Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

Waste Chemistry Envelope for the Determination of Pitting Corrosion Susceptibility – 19554

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ABSTRACT

Liquid radioactive wastes at the Hanford and Savannah River sites are stored in large underground carbon steel tanks. The high-level wastes are processed in several of the tanks and then transferred by piping to other site facilities for further processing before they are stabilized in a vitrified or grout waste form. Based on waste removal and processing schedules, many of the tanks, will be required to be in service for times exceeding the initial intended life (i.e., greater than 60 years). Until the waste is removed from storage, transferred, and processed, the materials and structures of the tanks must maintain a confinement function by providing a barrier to the environment and by maintaining acceptable structural stability during design basis events, which include loadings from both normal service and abnormal (e.g., earthquake) conditions.

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. Chemistry controls are based on in-situ coupon tests, waste tank experience, and laboratory testing. These requirements comprise the technical standards for corrosion control. The standards are utilized then as guidelines for operational procedures.

The present waste chemistry controls for the Hanford DSTs were established in the 1980s in response to tank failures caused by stress corrosion cracking (SCC) at the DOE Savannah River Site (SRS). Portions of the SRS chemistry limits, which were developed at the Savannah River National Laboratory (SRNL) were coupled with corrosion testing results from Pacific Northwest National Laboratories (PNNL) and adopted for corrosion control of the double-shell tank (DST) waste at the Hanford Site. Since that time, the temperatures of the waste in the DSTs have decreased to less than 50 °C in most cases as the radioactive material has decayed. As a consequence, new chemistry controls were formulated for SCC in 2010. This testing however, did not address that potential for pitting in the supernatant and at the liquid-air interface. Indeed, initial tests indicated that the inhibitor requirements for SCC would be insufficient for the prevention of pitting.

In addition to lower waste temperatures, future retrieval and process changes may impact the DST waste chemistry. Initial projections suggest that the waste chemistry of the DSTs may shift to a broader range of pH and higher aggressive anion concentrations (e.g., chloride, sulfate, etc.) than the wastes that are presently stored. Additionally, processes within the vitrification facility may result in streams that are returned to the tank farm for evaporation. These streams may also contain high concentrations of aggressive species.

SRNL investigated the propensity for pitting of the carbon steel waste tanks at current and projected DST waste chemistries. A statistically designed series of tests provided a pitting factor that relates the ratio of the inhibitor species to the aggressive species and the probability of observing pitting. An acceptable pitting factor was determined and was utilized for the development of a new chemistry envelope. The new chemistry envelope was compared to the envelope that was established for SCC and was determined to be bounding. Validation of the new chemistry envelope was performed via model simulations and

comparison with historical experimental results and approaches to establishing chemistry envelopes. The new chemistry envelope will eventually be part of an overall assessment of the condition of the tanks and any changes made to the overall structural integrity program for the Hanford DSTs.

INTRODUCTION

The present waste chemistry controls for the Hanford DSTs were established in the 1980s in response to tank failures caused by stress corrosion cracking (SCC) at the DOE Savannah River Site (SRS). Portions of the SRS chemistry limits [1], which were developed at the Savannah River National Laboratory (SRNL) were coupled with corrosion testing results from Pacific Northwest National Laboratories (PNNL) [2, 3] and adopted for corrosion control of the double-shell tank (DST) waste at the Hanford Site. Since that time, the temperatures of the waste in the DSTs have decreased to less than 50 °C in most cases as the radioactive material has decayed. As a consequence, new waste chemistry controls were formulated for SCC in 2010 [4]. This testing however, did not address that potential for pitting in the supernatant and at the liquid-air interface. Indeed, initial tests indicated that the inhibitor requirements for SCC would be insufficient for the prevention of pitting [5].

The Tank Integrity Expert Panel (TIEP) Corrosion Subgroup (CSG) recommended that additional testing be performed to assess the potential for pitting and liquid air interface (LAI) corrosion. Since 2016, DNVGL, SRNL, and the Hanford Site laboratory have investigated pitting and LAI corrosion at current and anticipated DST chemistry [6-8] and SRNL undertook a statistically based investigation of the role of nitrate and halide ion induced pitting corrosion. The objective was to develop comprehensive control limits for the simultaneous minimization of the pitting and cracking corrosion risks caused by halide and nitrate ion.

In addition to lower waste temperatures, future retrieval and process changes may impact the DST waste chemistry. For example, during feed preparation of the liquid waste for eventual stabilization by vitrification or grout formulation, the waste is retrieved from SSTs that are suspected leakers and transferred to DSTs. This transference of waste can impact the waste chemistry of the DST. Initial projections suggest that the waste chemistry of the DSTs may shift to a broader range of pH and higher aggressive anion concentrations (e.g., chloride, sulfate, etc.) than the wastes that are presently stored. Additionally, processes within the vitrification facility may result in streams that are returned to the tank farm for evaporation [9]. These streams may also contain high concentrations of aggressive species.

This paper summarizes the technical basis for the waste chemistry envelope to minimize the potential for pitting corrosion based upon the nitrate and halide ion. Validation of these tests by simulation and comparison with previous laboratory tests was performed.

PITTING FACTOR DEVELOPMENT

SRNL has conducted laboratory tests to investigate pitting corrosion at current and anticipated DST waste chemistries since 2016. The testing utilized a protocol for cyclic potentiodynamic polarization (CPP) to assess the susceptibility of carbon steel to pitting corrosion in DST chemistries [10]. The “pass” or “fail” condition was determined from the six categories specified by the CPP test protocol. Categories 1 and 2, for which CPP test indicated either a negative hysteresis or a significantly noble repassivation potential with respect to the initial open circuit potential (OCP) (>200 mV), respectively, were assigned a “0” or pass rating. Alternatively, categories 4, 5, and 6, which had positive hysteresis with a repassivation potential that was only slightly noble compared with the initial OCP (< 200 mV), a negative value when compared to the initial OCP, or indicated general corrosion, respectively, were assigned a “1” or fail rating. A category 3, or mixed hysteresis condition that was considered inconclusive, was re-tested using a modified ASTM G192 test method [11]. The modified ASTM G192 method is based on the Tsujikawa-

Hisamatsu Electrochemical (THE) method [12] and can be used to determine the repassivation potential. In this case, it was used to provide a definite categorization of pass or fail for borderline cases that showed mixed hysteresis. If the results were a pass, “0” was used and if it was a fail “1” was used.

Statistically designed test matrices were utilized to explore the boundaries of the DST chemistry envelope as well as interior points within the envelope [6, 7]. Table 1 shows the species that were investigated and the range of compositions for each.

Table 1. Composition Ranges for Statistical Tests

Species	**Minimum**	**Maximum**
Hydroxide (M)	**0.0001**	**1.2**
Nitrate (M)	**0**	**5.5**
Nitrite (M)	**0**	**1.2**
Chloride (M)	**0**	**0.4**
Fluoride (M)	**0**	**0.3**
Sulfate (M)	**0**	**0.2**
TIC (M)	**-**	**0.1**
Temperature (°C)	**25**	**50**

During FY16, the major variables affecting pitting corrosion were determined from Plackett-Burman and Box-Behnken statistical design matrices. The significant concentration variables were nitrate, nitrite, hydroxide, and chloride. For FY17, the original FY16 test matrix was augmented to include hydroxide concentrations up to 1.2 M [7]. These results were combined with the previous results from Plackett-Burman and Box-Behnken statistical design [6] for a total of 80 conditions. Finally, 15 interior chemistry conditions were tested to assess the robustness of the statistical model. These 95 data points were utilized to establish a statistical model. Finally, in FY18, margins tests were performed to better understand the chemistry envelope should be established [8]. A second series of tests were performed to determine if the effects of the fluoride and chloride concentrations could be distinguished. This is particularly significant for solutions with relatively low chloride concentrations, but somewhat higher fluoride concentrations.

Logistic regression analysis was performed to develop a model for pitting susceptibility prediction [7]. Logistic regression assumes a binary response, pass or fail in this instance. The probability of a failure, as determined from the CPP test, is calculated as shown in Equation 1. [Note: “1” is indicative of a failure, while “0” indicates a pass condition). Equation 2 is the linear relationship between the statistically significant variables. The statistically significant variables were hydroxide, nitrate, nitrite, and chloride. Inhibitor species are indicated by a positive coefficient, while aggressive species have a negative coefficient.

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

$$\text{Lin}(0) = a + b\,[OH^-] + c\,[NO_2^-] - d\,[NO_3^-] - e\,[Cl^-] - f\,[F^-] \quad \text{(Eqn. 2)}$$

The coefficients calculated from the statistical analysis are shown in Equation 3.

$$\text{Lin}(0) = 1.99 + 15.54\,[OH^-] + 2.99\,[NO_2^-] - 1.93\,[NO_3^-] - 32.11\,[Cl^-] - 10.7\,[F^-] \quad \text{(Eqn. 3)}$$

The coefficients for the species variables generated from the probability model were utilized in the development of an empirical "pitting factor" to provide a criterion for pitting susceptibility. Equation 4 shows the final form of the pitting factor. The pitting factor is a weighted ratio of the inhibitor species to the aggressive species.

$$Pitting\ Factor = \frac{8.06*[Hydroxide]+1.55*[Nitrite]}{[Nitrate]+16.7*[Chloride]+5.7*[Fluoride]} \quad \text{(Eqn. 4)}$$

CHEMISTRY ENVELOPE

Table 3 presents the chemistry envelope where the test results indicate minimal probability of corrosion. The nitrite/nitrate ratio was maintained for nitrate SCC prevention. The basis for the two-tiered approach for the pitting factor as determined by the hydroxide concentration will be elaborated on below. For unanticipated chemistry/temperature conditions outside these ranges, pitting corrosion and SCC tests are recommended to ensure that the tank is protected from these degradation mechanisms.

VALIDATION OF WASTE CHEMISTRY ENVELOPE

Two approaches were utilized to validate the envelope to minimize the potential for pitting corrosion: 1) simulations based on calculated pitting probabilities, and 2) comparison with historical experimental data. The simulations were performed with an EXCEL^{TM} spreadsheet. Up to 2000 random solutions were generated from concentrations of hydroxide, nitrite, nitrate, chloride, and fluoride. Ranges on the random compositions for each species were incorporated based on the requirements in Table 3 (e.g., a minimum nitrite concentration of 0.2 M, a maximum nitrate concentration of 5.5 M etc.). For each composition, the pitting probability and the pitting factor were calculated. Figure 1 plots the pH vs. the pitting factor and shows the probability of failure for each of the random simulations. Table 4 shows the relationship between the color in the figure and the probability of pitting.

Table 3. Waste Chemistry Envelope

Species	Minimum	Maximum
Nitrate (M)	-	5.5
Nitrite (M)	0.2	
Nitrite ion/Nitrate ion	0.15	
Temperature (°C)	-	50
AND		
Hydroxide (M)	0.001	0.1
Pitting Factor	2	-
Hydroxide (M)	0.1	6
Pitting Factor	1.5	-

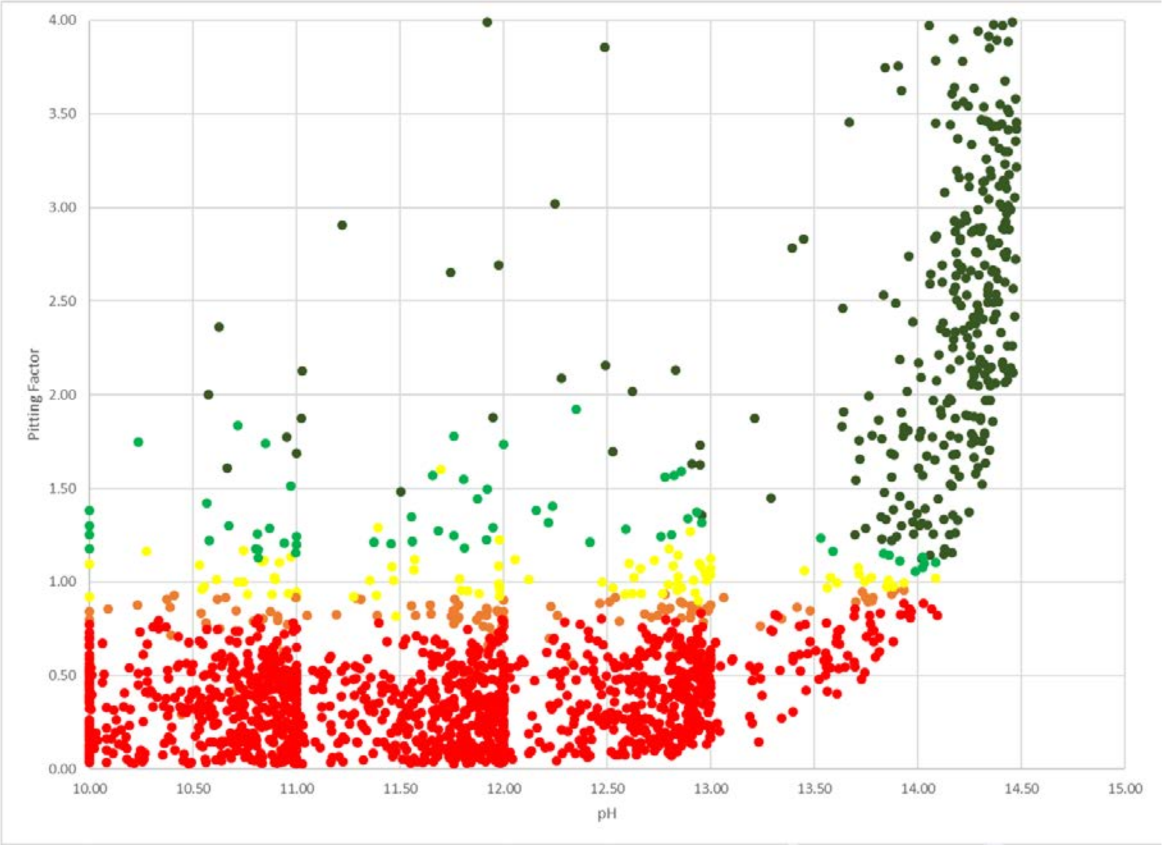

Figure 1. Simulation results for random waste chemistry compositions.

Table 4. Legend for Figure 1 Probabilities

Color	Probability
Dark Green	< 0.01
Green	$0.01 < P < 0.05$
Yellow	$0.05 < P < 0.20$
Orange	$0.2 < P < 0.5$
Red	$P > 0.5$

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. Thus, a composition with a pitting factor less than 1 presents a likely condition for pitting. For a pitting factor greater than 2, the probability of pitting is less than 0.01, which indicates that pitting is an unlikely occurrence at these conditions. For a pitting factor between 1 and 2, the probability ranges between less than 0.01 to less than 0.2. This pitting factor range clearly represents a transition between a likely pitting event and an unlikely pitting event. The pH is also a factor in the probability that is observed. For example, a pH greater than 13 with a pitting factor greater than 1.5 the pitting probability was always less than 0.01. However, for a pH less than 13 with a pitting factor greater than 1.5, there are several instances where the probability is up to 0.05 and one case where it approaches 0.1. Based on these observations a two-tiered approach for the chemistry envelope is proposed as shown in Figure 2.

Figure 2 does not reveal the basis for the minimum nitrite and pH requirements. 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 [14]. At extremely dilute concentrations (e.g., nitrate 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. A minimum of 0.2 M nitrite for these cases is expected to provide protection in these situations. The minimum pH was tied to two factors. First, pH 11 is coincident with the SCC chemistry controls and thus would not create an unnecessary gap between the two. Secondly, at less than pH 12 nitrite becomes the primary inhibitor per the pitting factor model. This result correlates with experimental observations that there was no significant difference between pitting tests performed at pH 10 vs. pH 12 [15].

The second method for validation was to compare historical experimental data with the new chemistry envelope. The historical results are plotted in Figure 3 along with the new chemistry envelope [Note: Some of the historical results were not performed with the present CPP protocol. However, these results have been shown to be similar [5]). The test conditions are summarized in Table 5.

Approximately 80% of the tests performed at a pitting factor less than 1 failed. There were some isolated cases where the pitting factor was above 1 and failed, the majority of these occurred at a pH less than 13. At SRS, the chemistry envelope for pitting were established by plotting the test results on a log-log aggressive species vs. nitrite graph [14]. A least-squared fit line that forms a boundary between the pass and no-pass test conditions was then determined. A 50% safety margin was added to the line (i.e., effectively increasing the minimum nitrite to aggressive species ratio by a factor of 1.5). The safety margin accounted for analytical error and uncertainties in the local chemistry of the tank. For the tests that failed at a pH less than 13, the maximum pitting factor was approximately 1.3. If the same 50% factor utilized at SRS was implemented, the criteria for the cut-off would be 1.95 or approximately 2. Above pH 13, there was one data point slightly above a pitting factor of 1 (i.e., 1.06). A factor of 1.5

would increase the criteria to 1.6. However, given the significant quantity of data, and the results of the simulation above accepting a pitting factor criterion of 1.5 is reasonable.

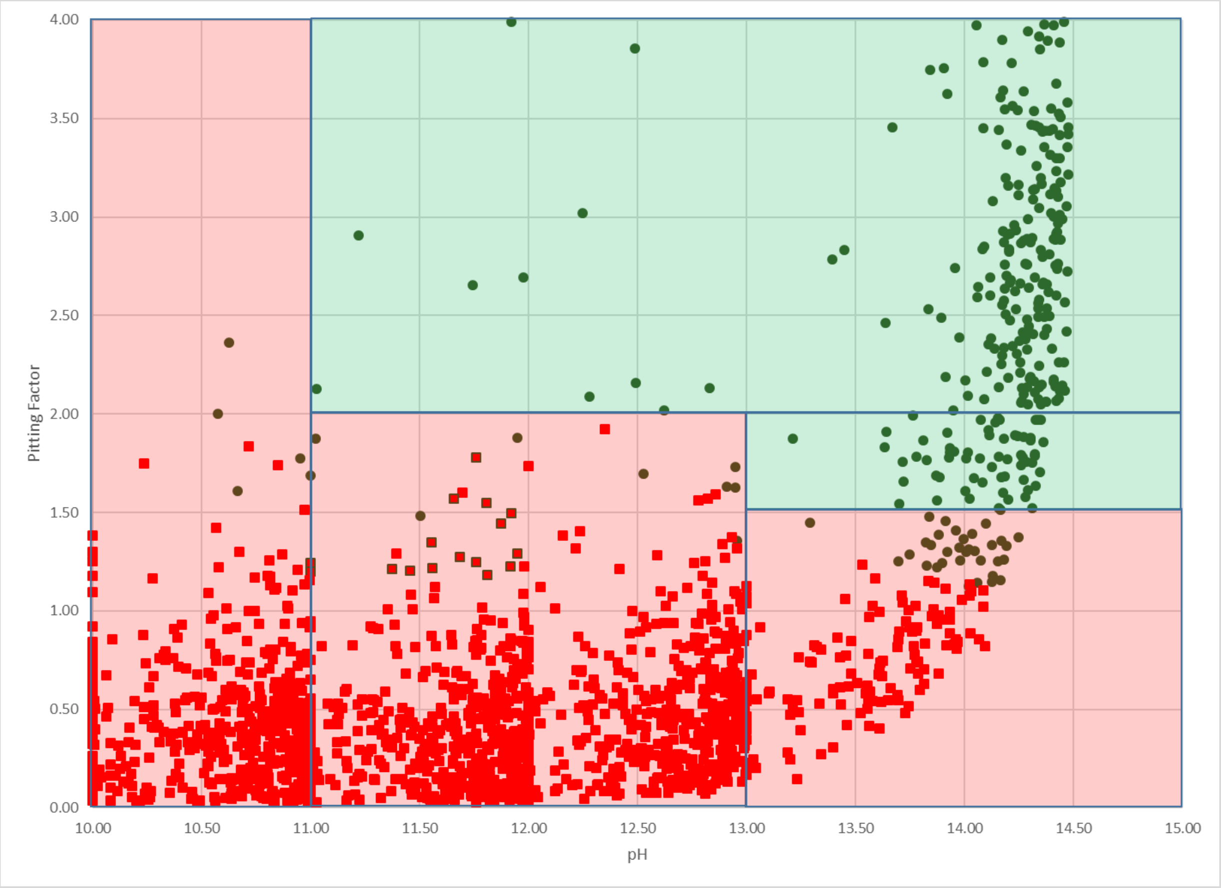

Figure 2. Proposed pitting factor chemistry envelope for waste chemistry control. Probability of pitting less than 0.01 is represented by the circles, while all probabilities greater than 0.01 are represented by the squares. Green shaded area is an acceptable region, while red shaded area is unacceptable.

CONCLUSIONS

SRNL investigated the propensity for pitting of the carbon steel waste tanks at current and projected DST waste chemistries. A statistically designed series of tests provided a pitting factor that relates the ratio of the inhibitor species to the aggressive species and the probability of observing pitting. An acceptable pitting factor was determined and utilized for the development of new chemistry envelope. The new chemistry envelope was compared to the envelope that was established for SCC and was determined to be bounding. Validation of the new chemistry envelope was performed via model simulations and comparison with historical experimental results and approaches to establishing chemistry envelope. The new chemistry envelope will eventually be part of an overall assessment of the condition of the tanks and any changes made to the overall structural integrity program for the Hanford DSTs.

Table 5. Range of Compositions and Temperatures for Historical Tests

Species/Temperature	Minimum	Maximum
Hydroxide (M)	0.0001	7.3
Nitrite (M)	0	7
Nitrate (M)	0	5.5
Fluoride (M)	0	0.58
Chloride (M)	0	0.4
Sulfate (M)	0	0.48
TIC (M)	0	2.1
Temperature (°C)	20	50

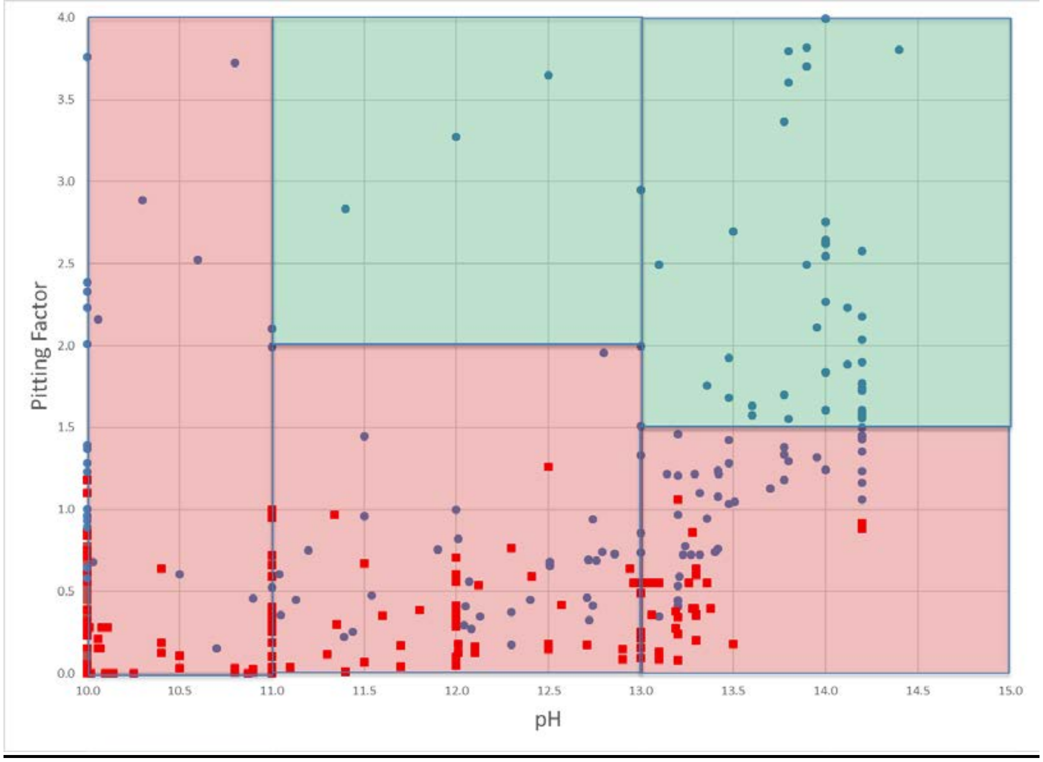

Figure 3. Historical experimental results. Circles indicate a test condition that was a pass, while squares indicate a test condition that failed. Green shaded area is an acceptable region, while red shaded area is unacceptable.

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ACKNOWLEDGEMENTS

The authors wish to acknowledge the contributions of Dr. Leon Stock, Mr. Ryan Murray, Dr. John Beavers, Dr. Narasi Sridhar, Dr. Scott Lillard, Dr. Stephen Harris, Dr. Brenda Garcia-Diaz, Dr. Russell Jones, and Mr. Todd Martin.