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EVALUATION OF SRAT SAMPLING DATA IN SUPPORT OF A SIX SIGMA YELLOW BELT PROCESS IMPROVEMENT PROJECT

Thomas B. Edwards

June 2005

Statistical Consulting Section
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SRNL
SAVANNAH RIVER NATIONAL LABORATORY

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EXECUTIVE SUMMARY

As part of the Six Sigma continuous improvement initiatives at the Defense Waste Processing Facility (DWPF), a Yellow Belt team was formed to evaluate the frequency and types of samples required for the Sludge Receipt and Adjustment Tank (SRAT) receipt in the DWPF. The team asked, via a technical task request, that the Statistical Consulting Section (SCS), in concert with the Immobilization Technology Section (ITS) (both groups within the Savannah River National Laboratory (SRNL)), conduct a statistical review of recent SRAT receipt results to determine if there is enough consistency in these measurements to allow for less frequent sampling. As part of this review process, key decisions made by DWPF Process Engineering that are based upon the SRAT sample measurements are outlined in this report. For a reduction in SRAT sampling to be viable, these decisions must not be overly sensitive to the additional variation that will be introduced as a result of such a reduction.

Measurements from samples of SRAT receipt batches 314 through 323 were reviewed as part of this investigation into the frequency of SRAT sampling. The associated acid calculations for these batches were also studied as part of this effort.

The results from this investigation showed no indication of a statistically significant relationship between the tank solids and the acid additions for these batches. One would expect that as the tank solids increase there would be a corresponding increase in acid requirements. There was, however, an indication that the predicted reduction/oxidation (REDOX) ratio (the ratio of Fe^{2+} to the total Fe in the glass product) that was targeted by the acid calculations based on the SRAT receipt samples for these batches was on average 0.0253 larger than the predicted REDOX based upon Slurry Mix Evaporator (SME) measurements. This is a statistically significant difference (at the 5% significance level), and the study also suggested that the difference was due to predictions of the formate and Mn concentrations in the SME product that were made at the time of the acid addition in the SRAT. For each of these analytes, the SRAT version was statistically different from the SME version (units are moles/kg SME product slurry): the SRAT values were, on average, 0.0914 larger than the SME values for formate and 0.0089 smaller than the SME values for Mn. A look at the signs of the terms corresponding to these two analytes in equation (2) indicates that both of these differences contribute to the calculated REDOX differences between the SRAT and SME product.

Based upon the results from this study, when targeting a stoichiometric factor of 155% using average measurements for the SRAT receipt, the actual factor realized for any given batch would be expected to fall within the interval from 133.3% to 176.7% with 95% confidence. When targeting a REDOX of ~0.2 using average measurements, the actual factor realized for any given batch would be expected to fall within the interval from 0.166 to 0.234 with 95% confidence.

Based on the results of this study, the following recommendations are made:

- DWPF should consider adjusting their acid calculation to align the Mn concentration in SRAT receipt with the Mn concentration in the SME product.
- DWPF should consider adjusting their acid addition strategy to introduce a 9.7% loss (as a 0.903 correction factor) as part of the evaluation of formate in the SME product portion of their spreadsheet.
- DWPF should evaluate how a $\pm 14\%$ uncertainty in their targeted stoichiometric factor and a $\pm 17\%$ uncertainty in the targeted REDOX may affect the success of their acid addition strategy.

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LIST OF ACRONYMS

DWPF	Defense Waste Processing Facility
HLW	High Level Waste
ITS	Immobilization Technology Section
JMP	Pronounced “jump.” It’s a statistical software package, a registered trademark of SAS Institute, Inc.
SCS	Statistical Consulting Section
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

1.0 INTRODUCTION AND BACKGROUND

The Defense Waste Processing Facility (DWPF) Analytical Laboratory routinely conducts chemical analyses of tank samples at several points during the processing of High Level Waste (HLW) at the DWPF. Included in the samples submitted to the laboratory for such analyses are samples of the Sludge Receipt and Adjustment Tank (SRAT) after the receipt of each process batch (designated as SRAT receipt samples) and just prior to the transfer of the SRAT material to the Slurry Mix Evaporator (SME) (designated as SRAT product samples). Currently, the time required to take, analyze, report, and interpret the results from these SRAT samples does not delay the processing in DWPF, but in the future, with the incorporation of possible salt streams into the feed going to DWPF and with other facility improvements, it could. In addition, analyzing the samples requires the time of both laboratory personnel and equipment and interpreting the sample results requires the time of process engineers. All of these resources are in limited supply, and there is a need to leverage their use for maximum impact on the DWPF operation. Finally, the processing of samples in the laboratory generates waste with a corresponding disposal cost. Reducing the number of samples processed reduces the waste and, thus, reduces these disposal costs.

As part of the Six Sigma continuous improvement initiatives at the DWPF, a Yellow Belt team was formed to evaluate the frequency and types of samples required for the SRAT receipt and SRAT product in the DWPF. The team asked, via a technical task request (TTR) [1], that the Statistical Consulting Section (SCS), in concert with the Immobilization Technology Section (ITS) (both groups within the Savannah River National Laboratory (SRNL)), conduct a statistical review of recent SRAT receipt results to determine if there is enough consistency in these measurements to allow for less frequent sampling or for fewer analyses per sample. As part of this review process, the decisions made by DWPF Process Engineering that are based upon the SRAT sample measurements and other process information are outlined in this report. For a reduction in SRAT sampling to be viable, these decisions must not be overly sensitive to the additional variation that will be introduced as a result of such a reduction.

The purpose of this report, as directed by the task technical and quality assurance plan [2], is to quantify the additional variation that would be expected if there were a reduction in the SRAT sampling frequency, to propagate this variation through the calculations conducted by Process Engineering, and to offer a recommended path forward for SRAT receipt sampling and for the Engineering calculations that rely on the information generated from the SRAT receipt samples.

2.0 RESULTS

The SRAT receipt measurements are used by DWPF's Process Engineering group to perform the acid calculation for the SRAT batch. This calculation utilizes predictive models: one equation predicts the total acid requirements for the batch and the other equation predicts the reduction/oxidation (REDOX) state of the glass product that will be produced by processing the batch. The inputs to these equations are either directly or indirectly related to measurements derived from the SRAT receipt samples.

If the SRAT receipt is sampled less frequently than every batch, then a set of average measurements would be used to drive the predictions from these two equations for the un-sampled batches. How much might the predictions generated from using these averages differ from the predictions that would have been generated from using measurements from samples of the individual SRAT receipt batch? This question is tackled in the sections below.

To start off, the two predictive equations are discussed. Secondly, SRAT receipt measurement data for samples from batches 313 through 323 are presented and a statistical analysis of these measurements is

provided. Then, comparisons are presented between the REDOX predictions made using the SRAT receipt and those made using Slurry Mix Evaporator (SME) measurements. Finally, different approaches are used to evaluate the impact of less frequent sampling on the acid addition process. The statistical analyses presented as part of these discussions were carried out using JMP® Version 5.1.2 [3] from SAS Institute, Inc.

2.1 DWPF's Acid Addition Strategy

On its simplest level, DWPF's acid addition strategy consists of two decisions: (1) How much total acid (the total number of moles) should be added to the SRAT batch? and (2) What is the relative proportion of formic to nitric acid that should be used to appropriately target REDOX in meeting the total acid requirement? To answer the first question, DWPF utilizes an equation that was presented in [4] that relates the total acid requirement for a SRAT batch to key characteristics and measurements of the SRAT receipt. The relationship is given by equation (1):

$$A_T = \text{moles acid} = V_S * \left[1.0 * \text{B.E.} + \rho_S * \left(\frac{0.75 * \text{NO}_2^-}{46.007} + \frac{\text{Hg}}{200.6} + \frac{2.0 * \text{TIC}}{12.01} + \frac{1.2 * \text{Mn}}{54.938} \right) \right] * \text{factor} \quad (1)$$

where

A_T is the total acid requirement in moles,
 V_S is the SRAT receipt slurry volume, L,
 ρ_S is the SRAT receipt slurry density, kg/L,
 B.E. is the SRAT receipt base equivalents at pH 7, equivalent moles OH-/L,
 NO_2^- is the SRAT receipt mass of nitrite ion per unit mass slurry,
 TIC is the SRAT receipt mass to total inorganic carbon (TIC) per unit mass slurry,
 Hg is the SRAT receipt mass of mercury per unit mass slurry,
 Mn is the SRAT receipt mass of manganese per unit mass slurry, and
 factor is a multiplier (called the stoichiometric value or factor) to increase the total acid above that predicted by the four terms.

In addition to adjusting the rheology of the SRAT material, the added acid must satisfy two goals during SRAT processing: the amount of nitrite in the SRAT material must be destroyed to below the level of concern and the amount of hydrogen generated during subsequent processing must be below the DWPF safety basis limit. The minimum acid, required to destroy the nitrite, and the maximum acid, that can be added before the generation of hydrogen at problem levels, define the "operating window" for the acid addition strategy. The operating window may be represented using an interval of values for the stoichiometric factor of equation (1). For batches 314 through 323 (the focus of this study), the stoichiometric factors were near 1.55 or 155%.

The answer to the second question above is determined using an equation from [5] that predicts the REDOX of DWPF's glass product. In this case, REDOX is represented as the ratio of Fe^{2+} to the total iron in the glass. The REDOX equation relates this ratio to the electron equivalents, ξ , for critical components of the slurry product that is fed to DWPF's melter. The overall relationship between the REDOX ratio and ξ may be expressed as in equation (2):

$$\frac{\text{Fe}^{2+}}{\Sigma\text{Fe}} = f \left[\left(2[\text{F}] + 4[\text{C}] + 4[\text{O}_T] - 5[\text{N}] - 2[\text{Mn}] \right) \frac{45}{\text{T}} \right] = f[\xi] \quad (2)$$

where

- f = indicates a function
- [F] = formate (mol/kg feed)
- [C] = coal (carbon) (mol/kg feed)
- [O_T] = oxalate_{Total} (soluble and insoluble) (mol/kg feed)
- [N] = nitrate + nitrite (mol/kg feed)
- [Mn] = manganese (mol/kg feed)
- T = total solids (wt%)

$$\text{and } \xi \text{ (mol/kg feed at 45 wt\% solids)} = \frac{(2[F] + 4[C] + 4[O_T] - 5[N] - 2[Mn])}{T} \cdot 45$$

The final form of the REDOX equation from [5] may be expressed as equation (3):

$$\frac{\text{Fe}^{2+}}{\Sigma\text{Fe}} = 0.1942 + 0.1910\xi \tag{3}$$

For REDOX, the operating window is the interval of values from 0.01 to 0.33 [5]. Typically, DWPF targets a value near 0.2 for REDOX. This was the case for batches 314 through 323.

Before leaving this section, one additional aspect of the REDOX equation should be explored. Note that the inputs to equation (2) are expressed in terms of melter feed, which may be thought of equivalently as the SME product. Figure 2-1 provides an overview of critical steps in the DWPF processing that occur from acid addition at the SRAT to the formation of the SME product.

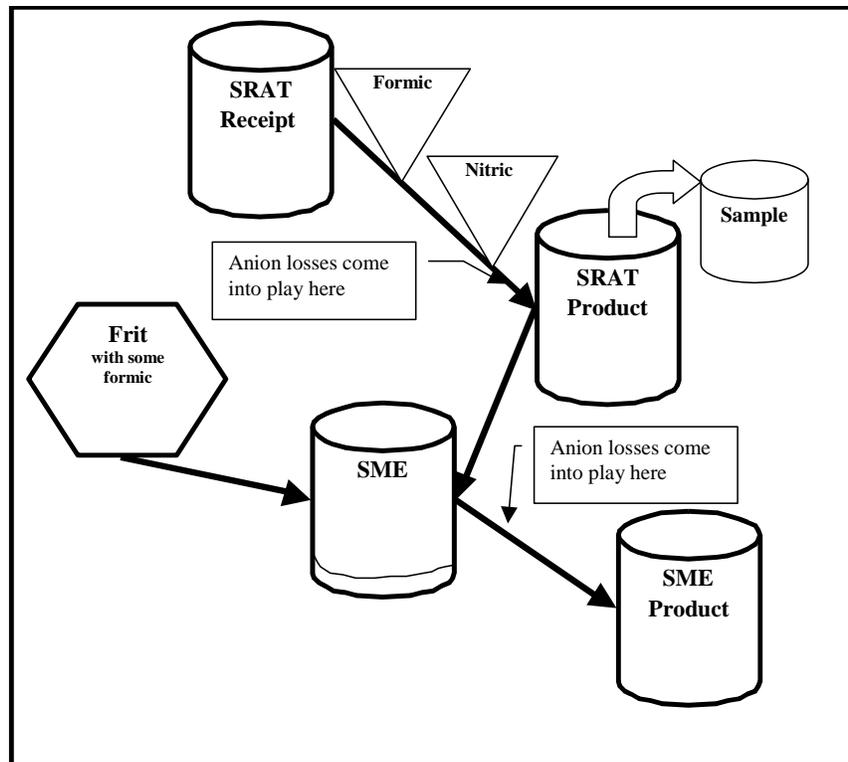


Figure 2-1 Overview of Critical Steps in the DWPF Process that Influence Inputs to REDOX Equation

Since the acid calculation for a process batch is conducted at the SRAT receipt step (as indicated in the figure), there are three categories of information used to estimate the REDOX of the SME product that will be produced for this batch: the SRAT receipt measurements, the nitric and formic acid additions, and some insight, through assumptions and process experience, of what happens to the SRAT receipt material as it makes its way through to the melter. A closer look at these assumptions and at the use of process experience to aid these calculations is presented later in this report.

2.2 SRAT Receipt Measurements for Batches 314 through 323

Table A1 in the Appendix provides a listing of the measurements of the SRAT receipt for batches 314 through 323 that were used as inputs for the acid calculation for these batches. Exhibit A1 in the Appendix provides plots of these data by batch number. The values are reasonably stable although some trending may be indicated for some of the analytes over these data. Figure 2-2 provides a scatterplot matrix of the average values over the batches for these measurements. This plot reveals some strong correlations among certain pairs of measurements. This is also reflected in Table 2-1, which provides the pairwise linear correlations for these data. Some of these correlations are at or above 0.90.

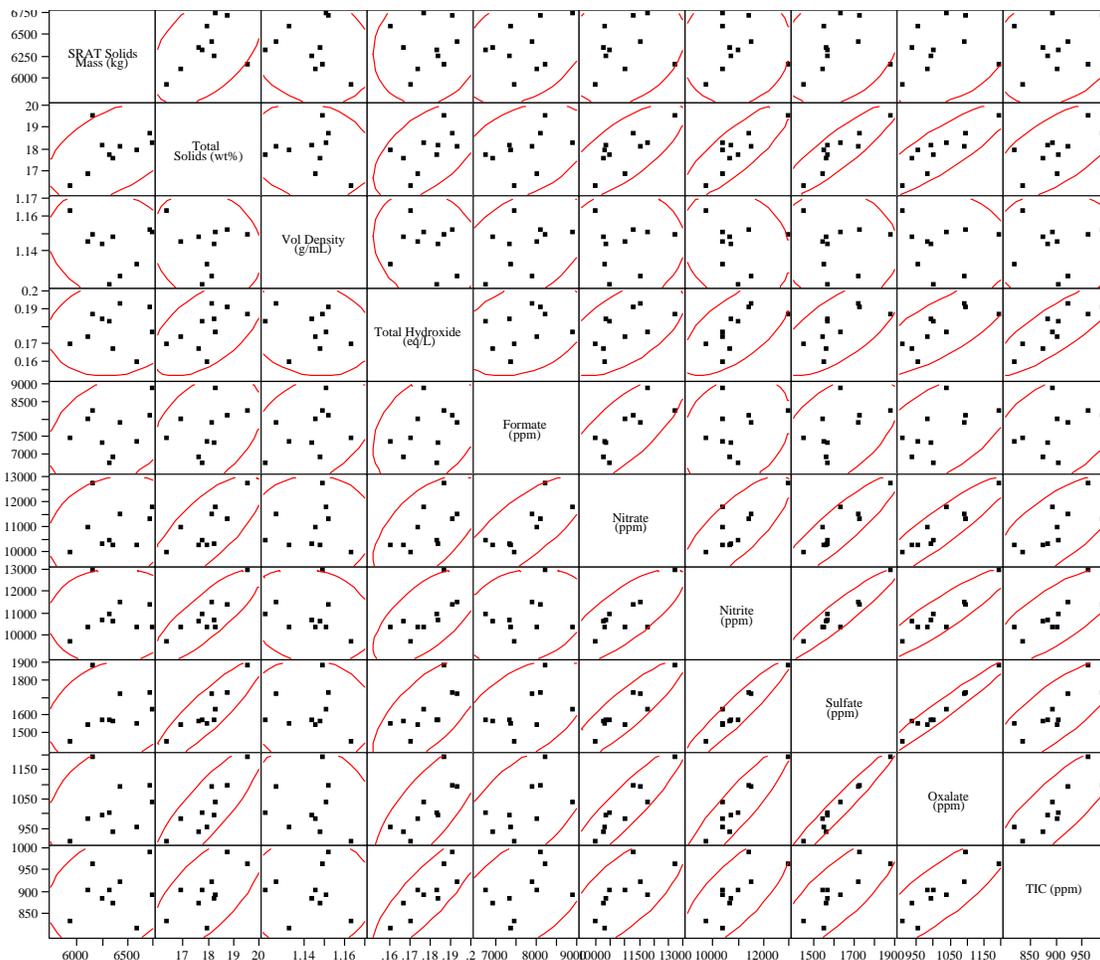


Figure 2-2 Scatterplot Matrix of the Average Measurements by Batch

Table 2-1 Correlations between Average Measurements by Batch

	SRAT Solids Mass (kg)	Total Solids (wt%)	Vol Density (g/mL)	Total Hydroxide (eq/L)	Formate (ppm)	Nitrate (ppm)	Nitrite (ppm)	Sulfate (ppm)	Oxalate (ppm)	TIC (ppm)
SRAT Solids Mass (kg)	1.0000	0.4827	-0.2210	0.1120	0.3514	0.2217	0.0647	0.2701	0.2386	0.2309
Total Solids (wt%)	0.4827	1.0000	-0.1543	0.5594	0.3835	0.7376	0.8462	0.8969	0.8613	0.6663
Vol Density (g/mL)	-0.2210	-0.1543	1.0000	-0.1807	0.3822	0.0549	-0.1931	-0.0758	-0.0968	0.0174
Total Hydroxide (eq/L)	0.1120	0.5594	-0.1807	1.0000	0.3201	0.5773	0.6568	0.6788	0.7684	0.8409
Formate (ppm)	0.3514	0.3835	0.3822	0.3201	1.0000	0.7674	0.2482	0.5092	0.5710	0.4354
Nitrate (ppm)	0.2217	0.7376	0.0549	0.5773	0.7674	1.0000	0.7856	0.9017	0.9237	0.7200
Nitrite (ppm)	0.0647	0.8462	-0.1931	0.6568	0.2482	0.7856	1.0000	0.9484	0.9190	0.7625
Sulfate (ppm)	0.2701	0.8969	-0.0758	0.6788	0.5092	0.9017	0.9484	1.0000	0.9775	0.8047
Oxalate (ppm)	0.2386	0.8613	-0.0968	0.7684	0.5710	0.9237	0.9190	0.9775	1.0000	0.8424
TIC (ppm)	0.2309	0.6663	0.0174	0.8409	0.4354	0.7200	0.7625	0.8047	0.8424	1.0000

The sample measurements were used to develop an estimated volume (in gallons) for each SRAT batch by DWPF Engineering. The estimated tank volumes and the acid addition volumes determined by DWPF Engineering for these batches are presented in Table 2-2. Not listed, but of importance for both the total acid and REDOX equations, is the concentration of Mn (3.67 wt% on a dried solids basis) that is used for each of these batches. Exhibit A2 in the Appendix provides plots of these data by batch number.

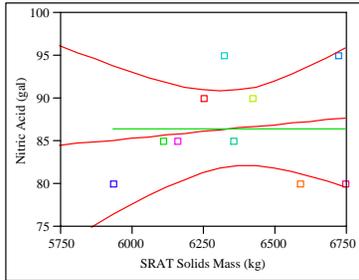
Table 2-2 Tank Volume, Nitric Acid Addition, and Formic Acid Addition by Batch

Batch	Volume (gal)	Nitric (gal)	Formic (gal)
314	8375	95	350
315	7345	85	345
316	8325	90	365
317	8225	95	365
318	8475	80	340
319	7950	90	335
320	8385	85	345
321	8225	80	325
322	8525	80	325
323	8350	85	350

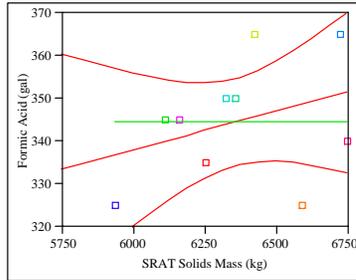
Figure 2-3 provides the results of fitting the values for nitric acid, formic acid, and total acid (in gallons) to the total solids of the SRAT receipt to see if any of these critical acid addition amounts appeared to be closely tied to this measure of the SRAT receipt. Each plot shows the average value (as a horizontal line)

for the measurements on the y-axis along with a trend line and its 95% confidence interval. None of the trends lines are statistically significant at the 5% significance level. Thus, there is no indication of a statistically significant relationship between the tank sludge solids and the acid addition volumes. One would have expected that as the tank solids increase there would be a corresponding increase in the acid requirements.

Bivariate Fit
Nitric (gal) By Total Solids (kg)



Bivariate Fit
Formic (gal) By Total Solids (kg)



Bivariate Fit
Total acid(gal) By Total Solids (kg)

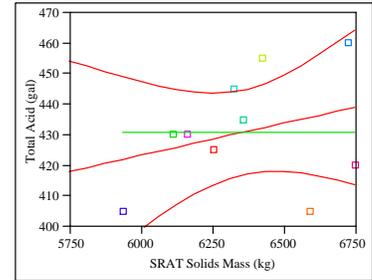


Figure 2-3 Acid Additions versus SRAT Receipt Total Sludge Solids

2.3 REDOX Predictions at SRAT Receipt versus REDOX Predictions at the SME

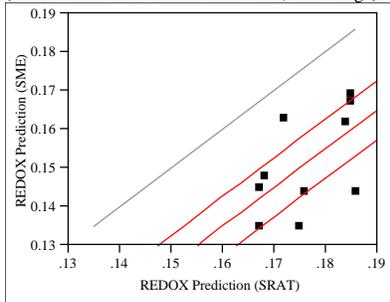
Comparisons between the predictions of the SME product at the time of the acid additions in the SRAT¹ and the measurements of the SME product taken much later in the process were another area of interest in this study. Table 2-3 provides the data for these comparisons, and the comparisons are provided in Figure 2-4.

Table 2-3 Comparisons of Melter Feed Predictions at the SRAT to SME Measurements

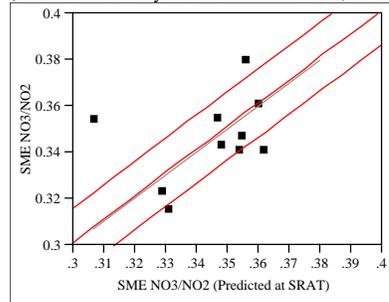
Batch	REDOX Prediction (SRAT)	REDOX Prediction (SME)	<i>(concentrations are in moles/kg of slurry)</i>					
			SME Formate (Predicted at SRAT)	Actual SME Formate	SME NO ₃ /NO ₂ (Predicted at SRAT)	Actual SME NO ₃ /NO ₂	SME Mn (Predicted at SRAT)	Actual SME Mn
314	0.185	0.167	0.988	0.886	0.362	0.341	0.128	0.137
315	0.184	0.162	0.948	0.906	0.347	0.355	0.126	0.137
316	0.185	0.169	0.981	0.939	0.36	0.361	0.128	0.139
317	0.186	0.144	0.977	0.928	0.356	0.38	0.13	0.155
318	0.175	0.135	0.943	0.807	0.354	0.341	0.133	0.149
319	0.172	0.163	0.871	0.815	0.329	0.323	0.126	0.116
320	0.168	0.148	0.922	0.847	0.355	0.347	0.124	0.136
321	0.176	0.144	0.888	0.844	0.307	0.354	0.115	0.132
322	0.167	0.135	0.938	0.734	0.331	0.315	0.134	0.129
323	0.167	0.145	0.988	0.824	0.348	0.343	0.132	0.135

¹ Please note that this wording may be somewhat misleading. The REDOX predictions described as being at the time of the acid additions in the SRAT are actually the REDOX predictions based upon the SRAT product, after accounting for the formate and nitrate losses during SRAT processing. The REDOX predictions at the time of the acid additions in the SRAT were not available for batches 314 through 323.

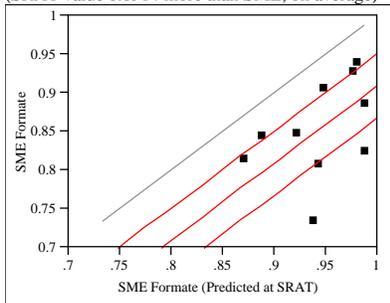
REDOX Prediction (SME) By REDOX Prediction (SRAT)
(SRAT value 0.0253 more than SME, on average)



SME NO3/NO2 By SME NO3/NO2 (Predicted at SRAT)
(SRAT value is only 0.0011 more than SME, on average)



SME Formate By SME Formate (Predicted at SRAT)
(SRAT value 0.0914 more than SME, on average)



SME Mn By SME Mn (Predicted at SRAT)
(SRAT value 0.0089 less than SME, on average)

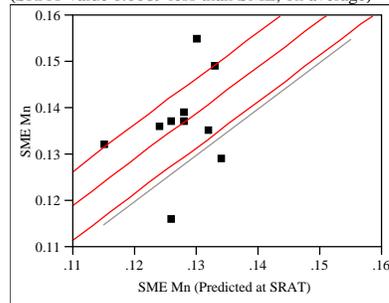


Figure 2-4 Paired Comparisons of SME Measurements versus SRAT Predictions

Figure 2-4 shows (in the upper left plot) that the predicted REDOX that is targeted for the acid calculations at the SRAT receipt is on average 0.0253 more than the predicted REDOX assessed based upon SME measurements. This is a statistically significant difference, and the other plots of Figure 2-4 suggest that it is due to the formate and Mn concentrations that are predicted for the SME product during the SRAT acid calculations. For each of these analytes, the SRAT prediction for the SME is statistically different (at the 5% significance level) from the SME measurement (the units are moles/kg of SME product slurry): the SRAT values are, on average, 0.0914 larger than the SME values for formate and 0.0089 smaller than the SME values for Mn. A look at the signs of the terms corresponding to these two analytes in equation (2) indicates that both of these differences between their SME and SRAT versions contribute to the REDOX differences between the SRAT and SME.

How might DWPF use the results from this section to make improvements in their acid addition strategy? Since the Mn concentration in the SRAT receipt is actually already an average value that is being used by DWPF, the results presented here suggest that the value currently being used in the SRAT (in the units of moles/kg of SME product slurry) is 0.0089 too small. On a percentage basis, since the SRAT Mn moles/kg of SME product slurry averages (for batches 314 through 323) 0.1276 moles/kg, the value should be $100\% \times (0.0089/0.1276)$ or 7% larger. Thus, instead of using 3.67 wt% as the value for the concentration of Mn on a dried solids basis, a value of $3.67 \times 1.07 = 3.92$ wt% might be used instead. As an alternative, there are assumptions regarding the weight percent dried solids for the SRAT product that may be affecting the Mn concentration predicted for the SME product. Adjustments to the acid calculations that eliminate the effect of these assumptions on the Mn concentration may be considered. Monitoring of the Mn assumed in the SRAT receipt versus the concentrations seen in the SME product should provide the data necessary to guide these decisions and to provide feedback as to their successful resolution.

Another suggestion revolves around the evaluation of formate. Since DWPF is already adjusting for the formate and nitrate losses in the SRAT product from the SRAT receipt (as soon as these losses are realized), they are not the source of the formate discrepancy (of 0.0914 moles/kg of SME product slurry) between the SRAT and SME. Based upon the fact that this discrepancy is about $100\% \times (0.0914/0.9444)$ or 9.7% and that the SRAT versus SME nitrate/nitrite values do not indicate a similar problem, the most likely source of the discrepancy is believed to be a formate loss during SME processing. Thus, DWPF may want to consider adjusting their acid calculation to introduce a 9.7% loss (as a 0.903 correction factor) as part of the evaluation of formate in the SME product portion of their acid calculation spreadsheet.

2.4 Variation in Acid Addition Amounts and REDOX Predictions

Assume that the acid calculation conducted by DWPF Engineering, which relies on the SRAT receipt measurements for each batch, yields the best estimates for the required amounts of formic and nitric for that batch. How much variation around these “best estimates” will be introduced if a set of average measurements is used for several SRAT batches instead of the individual measurements for each of these batches? That is, there is process variation from one batch to the next that the SRAT sample measurements capture and reflect that will be lost to the decision makers if they were to rely only on the average measurements from a set of previous SRAT receipt batches. The answer to this question is explored in this section.

Three different methods were used to help answer the question of the likely variation that may be introduced into the acid calculation by a less frequent sampling of the SRAT receipt. The first approach was an error propagation of the process variation through the acid calculation. The second approach was a simulation of the impact of process variation on the acid calculation. Finally, the third approach is to reenact the acid calculations for batches 314 through 323 using the average of the measurements from these batches. Since there was a common goal for these approaches there should be a consistency in their outcomes.

2.4.1 Error Propagation of Process Variations

The propagation of errors through equations (1) and (2) was a reasonably straightforward process (see for example Appendix B of [6]); it was, however, more difficult for equation (2) than equation (1) due to the imbedded nature of the SRAT receipt measurements in that equation. The process variation was estimated based upon the data in Table A1. The averages and standard deviations of these measurements are provided in Table 2-4. For Mn and Hg, the values already remained relatively fixed (i.e., the SRAT receipt samples are not routinely analyzed for Mn nor for Hg, so the values don't change often).

Table 2-4 Descriptive Statistics for the Measurements from SRAT Receipt Batches 314 through 323

Measurement	Average	Standard Deviation	% Relative Standard Deviation
SRAT Solids Mass (kg)	6361.8947	264.929	4.16
Total Solids (wt%)	17.9530	0.897	5.00
Density (g/mL)	1.1433	0.013	1.12
Vol Density (g/mL)	1.1432	0.013	1.13
Total Hydroxide (eq/L)	0.1786	0.011	6.07
Formate (ppm)	7697.5000	650.100	8.45
Nitrate (ppm)	10964.5000	866.273	7.90
Nitrite (ppm)	10918.2500	893.493	8.18
Sulfate (ppm)	1620.7500	122.792	7.58
Oxalate (ppm)	1020.2000	86.880	8.52
TIC (ppm)	899.3075	52.861	5.88
SRAT Volume (gal)	8218.0000	345.730	4.21

For equation (1), recall that the operating window for DWPF could be expressed as the target interval for the stoichiometric factor. The results from the error propagation suggest the following:

- that if the variations from batch to batch in the values of the critical inputs to equation (1) were uncorrelated the % relative standard deviation in the stoichiometric factor would be 3.1%.
- that if the variation from batch to batch in the values of the critical inputs to equation (1) were perfectly correlated the % relative standard deviation in the stoichiometric factor would be 26.5%.

For equation (2), the results from the error propagation suggest the following:

- that if the variations from batch to batch in the values of the critical inputs to equation (2) were uncorrelated the %RSD in the REDOX prediction would be 7.0%.
- that if the variation from batch to batch in the values of the critical inputs to equation (2) were perfectly correlated the %RSD in the REDOX prediction would be 7.54%.

2.4.2 A Simulation of the Sensitivity of the Acid Calculation to Process Variation

Expanding on the methodology developed in [7], a simulation of the acid calculation was conducted as part of this investigation. In the original simulation [7], the sensitivity of the acid addition strategy to measurement uncertainty was investigated whereas in this simulation, the sensitivity of the strategy to process variation was studied. Underlying this approach was an assumption that the process variations in the inputs to equations (1) and (2) were uncorrelated.

The results for equation (1) suggest that:

- if the variations from batch to batch in the values of the critical inputs to equation (1) were uncorrelated the %RSD in the stoichiometric factor would be 3.8%.

For equation (2), the results from the error propagation suggest that:

- if the variations from batch to batch in the values of the critical inputs to equation (2) were uncorrelated the %RSD in the REDOX prediction would be 8.1%.

2.4.3 Reenactment of the Acid Calculation for Batches 314 through 323

DWPF Engineering used the average measurements in Table 2-4 as input for a second round of acid calculations for each of these batches. For each batch, a value of 155% was used as the targeted stoichiometric factor and a value for the total moles of required acid was determined based on the average measurements. The results are presented in Table 2-5, which provides these values as well as the value for the total moles of required acid based upon the receipt measurements for each SRAT batch. The actual targeted stoichiometric factor for each batch is also presented in this table.

Table 2-5 Outcome from Reenactment of Acid Additions for SRAT Receipt Batches 314 through 323

SRAT Batch	Targeted Stoich. Factor	Total Moles of Acid Required Based Upon Averages	Total Moles of Acid Used Based Upon SRAT Receipt Measurements	Calculated Stoich. Factor Based Upon SRAT Measurements
314	155	34927.4	35057.3	154.43
315	155	31048.9	34275.4	140.41
316	155	34801.0	36259.0	148.77
317	155	34822.0	37120.7	145.40
318	155	35875.9	35442.9	156.89
319	155	33494.0	33570.2	154.65
320	155	35391.1	34234.7	160.24
321	155	35011.7	32293.5	168.05
322	155	35728.4	32291.9	171.50
323	155	35285.7	34108.5	160.35

The results from Table 2-5 suggest that when a set of average measurements was used to conduct the acid addition strategy for batches 314 through 323 at a targeted stoichiometry of 155%, the actual stoichiometric factors that could have been realized ranged from 140.4% to 171.5%. Figure 2-5 provides a closer look at these values. The standard deviation of 9.63 translates into a %RSD of 6.2%. This value is between the estimated %RSDs from the simulation and uncorrelated error propagation (3.8% and 3.1%, respectively) and the %RSD from the correlated error propagation (26.5%).

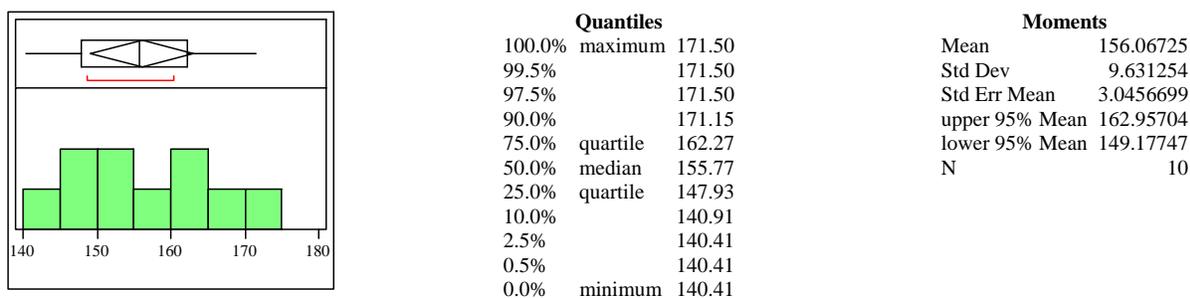


Figure 2-5 Descriptive Statistics of Actual Stoichiometric Factors versus the Anticipated Target of 155%

Table 2-6 provides the results of the impact on REDOX predictions of the reenactment of the acid addition strategy for batches 314 through 323. For each batch, as the acid calculation was reenacted the target for the predicted REDOX ratio was ~ 0.2. The actual targeted REDOX ratios ranged from 0.184 to 0.233, as seen in Table 2-6.

Table 2-6 Descriptive Statistics for the Measurements from SRAT Receipt Batches 314 through 323

SRAT Batch	REDOX targeted using Averages	Actual targeted REDOX based upon SRAT Measurements	Difference in REDOX Predictions
314	0.206	0.211	-0.005
315	0.206	0.184	0.022
316	0.207	0.202	0.005
317	0.207	0.202	0.005
318	0.200	0.193	0.007
319	0.197	0.201	-0.004
320	0.201	0.233	-0.032
321	0.197	0.213	-0.016
322	0.201	0.216	-0.015
323	0.198	0.205	-0.007

Figure 2-6 provides summary statistics of the differences in the REDOX targets. The standard deviation of the differences is 0.015. When expressed as a percentage of the 0.2 target, the value is 7.5%.

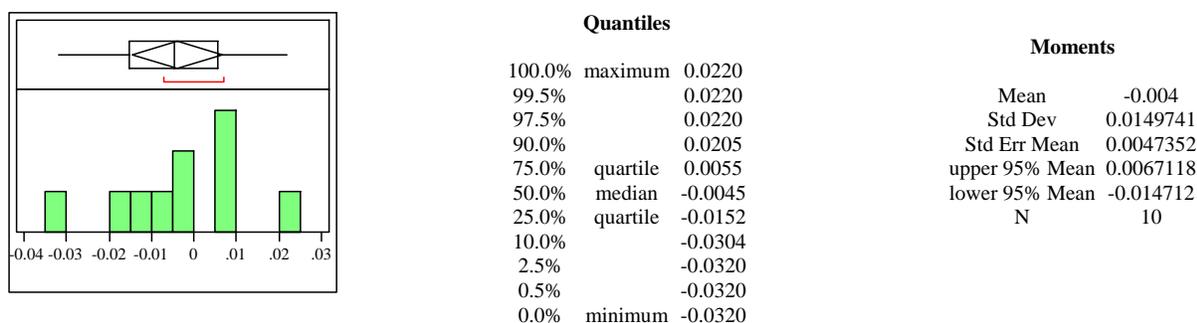


Figure 2-6 Descriptive Statistics of REDOX Differences

2.4.4 Summarizing the Results

Looking back over the three methods used to explore the impact of process variation on the acid addition strategy, there is a consistency in outcomes. For the total acid requirements, the %RSDs for stoichiometric factors ranged from lows of 3.1% (uncorrelated error propagation) and 3.0% (uncorrelated simulation) to a high of 16.5 (correlated error propagation). The %RSD for the reenactment was 6.2%. This value falls within the interval of values seen for the other methods as would be expected and this value is believed to be the best estimate of the %RSD. The value for the degrees of freedom for the %RSD of 6.2% is the same as that for the degrees of freedom (9) of the standard deviations of the SRAT receipt measurements. Thus, the 95% uncertainty for the stoichiometric factor is given by (see [6]):

$$\text{Stoichiometric Factor Uncertainty}_{@ 95\% \text{ confidence}} = t_{0.025, 9} \times (\%RSD) = 2.262 \times 6.2\% = 14\%$$

where $t_{0.025, 9}$ is the upper 2.5%-tail of the Student's t distribution with 9 degrees of freedom. Thus, when targeting a stoichiometric factor of 155% using average measurements, the actual factor realized for any given batch would be expected to fall within the interval from $155 \times 0.86 = 133.3\%$ to $155 \times 1.14 = 176.7\%$ with 95% confidence.

The %RSDs for REDOX from the three methods also show consistency. The %RSDs range from a low of 7.0 for the uncorrelated error propagation to 8.1% for the uncorrelated simulation with a value of 7.54% for the correlated error propagation. The %RSD for the reenactment was 7.5%. This value falls within the interval of values for the other methods as would be expected and this value is believed to be the best estimate of the %RSD. The value for the degrees of freedom for the %RSD of 7.5% is the same as that for the degrees of freedom (9) of the standard deviations of the SRAT receipt measurements. Thus, the 95% uncertainty for the targeted REDOX is given by:

$$\text{Targeted REDOX Uncertainty}_{@ 95\% \text{ confidence}} = t_{0.025, 9} \times (\% \text{RSD}) = 2.262 \times 7.5\% = 17\%$$

where, as above, $t_{0.025, 9}$ is the upper 2.5%-tail of the Student's t distribution with 9 degrees of freedom. Thus, when targeting a REDOX of ~0.2 using average measurements, the actual value realized for any given batch would be expected to fall within the interval from $0.2 \times 0.83 = 0.166$ to $0.2 \times 1.17 = 0.234$ with 95% confidence.

From the perspective of stoichiometric factors and targeted REDOX values, it appears that the biggest challenge facing DWPF Engineering is the uncertainty of the stoichiometric factor. The question that must be addressed is whether or not both goals (nitrite destruction and hydrogen avoidance) associated with the acid addition strategy can be met at an adequate confidence level.

3.0 CONCLUSIONS

Measurements from samples of SRAT receipt batches 314 through 323 were reviewed as part of this investigation into the frequency of SRAT receipt sampling. The acid calculations for these batches were also studied as part of this effort.

The results from this investigation showed no indication of a statistically significant relationship between the tank solids and the acid additions for these batches. One would have expected that as the tank solids increase there would be a corresponding increase in the acid requirements. There was, however, an indication that the predicted REDOX values that were targeted by the acid calculations based on the SRAT receipt samples for these batches were on average 0.0253 larger than the predicted REDOX values assessed based upon SME product measurements. This was a statistically significant difference, and the study also suggested that the difference was due to predictions of SME product formate and Mn concentrations that were made in the SRAT acid calculation. For each of these analytes, the SRAT version was statistically different from the SME version (the units are moles/kg of SME product slurry): the SRAT values were, on average, 0.0914 larger than the SME values for formate and 0.0089 smaller than the SME values for Mn. A look at the signs of the terms corresponding to these two analytes in equation (2) indicates that both of these differences between their SME and SRAT versions contribute to the REDOX differences between the SRAT and SME.

Based upon the results of this study, when targeting a stoichiometric factor of 155% using average measurements, the actual factor realized for any given batch would be expected to fall within the interval from 133.3% to 176.7% with 95% confidence. When targeting a REDOX of ~0.2 using average measurements, the actual value realized for any given batch would be expected to fall within the interval from 0.166 to 0.234 with 95% confidence.

4.0 RECOMMENDATIONS

Based on the results of this study, the following recommendations are made:

- DWPF should consider adjusting their acid calculation to align the Mn concentration in SRAT receipt with the Mn concentration in the SME product.
- DWPF should consider adjusting their acid calculation to introduce a 9.7% loss (as a 0.903 correction factor) as part of the evaluation of formate in the SME product portion of their spreadsheet.
- DWPF should evaluate how a $\pm 14\%$ uncertainty in their targeted stoichiometric factor and a $\pm 17\%$ uncertainty in the REDOX prediction may affect the success of their operating strategy.

5.0 REFERENCES

- [1] Patel, PM, "Technical Task Request: Evaluation of SRAT Sampling Data (U)," HLW/DWPF/TTR-2005-0006, Revision 1, May 2, 2005.
- [2] Edwards, TB, "Task Technical and Quality Assurance Plan: Evaluation of SRAT Sampling Data (U)," WSRC-RP-2005-01453, May 2, 2005.
- [3] SAS Institute, Inc., **JMP Statistics and Graphics Guide**, SAS Institute, Inc., Cary, NC, 2002.
- [4] Hsu, CW, "Defense Waste Processing Facility Nitric Acid Requirement for Treating Sludge (U)," WSRC-RP-92-1056, 1992.
- [5] Jantzen, CM, JR Zamecnik, DC Koopman, CC Herman, and JB Pickett, "Electron Equivalents Model for Controlling Reduction-Oxidation (REDOX) Equilibrium During High Level Waste (HLW) Vitrification (U)," WSRC-TR-2003-00126, Revision 0, 2003.
- [6] Coleman, HW and WG Steele, **Experimentation and Uncertainty Analysis for Engineers**, John Wiley & Sons, Inc., New York, 1989.
- [7] Edwards, TB and JR Harbour, "Sensitivity of Acid Addition Strategy to Input Uncertainties at DWPF for SB3," SRT-SCS-2003-00027, June 19, 2003.

6.0 ACKNOWLEDGEMENTS

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APPENDIX
Supporting Tables and Exhibits

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Table A1. SRAT Receipt Measurements for Batches 314 through 323

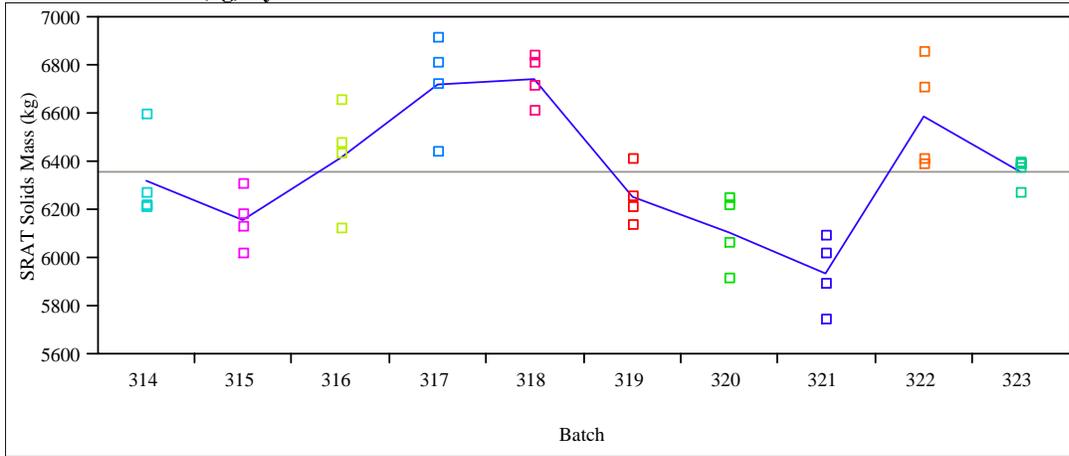
SRAT Receipt Batch	Sample	Total Solids (wt%)	Vol Density (g/mL)	Total Hydroxide (eq/L)	Formate (ppm)	Nitrate (ppm)	Nitrite (ppm)	Sulfate (ppm)	Oxalate (ppm)	TIC (ppm)
314	1	18.62	1.117	0.183	6750	10600	11200	1600	992	946.5
314	2	17.55	1.127	.	6750	10500	11000	1560	1010	890.9
314	3	17.53	1.117	.	6780	10300	10900	1560	997	888.3
314	4	17.47	1.123	.	6770	10400	10900	1560	1010	894.3
314	5	17.74
315	1	18.83	1.15	0.187	8280	14000	13000	1890	1200	1021.8
315	2	19.31	1.152	.	8190	12500	13100	1910	1190	959.8
315	3	19.82	1.144	.	8220	12100	12800	1850	1190	962.9
315	4	19.15	1.151	.	8230	12300	13000	1870	1200	913.4
315	5	20.06
315	6	20.12
316	1	17.33	1.121	0.193	8040	11700	11800	1760	1120	937.5
316	2	18.26	1.126	.	8090	11800	11800	1760	1120	901.5
316	3	18.08	1.129	.	7760	11400	11200	1680	1060	955.9
316	4	18.72	1.128	.	7690	11200	11300	1680	1070	900.5
316	5	18.37
316	6	18.18
317	1	18.86	1.16	0.191	8070	11400	11500	1730	1090	1011.6
317	2	18.7	1.154	.	8150	11200	11300	1730	1100	947.7
317	3	18.09	1.144	.	8090	11300	11400	1730	1100	1016.2
317	4	19.29	1.151	.	8160	11300	11400	1710	1090	991.9
317	5	18.77
318	1	18.5	1.132	0.177	8890	12000	10500	1630	1040	945.1
318	2	18.21	1.132	.	8890	11700	10300	1630	1040	893.4
318	3	18.26	1.163	.	8850	11700	10500	1630	1040	877.2
318	4	18.13	1.176	.	8940	11700	10300	1640	1040	859.3
318	5	18.26
318	6	18.36
319	1	18.21	1.134	0.184	7420	10600	10900	1580	1000	965.8
319	2	17.91	1.138	.	7320	10200	10600	1570	990	865.8
319	3	18.31	1.135	.	7340	10400	10800	1580	1000	847.6
319	4	18.23	1.169	.	7230	10100	10500	1550	989	856.9
319	5	17.99
319	6	18.63
320	1	16.53	1.155	0.174	8000	11700	11200	1540	977	938.1
320	2	17.25	1.141	.	8050	11500	10400	1550	973	919.6
320	3	16.32	1.142	.	8010	10400	9980	1550	990	889.7
320	4	17.12	1.144	.	7960	10400	10000	1530	992	864.2
320	5	17.26
321	1	16.59	1.141	0.17	7540	10100	9780	1460	908	848.1
321	2	16.25	1.135	.	7460	10000	9650	1460	911	823.9

Table A1. SRAT Receipt Measurements for Batches 314 through 323

SRAT Receipt Batch	Sample	Total Solids (wt%)	Vol Density (g/mL)	Total Hydroxide (eq/L)	Formate (ppm)	Nitrate (ppm)	Nitrite (ppm)	Sulfate (ppm)	Oxalate (ppm)	TIC (ppm)
321	3	16.2	1.193	.	7380	9870	9730	1440	906	841.1
321	4	16.54	1.183	.	7450	9980	9740	1450	907	824.8
321	5	16.3
321	6	16.19
322	1	18.97	1.12	0.16	7370	10300	10300	1550	957	846.7
322	2	17.95	1.158	.	7410	10200	10400	1560	959	789.8
322	3	17.58	1.13	.	7350	10400	10500	1570	956	816
322	4	17.64	1.122	.	7340	10300	10400	1530	944	819.2
322	5	17.72
322	6	17.84
323	1	17.44	1.138	0.167	7140	9730	9650	1610	967	910.3
323	2	17.53	1.154	.	7020	10700	11300	1600	953	864.5
323	3	17.33	1.163	.	7110	10300	10900	1600	963	871.5
323	4	17.77	1.137	.	6410	10300	10800	1440	867	853
323	5	17.76
323	6	17.83

Exhibit A1. Plots of the SRAT Receipt Measurements by Batch Number

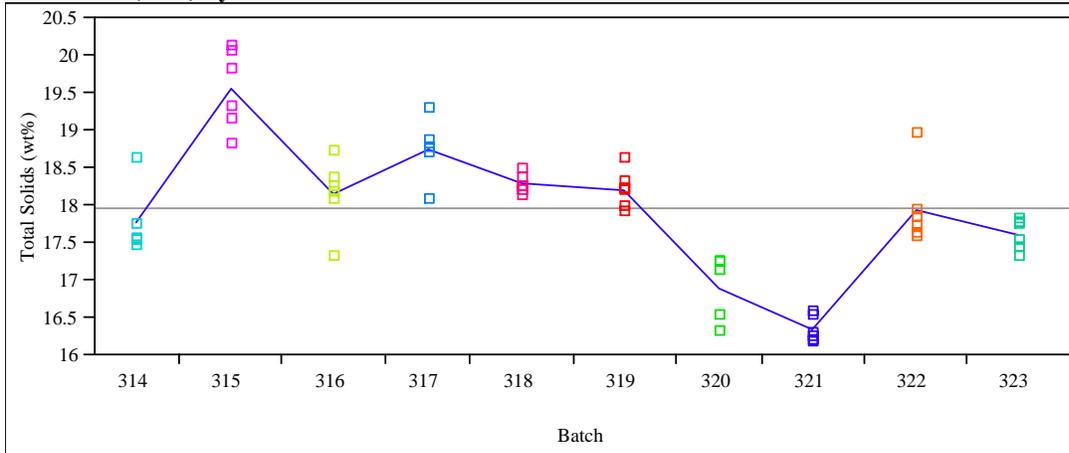
SRAT Solids Mass (kg) By Batch



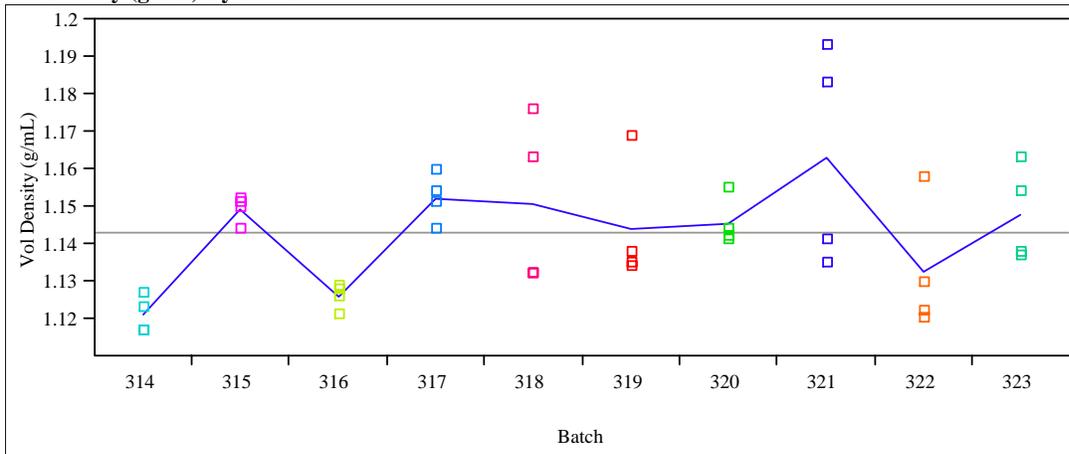
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Total Solids (wt%) By Batch



Vol Density (g/mL) By Batch

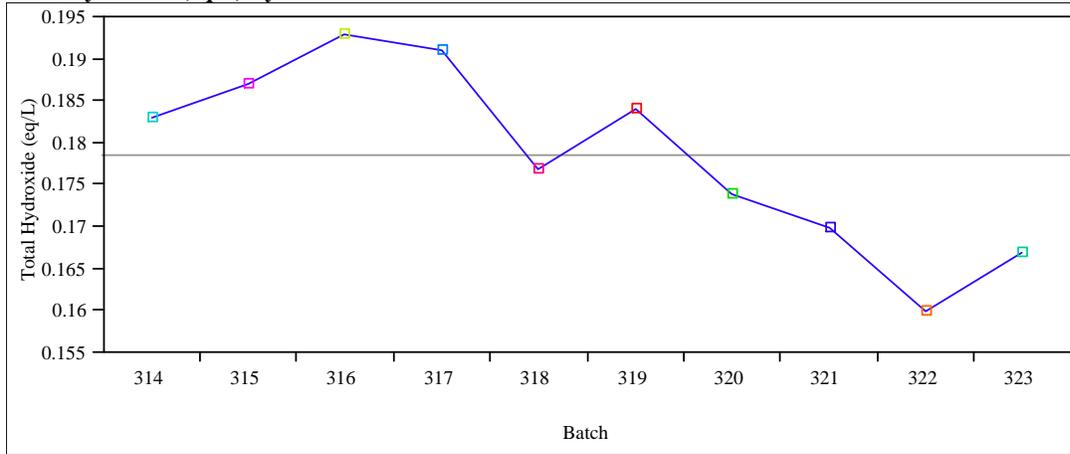


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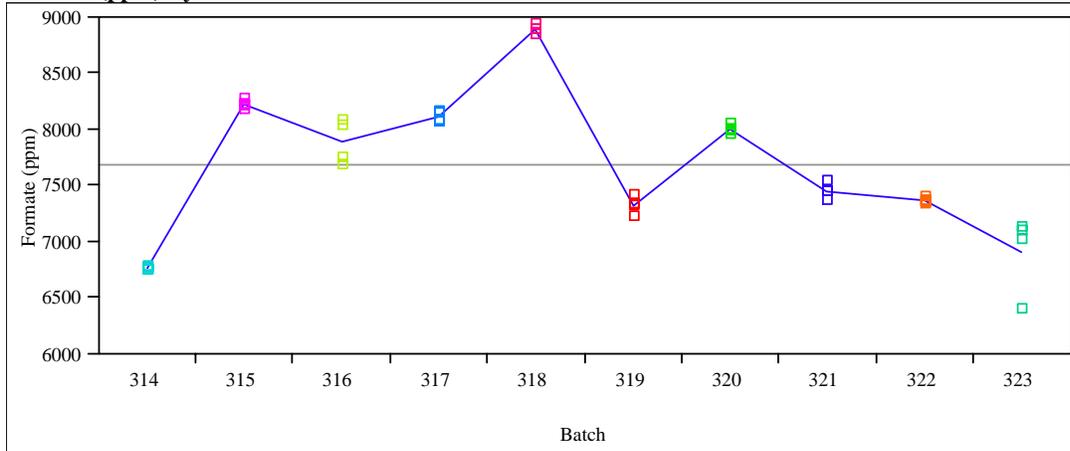
Exhibit A1. Plots of the SRAT Receipt Measurements by Batch Number

Total Hydroxide (eq/L) By Batch



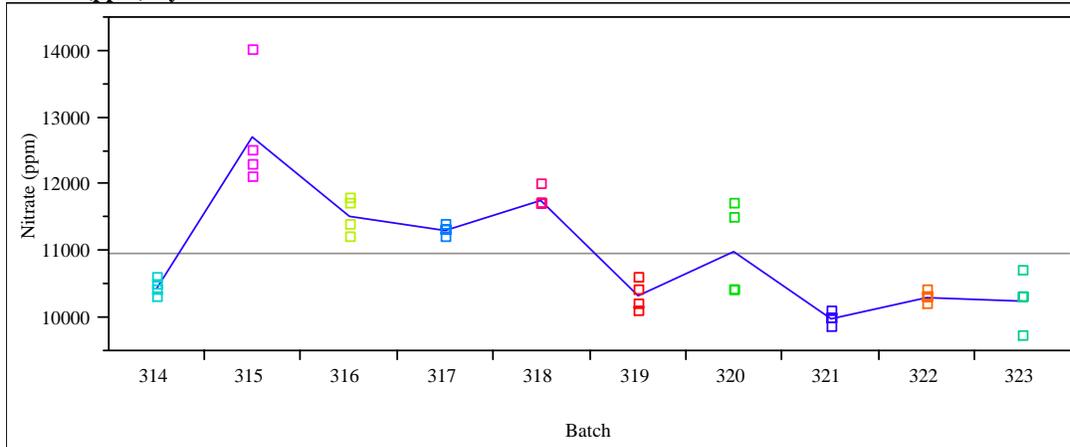
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Formate (ppm) By Batch



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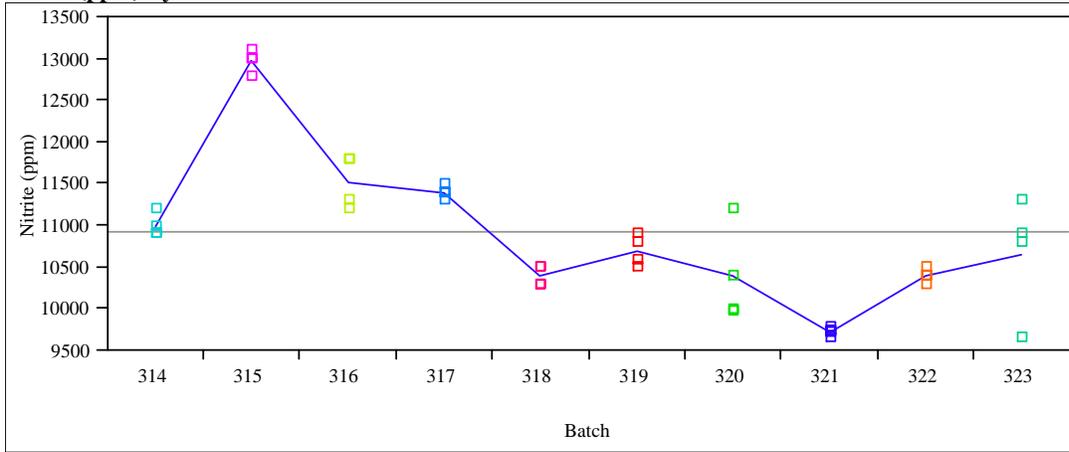
Nitrate (ppm) By Batch



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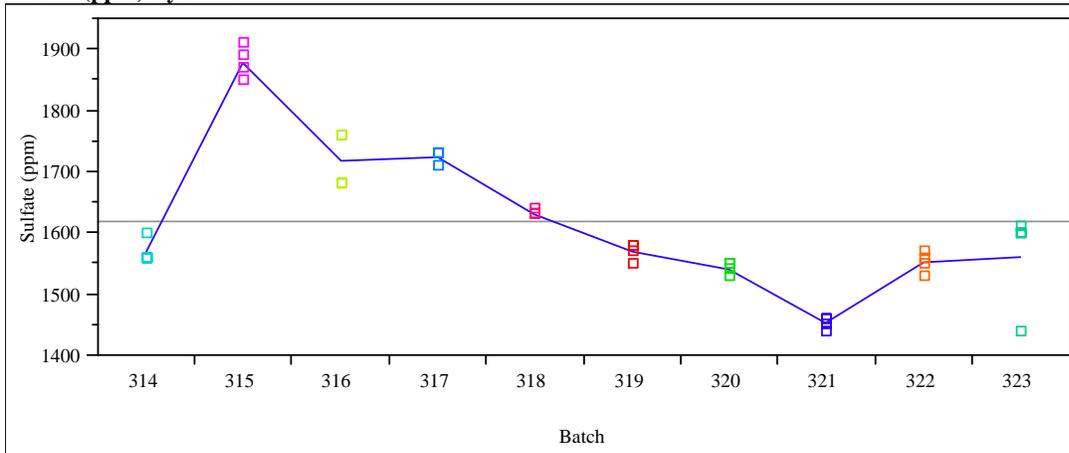
Exhibit A1. Plots of the SRAT Receipt Measurements by Batch Number

Nitrite (ppm) By Batch



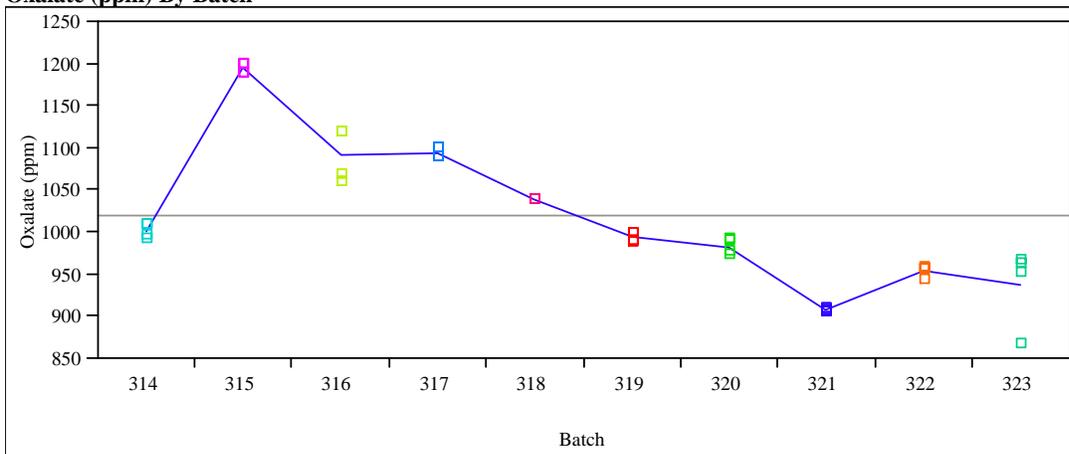
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Sulfate (ppm) By Batch



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17

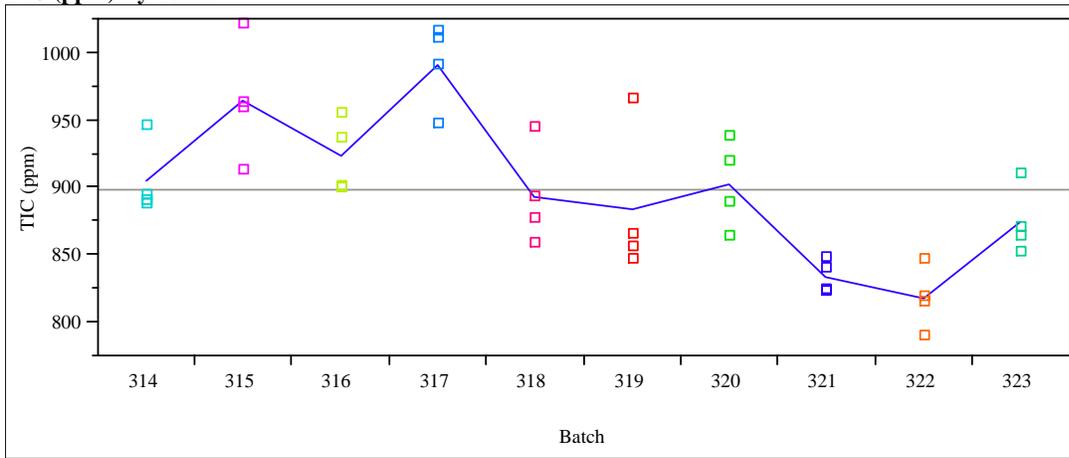
Oxalate (ppm) By Batch



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17

Exhibit A1. Plots of the SRAT Receipt Measurements by Batch Number

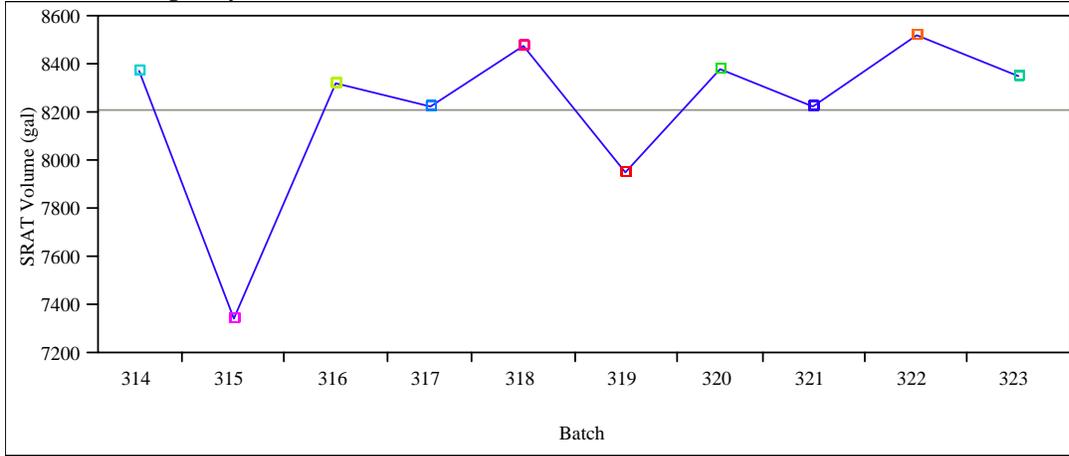
TIC (ppm) By Batch



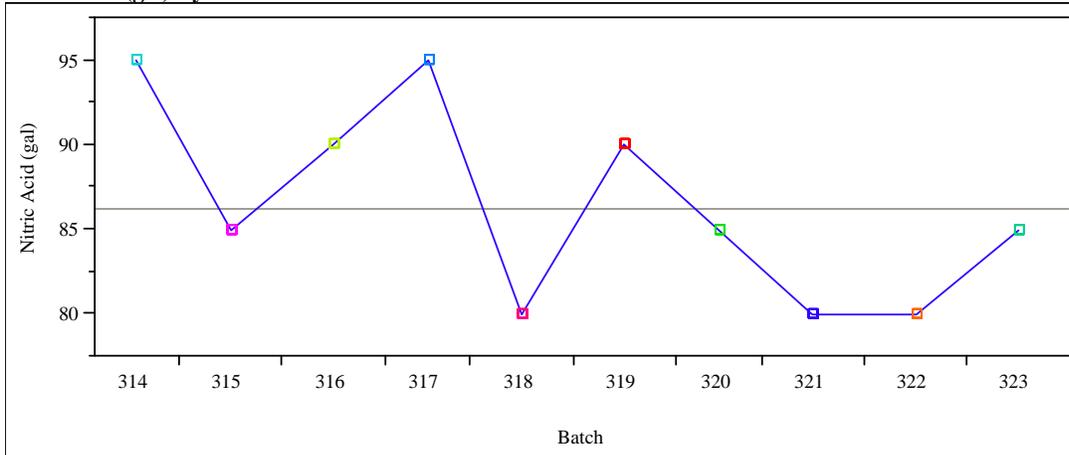
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Exhibit A2. Plots SRAT Volumes, Nitric Acid Additions, and Formic Acid Additions by Batch Number

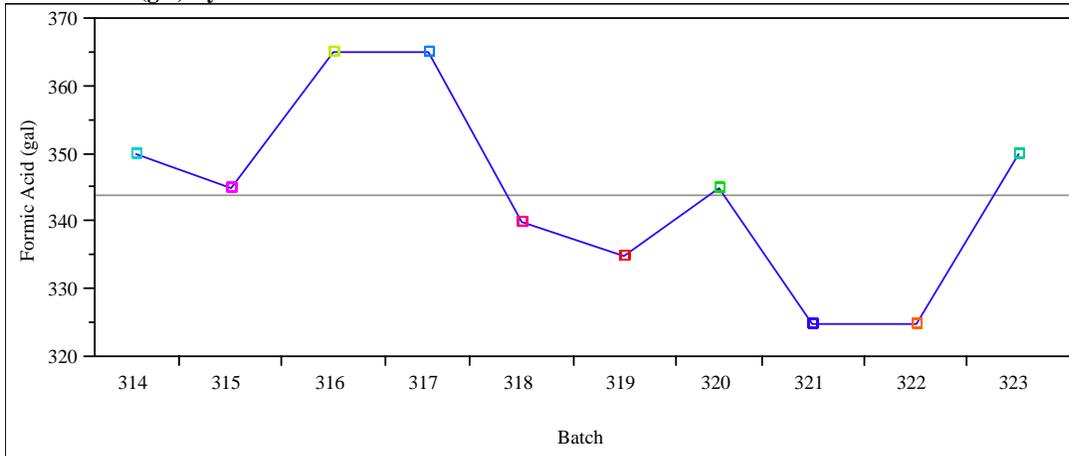
SRAT Volume (gal) By Batch



Nitric Acid (gal) By Batch



Formic Acid (gal) By Batch



Distribution:

N.E. Bibler, 773-A	W.L. Melton III, 704-28S
D.R. Best, 786-1A	J.E. Occhipinti, 704-S
T.B. Calloway, 999-W	P.M. Patel, 704-27S
J.N. Chen, 704-27S	F.M. Pennebaker, 773-A
J.E. Cook, 210-S	D.K. Peeler, 999-W
D.A. Crowley, 773-A	J.W. Ray, 704-S
T.B. Edwards, 773-42A	E.P. Shine, 773-42A
M.T. Feller, 704-28S	J.A. Smith, 704-29S
T.L. Fellingner, 773-A	M.E. Smith, 773-42A
C.C. Herman, 773-42A	T.K. Snyder, 999-W
R.M. Hoeppe, 704-27S	M.E. Stone, 999-W
E.W. Holtzscheiter, 773-A	R.C. Tuckfield, 773-42A
C.M. Jantzen, 773-A	J.P. Vaughan, 773-41A
R.N. Mahannah, 704-28S	F.A. Washburn, 704-28S
S.L. Marra, 999-W	P.M. Woodward, 704-28S