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The Development of the Corrosion Control Limits for Direct Feed Low-Activity Melter Off Gas Returns to Hanford Tank Farms

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Abstract

The Savannah River National Laboratory has been developing a corrosion model to facilitate implementation of Hanford's Direct Feed Low Activity Waste (DFLAW) flowsheet. Laboratory testing and statistical analysis has been used to determine the necessary corrosion controls for returning effluent from the Hanford Waste Treatment and Immobilization Plant's Low Activity Waste Vitrification melter off-gas treatment system to the tank farms. The stream compositions are projected to contain components at relative concentrations that are significantly more corrosive toward carbon steel, specifically halide and sulfate anions, than the current waste compositions in the tank farms. Administrative programs are in place to mitigate potential corrosion mechanisms and thereby maintain the structural and leak integrity functions of these waste tanks throughout their intended service life. Waste chemistry and temperature control are the means by which corrosion degradation of the waste tanks is minimized. The current administrative specification for chemical composition and temperature for the underground carbon steel waste tanks are not designed to control the higher halide or sulfate composition.

The content of the waste streams will be diverse and depend on several factors, such as the melter feed composition, and melter idle time. Other factors such as, effluent management of the off gas water collections will impact the variability of the return streams even more. The work performed by the Savannah River National Laboratory has confirmed that the halide ions are the most aggressive species in the return stream compositions based on operation computer simulation results, and nitrite is the most effective inhibitor at pH 10 and 40°C. This test program has employed statistically designed test matrices to determine the dependent variables and the interaction terms between the variables that are significant for the corrosion model and definition of the corrosion control specifications. The first phase of testing focused on identifying aggressive species in off-gas condensate return compositions that present a propensity for localized corrosion attack, namely pitting corrosion. The second phase of testing focused on developing a corrosion model from the interaction terms that will predict the susceptibility of pitting in the double shell tank system based on waste composition and the required amount of corrosion inhibitor. The data collected from this testing program in conjunction with other testing programs, both at the Savannah River Site and the Hanford Site, along with operations knowledge, has determined the chemistry ranges and chemical species requirements for corrosion control in the Hanford double-shell tank system for the effluents generated in the DFLAW facility.

Introduction

The Savannah River National Laboratory has been developing a corrosion model to facilitate implementation of Hanford's Direct Feed Low Activity Waste (DFLAW) flowsheet with the focus on returning waste residues, specifically off gas collections from the Low Activity Waste (LAW) melter to tanks farms. The return stream effluent will be generated by condensing and scrubbing the off-gas stream from the LAW melter. The primary option for management of this waste stream is to recycle the collection to the LAW melter after volume reduction by an evaporator. As the Tank Waste Disposal Integrated Flowsheet (TWIDF) matures, the management plan for this waste stream includes a strategy to return a percentage of this stream to tank farms as evaporator feed or evaporator bottoms.[1]

The aqueous collections will be high in chloride, fluoride, and sulfate ion, and potentially small amounts of mercury. All of which can be detrimental to the carbon steel waste tanks through localized corrosion mechanisms if not chemically inhibited. The current corrosion control protocols for the Double Shell Tank System (DSTs) in the Hanford Tank Farms will be expected to handle these waste streams. At present the tank farm facility has no corrosion control measures for the waste tanks or the 242-A evaporator that address the halides and sulfate anions. The Savannah River Site (SRS) has data on chlorides and sulfates that may apply to the Hanford waste tanks.[2] However, application of the data at Hanford would require addition of a significant quantity of inhibitor and dilution water to first reduce the halide and sulfate concentrations into the range for which the SRS data was developed.[3]

This paper discusses the corrosion control specification development for high-halide content waste for the Hanford DSTs. This work is one example of an appropriate approach taken to understand and determine the corrosion mechanisms, to identify aggressive species, and determine appropriate inhibitor concentration and temperature requirements necessary to mitigate corrosion.[4] Here we demonstrate how statistical methods are used to optimize testing and uncertainty analysis to supplement the mechanistic understanding of the corrosion process and provide an all-encompassing corrosion specification for the high-halide return streams.[5]

Experimental Methods

The off-gas return streams are expected to have a wide range of compositions that results from the range of compositions of LAW treated and immobilized in the DFLAW flowsheet. This range directly impacts the composition of return streams to tank farms. The testing range for aggressive ions, such as sulfate, chloride, fluoride, and nitrate, were increased by 30% of the maximum expected concentration and the inhibitor species, such as nitrite, were decreased by 30% of the minimum expected concentration. The test ranges for the anticipated chemistry are given in Table 1. The compositions were all adjusted to a pH of 10 and tested at 40°C.

Table 1.

Variables and Constants for Anticipated Stream Conditions

Independent variable Concentration in moles per liter (M)			Dependent Variables	Constants	
	Minimum	Maximum	E_{rp} (V)	Potassium	0.01
Sulfate	0.0	0.45	E_{corr} (V)	pH	10
Chloride	0.01	1.63	E_{rp} - E_{corr} (V)	Temperature (°C)	40
Fluoride[a]	0.0	1.04			
Nitrite	0.0	4.0			
Nitrate	0.01	2.6			
Carbonate [b]	0.0	0.07			
Phosphate [b]	0.0	0.013			

[a] Fluoride was omitted in later test matrices due to solubility issues at high concentration.

[b] These constituents were held constant at the midpoint concentrations for the Box-Behnkin Test Matrix at 0.035 M for Carbonate and 0.013 M for Phosphate .

Test matrices were statistically designed to satisfy specific elements of the corrosion control development process. The initial test matrix of 19 test conditions used a constrained Plackett-Burman statistical design. The results from this test were used to design a second experimental matrix of 28 tests to refine the model and estimate the interaction terms between the variables. The second experimental matrix was designed using a Box-Behnkin statistical design. Using this methodology, four other test matrices were designed and the results were analyzed, each set of results guiding the next test matrix in order to optimize the corrosion control requirement to inhibit chloride pitting.

Electrochemical corrosion tests were performed to screen chemistry compositions for pitting corrosion using the Hanford testing protocol.[6]\Martin] The technical details of the protocol and methods of analysis are described elsewhere.[7,8] \NACE 2017, \Wyrwas 2017] Briefly, Cyclic Potentiodynamic Polarization tests were performed using the parameters defined in the Hanford testing protocol. The protocol defines standardized categories to for results interpretation and an additional potentiostatic-type of test to be performed when the tests results are borderline. This testing focused on the boundary region of the aggressive-inhibitor species relationship. Testing in and around boundary regions can give mixed results in electrochemical corrosion testing. In interpreting the results for the development of the model, the worst-case scenario was assumed from the electrochemical tests. The electrochemical tests are performed in duplicate and can sometimes yield no pitting for one test and pitting for the duplicate test. The Hanford testing protocol delineates how to decisively define pitting and non-pitting cases based on the electrochemical data, but does not define how to handle differing results between duplicate scans. A low risk, safe approach is to consider one failure as a failing result. In this testing, particularly the later test matrices that focused around the boundary, split results were more common and are represented as pitting results in the data presented.

Results and Discussion

The results from the Plackett-Burman test matrix showed that the chloride ion is the most aggressive ion in the DFLAW recycle stream and the nitrite ion is the best inhibitor species present.[8]\NACE 2016] The statistical analysis further determined the sulfate and nitrate ions to be the next most significant species in the testing. These results were as expected based on prior experience.[9,10] \RIE 2015, \Hoffmann 2011]

The Box-Behnkin test matrix used the results from the Plackett-Burman test to determine the interaction terms among nitrite, chloride, nitrate, and sulfate (i.e., the more statistically significant variables). The carbonate and phosphate species were found to have little significance on the corrosion of carbon steel, so the concentration values for these compounds were held constant at the respective mid-point concentration. Using this analysis, fluoride was excluded from the remainder of the test matrices for the following reasons:

- Thermodynamic modeling predicted that fluoride would precipitate with sulfate; this was confirmed by laboratory trials. This constraint complicated the statistical design of the test matrix.
- Literature data and the results from the Plackett-Burman testing indicate fluoride is less aggressive than chloride; when compounded with the limited solubility of fluoride in the more concentrated streams, i.e. evaporator bottom streams, the chloride concentration could be used as a total halide limit.
- Fluoride was found to be only moderately significant in the Plackett-Burman tests.
- Sulfate has been shown to be aggressive toward carbon steel and was only found to be moderately significant in the Plackett-Burman tests. However, this may have been due to the presence of and interaction with fluoride.

The results from the Plackett-Burman test matrix and the Box-Behnkin test matrix were combined to yield a relationship response between chloride and nitrite. A logistical regression analysis was used where the tests results were defined to be either as a pitting or non-pitting result. Equation 1 and Equation 2 below represent the results of the regression analysis, where P(1) is the probability of pitting. The nitrite required to inhibit chloride pitting can be represented as the boundary given in Equation 3 for P(1)= 0.95 confidence limit. The test results and corrosion control boundary equation as plotted in Figure 1 with historic data, related to the development of this project.[9]\RIE] Points that fall below the line have a higher probability of pitting than points above the line and the probability increases the further away from the line.

Equation 1

$$P(1) = \frac{1}{1 + \text{Exp}([\text{Lin}(0)])},$$

Equation 2

$$\text{Lin}(0) = -15.5 + 0.465\ Na_2SO_4 - 76.2\ NaCl + 15.7\ NaNO_2 + 0.192\ NaNO_3$$

Equation 3

$$[\text{Nitrite}] = 0.805 + 4.9\ [\text{Chloride}]$$

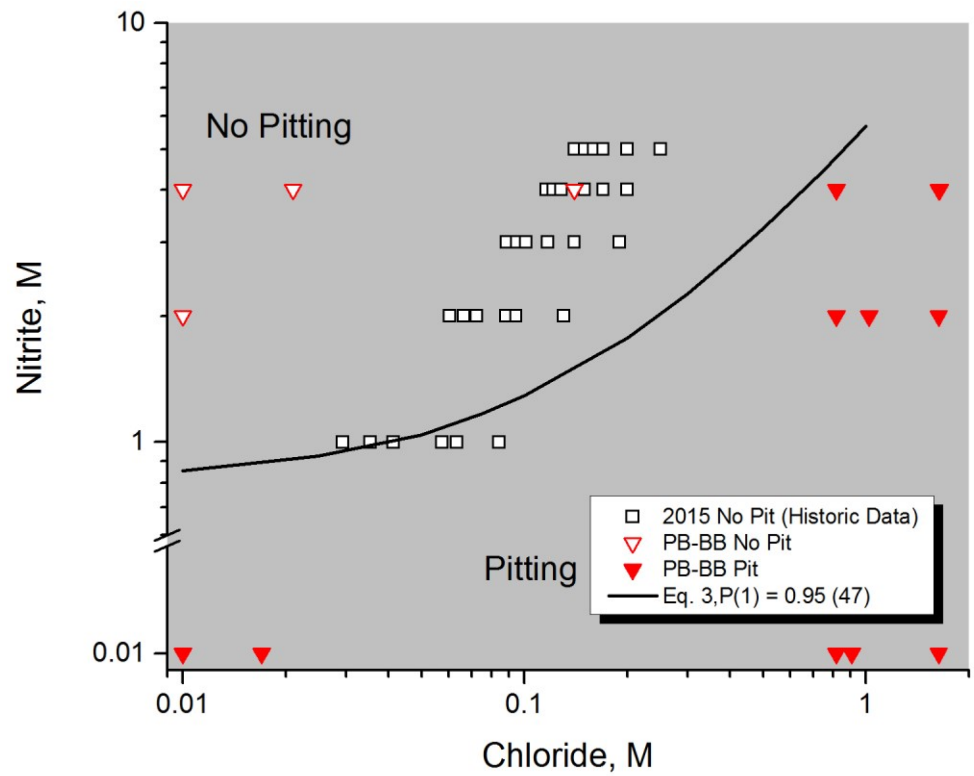

Figure 1. Test matrix points for Plackett-Burman (PB) and Box-Behnkin (BB) plotted with the preliminary boundary equation. Solid symbols indicate pitting corrosion. Historic data is also plotted for reference.

After establishing the relationship between these two variables, testing focused on optimizing the nitrite requirement and exploring the impact on other corrosion inhibitors, specifically pH. Four independent test matrices were designed with key independent variables in mind: pH 12 test matrix, gap specific testing, boundary validation, and confirmatory testing. A Box-Behnkin test matrix was designed to investigate the impact of operating at pH 12. These test results indicated that there was no significant impact at pH 12. This result was in agreement with testing for Nitrate induced pitting corrosion and that higher pH values were needed to inhibit pitting.[11]\Roderick

Once Equation 1 was established as a boundary between the pitting and no-pitting domains, testing focused on the data gaps along that boundary. More specifically, there were very few pitting cases at halide concentrations less than 0.1 M halide. Historically, there are many in this region and the desire is to have the model cover the dilute range as well. The second region between 0.2 and 0.8 M chloride did not have many data points near the boundary line. The plot in Figure 2 shows the Margin test conditions along with the results for those tests.

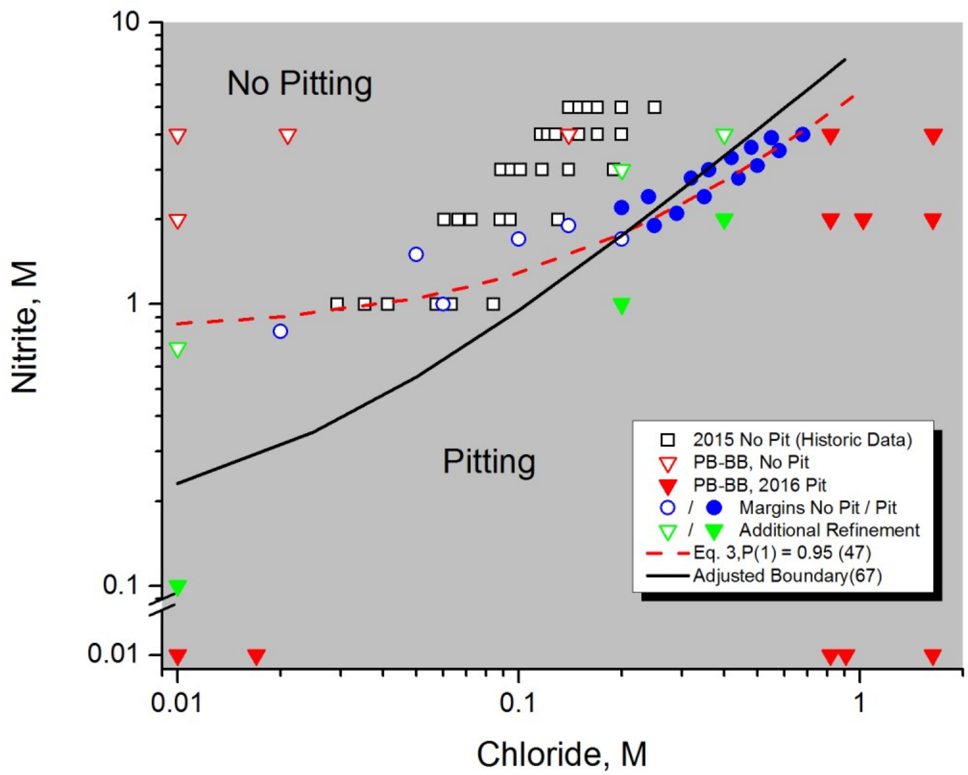

Figure 2. Plot of the Margin test points and adjusted boundary equation.

A series of 6 additional tests points were identified as significant tests for model refinement. These tests are indicated by the green triangles in Figure 2. The model defining the boundary could then be refined using the results of these points and the adjusted result is also shown in Figure 2.

The final step in the process was to confirm the refined preliminary model. The test matrix to confirm the model was designed to address two criteria: 1) Adequately cover the range of test variables, and 2) Adequately validate the model equation around the boundary conditions. Figure 3 shows the final test matrix conditions that satisfy these conditions.

Figure 4 shows the results of the final test matrix along with the final boundary that is defined by Equation 4. The final equation was optimized with more data points than the previous equations along with a lower confidence interval than the previous iterations, P(1) = 0.05 which translate to P(0) = 0.95. The lower confidence limit, or the higher confidence limit to find non-pitting conditions, provides an all-encompassing corrosion specification with an appropriate margin of safety that minimizes the risk of the tanks operating within this chemistry regime.

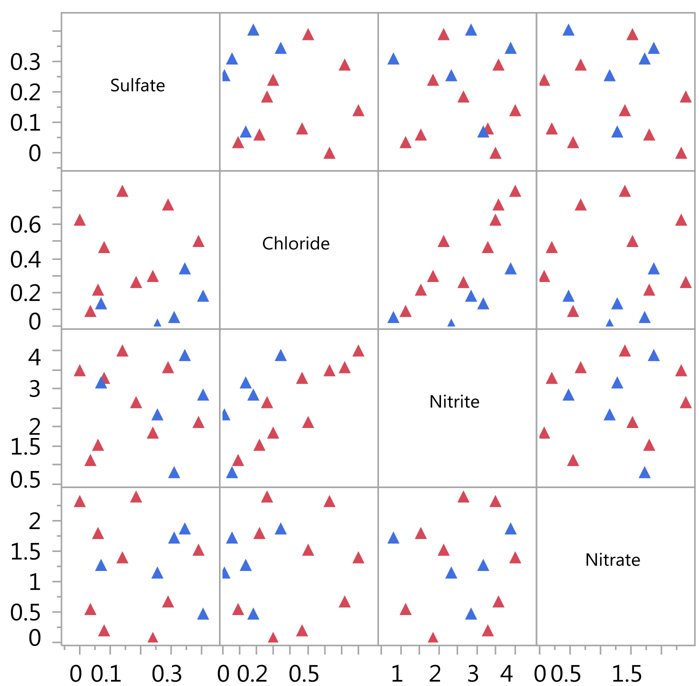

Figure 3. The final test matrix used to confirm the corrosion model and boundary equation.

In the development of Equation 4, which is the optimized equation for chloride induced pitting of carbon steel, there are a few considerations that should be discussed. This specification does not stand alone however, as other waste compositions are present in the Hanford DSTs, such wastes are high in nitrate. In the waste compositions where nitrate is much greater than the halide concentration, the current Hanford DSTs corrosion specification may suffice since additional inhibitor requirements, such as hydroxide, are adequate to inhibit the lower halide content as well.

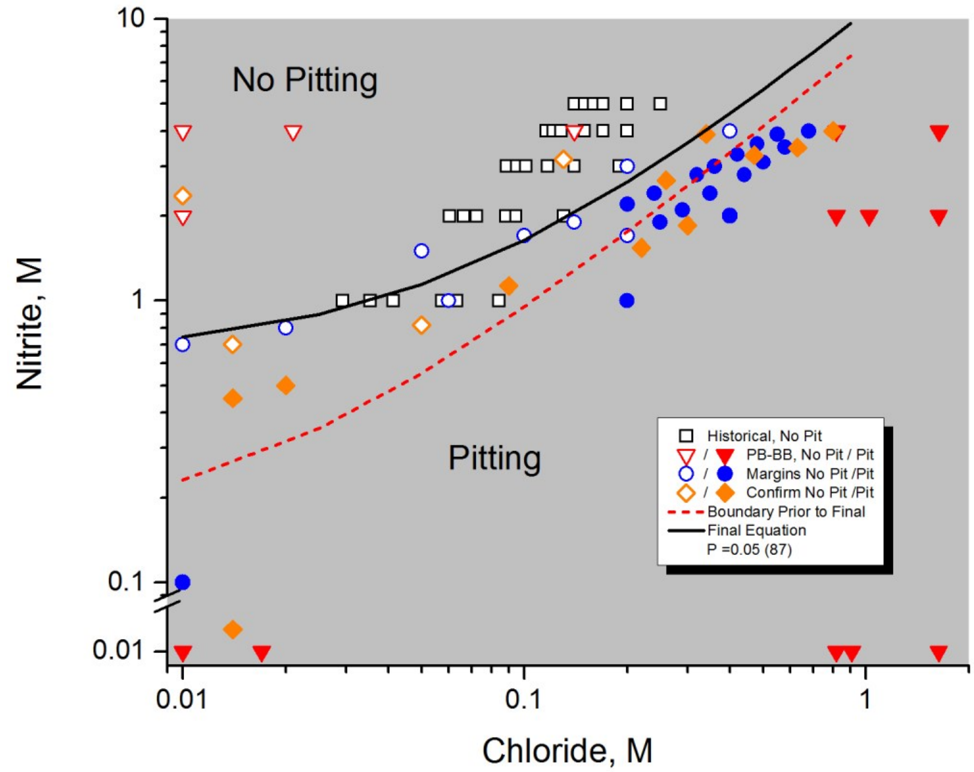

Figure 4. Confirmatory results and final optimized corrosion model to inhibit chloride induced pitting.

Equation 4

$$[NO_2^-] = 9.97\ [\text{Chloride}] + 0.65$$

Conclusions

The final corrosion model to inhibit high-halide waste in the Hanford DSTs has been defined in Equation 4. This specification was developed using a combination of corrosion mechanism knowledge combined with statistical methods of design and analysis to optimize testing. This iterative process has provided a chemical inhibitor scheme that will be incorporated with other testing program results, process knowledge, and waste tank storage knowledge from SRS to provide a revised corrosion control specification for the Hanford Tank Farms.

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