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Relationship Between the Marginal Probability of Failure for a CPP Test and the Recommended Corrosion Control Requirements for Hanford Double Shell Waste Tanks

B. J. Wiersma

S. P. Harris

March 2022

SRNL-STI-2022-00060, Revision 0

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Printed in the United States of America

Prepared for
U.S. Department of Energy

Keywords: *Hanford Double Shell Tanks, Chemistry Control, Pitting Factor*

Retention: *Permanent*

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Savannah River National Laboratory is operated by Battelle Savannah River Alliance for the U.S. Department of Energy under Contract No. 89303321CEM000080.

REVIEWS AND APPROVALS

AUTHORS:

____
B. J. Wiersma, Environmental and Legacy Management Directorate, Materials Technology Division
Date

____
S. P. Harris, Science, Engineering and Energy Directorate, Computation and Modeling Division Date

TECHNICAL REVIEW:

____
J. T. Boerstler, Environmental and Legacy Management Directorate, Materials Technology Division
Date

APPROVAL:

____
J. Manna, Manager Date
Environmental and Legacy Management, Materials Technology Division

____
J. S. Page, Manager Date
Washington River Protection Solutions, Tank and Pipeline Integrity

____
R. J. Nelson, Manager Date
Washington River Protection Solutions, Program Manager

EXECUTIVE SUMMARY

The Hanford Site in Washington State currently stores millions of gallons of radioactive waste in underground, carbon steel, double shell tanks (DSTs) that were constructed between 1968 and 1986. A chemistry control and monitoring program has been established mitigate corrosion in order to extend the service life for the DSTs. The current waste temperatures in the DSTs are at historical lows (i.e., typically less than 50 ◦C). The previous chemistry control requirements were determined for conditions at temperatures significantly higher. SRNL undertook a statistically based investigation of the role of nitrate and halide ion (i.e., chloride and fluoride) induced pitting corrosion. The objective was to develop a comprehensive waste chemistry envelope for the simultaneous minimization of the pitting and SCC risks caused by halide and nitrate ions at the lower temperature conditions. On the basis of these tests, new chemistry control requirements were proposed and have since been implemented for pitting corrosion control.

In the fall of 2021, the Corrosion Sub-group (CSG) of the TIEP performed a review of the newly implemented chemistry control requirements for the Hanford DSTs. The primary considerations during the three meetings were:

1) Observations of a CPP test “pass” condition, even though the PF calculation predicted a “fail”.
2) For dilute solutions, the PF limit may be non-conservative with respect to the probability of failure of the CPP test.
3) A direct mathematical relationship between the PF and the probability of failure had not been established.
4) The Log [OH-] vs. PF plot did not clearly show the risk or probability of failure. The plot also did not definitively illustrate the effect of the other new chemistry limit controls (e.g., a minimum [NO_2^-].

This document summarizes the conclusions and recommendations from the discussions at these meeting.

The following conclusions and recommendations were made based on this review.

- Three mathematical representations are helpful in visualizing the relationship between the probability of failure and the ratio of the weighted inhibitor concentrations and the weighted aggressive species concentrations, the minimum weighted inhibitor concentration, and probability of failure of a CPP test.
- Probability profiles (gradients) and contours can be added to figures to help visualize the relationship between the probability of failure of a CPP test and the new chemistry limits.
- Individual inhibitor or aggressive species could not be mathematically related to the probability of failure. Instead, weighted inhibitor and weighted aggressive species concentrations were mathematically related. The weights for each species were tied to the logistic regression model for the experimental CPP data.
- Probability contours and profiles (or gradients) indicate that maintaining the inhibitor levels above the new chemistry limits ensure that the environment is benign with respect to pitting corrosion (i.e., a low marginal probability of failure).
- Historical CPP tests validated that in low probability regions (i.e., less than 12%), all tests were a “pass” condition.
- Historical CPP tests with high concentrations of TOC or high concentrations of TOC resulted in a “pass”, even though PF was significantly less than 1.2. It should be noted that the minimum hydroxide and nitrite concentrations were exceeded for the tests with high TOC, whereas this was not necessarily true for the very dilute TIC solutions.

- The profiler function for the JMP™ statistical package may be utilized to perform simulations for anticipated waste chemistries based on the statistical model and the anticipated DST waste compositions.
- Further CPP testing at more dilute solutions with lower levels of aggressive species (e.g., chloride) may provide additional data that would refine the model and allow for lower minimum inhibitor requirements.
- Further CPP testing may be utilized to incorporate TOC and TIC into the logistic regression model.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

SRNL	Savannah River National Laboratory
CPP	Cyclic Potentiodynamic Polarization
PF	Pitting Factor
WRPS	Washington River Protection Solutions
TIEP	Tank Integrity Expert Panel
DST	Double Shell Tank
LAI	Liquid Air Interface
CSG	Corrosion Sub-Group

1.0 Introduction

The Hanford Site in Washington State currently stores millions of gallons of radioactive waste in underground, carbon steel, double shell tanks (DSTs) that were constructed between 1968 and 1986. Most of these tanks have been in service for more than 35 years and it is anticipated that they will be needed for several more decades. Corrosion mechanisms are the most likely form of degradation for the carbon steel tank. A chemistry control and monitoring program was established mitigate corrosion during their service [1].

In light of the failure of tank AY-102 due to pitting corrosion of the tank bottom, Washington River Protection Solutions (WRPS), the Hanford site contractor for the DST facility, has utilized the Tank Integrity Expert Panel (TIEP) Corrosion Sub-group (CSG) to advise and recommend necessary testing to promote the mitigation of corrosion degradation of the DSTs. Since 2015, DNV-GL, a corrosion testing laboratory in Ohio, the Savannah River National Laboratory (SRNL), and the 222-S laboratory at the Hanford Site laboratory have collaborated to investigate pitting and LAI corrosion at current and anticipated DST chemistries. The current waste temperatures in the DSTs are at historical lows (i.e., typically less than 50 ◦C). The current chemistry control requirements were determined for conditions at temperatures significantly higher. SRNL undertook a statistically based investigation of the role of nitrate and halide ion (i.e., chloride and fluoride) induced pitting corrosion. The objective was to develop a comprehensive waste chemistry envelope for the simultaneous minimization of the pitting and SCC risks caused by halide and nitrate ions at the lower temperature conditions.

SRNL conducted electrochemical tests to investigate pitting corrosion at current and anticipated DST waste chemistries and temperatures between 2015-2019 [2-6]. The testing utilized a protocol for cyclic potentiodynamic polarization (CPP), developed in conjunction with the Tank Integrity Expert Panel Corrosion Sub-group (TIEP-CSG), to assess the susceptibility of carbon steel to pitting corrosion in DST chemistries [7]. The "pass" or "fail" condition was determined from the six categories specified by the CPP test protocol. Statistically designed test matrices were utilized to explore the boundaries of the DST chemistry envelope as well as interior points within the envelope [2, 3]. CPP tests at 110 simulated waste conditions were performed and evaluated.

Logistic regression analysis (LRA) was performed to develop the model for pitting susceptibility prediction [4-6]. Logistic regression assumes a binary response, pass or fail in this instance. The marginal probability of a failure, as determined from the CPP test, is predicted from Equation 1. (Note: "1" is indicative of a failure, while "0" indicates a pass condition). The statistical analysis indicated that a linear relation existed between the statistically significant variables. The statistically significant variables were hydroxide, nitrate, nitrite, chloride and fluoride. Equation 2 shows the linear relationship between the statistically significant variables and the coefficients calculated from the statistical analysis. Inhibitor species are indicated by a positive coefficient, while aggressive species have a negative coefficient.

$$P(1)=\frac{1}{1+e^{Lin[0]}} \qquad \text{Equation 1}$$

$$Lin\,(0) = 1.99 + 15.54\,[OH^-] + 2.99\,[NO_2^-] - 1.93\,[NO_3^-] - 32.11\,[Cl^-] -10.7\,[F^-] \qquad \text{Equation 2}$$

The probability in Equation 1 may be considered a "marginal probability" and provides a snapshot in time of the relative probability of whether a given waste chemistry is aggressive or benign. The coefficients for the species variables generated from the probability model were utilized in the development of an empirical "pitting factor", PF, to provide a criterion for pitting susceptibility the could be utilized for the DST chemistry control program [6, 7]. Equation 3 shows the final form of the pitting factor. The pitting factor is a weighted ratio of the inhibitor species to the aggressive species.

$$PF = \frac{8.06*[Hydroxide]+1.55*[Nitrite]}{[Nitrate]+16.7*[Chloride]+5.7*[Fluoride]} \qquad \text{Equation 3}$$

The correlation between PF and the hydroxide concentration, the principal inhibitor, was initially used to illustrate the recommended waste chemistry control boundaries. The PF for each of the CPP tests that were used to develop the LRA model was calculated and correlated with the free hydroxide concentration for each of the tests as shown in Figure 1-1. The blue dots are test conditions that yielded a "pass", while the red squares are test conditions that resulted in a failure of the CPP test. The green region indicates a chemistry regime where the likelihood of pitting susceptibility is low, while the red region indicates a chemistry regime where pitting susceptibility is more likely. These diagrams provide initial direction toward the development of the new chemistry limits [Wiersma, Stock, Fuentes]

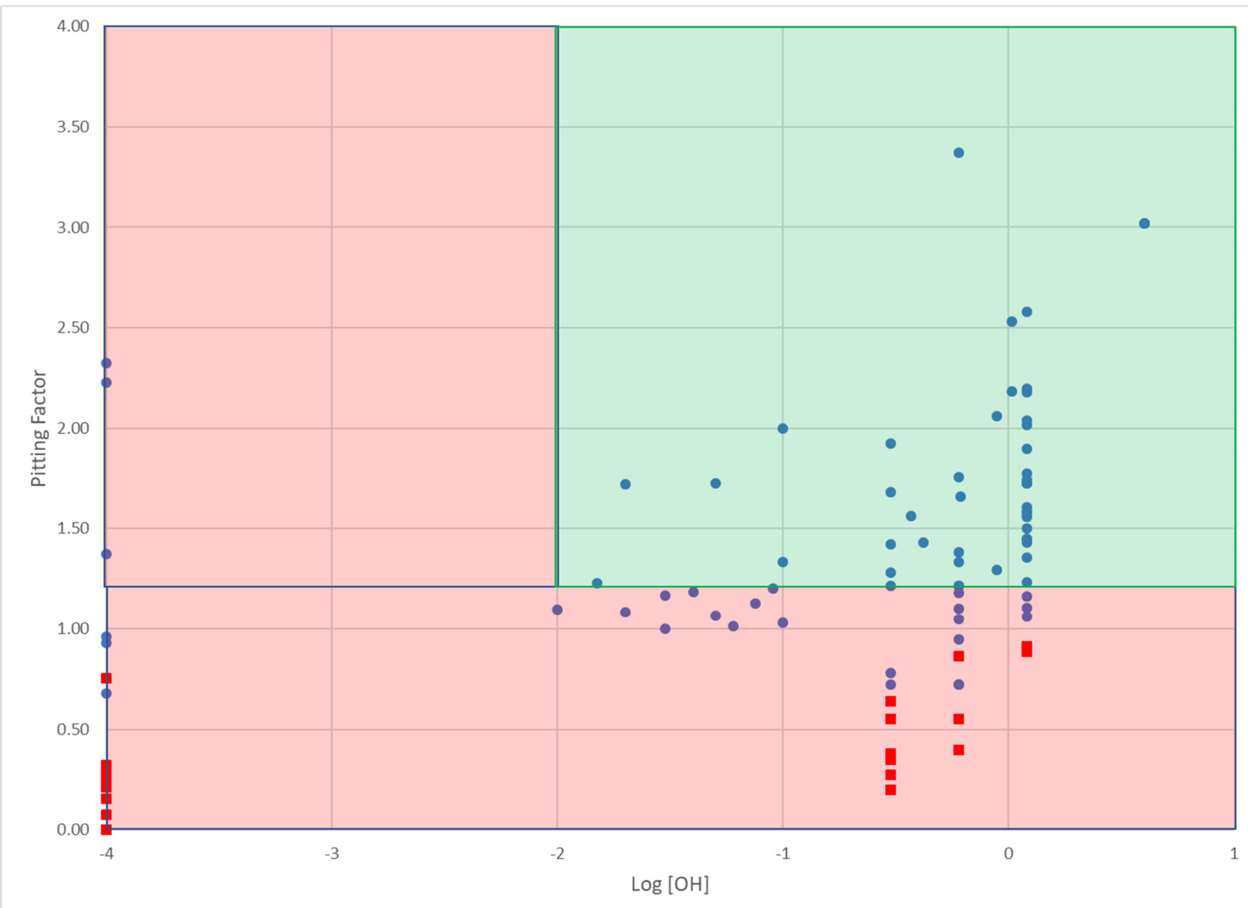

Figure 1-1. Summary of testing data utilized to develop the logistic regression model for 50 °C or less. The blue circles indicate a "pass" condition, while the red squares indicate a "fail" condition. Note that several tests were performed at Pitting Factors greater than 4. All these conditions were a "pass" or no pitting condition.

The waste chemistry envelope for pitting corrosion control was verified by two methodologies: (i) randomized parameter simulation studies and (ii) comparison with historical data [reference]. Randomized parameter simulation studies investigated the marginal probability of failure of a CPP test for possible DST chemistries. The simulations were performed with an EXCEL™ spreadsheet. Up to 2000 random waste chemistries were generated from concentrations of hydroxide, nitrite, nitrate, chloride, and fluoride. Ranges on the random compositions for each species were simulated based on the chemistry envelope shown in Table 2 (e.g., a minimum nitrite concentration of 0.20 M, a maximum nitrate concentration of 5.5 M etc.). For each composition, the pitting probability and pitting factor were correlated.

Figure 1-2 shows the log [OH^-] vs. the pitting factor and the probability of failure for each of the random simulations. Table 1-1 shows the relationship between the colors in the figure and the probability of pitting. For a pitting factor less than 1, the probability of pitting is typically greater than 0.2, with most of this range having a pitting probability greater than 0.5. For a pitting factor greater than 2, the probability of pitting was always less than 0.01. For a pitting factor between 1 and 2, the probability ranges between less than 0.01 to less than 0.2. Clearly, the hydroxide ion concentration has a significant influence on the probability that is observed. The initial chemistry boundaries from Figure 1-1 (i.e., acceptable vs. unacceptable chemistry regimes) were superimposed on the simulation results. For example, when the hydroxide concentration was greater than 0.1 M with a pitting factor greater than 1.2, the pitting probability was always observed to be less than 0.01. However, for a hydroxide concentration less than 0.1 M, but greater than 0.01 M, with a pitting factor between 1.2 and 2, there were several instances where the probability of pitting is up to 0.03.

Results from historical CPP tests were also reviewed to validate the corrosion chemistry requirement envelope (see Figure 1-3). The environmental conditions for the historical tests are shown in Table 1-2. Not all tests were performed with the presently accepted pitting protocol test methodology. However, historical results were validated with the new pitting protocol and observed to produce consistent outcomes [8]. Initially, the PF was calculated for the historical data that were at temperatures less than 50 °C.

The historical data provide confirmation of the pitting susceptibility envelope (i.e., red region) at hydroxide concentrations between 0.0001 and 0.01 M and for PF values less than 1. As can be seen from Figure 1-3, the data collected during the model development did not contain much data in this region. Approximately 80% of the CPP tests performed at waste chemistries with a PF less than 1 failed. This region typically correlates to marginal probabilities as calculated from the model of greater than 0.2. There were no CPP test failures at PF greater than 1.2 and at hydroxide concentrations greater than 0.01 M. For hydroxide concentrations greater than 0.1 M, the marginal probability is less than 0.01, while for hydroxide concentrations between 0.01 M and 0.1 M the marginal probabilities as calculated from the model are less than 0.03. This slightly higher relative probability range demonstrates the influence of the hydroxide concentration on the corrosivity of the waste chemistry.

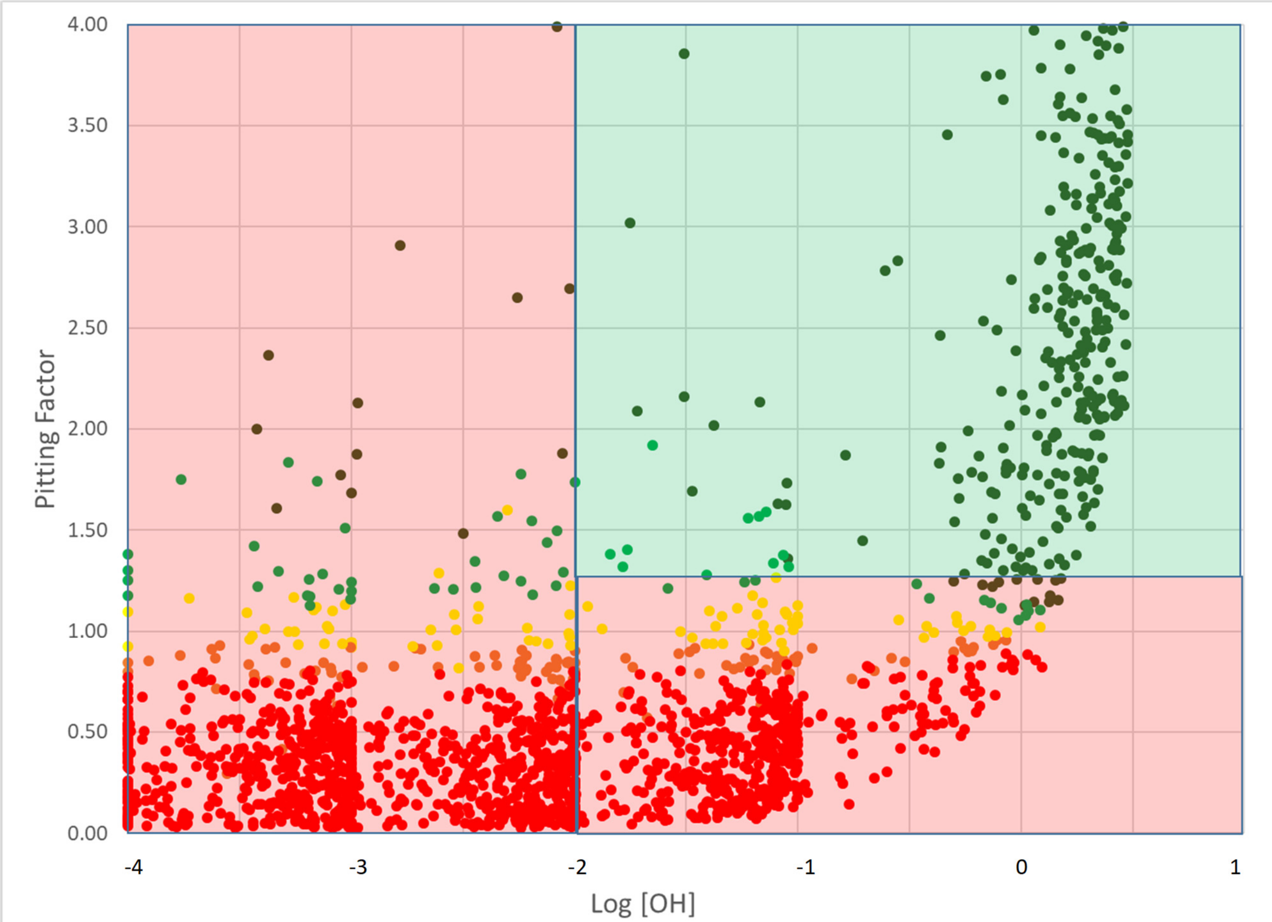

Figure 1-1. Randomized Parametric Simulation. Marginal probability of pitting less than 0.01 is represented by the dark green circles, while all probabilities greater than 0.01 are represented by the red circles. The green shaded area is an acceptable region, while the pink shaded area is unacceptable.

Table 1-1 Legend for Figure 1-1 Probabilities

Color	Marginal Probability of Pitting
Dark Green	< 0.01
Green	0.01 < P < 0.05
Yellow	0.05 < P < 0.20
Orange	0.2 < P < 0.5
Red	P > 0.5

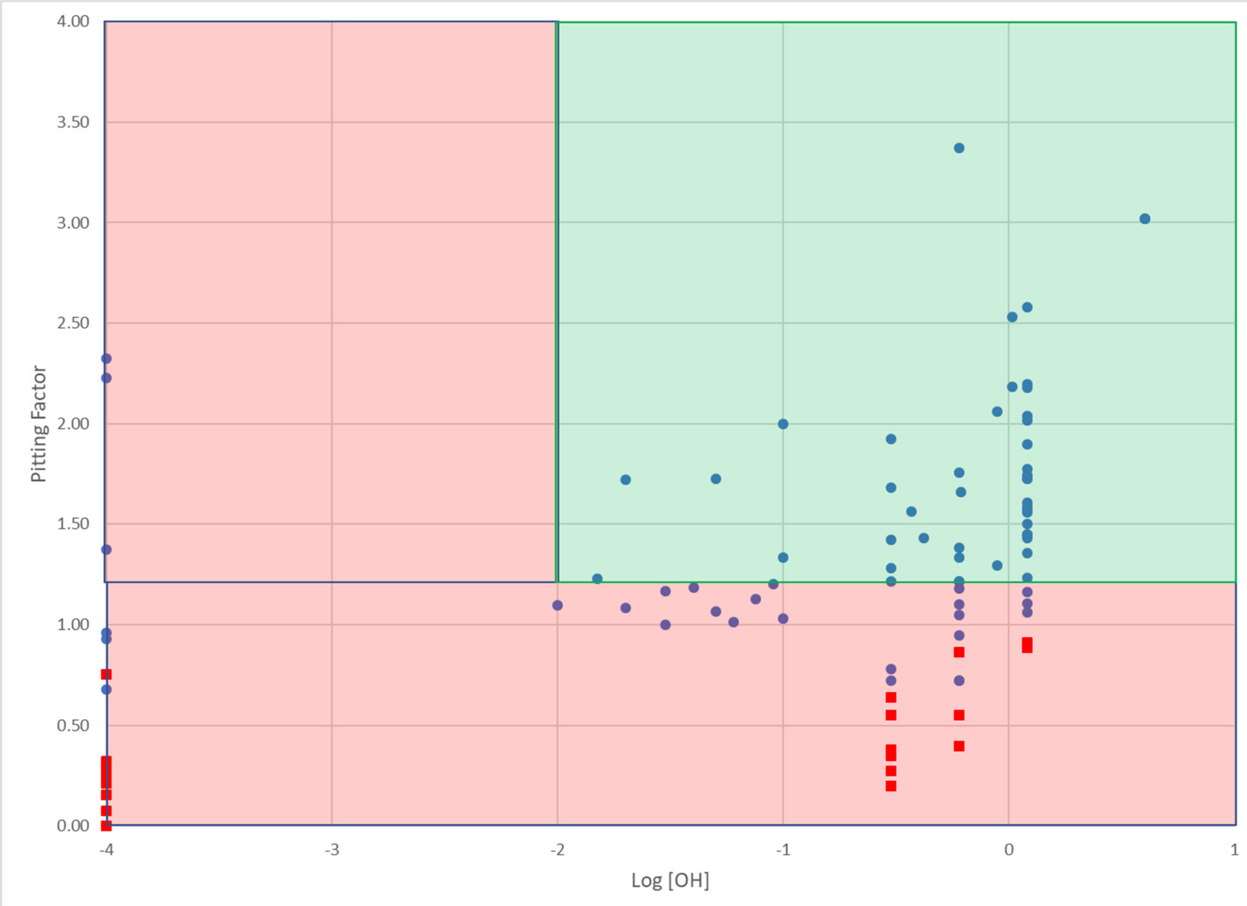

Figure 1-2. Summary of testing data utilized to develop the logistic regression model for 50 °C or less. The blue circles indicate a "pass" condition, while the red squares indicate a "fail condition. Note that several tests were performed at Pitting Factors greater than 4. All these conditions were a "pass" or no pitting condition.

Table 1-2. Range of Compositions and Temperatures for Historical Tests

Species/Temperature	Minimum	Maximum
Hydroxide (M)	0.0001	7.3
Nitrite (M)	0.0	7.0
Nitrate (M)	0.0	5.5
Fluoride (M)	0.0	0.58
Chloride (M)	0.0	0.40
Sulfate (M)	0.0	0.48
TIC (M)	0.0	2.1
Temperature (°C)	20	75

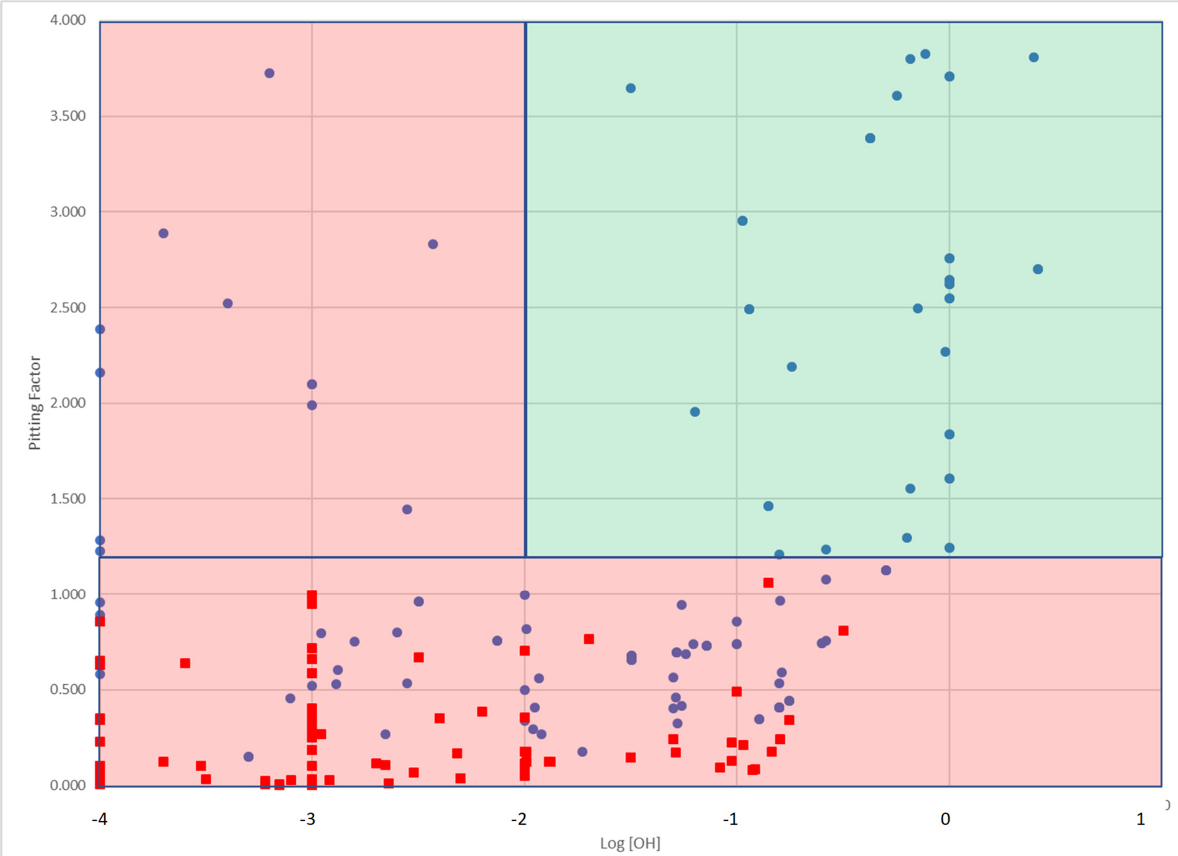

Figure 1-3. Historical experimental results at temperatures between 25 and 50 °C. Circles indicate a test condition that was a "pass", while squares indicate a test condition that was a "fail". Green shaded area is an acceptable region, while pink shaded area is unacceptable.

The chemistry control limits for pitting that were formulated through these investigations are shown in Table 1-3.

Table 1-3. Control Limits for Pitting Corrosion

Limit	Minimum	Maximum
Hydroxide, M	0.01	6.0
Nitrite, M	0.20	
Nitrate, M		5.5
PF	1.2	
Temperature, °C		75

The Log [OH^-] vs. PF relationship does not illustrate the influence of the aggressive species on the determination of the appropriate limits. For example, the pitting susceptibility of carbon steel in dilute nitrate wastes (i.e., on the order of less than 0.1 M). Previous testing at SRS and other labs has shown that, for dilute solutions, a minimum nitrite concentration is required in order to ensure that pitting has been effectively mitigated [9]. At extremely dilute concentrations (e.g., nitrate concentrations less than 0.1 M), higher nitrite/aggressive species ratios are required than are necessary for more concentrated solutions to minimize the likelihood of pitting. This series also demonstrated that, if the nitrite is eliminated, Category 3 and 4 behavior is possible even at PF greater than 1.2 [5]. Additional testing, performed with a minimum nitrite concentration of 0.2 M, and a review of historical data indicated that this level of nitrite in addition to the minimum hydroxide concentration is sufficient to reduce the likelihood of pitting susceptibility in dilute solutions [6].

This initial envelope was a compromise with the present corrosion chemistry requirements, which allow a minimum hydroxide concentration of 0.01 M hydroxide. The restriction on the minimum free hydroxide concentration ensures that carbon steel will experience principally localized forms of attack such as pitting or stress corrosion cracking. Investigations have shown that for pH greater than 9.5 localized attack is favored, while at lower hydroxide concentrations repair of the oxide film does not occur and general corrosion ensues [10]. Pitting attack on carbon steel appears to be broad and shallow, with some patches of localized general corrosion.

It is clear from the previous discussion that the PF approach to chemistry control minimizes the pitting risks associated with nitrate and halide ions, but no maximum concentrations for fluoride and chloride ions are presented in the table. The upper limits used in the statistical testing program were 0.30 and 0.40 M, respectively. But other observations in the historical work strongly suggest that the risks associated with higher concentrations of halide ions can be controlled by adequate concentrations of hydroxide and nitrite ions.

2.0 Discussion on Effectiveness of New Chemistry Controls for DSTs

In the fall of 2021, the Corrosion Sub-group (CSG) of the TIEP performed a review of the newly implemented chemistry control requirements for the Hanford DSTs. The primary considerations during the three meetings were:

1) Observations of a CPP test “pass” condition, even though the PF calculation predicted a “fail”.
2) For dilute solutions, the PF limit may be non-conservative with respect to the probability of failure of the CPP test.
3) A direct mathematical relationship between the PF and the probability of failure had not been established.
4) The Log [OH-] vs. PF plot did not clearly show the risk or probability of failure. The plot also did not definitively illustrate the effect of the other new chemistry limit controls (e.g., a minimum $[NO_2^-]$.

A brief description of each issue follows.

Two historical test environments produced the majority of the cases where a “pass” for the CPP test was observed, while the PF calculation would predict a “fail”. The first environment had a high total inorganic carbon (TIC) concentration. The TIC for these solutions was typically greater than 1 M, while the nitrate concentrations were extremely low on the order of less than 0.1 M. These conditions are representative of tanks such as AY-101 and formerly of AY-102 [references]. The second environment had a high total organic carbon (TOC) concentration. The TOC for these solutions was typically greater than 2 M, while the hydroxide concentration was typically less than 0.01 M. These conditions are representative of tanks such as AN-102 and AN-107 [3, 5]. It should be noted that the TIC utilized in test matrix for the CPP tests was 0.1 M and no TOC was utilized for the test simulants. Other tests have shown that both of these carbonate forms may provide some level of inhibition, although the effects have not been quantitatively defined for the model [11].

During the discussions, J. Belsher of WRPS introduced a concern relative to dilute solutions. The postulated process involved dilution of a concentrated waste supernate, in this case AZ-102, with a more dilute waste from AX-103. Various levels of mixing of the two streams were examined and the concentrations of critical species were calculated. The mixing fraction is defined as the volume of AZ-102 waste divided by the sum of the volumes of wastes from AZ-102 and AX-103. Equations 1 and 4 were utilized to calculate the probability failure for the CPP test and the PF, respectively. Each of these parameters were calculated as a function of the mixing fraction and then plotted as shown in Figure 2-1. At mixing fractions less than or equal to 0.1, both the PF and probability of failure increase exponentially. The increase in the probability of failure is not surprising, however, an increase in the PF is usually accompanied by a decrease in the probability of failure (i.e., increasing the ratio of inhibitor species concentration to aggressive species concentration would result in a more benign corrosion environment). This situation will be more closely examined by constructing a PF vs. probability of failure plot.

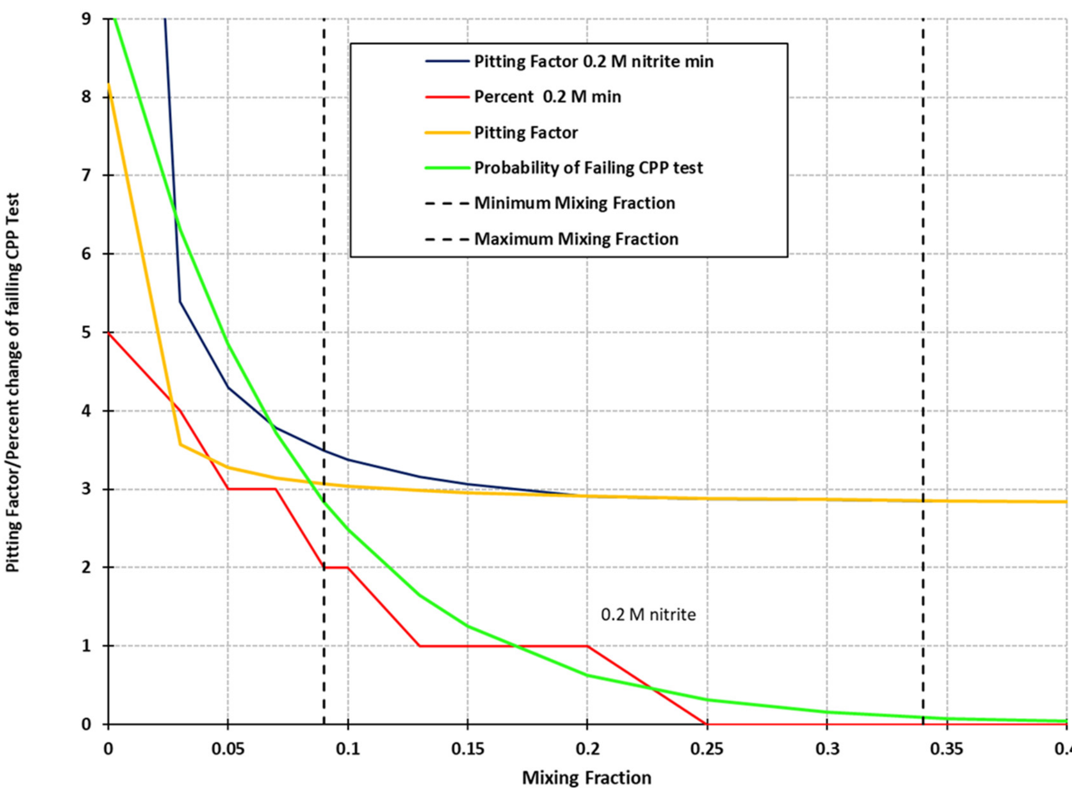

Figure 2-1. Pitting Factor and P(1) vs. Mixing Fraction for Dilute Solutions.

Both of these observations raised questions as to the effectiveness of the pitting factor approach in establishing chemistry regimes where the risk of pitting susceptibility is low. One of the concerns was that a mathematical relationship between the pitting factor and the probability of failure had not been developed. Similarly, an adequate means of visualizing all the chemistry limits (i.e., PF, nitrite, and free hydroxide) on a single plot had not been adequately developed. The next section will develop these mathematical relationships and present more effective ways of visualizing the new chemistry limits.

3.0 Development of the Mathematical Relationship between the Probability of Pitting and the Pitting Factor

3.1 Direct Relationship Between the Probability of Failure and the Pitting Factor

The development of the mathematical relationship began with an examination of equations 1 through 3. Equation 2 provides the linear function that relates the inhibitor species and the aggressive species.

$$Lin(0) = 1.99 + 15.54[OH] + 2.99[NO2] - 1.93[NO3] - 32.11[Cl] - 10.7[F] \quad (2)$$

The aggressive species can be defined as A by Equation 4.

$$A = 1.93\{[NO3] + 16.7[Cl] + 5.7[F]\} \quad (4)$$

Then, Eq. 2 can be transformed using Eq. 3 and 4 as:

$$1 + \frac{Lin(0)}{A} = \frac{1.99}{A} + PF \quad (5)$$

Eq. 5 can be re-written as:

$$Lin(0) = 1.99 - A + (A \times PF) \quad (6)$$

Using Eq. 6 and 1, a plot PF vs. P(1) can be constructed as shown in Figure 3-1.

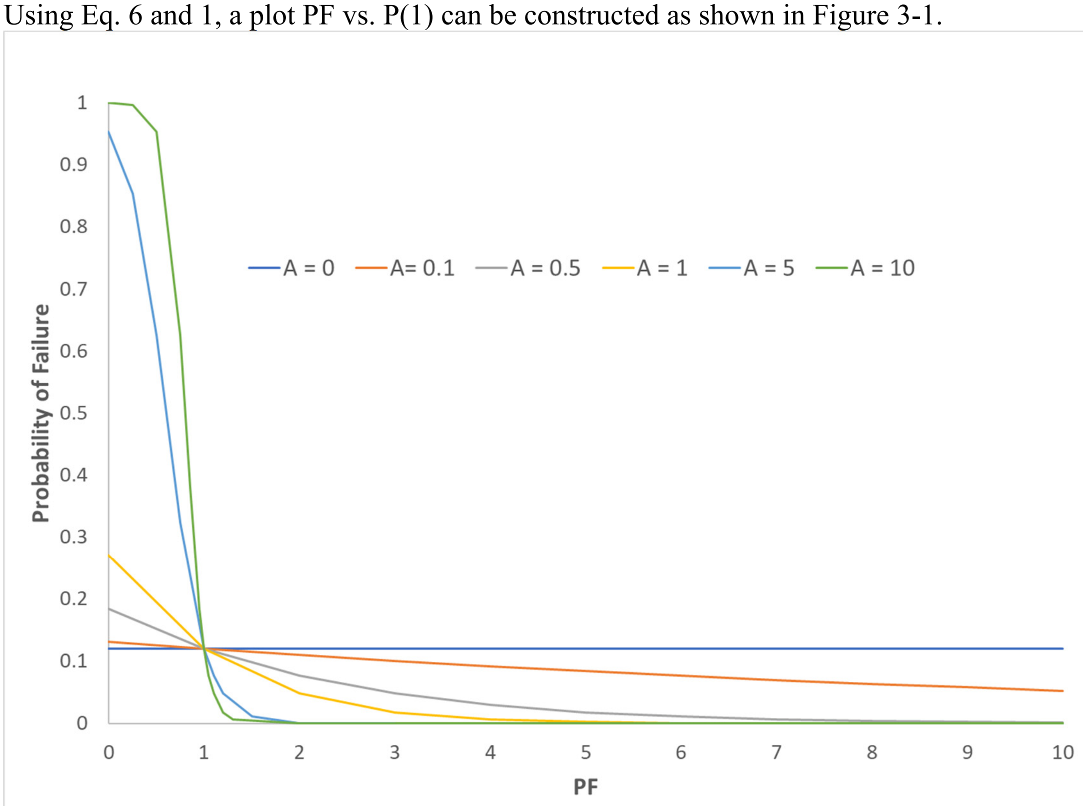

Figure 3-1. Dependence of probability of pitting on PF as a function of the aggressive species as defined by A.

The plot illustrates unique features of the relationship between PF and the probability of failure. At PF=1, the probability of failure is independent of the value of A. This inflection point has consequences for the probability of failure depending on PF and the value of A. For PF < 1 and A > 5, it is extremely likely that a failure will occur. However, for the same PF region a more dilute solution (e.g., A < 1) there is a lower probability of failure. The probabilities are still significant (i.e., between 12 to 28%), but considerably less than the more concentrated solutions. For PF > 1 the opposite trends are observed. For A > 5, the probability of failure is very low for nearly all values of PF. On the other hand, for dilute solutions (A < 1), the probability of failure is slightly higher. For example, at PF = 2, the probability of failure ranges from 0.05 to 0.12. Although this is not an extremely high probability of failure, it does suggest that further constraints on the chemistry limits for dilute solutions are warranted.

3.2 Relationship Between the Weighted Inhibitor Species and the Weighted Aggressive Species Concentrations

The effects of the aggressive species concentrations on the required inhibitor species concentration may be visualized by simply taking the logarithm of Equation 3.

The pitting factor is given by:

$$PF = \frac{8.06(OH)+1.55(NO2)}{NO3+16.7(Cl)+5.7(F)} \qquad (3)$$

Let A’ = (NO3)+16.7(Cl)+5.7(F) (7)

Let B’ = 8.06(OH) +1.55(NO2) (8)

Substituting Equations (7) and (8) into (3) and taking the log of the result yields Equations 9 and 10.

Log PF = Log B’ – Log A’ (9)

Log B’ = Log PF + Log A’ (10)

Thus, a linear relationship on a log-log plot exists between A’ and B’ with the slope determined by PF. Furthermore, Equation 2 may be re-written in terms of A’ and B’.

Lin(0) = 1.99+ 1.93*(B’-A’) (12)

This equation may be substituted into Equation 1 and the probability of failure may be calculated for each value of (A’, B’). This information may be included in the log-log plot and will demonstrate the gradient or profile of the probability of failure for a given PF value.

Figure 3-2 shows the logarithmic relationship between A’ and B’ along with the gradients for the probability of failure for a range of PF values between 0.5 and 3. The color scheme that shows the probability failure along each line is the same that was described in Table 1-1. Similar conclusions that were drawn from the direct relationship between the PF and the probability of failure may be drawn based on observations from this plot. For example, at PF = 1, the probability of failure is constant at 12% and is independent of the concentration of the species and dilution level. At PF < 1 and A’ > 1, the probability of failure is quite high. On the other hand, as A’ decreases (or the concentration becomes more dilute) the probability of failure decreases to values that are still significant, but clearly not as great. In contrast, at

PF > 1 and A' > 1, the probability of failure is reduced to very low values, while at A' < 1, the probability of failure increases to values slightly less but comparable to those that were observed with PF < 1 and A' < 1. Thus, it appears that the probability of failure in dilution solutions is not minimized solely by a ratio of inhibitor to aggressive species (PF), but also must have minimum requirement of inhibitors (B').

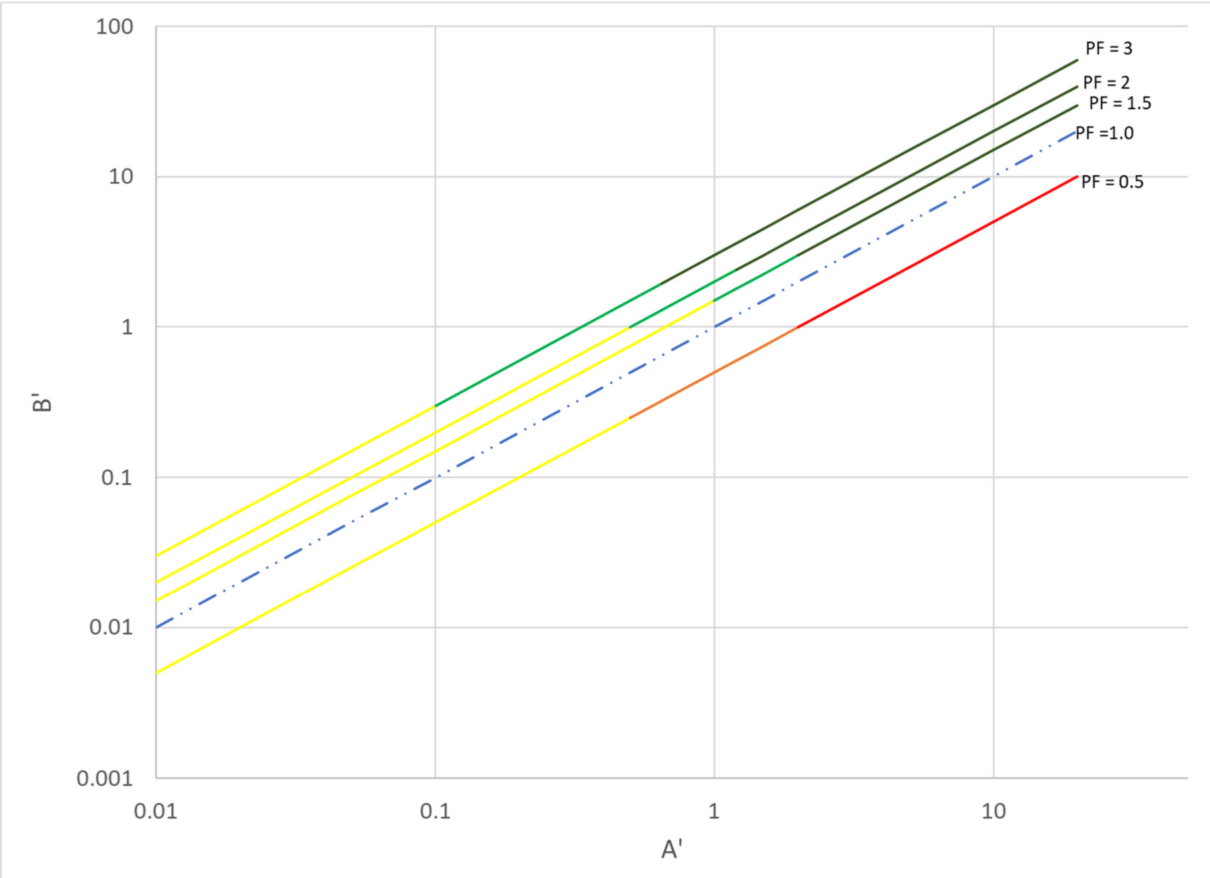

Figure 3-2. A' vs. B' for various values of PF. The probability gradient or profile is also illustrated.

3.3 <u>Relationship Between the Pitting Factor and the Log Weighted Inhibitor Species Concentration</u>

Previously a plot of the free hydroxide vs. the PF was plotted to show the boundaries for the new chemistry control limits (see Figure 1-1). However, this plot did not illustrate the minimum nitrite concentration limit and also did not illustrate the probability of failure very well. A direct mathematical relationship between PF and Log [OH] does not exist. On the other hand, a relationship between PF and B', the weighted total inhibitor concentration, does exist as shown next.

As shown, above Equation 2 may be re-written as Equation 12.

Lin (0) = 1.99 + 1.93*(B'-A') (12)

Therefore, Equation 1 may be re-written as:

P (1) = 1/(1+exp(1.99+1.93*(B'-A'))) (13)

The gradient or profiles for the probability of failure for each value of A' were also determined. The plot of Log B' vs. PF is shown. The color scheme for the probability of failure is the same as described in Table 1-1.

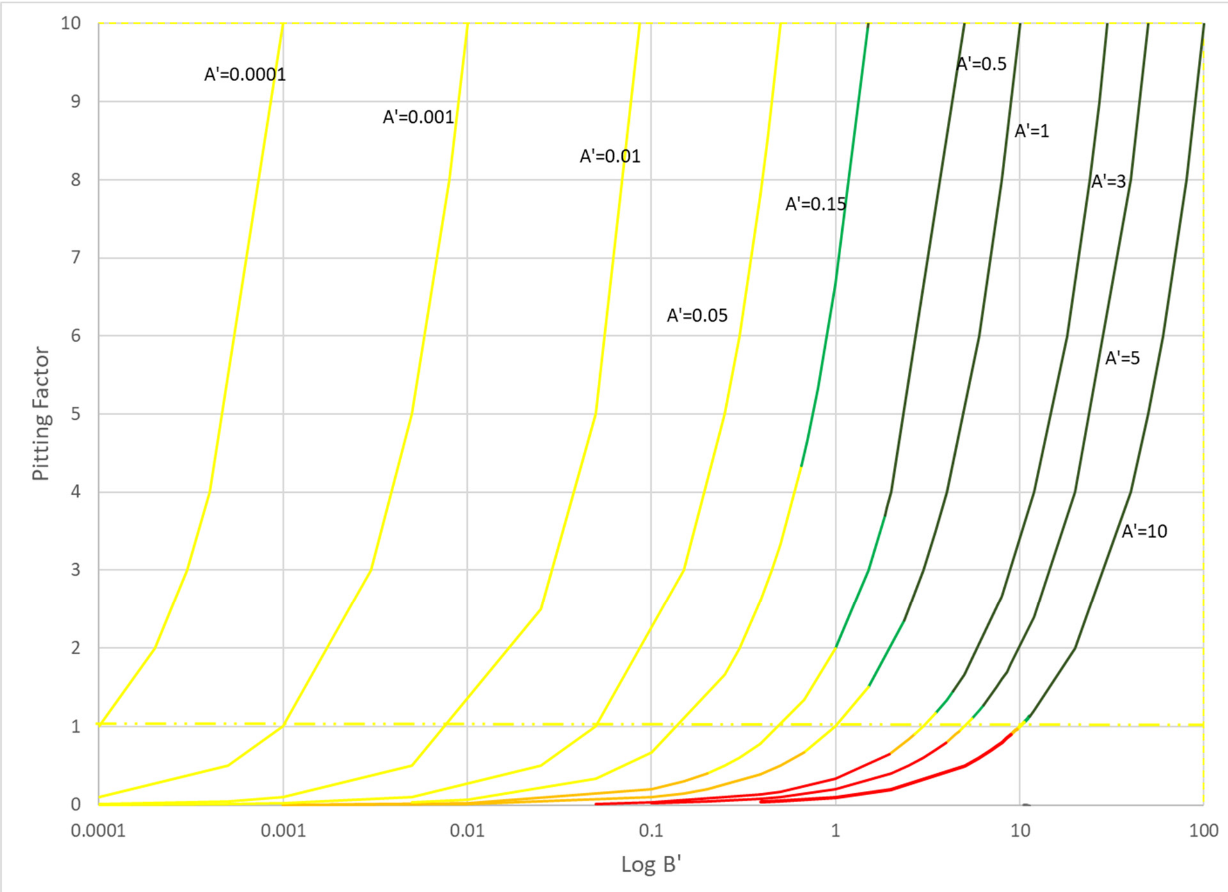

Figure 3-3. Log B' vs. PF. Dark green: P(1) < 0.01; Light Green: 0.01<P(1)<0.05; Yellow: 0.05<P(1)<0.2; Orange: 0.2<P(1)<0.5; Red: P(1)>0.5. Solid lines mean that the profiles are within the acceptable region, while the dashed lines mean that the profiles are outside the acceptable region.

At PF = 1, once again the probability of failure is independent of both B' and A'. The probability of failure was also the independent of B' and A' and equal to 12%. For PF < 1, and values of A' and B' greater than 1, the probability of failure is typically greater than 20%. For PF < 1, and values of A' and B' less than 1 (i.e., more dilute solutions), the probability of failure is between 12 and 20%. For PF > 1, and values of A' and B' greater than 1, the probability of failure is predominantly less than 5%. For PF > 1, and values A' and B' less than 1, the probability of failure ranges between 5 and 12%. Thus, the probability of failure can be reduced by maintaining the PF at values greater than 1 and B' at a value somewhere between 0.1 and 1. The probability of failure profiles for each A' can be connected to establish probability of failure contours (see Figure 3-4).

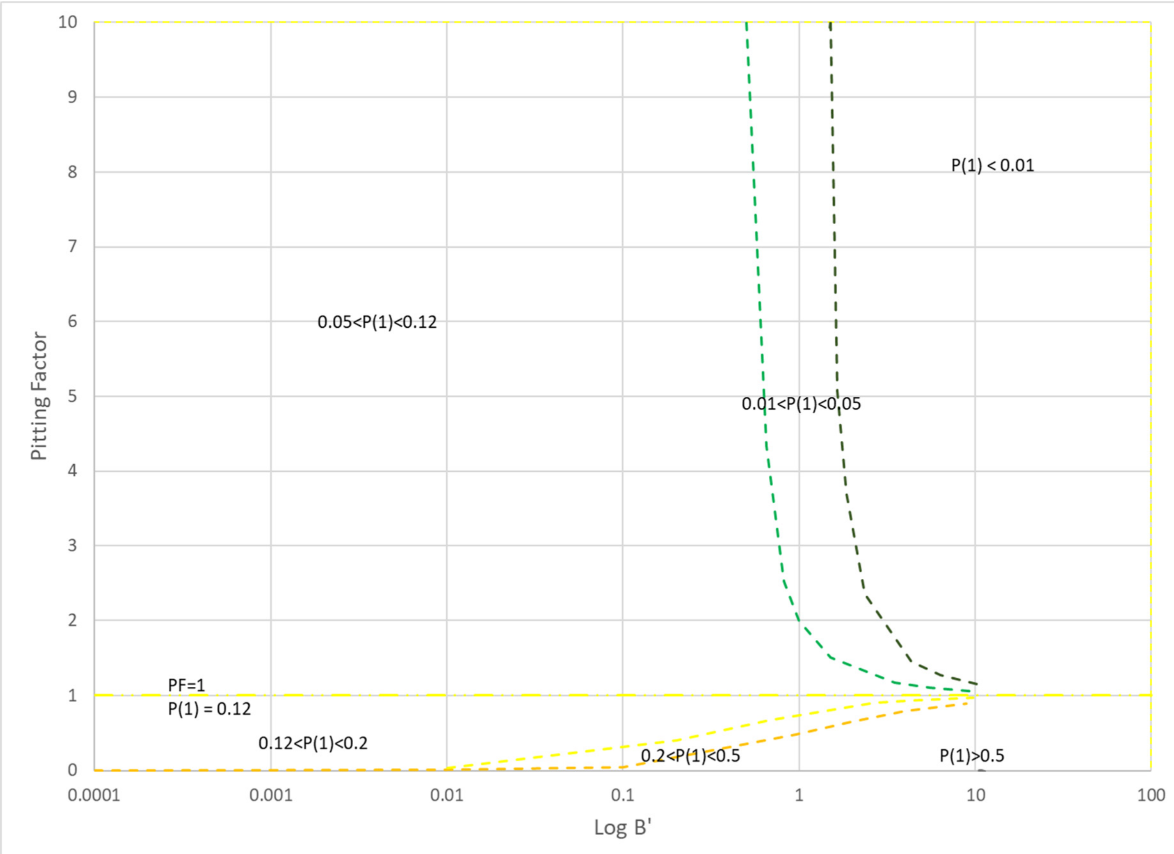

Figure 3-4. Log B' vs. PF. Dark green: P(1) < 0.01; Light Green: 0.01<P(1)<0.05; Yellow: 0.05<P(1)<0.2; Orange: 0.2<P(1)<0.5. Dashed lines show P(1) contour regions.

4.0 Projection of New Chemistry Control Limits on to the Plot Showing the Mathematical Relationships

4.1 Pitting Factor vs. Probability of Failure

As stated previously, new limits require a minimum PF of 1.2, minimum hydroxide concentration of 0.01 M and a minimum nitrate concentration of 0.2 M. If the hydroxide and nitrite minimum values are substituted into Equation 2, Lin (0) becomes:

$$Lin\ (0) = 2.7434 - A \quad (14)$$

Note that this means that the probability of failure would not be a function of PF. The probability of failure vs. the PF was plotted again in Figure 4-1. The probability for the dashed lines uses equation 14, while the solid lines use equation 2. By examining the calculated probabilities for three values of A, the effect of utilizing the minimum inhibitor concentrations is exhibited. For A = 0.3 and PF > 2.5, the minimum probability is given by the curve determined by Equation 2, that is, this limit requires a relatively higher weighted inhibitor concentration than that required by Equation 13 for this given value of A. On the other hand, for PF less than 2.5, but greater than 1.2, the minimum probability is given by

Equation 13. That is, the weighted inhibitor concentration provides the boundary for the minimum probability. Thus, the maximum probability, given a value of A = 0.3 with the minimum inhibitor requirements is approximately 8%. For A = 1, the minimum probability, as given by Equation 2, always gives the minimum probability when PF is greater than 1.2. The maximum probability occurs at PF = 1.2 and is approximately 10%. In this case, the combined weighted inhibitor concentration is always greater than the minimum required weighted average. For A = 0.63, Equation 2 and Equation 13 are equal when PF = 1.2. Equation 2 represents the minimum probability of failure for all values of PF > 1.2 in this case. The maximum probability is ~10.7% at a PF = 1.2. For all values of A > 0.63, Equation 2 is used exclusively. It should be noted that the weighted inhibitor concentration may exceed the minimum requirement, however, this does not necessarily imply that the individual inhibitors (nitrite and hydroxide) meet the minimum requirements. While this may not be critical for situations where the hydroxide concentration is high (e.g., greater than 0.1 M), however, for dilute solutions, where the hydroxide concentration is low it is more important to maintain the minimum nitrite concentration.

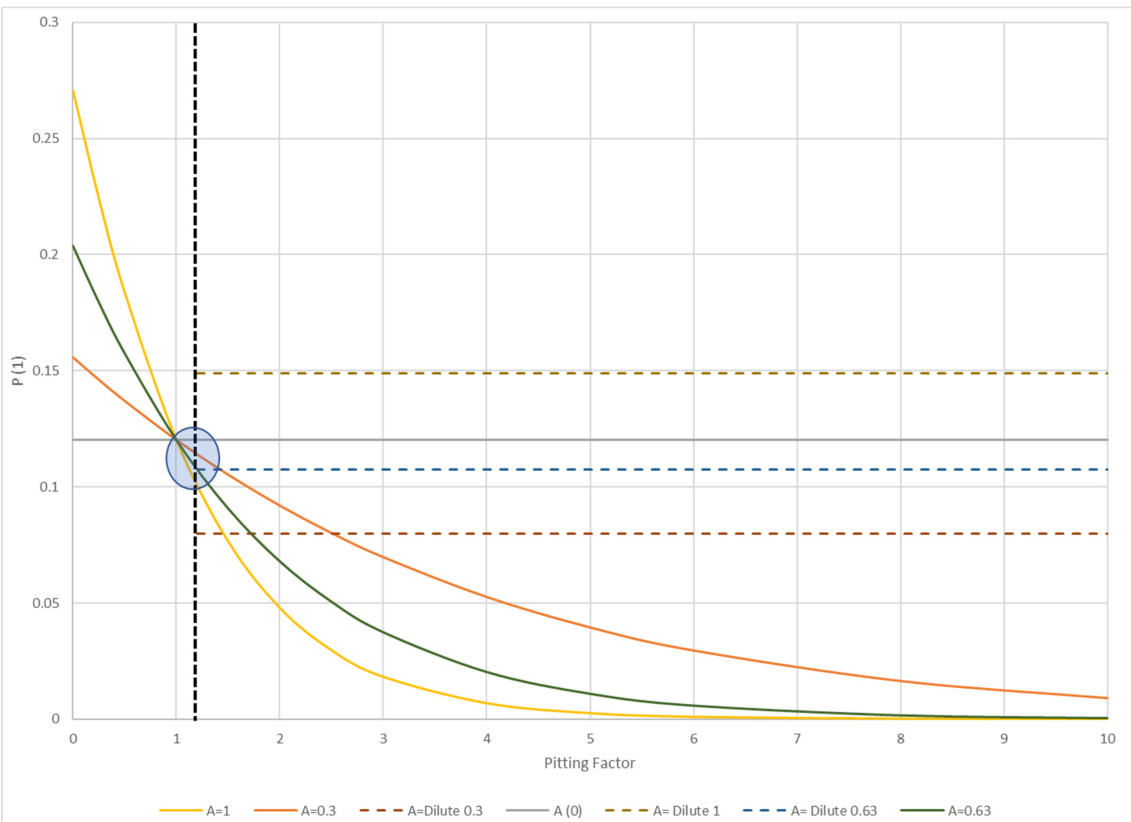

Figure 4-1. Illustration of the constraints of the new chemistry control limits on the probability of failure.

4.2 <u>Log of the Weighted Aggressive Species Concentration vs. Log of the Weighted Inhibitor Species Concentration</u>

The log A' vs. B' plot may also be utilized to illustrate the effects of the new chemistry limits on the probability of failure. Recall that:

Log B’ = Log PF + Log A’ (10)

For the minimum requirements of 0.01 M hydroxide and 0.2 M nitrite, B’=0.3906 M. Thus, B’ must always be greater than this value. For PF = 1.2 and B’ = 0.3906 M, the value of A’ is 0.3255 M. Figure 13 shows that for A’ < 0.3255 M, that B’ is bounded by the horizontal line at B’ =0.3906 M. On the other hand, for A’ > 0.3255 M, the minimum inhibitor requirement is bounded by PF = 1.2, which is the minimum ratio of B’ to A’.

Additionally, the probability may be calculated as:

Lin (0) = 1.99+ 1.93*(B’-A’) (12)

P (1) = 1/ (1+exp (Lin (0))) (1)

This Equation was utilized to construct the probability of failure gradient or profiles shown in Figure 4-2. The highest probability of failure (10.7%) occurs at the intersection of the horizontal and diagonal lines. Note that A’ > 0.3255, the probability of failure decreases as A’ increases, while for A’ < 0.3255, the probability decreases as A’ decreases.

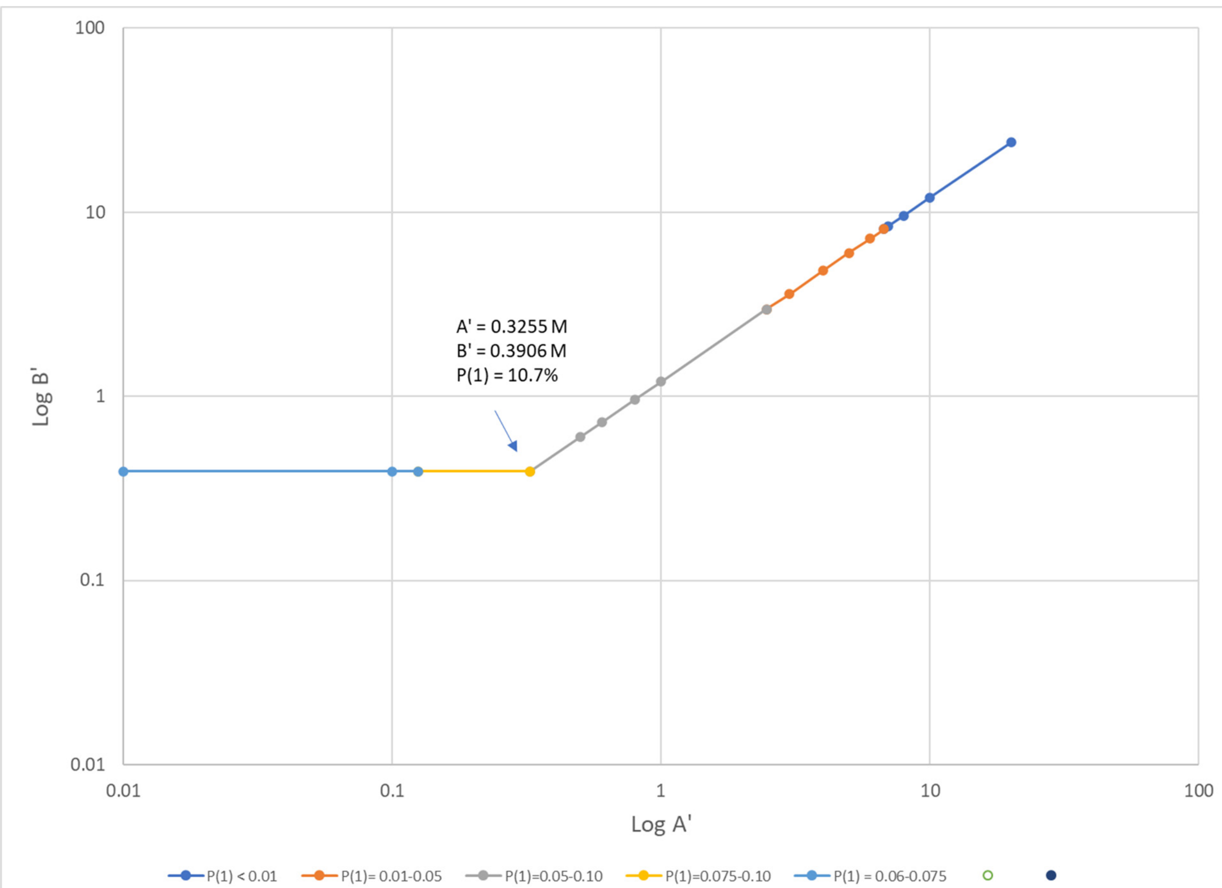

Figure 4-2. Log A’ vs. Log B’ for PF = 1.2 and B’ = 0.3906 M.

The effect of increasing the minimum PF requirement to 2, while maintaining the same minimum weighted inhibitor requirement (B') was investigated (see Figure 4-3). The plot demonstrates that the A' value at the intersection of the horizontal and the PF = 2 line shifts to a value of approximately 0.195 M. The result is that the ratio of that maximum probability of failure is reduced to 8.5%. This result is not unexpected given the minimum ratio of the concentrations of the inhibitors to the aggressive species has been increased.

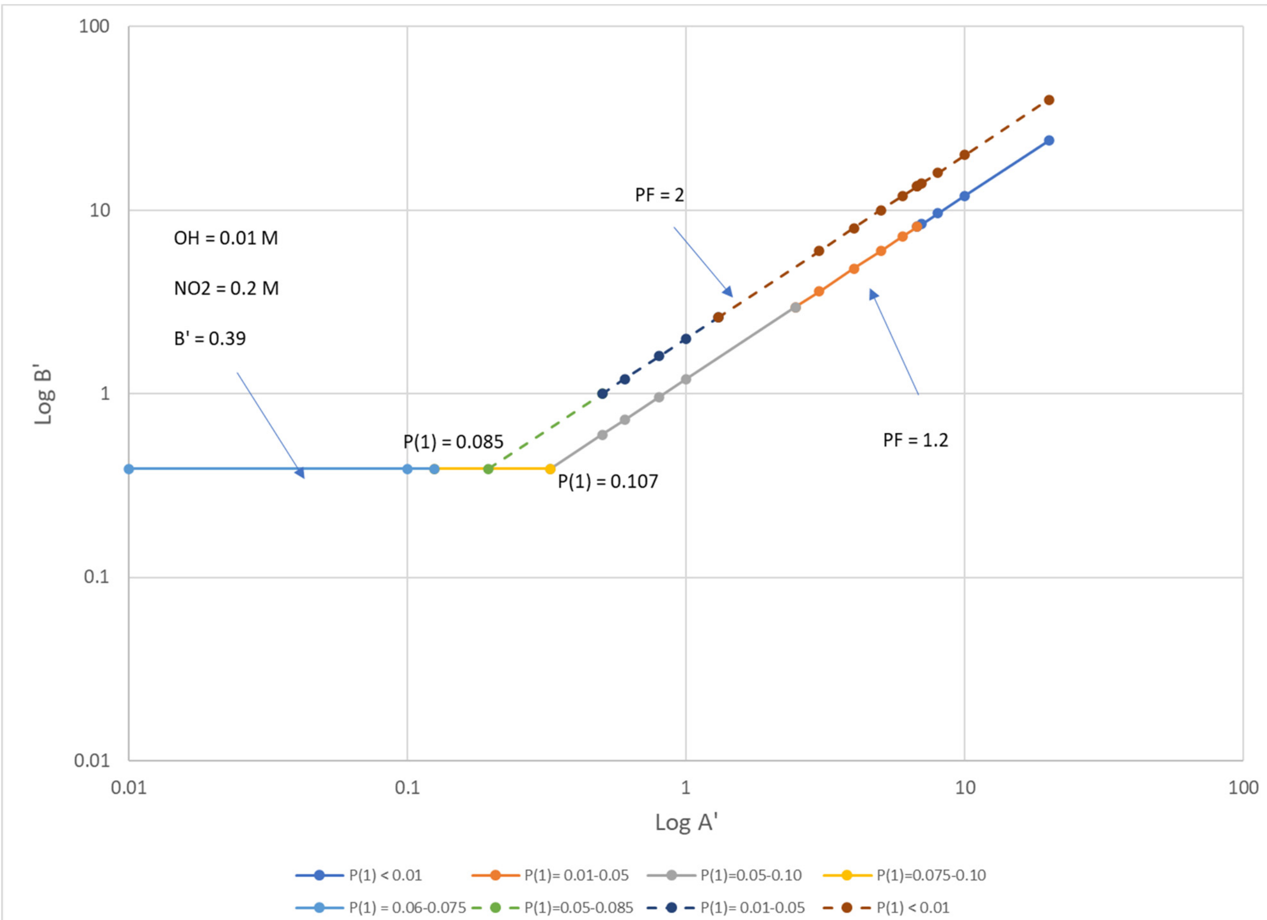

Figure 4-3. Log A' vs. Log B' for PF = 2 and B' = 0.3906 M.

The effect of increasing B', the minimum weighted inhibitor concentration, while maintaining the same minimum PF value was investigated. In this case B' = 1 and PF = 1.2. Increasing B' could result from either an increase in the minimum nitrite or hydroxide requirements. From Figure 4-4 it is observed that the A' value at the intersection of the horizontal and the PF = 2 line shifts to a value of approximately 0.834 M. The new weighted inhibitor requirement would be adequate for higher concentrations of the weighted aggressive species concentrations. The maximum probability of failure occurs at the intersection of the horizontal and diagonal lines and is approximately 9%.

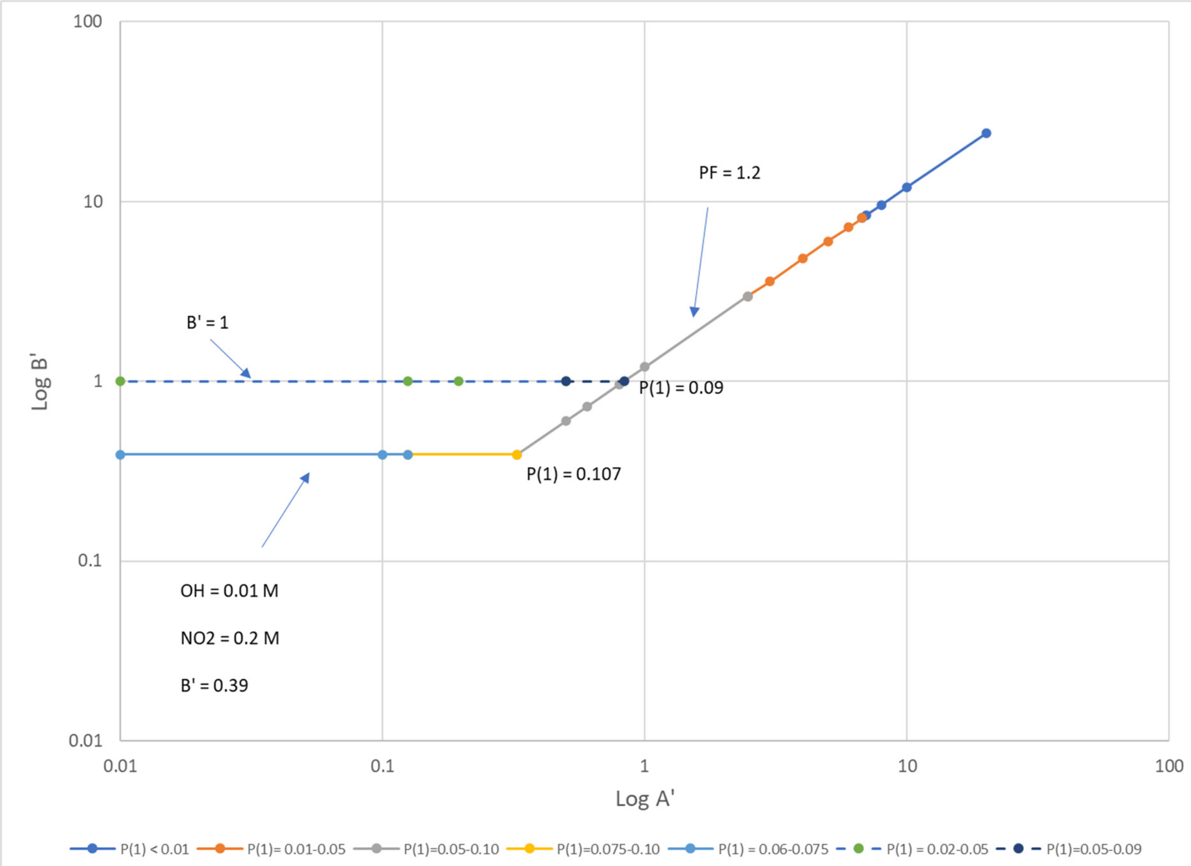

Figure 4-4. Log A' vs. Log B' for PF = 1.2 and B' = 1 M.

Finally, the effect of increasing both PF and B' was investigated. In this case, the values were PF=2 and B'=1 M. From Figure 4-5 it is observed that the A' value at the intersection of the horizontal and the PF = 2 line shifts to a value of approximately 0.5 M. These values represent both an increase in the minimum inhibitor requirements and the minimum ratio of the weighted inhibitor concentration and the weighted aggressive species. The maximum probability of failure occurs at the intersection of the horizontal and diagonal lines and is approximately 5%.

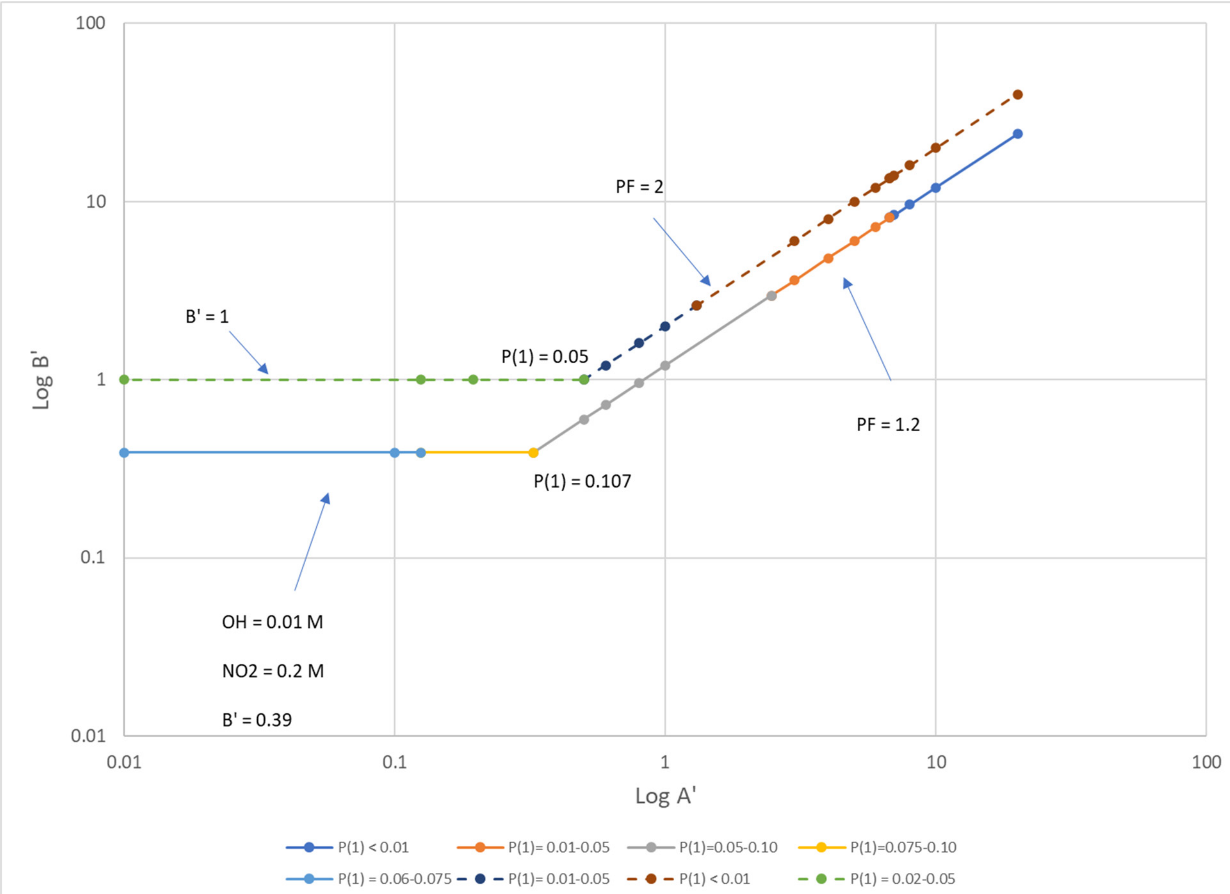

Figure 4-5. Log A' vs. Log B' for PF = 2 and B' = 1 M.

4.3 Weighted Inhibitor Concentration vs. Pitting Factor

Finally, the new chemistry control limits were examined on the PF vs. Log B' plot (See Figure 4-6). The probability contours in Figure 3-4 were also utilized in this visualization. The green box on the plot illustrates the region defined by the new chemistry control limits. The vertical line for the box is defined by the weighted inhibitor concentration (B'), while the horizontal line is defined by the minimum ratio (PF). The red area defines the weighted inhibitor concentrations and the ratios that are outside the new chemistry control requirements.

The probability of failure in the green box is predominantly less than 5%. There is only a small region where the probability exceeds this value. The maximum probability of failure occurs at the intersection of the horizontal and vertical lines (i.e., minimum PF and B') and is 10.7%. In this case, dilute solutions are represented by low values of B'. For B' < 0.4 M, the probability of failure ranges between 5 and 20%, except for very low values of PF. Thus, the probability of failure could be maintained at levels similar to the those in the green region by maintaining a high PF value.

However, for the dilute solutions, as can be seen by evaluating the equation for B', this may mean that a large quantity of nitrite relative to the aggressive species would be necessary. This is particularly true if the hydroxide is less than 0.01 M. SRS has used the practice of adding nitrite to inhibit dilute solutions that occur during waste retrieval, vitrification feed preparation and vitrification facility returns [ref.]. At the chemistry limit boundaries for SRS, the PF is typically around 1.66 and minimum B' ranges between 0.05 to 0.5 M. Thus, at the boundaries of the chemistry control limits, the SRS corrosion chemistry requirements are similar to the new limits for chemistry control for the Hanford DSTs.

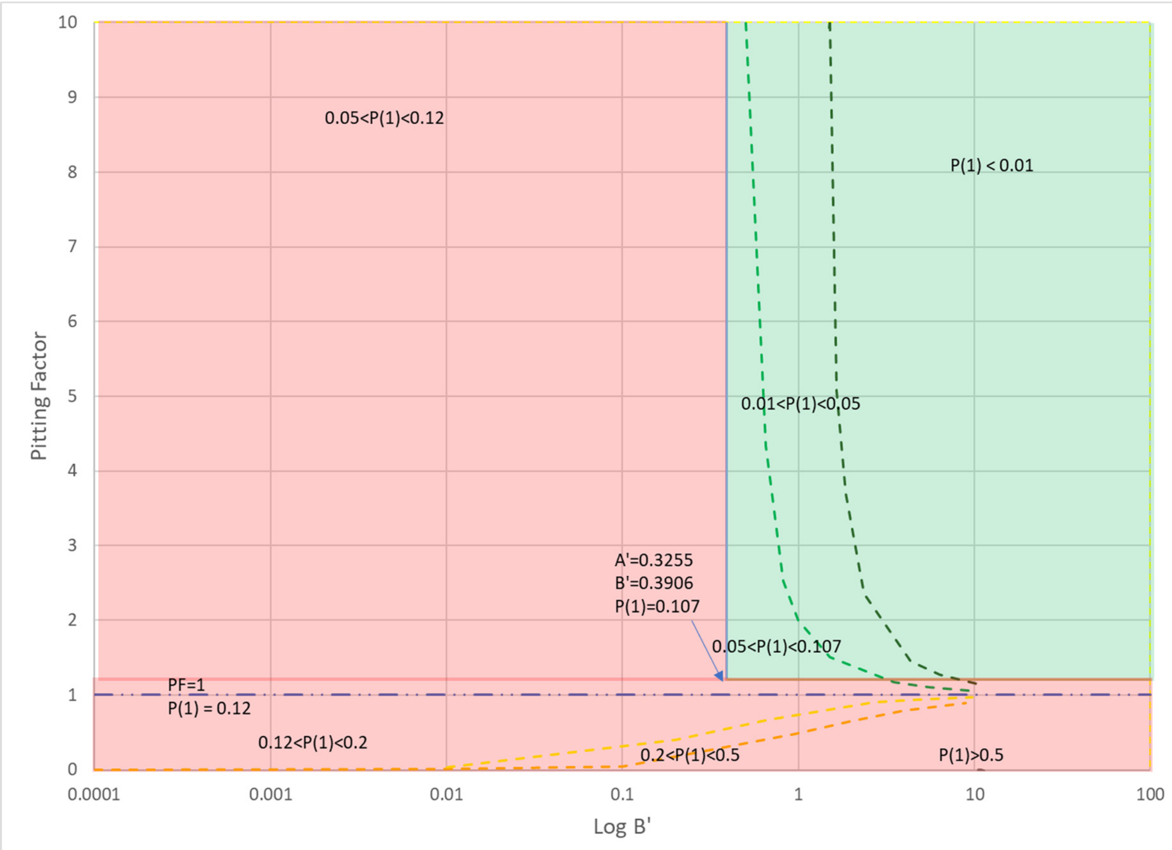

Figure 4-6. Log B' vs. Pitting Factor that illustrates the new chemistry control limits. The green region is the acceptable chemistry and the red region is unacceptable. Probability of failure contours are also illustrated.

5.0 Historical Data Evaluation Projected on to the Plots Showing the Mathematical Relationship

The historical data set of 300+ CPP tests that was originally utilized to verify the chemistry limits was evaluated on the Log B' vs. Log A' and the PF vs. Log B' plots. In addition, data from SRNL tests performed in 2014 were added to this data set [12]. The values for A' and B' in several of these tests had values less than 0.4 M, whereas for the previous historical data, both of these values were typically greater than this value. These dilute compositions were typically associated with testing related to vitrification feed preparation and storage of dilute wastes.

5.1 Weighted Aggressive Species Concentration vs. Weighted Inhibitor Species Concentration

Figure 5-1 shows the historical CPP data on a Log A' vs. Log B' plot. The new chemistry control requirements are also depicted. Principally the data represents conditions where A' is greater than 1. Much of the testing for WRPS has been for waste simulants that represent DST storage conditions, which tend to be the more concentrated wastes. In this region, for all cases where B' was such that PF was greater 1.2, the CPP test resulted in a "pass" condition. Below this ratio, approximately 80% of the CPP tests were failures. For PF < 1, greater than 95% of the CPP tests were failures. The notable exceptions were CPP tests that "passed" in simulants of AN-102 and AN-107 wastes. Both wastes contained significant quantities of total organic carbon (TOC), which was on the order of 2 M. TOC has been observed to be a weak inhibitor of corrosion of carbon steel [ref.]. However, both of these wastes have significant quantities of nitrite present as well (i.e., greater than 1 M). It should also be noted that for the SRNL tests the principal aggressive species was nitrate [ref.]. Chloride and fluoride concentrations were very minor contributors.

For A' < 1, all CPP tests were a "pass" for B' greater than 0.39 M. In fact, the majority of the CPP tests resulted in a "pass", even several that were less than the minimum required B'. This result may reflect the observation from previous plots that the probability of failure is relatively low in most cases (< 12%). Of particular note are the results where B' was less than 0.01. These tests were performed in AY-101 and AY-102 interstitial liquid. These tests were performed in simulants that were very dilute in both inhibitor species and aggressive species. However, the total inorganic carbon (TIC) was relatively high (i.e., 1-1.84 M). This TIC concentration is much higher than that utilized to determine the new limit requirements. TIC has also been shown to be a weak inhibitor for carbon steel in these simulants [13]. However, previous attempts to define thresholds requirements for TIC have not been successful.

5.2 Weighted Inhibitor Concentration vs. Pitting Factor

The log B' vs. PF plot was also used to evaluate the historical data. The historical data, including the 2014 SRNL data, were plotted on Figure 18 along with the probability contours and the green and red regions that illustrate the chemistry control limits. All the historical CPP data in the green region were a "pass". There are practically no "fail" results for PF > 1. "Fail" conditions begin to be observed when the probability of failure exceeds 12%. It is observed that when B' < 0.3906 M and PF > 1.2, all the tests were passes. However, when PF < 1.2 the percentage of "fail" tests increases considerably. The same anomalies with the high concentrations of TIC and TOC were observed in these plots.

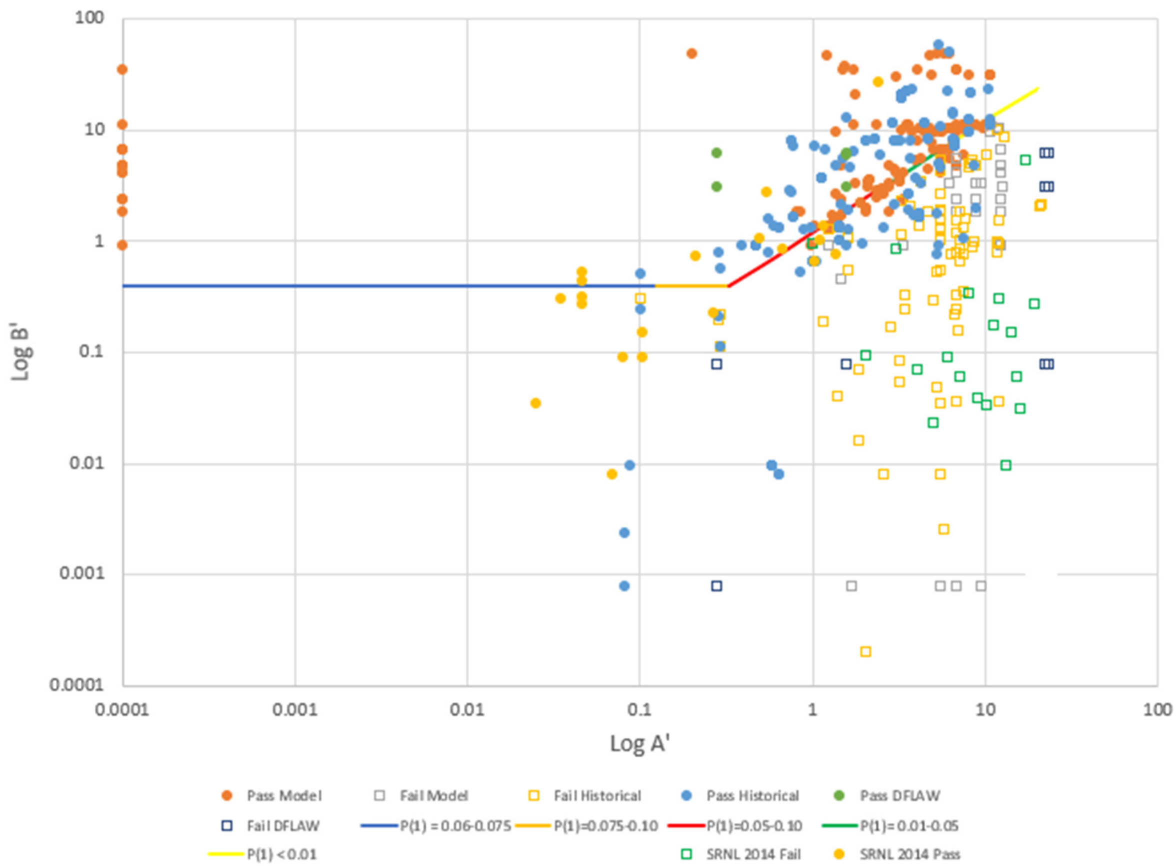

Figure 5-1. Log A' vs. Log B' for PF = 1.2 and B' = 0.3906 M. Historical data from Hanford and SRNL are shown. Closed symbols indicate a CPP test that "passed" and open symbols indicate a CPP test that "failed".

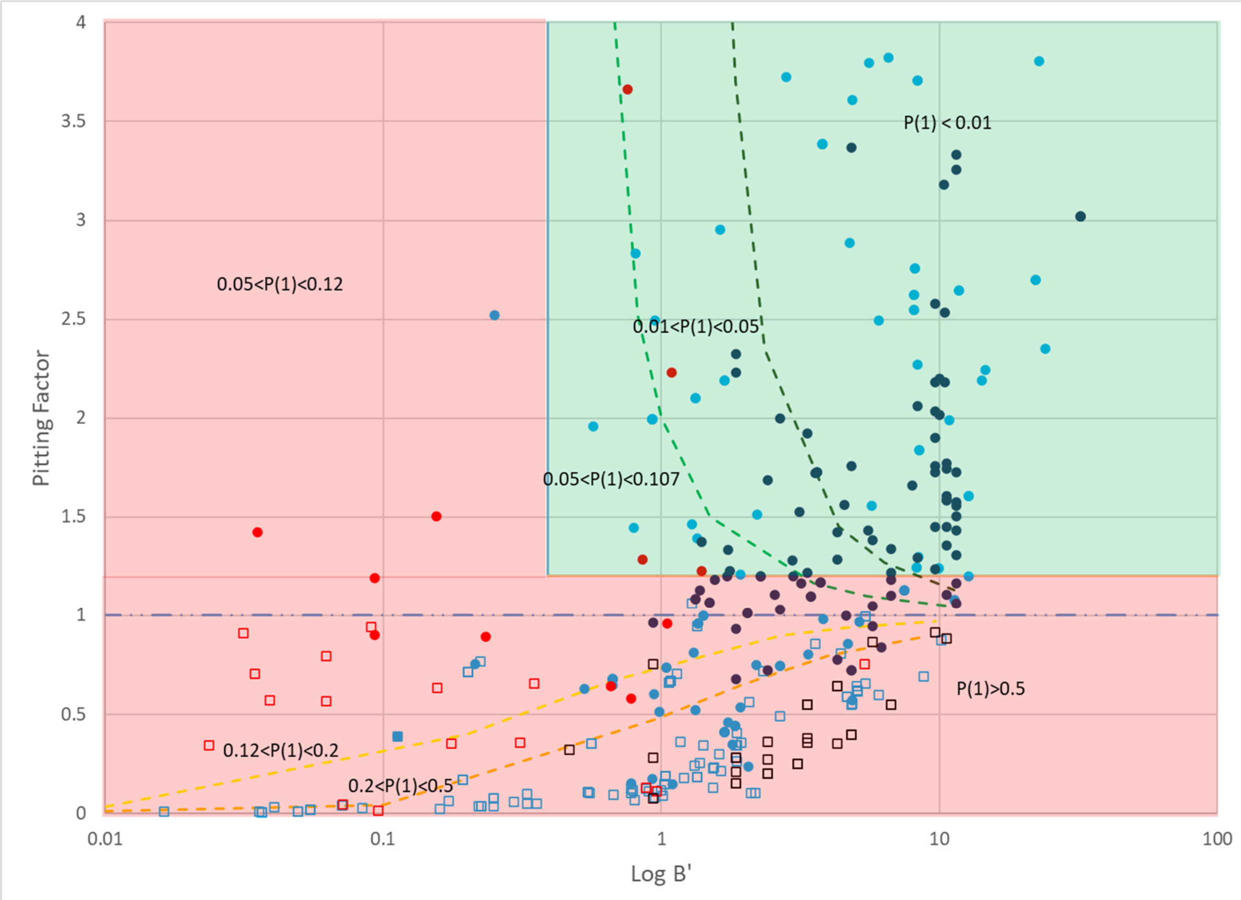

Figure 5-2. Log B' vs. PF with Historical Data. Dashed lines show probability of failure contour regions. The colors of the lines represent the following probabilities. Dark green: P (1) < 0.01; Light Green: 0.01<P(1)<0.05; Yellow: 0.05<P(1)<0.2; Orange: 0.2<P(1)<0.5; Red: P(1)>0.5. The green region represents the chemistries that meet the chemistry limits, while the red region represents chemistries that do not meet the requirements. The historical data is the same that was used for Figure 5-1. Closed circles represent a "pass" for a CPP test, while open squares represent a "fail"

6.0 Conclusions and Recommendations

The following conclusions and recommendations were made based on this review.

- Three mathematical representations are helpful in visualizing the relationship between the probability of failure and the ratio of the weighted inhibitor concentrations and the weighted aggressive species concentrations, the minimum weighted inhibitor concentration, and probability of failure of a CPP test. The relationships between P(1) vs. PF, Log B' vs. Log A', and PF vs. Log A' were investigated.
- Probability profiles (gradients) and contours can be added to the Log B' vs. Log A' and the PF vs. Log B' plots to help visualize the relationship between the probability of failure of a CPP test and the new chemistry limits.
- Individual inhibitor or aggressive species could not be mathematically related to the probability of failure. Instead, weighted inhibitor and weighted aggressive species concentrations were

mathematically related. The weights for each species were tied to the logistic regression model for the experimental CPP data.
- Probability contours and profiles (or gradients) indicate that maintaining the inhibitor levels above the new chemistry limits ensure that the environment is benign with respect to pitting corrosion (i.e., a low marginal probability of failure).
- For dilute solutions (A' typically less than 1), the probability of failure ranges between 5% to 20%. This value is reduced further if the ratio, PF = 1.2 is considered.
- For concentrated solutions (A' typically greater than 1), maintaining a high ratio, PF, reduced the probability of failure in most cases to less than 5%.
- Historical CPP tests validated that in low probability regions (i.e., less than 12%), all tests were a "pass" condition.
- Historical CPP tests with high concentrations of TOC or high concentrations of TOC resulted in a "pass", even though PF was significantly less than 1.2. It should be noted that the minimum hydroxide and nitrite concentrations were exceeded for the tests with high TOC, whereas this was not necessarily true for the very dilute TIC solutions.
- The profiler function for the JMP™ statistical package may be utilized to perform simulations that construct a PF vs. Log B' plot based on the statistical model and the anticipated DST waste compositions.
- Further CPP testing at more dilute solutions with lower levels of aggressive species (e.g., chloride) may provide additional data that would refine the model and allow for lower minimum inhibitor requirements.
- Further CPP testing may be utilized to incorporate TOC and TIC into the logistic regression model.

7.0 Reference

1. OSD-T-151-00007, 2018, Operating Specifications for the Double-Shell Storage Tanks, Rev. 22, Washington River Protection Solutions, LLC, Richland, Washington, 2018.
2. SRNL-STI-2016-00117, *Hanford Double Shell Waste Tank Corrosion Studies – Final Report FY2015*, R. E. Fuentes and R.B Wyrwas, May 2016.
3. SRNL-STI-2016-00721, *Hanford Double Shell Waste Tank Corrosion Studies – Final Report FY2016*, R. E. Fuentes, December 2016.
4. SRNL-STI-2018-00116, *Hanford Double Shell Waste Tank Corrosion Studies – Final Report FY2017*, R. E. Fuentes, April 2018.
5. SRNL-STI-2019-00114, *Hanford Double Shell Waste Tank Corrosion Studies – Final Report FY2018*, R. E. Fuentes, P. K. Shukla, B. Peters, D. Hitchcock, July 2019.
6. SRNL-STI-2020-00109, *Hanford Double Shell Waste Tank Corrosion Studies – Final Report FY2019*, R. E. Fuentes and P. K. Shukla, May 2020.
7. RPP-ASMT-60833, Rev. 0, *Tank Integrity Expert Panel Corrosion Sub-group March 2016 Meeting Outcomes"*, T. M. Martin, May 2016.
8. SRNL-STI-2019-00217, Rev. 0, *Chemistry Envelope for Pitting and Stress Corrosion Cracking Mitigation,* B. J. Wiersma, R. E. Fuentes, and L. M. Stock, September 2019.
9. WSRC-TR-90-512, *Minimum Nitrite Concentration for Washed Sludge,* P. E. Zapp, November 1990.
10. C. S. Brossia and G. A. Cragnolino, "Effect of Environmental Variables on Localized Corrosion of Carbon Steel," *Corrosion,* Vol. 56, No. 5, May 200.
11. RPP-RPT-61420, Rev. 0, *FY2018 DST and SST Chemistry Testing Report,* Washington River Protection Solutions LLC, Richland, Washington.
12. SRNL-STI-2014-00616, *Hanford Double Shell Waste Tank Corrosion Studies – Final Report FY2014*, R. E. Fuentes, B. J. Wiersma, and K.R. Hicks, December 2014.

13. DNV Report