Contract No:

This document was prepared in conjunction with work accomplished under Contract No. 89303321CEM000080 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Disclaimer:

Refinement of Salt Dissolution Inhibitor Requirements

Joshua T. Boerstler
Savannah River National Laboratory
Savannah River Site
Aiken, SC 29808
United States of America

Bruce J. Wiersma
Savannah River National Laboratory
Savannah River Site
Aiken, SC 29808
United States of America

Keisha B. Martin
Savannah River Mission Completion
Savannah River Site, Building 766-H
Aiken, SC 29808
United States of America

Andrea N. Bridges
Savannah River Mission Completion
Savanna River Site, Building 766-H
Aiken, SC 29808
United States of America

ABSTRACT

Corrosion control limits for High-Level Waste storage are being revisited to determine if a ratio of inhibiting and aggressive species, the Pitting Factor, is applicable to predicting localized corrosion in waste tank chemistries. An experimental matrix was designed to evaluate the use of the pitting factor for supernate chemistries, particularly during the salt dissolution process. Two electrochemical methods were identified to determine the susceptibility of A537 and A285 low-carbon steels to pitting corrosion within this chemistry envelope at temperatures up to 75 °C. The predominant electrochemical test method was Cyclic Potentiodynamic Polarization (CPP) studies. Where CPP was inconclusive, Modified ASTM G192 was successfully used to evaluate pitting susceptibility conditions and allowed for a pass/fail result to be determined. In all cases, the pitting factor was determined to be applicable to the simulants tested, with this metric accurately predicting incidences in which pitting occurred.

Key words: Corrosion Control, Pitting

INTRODUCTION

At Savannah River Site (SRS), High-Level Waste is stored in below-grade tanks constructed of carbon steel. This waste is composed of sludge, salt cake, and/or supernate. In part, preparation of this waste for future processing involves dissolution of the salt cake layer. The salt dissolution process can create conditions that leave the carbon steel tanks susceptible to a number of corrosion processes. The salt to be dissolved contains high concentrations of nitrate, that once released, create an environment that may be conducive to pitting corrosion of carbon steel.

The salt dissolution process also liberates interstitial liquid trapped between the salt crystals. This liquid is initially high in nitrite and hydroxide concentration. High pH and greater ratios of nitrite to nitrate act as inhibitors to minimize corrosion of carbon steel in high nitrate environments. However, as dissolution proceeds the concentration of nitrate will increase while the hydroxide and nitrite concentration of the interstitial liquid will deplete and become insufficient to prevent the onset of corrosion attack. Tank blending and addition of inhibitors are used to ensure adequate concentrations of hydroxide and nitrite. However, this is not desirable during salt dissolution as it can reduce process efficiency and increase the amount of waste that needs processed.

An administrative control program is in place that dictates the amount of inhibitors required for tank chemistries based on the concentration of nitrate present [1]. This program is based on experimental programs that have evaluated the susceptibility of UNS K12437 (A537) carbon steel to pitting corrosion and SCC in high nitrate concentration solutions with low concentrations of inhibitors [2-4]. The nitrate and inhibitor concentrations examined in these works are shown in Table 1. It has been proposed that these corrosion control limits be revisited to evaluate the corrosion susceptibility of carbon steel in environments that more closely resemble current operating conditions during salt dissolution.

Table 1

Compositional Ranges for Previous Testing [2-4]

Species	Concentration Range [M]	Temperature Range [°C]
Nitrate	5.5 - 8.5	50
Nitrite	0.01 - 0.1	
Hydroxide	0.01 - 0.1	
Chloride	0.1	
Sulfate	0.1	
Aluminate	0.5	
Carbonate	0.1	
Phosphate	0.05	

The compositional range of inhibiting species (nitrite and hydroxide) in these works are lower than current salt dissolution tank chemistries. Sulfate concentrations have also recently been observed to be higher than the 0.1 M that was previously evaluated. In addition, it is desirable to expand the temperature range to 75 °C from 50 ºC, to potentially allow for continued mixing during salt dissolution campaigns.

To evaluate the susceptibility of carbon steel to pitting corrosion in conditions more resembling the salt dissolution environment, corrosion testing was conducted at higher inhibitor concentrations and more realistic operating temperatures, shown in Table 2.

Table 2

Compositional Ranges for Proposed Testing

Species	Concentration Range [M]	Temperature Range [°C]
Nitrate	0.0 - 7.0 or saturation	25-75
Nitrite	0.0 - 1.2	
Hydroxide	0.0 - 1.2	
Chloride	0.0 - 0.4	
Sulfate	0.0 - 0.6	
Aluminate	0.5	
Carbonate	0.1	
Phosphate	0.05	

Coupons of A537 and UNS K02801 (A285) were subjected to cyclic potentiodynamic polarization (CPP) electrochemical experiments to help determine their pitting corrosion vulnerability in salt dissolution supernate simulants and other tank farm simulant chemistries at temperatures ranging from 25-75 °C. In some cases, CPP provided inconclusive results as to the susceptibility to pitting corrosion in a given chemistry. In such cases, a Modified ASTM(1) G192 test was used to further evaluate the pitting behavior of the material and ultimately draw conclusions on its susceptibility. This method employs galvanostatic and potentiostatic holds that differ from the constant ramp rate of the potential for CPP, allowing the system time to reach a steady state and elucidate details that may be missed during CPP analysis. The pitting factor was determined to accurately predict instances of pitting within the chemistry envelope evaluated, and control limits based upon this approach are proposed.

EXPERIMENTAL PROCEDURE

Cyclic Potentiodynamic Polarization (CPP) of Carbon Steel Coupons

A common method used to assess the pitting susceptibility of an alloy in a given environment is CPP. The resulting polarization curve from a CPP can be found in Figure 1 for reference. This method involves polarizing the sample anodically through the passive regime until breakdown occurs, due to the onset of pitting, and/or reaching transpassive conditions, then polarizing cathodically until the scan returns to the corrosion potential. From this process, a number of assessments can be made about the susceptibility of the material to pitting corrosion in that environment. The first characteristic value is the breakdown potential or pitting potential. This is typified by the large increase in current from the passive current that occurs as a result of increased anodic dissolution rates. The next characteristic that can be assessed is the nature of the hysteresis. A positive hysteresis, the reverse scan having higher current than the forward scan at the same potential value, indicates that pitting has occurred, and pits continue to grow even below the breakdown potential. A negative or no hysteresis likely indicates that no localized corrosion has occurred, or pit growth is no longer stable when the potential decreases. Lastly, the repassivation potential could be obtained if solution conditions are such that repassivation of active pits can occur. This parameter may not be possible to obtain if chemistries conducive to repassivation are not present or if repassivation occurs below the corrosion potential.

The OCP or corrosion potential of the material, along with the repassivation potential and breakdown potential, can be used to assess the severity of the material's susceptibility to pitting corrosion in a given

---

(1) American Society for Testing and Materials (ASTM) International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA, 19428-2959

environment. The relative potential values of the corrosion and breakdown potentials indicate how much the material must be polarized to support stable pit growth into the material. If the breakdown potential is close to the corrosion potential, pitting is more likely in the event of polarization of the material or if there is an increase in the OCP of the material with exposure time. The relative positions of the breakdown and repassivation potentials essentially indicate the range over which initiated pits will continue to grow, if pits are present. Therefore, materials with more noble repassivation potentials or those closer to the breakdown potential are desirable. Lastly, the relationship of the corrosion potential and the repassivation potential is an indicator of the likelihood of pitting in a material. If the repassivation potential is near the corrosion potential, there is an increased likelihood that the repassivation potential could be exceeded, and pits that initiated will continue to grow so long as the potential remains above the repassivation potential.

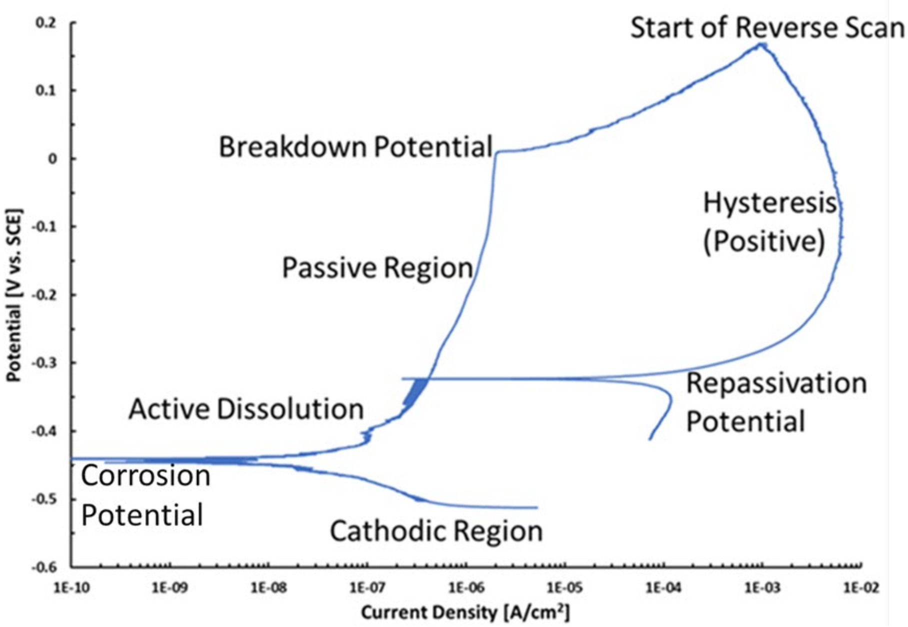


Figure 1: Example of CPP curve with regions and values of interest labelled.

The forward scan begins in the cathodic region and continues until the start of the reverse scan. The corrosion potential and breakdown potential can be determined in this region. The reverse scan begins at the end of the forward scan and ends once the potential is equal to the corrosion potential. The nature of the hysteresis (positive, negative, or mixed) along with the repassivation potential, when applicable, can be determined from this portion of the curve.

Three outcomes are possible based upon the presence or absence of stable localized corrosion during the polarization. A positive hysteresis is defined by the current of the reverse scan being greater than that of the forward scan. With these cases, the current density of the reverse scan should remain higher than the passive current density within the potential range of the passive region with the exception of decreases in current associated with repassivation, illustrated in Figure 1. This is indicative of stable localized corrosion taking place, which could be the result of pitting or crevice corrosion. Crevice corrosion can occur due to aggressive conditions forming in the narrow space between the sample and its mount. The crevice creates an occluded region where the localized chemistry can become different from the bulk chemistry as metal ions dissolve, creating a charge imbalance, and attracting negatively charged anions, some aggressive, into the crevice region. This can result in increasingly aggressive conditions that result in accelerated dissolution of the base material. Because these conditions represent a localized chemistry that is indicative of flaws in the experimental setup and not actual tank conditions, cases of positive hysteresis in the absence of pitting of the boldly exposed surface were rerun to ensure that pitting, not crevice corrosion, was the source of any localized attack. A failure is determined if all of the following three conditions are met:

1. A positive or mixed hysteresis was present on the CPP curve.
2. Pitting, not crevice, corrosion was observed on the sample surface.
3. Repassivation potential was not observed or the difference between repassivation potential and corrosion potential is less than 200 mV.

Pitting corrosion can only occur at potentials above the repassivation potential. Below this potential, any pits that were present would be passivated, meaning that a passive film is stable, and no further dissolution would occur. Therefore, the difference between the corrosion potential and the repassivation potential indicates how likely pitting corrosion would occur for a given material in an environment. A difference of more than 200 mV indicates that conditions favorable for pitting to occur are not anticipated absent any outside influence polarizing the surface substantially beyond typical OCP drift.

A negative hysteresis is defined by the current density on the reverse scan being less than the current on the forward scan. A negative hysteresis indicates that stable localized corrosion has not occurred during polarization. Neither pitting nor crevice corrosion was present in these cases. As such, trials with a negative hysteresis are defined as a pass condition.

The final potential outcome is a mixed hysteresis. A mixed hysteresis represents a condition in which the current density during the reverse scan displays behavior of both positive and negative hysteresis during portions of the reverse scan. This could occur due to localized corrosion to a lesser extent or because of changes to the sample surface during the forward scan that result in slightly different kinetics for dissolution on the reverse scan. These instances require further examination to determine whether a passing or failing condition for susceptibility to pitting corrosion has occurred. First, the sample is examined for the presence of pitting or crevice corrosion. If this examination is still inconclusive, meaning there is no clear indication of pitting or crevice corrosion, the sample is subjected then to a Modified ASTM G192 test, which will be discussed further in the next section.

Two types of carbon steel were examined to characterize the pitting behavior of Type IIIA and Type II waste tank materials of construction, A537 and A285, respectively. Disks (exposed area of approximately 2 cm^2) or squares (approximately 0.75-inch [1.91 cm] by 0.75-inch [1.91 cm]) were cut from bar or rectangular bar stock using a slow speed saw. Insulated lead wires were affixed to the back side of coupons with conductive silver epoxy to create an electrical connection outside of the test cell. The wired coupons were then cold mounted using acrylic to protect the electrical connection, exposing only the top face of the coupon, and to provide a means of handling the coupons for further sample preparation. Samples were ground to 800-grit using progressively higher grit silicon carbide (SiC) paper with water as lubrication to obtain a flat, uniform surface. The final grinding step was conducted within one hour of testing to prevent the development of corrosion products on the test surface from residual moisture or atmospheric conditions. Finally, the samples were rinsed with ethyl alcohol and blown dry to remove any residual organic material and water from the sample surface.

750 mL of test solution was batched for each test. Test solutions were made the same day as testing to prevent precipitation of salts at room temperature during storage. In general solutions were made at their respective test temperature with stirring using a magnetic stir bar on a hotplate/stirrer. However, exceptions were made dependent upon solution chemistry. The dissolution of sodium nitrate is endothermic, therefore, solutions containing higher nitrate concentrations (greater than 4 M) would have the temperature increased when necessary to account for the endothermic process and aid in complete dissolution. Another exception was due to the dissolution behavior of sodium sulfate. In high nitrate solutions, it was observed that sodium sulfate did not readily dissolve. In addition, sodium sulfate differs from the other solution constituents in that the solubility is highest between 30 and 40 °C then decreases with increasing temperature. For this reason, the temperature of the test solution would be lowered, if necessary, to accommodate the solubility characteristics of sodium sulfate. In some cases, precipitation

of salts was observed for highly concentrated solutions. As many of these solutions represent salt dissolution conditions, this was considered acceptable as operating conditions would represent an equilibrium, or at least steady state, between the supernate and precipitated salt layer.

The prepared solution was then added to a test vessel with ports for the working electrode or sample, a salt bridge containing a reference electrode, two graphite rods to serve as counter electrodes, and thermocouples to monitor test temperature and prevent overheating of the solution. The solution was heated on a hotplate with stirring until a steady test temperature was achieved. The hotplate contained an additional thermocouple to provide feedback for maintaining test temperature. After test temperature was achieved, the sample, counter electrodes, and salt bridge containing the reference electrode and a 0.1 M sodium nitrate solution were inserted into the test cell. Two graphite counter electrodes were used to promote more even current distribution to the working electrode. A saturated calomel electrode (SCE) was used as the reference electrode.

After the proper test conditions were established and the test apparatus was prepared, an OCP delay was initiated. The potential was measured once per second for a total of two hours. This was followed by the CPP experiment. The following parameters for the polarization were used:

Scan rate:	0.167 mV/s
Initial potential:	-0.1 V versus open circuit potential
Final potential:	1.2 V versus reference electrode
Current density limit:	1 mA/cm^2
Reverse scan rate:	0.167 mV/s
End potential:	0.0 V versus open circuit potential

The forward scan proceeded until either the final potential or the current density limit was reached, which was the current density limit in all cases. At this point the scan direction was reversed, and the reverse scan proceeded until the OCP at the beginning of the test was reached. The applied potential and the measured current were monitored for the duration of the cyclic polarization. After completion of the test, the sample was removed from the test solution, rinsed with deionized water, and dried. Samples were visually inspected for the presence of pitting and crevice corrosion and then placed in a desiccator for storage.

Modified ASTM G192

Results from CPP experiments were not always conclusive. In such cases, a secondary test method was used to clarify the pitting susceptibility of the material. Modified ASTM G192 is a test method by which the protection potential or repassivation potential can be determined [6]. This method predominantly differs from CPP in the time that the system remains at a given polarization. The initial potentiodynamic step is largely the same as the forward scan during a CPP test. While the CPP method uses a constant potential ramp rate on the forward scan immediately followed by the reverse scan, the Modified ASTM G192 method includes a 4-hour galvanostatic hold following the forward scan which allows any stable pits to grow at a stable current density. This period is then followed by the potential being stepped down with the potential being held for two hours at each value. These two-hour potentiostatic holds allow the system to reach a steady state, and either the current density increases, indicating stable pit growth, or remains constant or declines, indicating no localized corrosion. This process continues until the measured current falls below the passive current density observed during the potentiodynamic scan performed during this test. At the point where current density is less than the passive current density, the repassivation potential can be determined.
Sample preparation and setup for this test were carried out in an identical manner as the CPP tests through the two-hour OCP delay. The following test parameters were used:

Potentiodynamic
  Initial potential: -0.1 V vs. open circuit potential
  Final potential: 1.5 V vs. reference electrode
  Current density limit: 50 μA/cm^2
  Scan Rate: 0.1667 mV/s

Galvanostatic
  Hold current density: 50μA/cm^2
  Hold time: 240 min

Potentiostatic Staircase
  Potential step decrement: 25 mV
  Potential hold time: 120 min

The potential and the current were monitored for the duration of the test for all steps. After completion of the test, the sample was removed from the test solution, rinsed with deionized water, and dried. The sample was visually inspected for the presence of pitting and crevice corrosion and then placed in a desiccator for storage.

RESULTS AND DISCUSSION

Cyclic Polarization of Carbon Steel Coupons

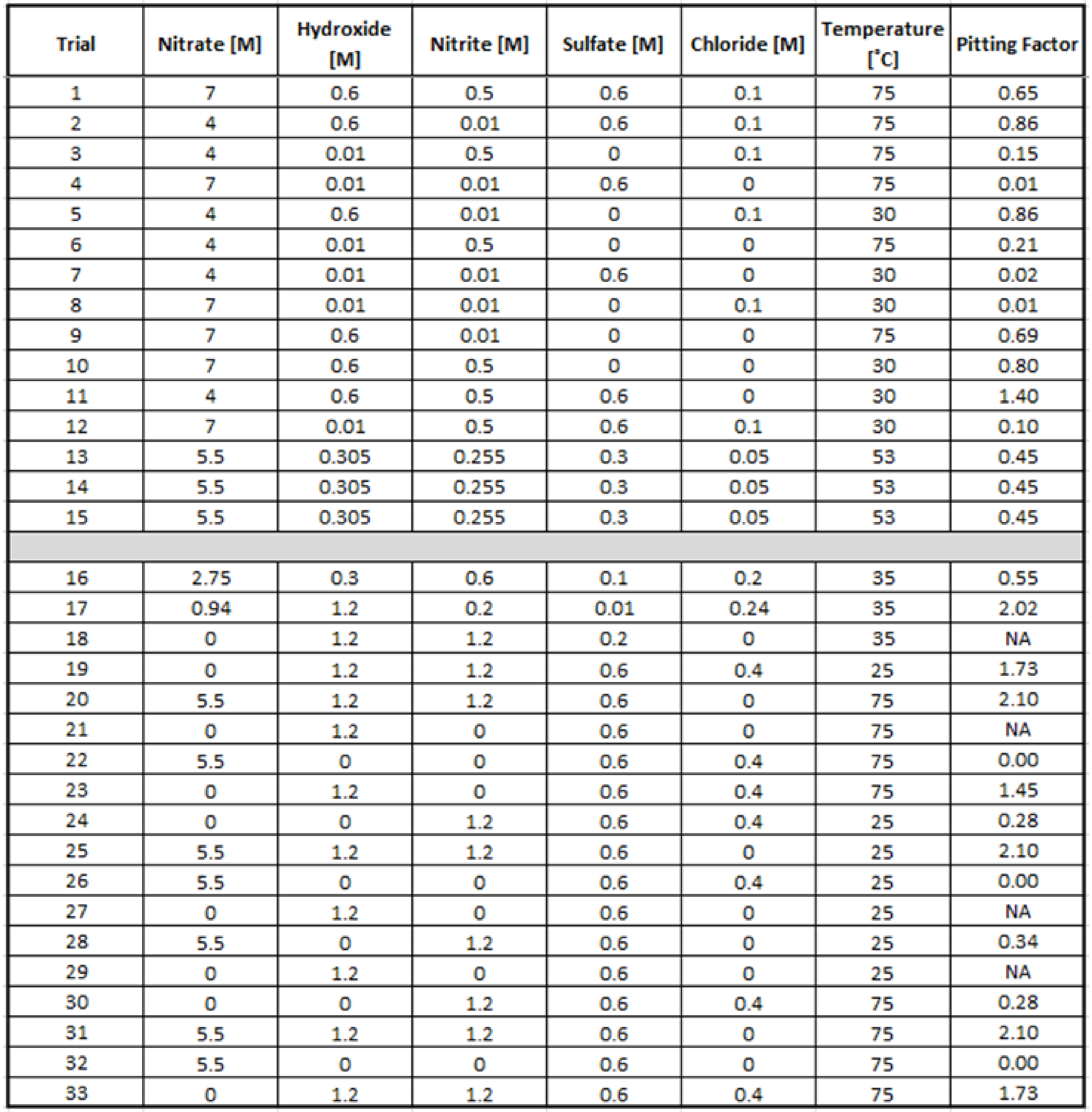
The experimental matrix used for CPP testing is shown below in Table 3. Trials 1 to 15 represent a range of simulated salt dissolution simulant chemistries. This matrix was statistically designed to span the compositional range of salt dissolution chemistries with nitrate concentration up to 7 M or saturation and increased inhibitor concentrations up to 0.6 and 0.5 M for hydroxide and nitrite, respectively. Aluminate, carbonate, and phosphate concentrations were held constant across the chemistry envelope, with these values found in Table 2. Trials 16 to 33 represent a screening matrix based upon work conducted for the mitigation of pitting and SCC of Hanford double-shell tanks [7]. In general, nitrate concentrations are lower, maximum inhibitor concentrations are higher, and chloride is present in higher quantities. In addition, sulfate concentration was also expanded from a maximum of 0.2 M to a maximum of 0.6 M to evaluate its influence on pitting corrosion. This second group of screening trials represents more general SRS tank farm chemistries. Both matrices were also expanded to include temperature up to 75 °C. The table also includes a metric called the pitting factor which is used to determine the susceptibility of the material to pitting corrosion in a given environment. The pitting factor is calculated by a ratio of inhibitor species (hydroxide and nitrite) to aggressive species (nitrate and halides) that are weighted based upon logistic regression of the influence of these species on pitting that resulted from CPP experimental campaigns [7]. The equation for the pitting factor is shown below in Equation 1.

$$\text{Pitting Factor} = \frac{8.06\,[\mathrm{OH}^-]+1.55\,[\mathrm{NO}_2^-]}{[\mathrm{NO}_3^-]+16.7\,[\mathrm{Cl}^-]+5.7[F^-]} \qquad (1)$$

A pitting factor of greater than 2 indicates an environment in which pitting is not anticipated. A pitting factor of less than 1 indicates a condition in which the probability of pitting is high and can occur. Pitting factor values between 1 and 2 represent conditions in which the probability of pitting is low and minor pitting could potentially occur. This metric was determined based upon tank chemistries at Hanford Site; therefore, it is being evaluated in this study for applicability to Savannah River Site waste tank chemistries. It should be noted that fluoride concentration is a factor in the calculation of the pitting factor as it applies to Hanford control programs. However, fluoride concentrations within waste streams at Savannah River are not significant enough to affect the calculation of the pitting factor and were not considered in this work.

Table 3

Chemistry envelope developed for evaluation of pitting corrosion in salt dissolution environments expanded for increased sulfate concentrations.

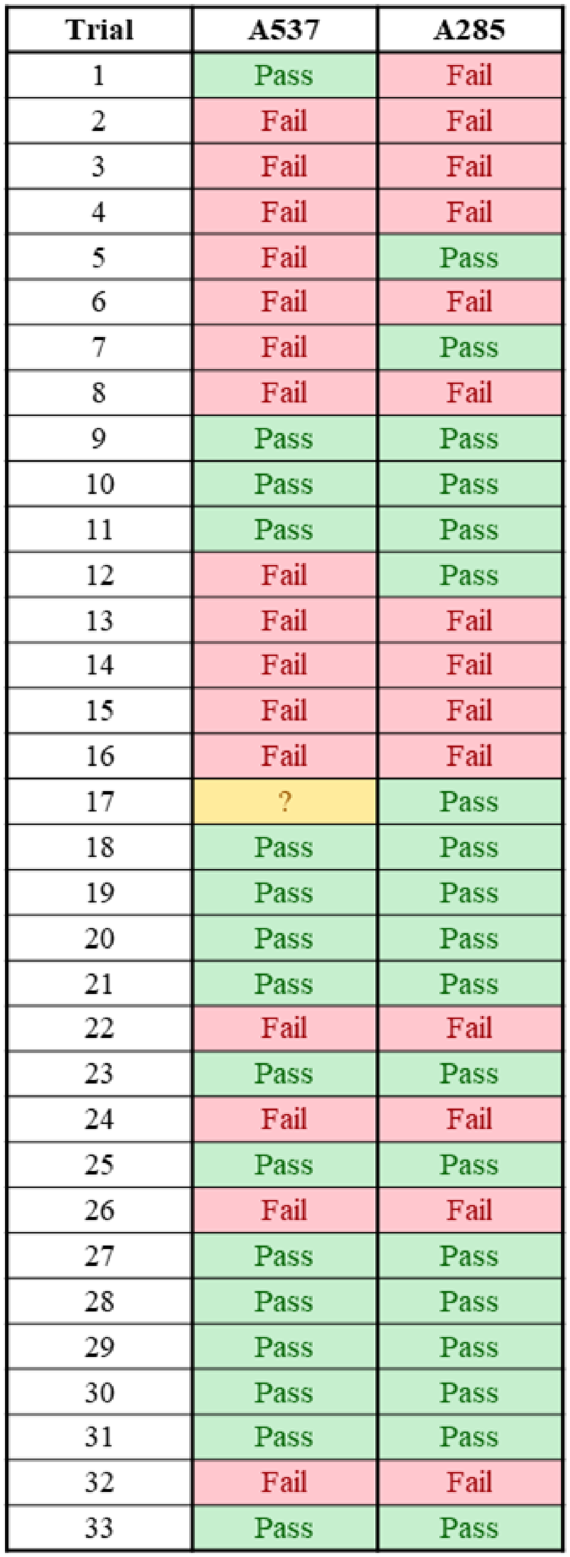


Trial	Nitrate [M]	Hydroxide [M]	Nitrite [M]	Sulfate [M]	Chloride [M]	Temperature [°C]	Pitting Factor
1	7	0.6	0.5	0.6	0.1	75	0.65
2	4	0.6	0.01	0.6	0.1	75	0.86
3	4	0.01	0.5	0	0.1	75	0.15
4	7	0.01	0.01	0.6	0	75	0.01
5	4	0.6	0.01	0	0.1	30	0.86
6	4	0.01	0.5	0	0	75	0.21
7	4	0.01	0.01	0.6	0	30	0.02
8	7	0.01	0.01	0	0.1	30	0.01
9	7	0.6	0.01	0	0	75	0.69
10	7	0.6	0.5	0	0	30	0.80
11	4	0.6	0.5	0.6	0	30	1.40
12	7	0.01	0.5	0.6	0.1	30	0.10
13	5.5	0.305	0.255	0.3	0.05	53	0.45
14	5.5	0.305	0.255	0.3	0.05	53	0.45
15	5.5	0.305	0.255	0.3	0.05	53	0.45
16	2.75	0.3	0.6	0.1	0.2	35	0.55
17	0.94	1.2	0.2	0.01	0.24	35	2.02
18	0	1.2	1.2	0.2	0	35	NA
19	0	1.2	1.2	0.6	0.4	25	1.73
20	5.5	1.2	1.2	0.6	0	75	2.10
21	0	1.2	0	0.6	0	75	NA
22	5.5	0	0	0.6	0.4	75	0.00
23	0	1.2	0	0.6	0.4	75	1.45
24	0	0	1.2	0.6	0.4	25	0.28
25	5.5	1.2	1.2	0.6	0	25	2.10
26	5.5	0	0	0.6	0.4	25	0.00
27	0	1.2	0	0.6	0	25	NA
28	5.5	0	1.2	0.6	0	25	0.34
29	0	1.2	0	0.6	0	25	NA
30	0	0	1.2	0.6	0.4	75	0.28
31	5.5	1.2	1.2	0.6	0	75	2.10
32	5.5	0	0	0.6	0	75	0.00
33	0	1.2	1.2	0.6	0.4	75	1.73

Table 4 displays whether each condition was a pass or fail based upon the criteria described above.

Table 4

Results (Pass/Fail) for all CPP trials for A537 and A285 carbon steels. A question mark (?) indicates that degradation occurred near the acrylic/metal interface that could not be attributed clearly to either crevice or pitting corrosion.



Trial	A537	A285
1	Pass	Fail
2	Fail	Fail
3	Fail	Fail
4	Fail	Fail
5	Fail	Pass
6	Fail	Fail
7	Fail	Pass
8	Fail	Fail
9	Pass	Pass
10	Pass	Pass
11	Pass	Pass
12	Fail	Pass
13	Fail	Fail
14	Fail	Fail
15	Fail	Fail
16	Fail	Fail
17	?	Pass
18	Pass	Pass
19	Pass	Pass
20	Pass	Pass
21	Pass	Pass
22	Fail	Fail
23	Pass	Pass
24	Fail	Fail
25	Pass	Pass
26	Fail	Fail
27	Pass	Pass
28	Pass	Pass
29	Pass	Pass
30	Pass	Pass
31	Pass	Pass
32	Fail	Fail
33	Pass	Pass

Trials 10, 11, 18, 19, 20, 21, 23, 25, 27, 28, 29, 30, 31, and 33 were determined to be passes based upon a negative hysteresis and no pitting observed for both materials. Additionally, Trials 1 and 9 for A537 and Trials 5, 7, 9, 12, and 17 for A285 were considered passes based upon the same criteria or a difference between the corrosion potential and repassivation potential greater than 200 mV. With the exception of Trial 17, the rest were fails based upon the presence of pitting determined visually and/or by a positive hysteresis. Trial 17 for A537 was ultimately determined to be a passing condition after further examination, which will be discussed in the following section. In general, A537 was determined to be more susceptible to pitting corrosion than A285 based upon the number of conditions in which fails occurred. Tanks constructed of A537 are stress relieved, however, this is not anticipated to significantly affect the pitting behavior but can contribute to degradation mechanisms in which mechanical stress is a factor, such as SCC.

These pass/fail results were used to analyze the predictive capability of the pitting factor in addition to examining the influence of sulfate concentration on pitting behavior. The presence of pitting compared to the pitting factor is displayed in Figure 2.

Figure 2: Chart displaying the pitting factor of trials with pitting and no pitting. Note: Trial 17 was shown to not exhibit pitting conclusively after further analysis.

These results indicate a few key points. First, no instances of pitting were observed with a pitting factor greater than 2. Even at the intermediate range between 1 and 2, no pitting occurred. The highest pitting factor to exhibit pitting was at a value of 0.86. This indicates that a pitting factor minimum of 1 would be conservative for the mitigation of pitting corrosion for the compositional ranges examined. Second, several trials with a pitting factor of less than 2, or even less than 1, were shown to not exhibit pitting. This again illustrated conservatism in the predictive capability of the pitting factor with many chemistries that would be deemed non-compliant not actually displaying pitting susceptibility. This generally occurred in environments where one or both inhibiting species were in high concentrations for their given matrix, but nitrate concentrations were sufficient to drive the pitting factor calculation below 1, such as Trials 9, 10, and 28. Therefore, it was concluded that the predictive capability of the pitting factor within the chemistry envelope and temperature range studied was adequate if not conservative.

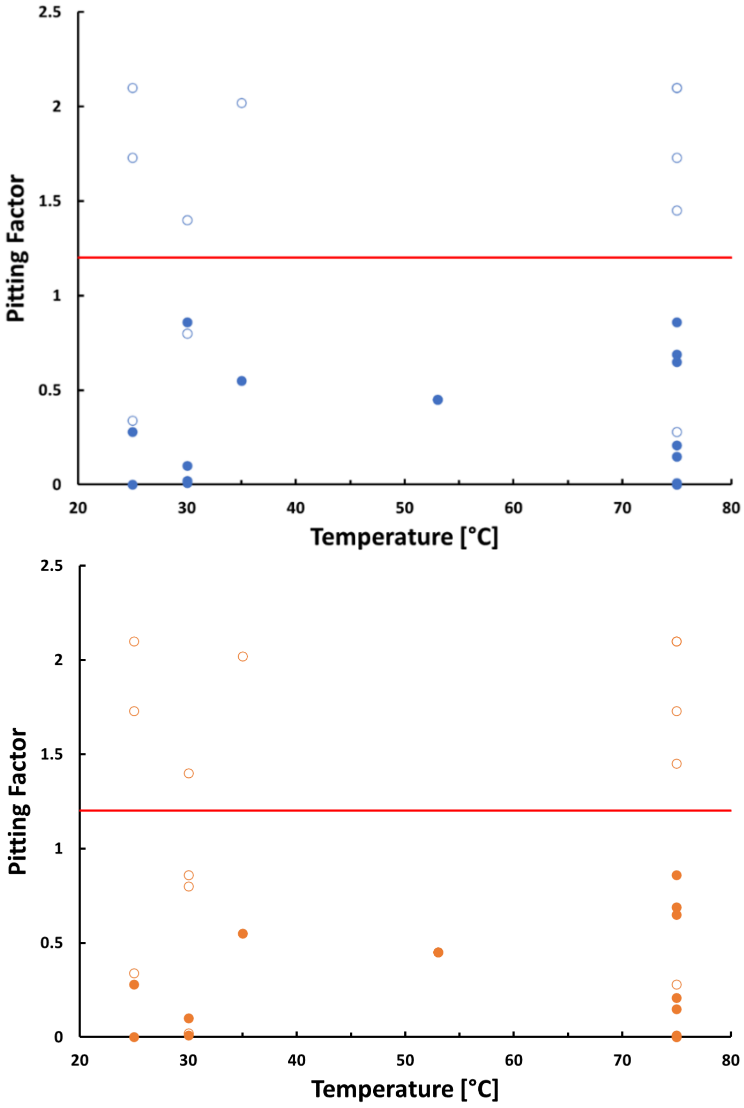


Figure 3: Plots of showing the influence of temperature on pitting incidence for A537 carbon steel (top) and A285 carbon steel (bottom). Open markers indicated trials in which no pitting was observed. The red line indicates the proposed 1.2 control limit for pitting factor.

While no instances of pitting were observed at pitting factors above 1, the region containing trials less than 1.2 (predicted failures) was evaluated to determine if temperature had an effect on pitting incidence. As can be seen in Figure 3, there was no observable temperature effect in the region defined by pitting factor greater than 1.2, with all tests resulting in no pitting. However, the trials with pitting factor less than 1.2 that did not pit seem to indicate an influence on temperature. Out of a total of eight such cases, six of the cases with no pitting and pitting factor less than 1.2 occurred at temperatures of 30 °C or less. The remaining two cases occurred at 75 °C. These results indicate a higher likelihood of pitting incidence within the region defined by pitting factor less than 1.2 at elevated temperatures. It is important to note that this finding does not affect the validity of the pitting factor used as predictive metric or defining a control limit, as no instances of pitting are observed at any temperature at pitting factor greater than 0.86. However, it represents an indication that increased operating temperatures and exposure to low pitting factor chemistries present an increased risk of pitting incidence.

In addition, statistical analysis of all variables within the test matrices was conducted to determine the relative influence of each variable on the outcome (pass or fail). For this analysis, four submatrices were evaluated individually: Trials 1-15 for A537 (A537-SD), Trials 16-33 for A537 (A537-HT), Trials 1-15 for

A285 (A285-SD), and Trials 16-33 for A285 (A285-HT). A Likelihood Ratio Chi Square test was conducted on these matrices to determine the relative influence of nitrate, hydroxide, nitrite, sulfate, and chloride concentrations on a pass or failure. The results are listed below in Table 6.

Table 5

Results of Likelihood Ratio Chi Square statistical analysis for determining the influence of chemical species on pitting susceptibility.

A537-SD

Source	L-R Chi Square	Prob > Chi Square
Nitrate	7.60E-08	0.9998
Hydroxide	35.13	<.0001*
Nitrite	4.65E-08	0.9998
Sulfate	1.95E-08	0.9999
Chloride	4.05E-07	0.9995

A285-SD

Source	L-R Chi Square	Prob > Chi Square
Nitrate	9.07E-04	0.9760
Hydroxide	7.64	0.0057*
Nitrite	0	1.0000
Sulfate	1.44E-04	0.9904
Chloride	13.29	0.0003*

A537-HT

Source	L-R Chi Square	Prob > Chi Square
Nitrate	1.18E-07	0.9997
Hydroxide	7.27	0.0070*
Nitrite	20.78	<.0001*
Sulfate	1.10E-07	0.9997
Chloride	2.19E-07	0.9996

A285-HT

Source	L-R Chi Square	Prob > Chi Square
Nitrate	1.18E-07	0.9997
Hydroxide	7.27	0.0070*
Nitrite	20.78	<.0001*
Sulfate	1.10E-07	0.9997
Chloride	2.19E-07	0.9996

Two values are presented in Table 5. The Likelihood Ratio Chi Square Value (L-R Chi Square) indicates a likelihood that a given variable influences the outcome more than the case where none of the variables have any effect on the result, i.e., the result is random and independent of the parameters. A L-R Chi Square value of greater than 0.05 indicates some level of correlation between a given parameter and the outcome of the test. The second value is the Prob > Chi Square, which indicates the probability that Chi Square value larger than the L-R Chi Square value is achievable assuming the hypothesis that all variables are unrelated and do not affect the outcome. Essentially this illustrates the probability that the calculated correlation between a variable and the outcome could be observed by chance if no real influence was present. This means that variables with a Prob > Chi Square at or near 1 exhibit no meaningful influence that could be distinguished from random chance. In general, this analysis shows that inhibitor levels (in particular hydroxide) had the greatest impact on the pass/fail result of the CPP test. Chloride was shown to exhibit a statistically significant influence in one subset of the test matrix; however, this result is not maintained when the entire test matrix is considered. The potential for sulfate to be considered as an additional aggressive species as discussed previously was also explored. As indicated by the Prob > Chi Square values in Table 6, there is a probability less than 1% in each subset of the matrix that sulfate concentration had an influence greater than any random, unrelated variable. Therefore, within the compositional range studied (up to 0.6 M), sulfate concentration was not predicted to have any meaningful influence on pitting susceptibility.

Modified ASTM G192

A conclusive result was not always attainable with CPP alone. This was the case with Trial 17 for A537 carbon steel. CPP results from this trial can be found in Figure 4. The initial CPP test (a) displayed a positive hysteresis, though the current density on the reverse scan was less than an order of magnitude different from the passive current density. Localized attack was observed on the sample surface; however, this attack was confined to at or near the interface between the acrylic and metal. Observation of the sample was inconclusive as to whether the attack initiated on the boldly exposed surface or within the crevice region. Therefore, the trial was repeated to elucidate whether attack could be attributed to experimental artifact. This CPP (b) revealed a negative hysteresis and no indications of localized attack. With conflicting results between the two tests, a separate electrochemical technique was used to determine the pitting characteristics of A537 exposed to the conditions of Trial 17. Modified ASTM G192 has been used previously to determine the repassivation behavior of carbon steels in similar simulants [6]. This method predominantly differs from CPP in the time that the system remains at a given polarization. The two-hour potentiostatic holds allow the system to reach a steady state, and either the current density increases, indicating stable pit growth, or remains constant or declines, indicating no localized corrosion. The results of this test can be found in Figure 5.

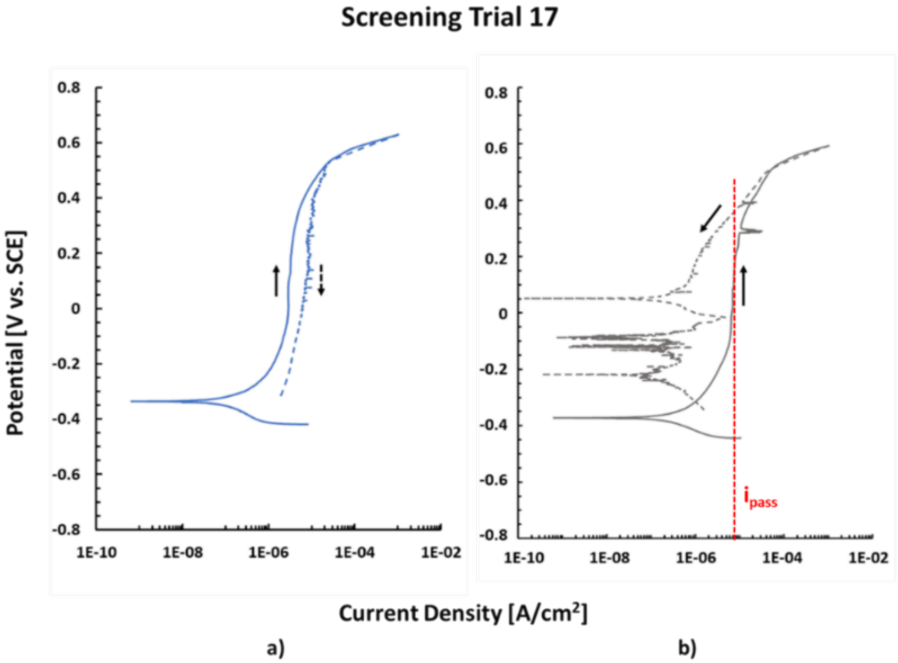


Figure 4: CPP curves for Trial 17 for A537. a) initial CPP curve b) subsequent CPP curve. The red dashed line indicates the passive current density used in the analysis of the Modified ASTM G192.

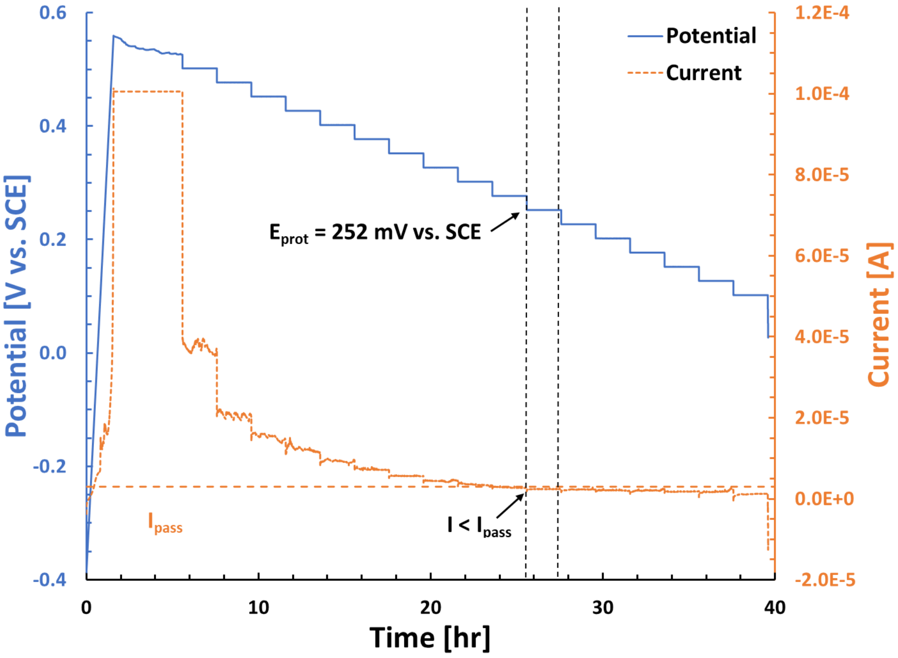


Figure 5: Modified ASTM G192 data for Trial 17 for A537

Stable increases in current were not observed for any of the potentiostatic steps. This indicated a lack of stable pit growth even during the initial potentiostatic holds. However, the protection potential requires that the measured current density be less than the passive current density. At a potential of 252 mV vs. SCE these two criteria were met, and a protection potential was established. The difference between this potential and the corrosion potential was greater than 600 mV. These results, coupled with the lack of any indications of localized corrosion upon visual inspection of the sample, resulted in a pass condition for Trial 17 for A537. The positive hysteresis and localized corrosion observed in the initial CPP for Trial 17 were attributed to crevice corrosion that was the result of less than adequate sample preparation.

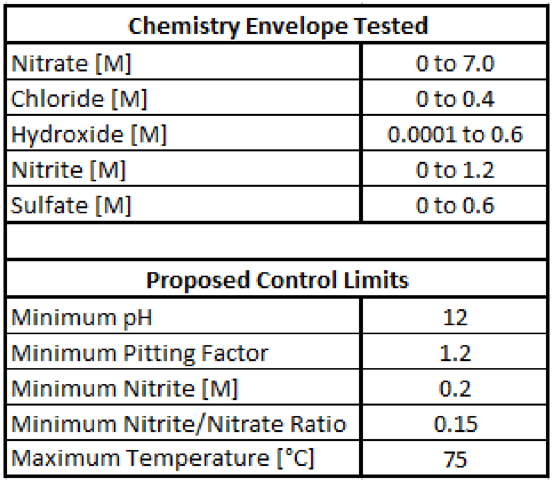
CONCLUSIONS

An experimental matrix was designed to evaluate the use of the pitting factor for supernate chemistries characteristic to SRS, particularly during the salt dissolution process. Two electrochemical test methods were utilized to determine the susceptibility of A537 and A285 low-carbon steels to pitting corrosion with this chemistry envelope at temperatures up to 75 °C. The predominant test method was CPP studies. Through CPP, the pitting factor was determined to accurately identify pitting susceptibility within the compositional range investigated. Additionally, sulfate was determined to have no significant influence on pitting behavior, at concentrations up to 0.6 M. The Modified ASTM G192 method was successfully used to evaluate conditions where CPP was inconclusive and allowed for a pass/fail result to be determined. In all cases the pitting factor was determined to be applicable to the simulants tested, with this metric accurately predicting incidences in which pitting occurred.

Table 6 summarizes the chemistry envelope over which pitting behavior was examined and recommends a minimum pitting factor of 1.2 for temperatures up to 75 °C. The chemistry envelope tested includes both the testing performed for this program and that performed for Hanford [8]. While a minimum pitting factor threshold of 1 was determined to be sufficient for the prediction of pitting corrosion, a pitting factor of 1.2 is being proposed to build in a safety factor and remain consistent with the Hanford Site approach [7]. Additionally, a minimum pH limit of 12 is proposed to ensure passivity and that localized corrosion is the primary form of corrosion degradation

Table 6

Summary of chemistry envelope and proposed control limits



Chemistry Envelope Tested	
Nitrate [M]	0 to 7.0
Chloride [M]	0 to 0.4
Hydroxide [M]	0.0001 to 0.6
Nitrite [M]	0 to 1.2
Sulfate [M]	0 to 0.6
Proposed Control Limits	
Minimum pH	12
Minimum Pitting Factor	1.2
Minimum Nitrite [M]	0.2
Minimum Nitrite/Nitrate Ratio	0.15
Maximum Temperature [°C]	75

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the assistance of B. Hill and T. Murphy in the execution of the testing program. The authors would also like to acknowledge Dr. Stephen Harris for his assistance with the statistical design and analysis of the experiments.

REFERENCES

1. K.B. Martin, “CSTF Corrosion Control Program: Program Description Document”, WSRC-TR-2002-00327, Rev. 9, December 16, 2015.
2. B. J. Wiersma, J. I. Mickalonis “Determination of Corrosion Inhibitor Criteria for Type III/IIIA Tanks During Salt Dissolution Operations”, WSRC-STI-2006-00029, Rev. 0, September 2007.
3. K. M. Counts, B. J. Wiersma, J. I. Mickalonis, “Determination of Corrosion Inhibitor Criteria for Type III/IIIA Tanks During Salt Dissolution Operations-Interim Report”, WSRC-STI-2007-00552, Rev. 0, December 2007.
4. B. L. Garcia-Diaz, J. I. Mickalonis, B. J. Wiersma, “Determination of Corrosion Inhibitor Criteria for Type III/IIIA Tanks During Salt Dissolution Operations-Summary Document”, SRNL-STI-2009-00600, Rev. 0, October 2009.
5. T. Martin, “Tank Integrity Expert Panel Corrosion Subgroup March 2016 Meeting Outcomes”, RPP-ASMT-60833, Washington River Protection Solutions LLC, Richland, WA, May 2016.
6. K.J. Evans, S. Chawla, K. Sherer, J. Gerst, J.A. Beavers, K. Boomer. The Use of ASTM G192 (Tsujikawa-Hisamatsu Electrochemical Method) to Evaluate the Susceptibility of Hanford Tank Steels to Pitting Corrosion. *Corrosion.* 2016.
7. B.J. Wiersma, R.E. Fuentes, L.M. Stock, “Chemistry Envelope for Pitting and Stress Corrosion Cracking Mitigation”, SRNL-STI-2019-00217, Rev. 0, September 2019.
8. K. J. Evans, N. Sridhar, B.C. Rollins, S. Chawla, J.A. Beavers, and J. Page. Long Term Evolution of Corrosion Potentials of Carbon Steel in Alkaline Radioactive Environments*.* *Corrosion*. 2019