effort in the extremely dilute regime failed to follow the mixture/amount model. When all the results of solutions containing less than 0.1 M nitrate are removed, the data supported the mixture/amount model. It is hypothesized that at the concentrations of nitrate less than 0.1 M, a separate chemical reaction involving the chlorides and sulfates is controlling the corrosion result [12]. This additional reaction creates a challenge when trying to incorporate the dilute solution sets into the mixture/amount model.

A contour plot depicting the pitting probabilities of the mixture/amount model in the region of 0.1 - 1.0 M nitrate is shown in Figure 4. For reference, the historical experimental limit is shown as well as the current chemistry control limit, which was created by incorporating a safety factor into the historical experimental limit.

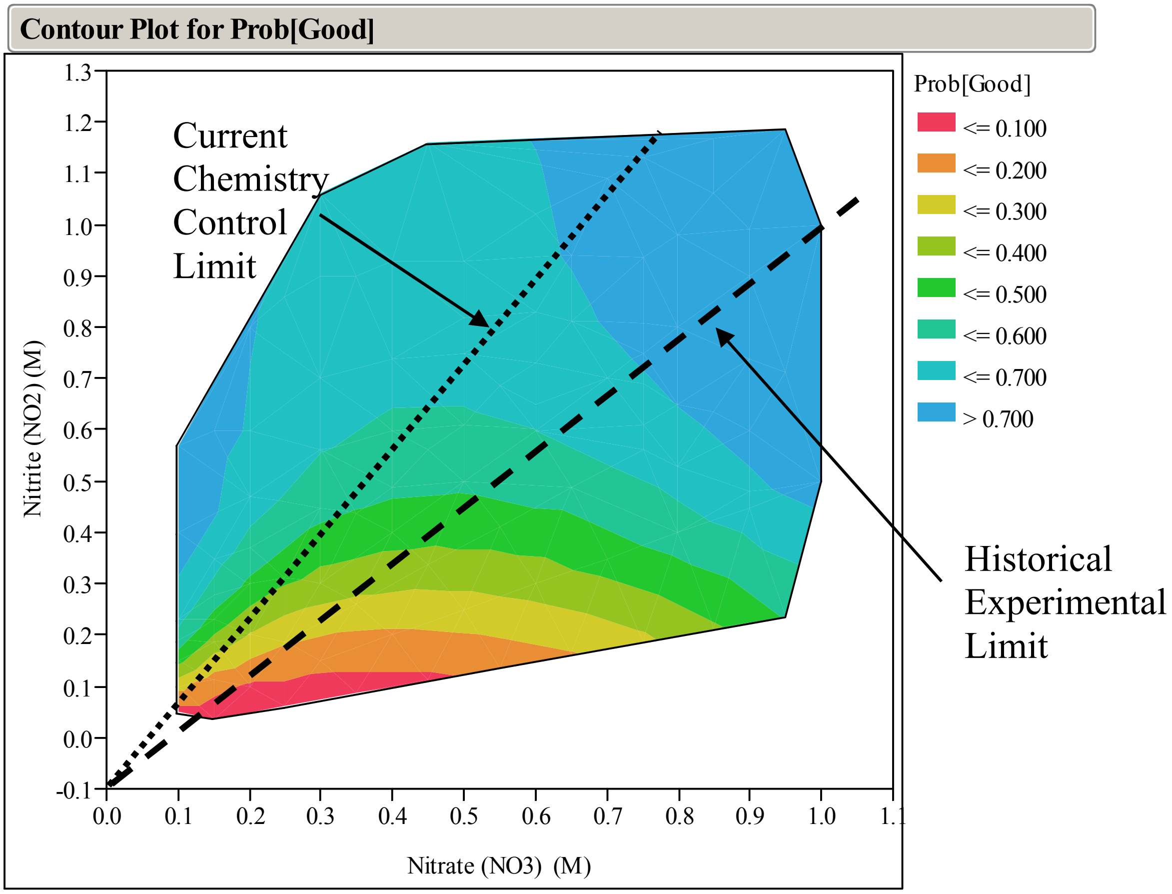


Fig. 4 Contour plot for probability of a "no corrosion" outcome developed from the FY09 and even trials of FY08 developed from the mixture/amount model. The shaded regions represent probabilities of a good outcome, i.e. no pitting.

Unlike a simple linear fit, the more complex mixture/amount model requires significantly more experimental data to ensure a degree of high probability. Based on the current amount of data, the model is only able to determine probability limits up to >70%. However, when comparing the probability contours of the mixture/amount to the current chemistry control limit follows the slope of the model contours in the nitrate concentration region of 0.1 - 0.4 M.

CONCLUSIONS

Localized corrosion, pitting and stress corrosion cracking, of ASTM A537 carbon steel tanks in contact with alkaline radioactive waste solutions is prevented or mitigated by adherence to the requirements of a formal chemistry control program. The program specifies minimum concentrations of the inhibitors sodium hydroxide and sodium nitrite based on the concentration of nitrate, the principal corrosive anion in the waste. In response to new operating challenges as the waste is prepared for vitrification and ultimate disposition, a statistically designed experimental study has been undertaken to improve in particular the effectiveness of the minimum nitrite concentrations to inhibit pitting corrosion. The study used cyclic potentiodynamic polarization testing as an accelerated method to measure the pitting susceptibility in solutions containing varying concentrations of nitrate and nitrite.

Analysis of the results indicated that pitting susceptibility in A537 carbon steel depends on the ratio of aggressive to inhibitive anions, as well as the concentration of each species. This relationship is termed a mixture/amount model. This model, which is applicable in the solution sets between 0.1 and 1.0 M nitrate, yields a probability of pitting as a function of nitrate and nitrite concentration. In the upper regime of nitrate concentration (0.8 - 1.0 M) the model suggests that less nitrite is needed compared to the intermediate regime of 0.4 - 0.8 M nitrate to achieve the same level of pitting probability. This result further supports the reduction of the chemistry control nitrite inhibitor concentration in the regime of 0.8 - 1.0 nitrate. A reduction in the inhibitor concentration in the region of 0.8 - 1.0 M nitrate leads to a cost savings in sodium nitrite additions as well as a conservation of waste volume.

REFERENCES

1. E.N. HOFFMAN, “Probability Based Corrosion Control for High Level Waste Tanks”, SRNL-STI-2008-00539, (2009).

2. T.B. EDWARDS to E.N. HOFFMAN, “A Statistically Designed Experiment to Support the Study of Corrosion Inhibition”, SRNL-SCS-2005-00024, Rev. 1, Savannah River Nuclear Solutions, (2008).

3. T.B. EDWARDS to E.N. HOFFMAN, “Statistical Analysis of Corrosion Data”, SRNL-L5100-2008-00002, Savannah River Nuclear Solutions, (2008).

4. R.L. SINDELAR, B.J. WIERSMA, “SRS High Level Waste Tank and Piping Systems – Structural Integrity Program and Topical Report”, WSRC-TR-95-0076, (1995).

5. “CSTF Corrosion Control Program”, WSRC-TR-2002-00327, Rev. 4, (2007).

6. P.E. ZAPP, “Recommended Nitrite Limits for Chloride and Sulfate in ESP Slurries”, Westinghouse Savannah River Company, WSRC-TR-94-0250, (1994).

7. P.E. ZAPP and D.T. HOBBS, “Inhibiting Pitting Corrosion in Carbon Steel Exposed to Dilute Radioactive Waste Slurries”, Paper no. 98, CORROSION/92, NACE, Houston, TX, (1992).

8. J.A. CORNELL, Experiments with Mixtures: Designs, Models, and the Analysis of Mixture Data, Third Edition, John Wiley & Sons, Inc., New York, (2002).

9. M. POURBAIX, “Applications of Electrochemistry in Corrosion Science and in Practice”, *Corrosion Science*, 14, (1974).

10. R. S. ONDREJCIN, “Chemical Compositions of Supernates Stored in SRP High Level Waste Tanks”, DP-1347.

11. W.S. TAIT, An Introduction to Electrochemical Corrosion Testing for Practicing Engineers and Scientists, Racine, WI: Pair O Docs Publications (1994).

12. J.W. CONGDON, and J.S. LOZIER, “Inhibition of Washed Sludge with Sodium Nitrite”, DPST-87-379, (1987).