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INVESTIGATION OF RHEOLOGICAL IMPACTS ON SLUDGE BATCH 3 AS INSOLUBLE SOLIDS AND WASH ENDPOINTS ARE ADJUSTED (U)

T.L. Fellinger

July 12, 2005

Immobilization Technology Section
Savannah River National Laboratory
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EXECUTIVE SUMMARY

The Defense Waste Processing Facility (DWPF) is currently processing and immobilizing radioactive sludge slurry into a durable borosilicate glass. The DWPF has already processed three sludge batches (Sludge Batch 1A, Sludge Batch 1B, and Sludge Batch 2) and is currently processing the fourth sludge batch (Sludge Batch 3). A sludge batch is defined as a single tank of sludge slurry or a combination of sludge slurries from different tanks that has been or will be qualified before being transferred to DWPF.

As a part of the Sludge Batch 3 (SB3) qualification task, rheology measurements of the sludge slurry were requested at different insoluble solids loadings.[1, 2] These measurements were requested in order to gain insight into potential processing problems that may occur as the insoluble solids are adjusted up or down (by concentration or dilution) during the process. As a part of this study, a portion of the “as received” SB3 sample was washed with inhibited water (0.015 M NaOH and 0.015 M $NaNO_2$) to target 0.5M Na versus a measured 1M Na in the supernate. The purpose of the “washing” step was to allow a comparison of the SB3 rheological data to the rheological data collected for Sludge Batch 2 (SB2)[3] and to determine if there was a dependence of the yield stress and consistency as a function of washing[4, 5]. The “as received” SB3 rheology data was also compared to SB3 simulants prepared by the Simulant Development Program[6] in order to provide guidance for selecting a simulant that is more representative of the rheological properties of the radioactive sludge slurry. Below is a summary of the observations, conclusions and recommendations from this rheology work.

Observations and Conclusions:

- The yield stress and plastic viscosity increased as the weight percent insoluble solids were increased for the “as received” and “washed” SB3 samples, at a fixed pH.
- For the same insoluble solids loading, the yield stress for the SB2 sample is approximately a factor of three higher than the “as received” SB3 sample. There also appears to be small difference in the plastic viscosity. This difference is probably due to the different Na concentrations of the slurries.
- The yield stress for the SB2 sample at 17.5 wt. % insoluble solids loading is four times higher than the “washed” SB3 sample at 16.5 wt. % insoluble solids. There also appears to be small difference in the plastic viscosity. The differences for the yield stress and consistency can be explained by the differences in the Fe and Na concentrations of the sludge slurry and the anion concentrations of the resulting supernates.
- The rheological properties (i.e. yield stress and plastic viscosity), as the insoluble solids are adjusted, for the “as received” and “washed” SB3 samples are different. The plastic viscosity curve for the “as received” SB3 sample was higher than the plastic viscosity curve for SB3 “washed” sample. The yield stress curve for the “washed” SB3 sample is slightly lower than the “as received” SB3 sample up until ~19 wt. % insoluble solids. The “washed” SB3 sample then exceeds the yield stress curve for the “as received” SB3 sample. This rheological behavior is probably due to the difference in the Na concentration of the supernate for the samples.
- No unusual behavior, such as air entrainment, was noted for the “as received” SB3 sample.
- The observed physical properties of the SB3 sample changed after washing. The “washed” SB3 sample entrained air readily at higher insoluble solids loadings (i.e. 14.1, 16.5, 19.5 wt. %) as it did for SB2. The air entrainment appeared to dissipate for the SB3 sample at the lower insoluble solids loadings (i.e. 9.7 and 11.7 wt. %).
- The physical behavior of SB3 can be influenced by controlling the Na concentration in the supernate and the wt. % insoluble solids. The cause for the air entrainment in the “washed” SB3 sample could be due to a change in the particle size during the washing step.

- The SB3 simulants prepared for the Simulant Development Program were approximately a factor of 1.6 to 4 times higher for yield stress and 2.6 to 4 times higher for the plastic viscosity over a similar range of insoluble solids loadings. The difference noted between the radioactive and simulant samples could be due to several factors including particle size, thermal treatment (i.e. aging of the sludge), shear history, etc.

Recommendations:

- In order to facilitate the understanding of the rheological differences between the radioactive SB3 sludge and the SB3 simulants, it is recommended that the particle size information for the radioactive SB3 sample be obtained and compared to the particle size information obtained for the simulants. This information coupled with rheological data will provide the necessary basis for developing a simulant that more closely mimics the rheological properties of the radioactive sludge slurry.
- In order to investigate the air entrainment issue observed for the “washed” sample, it is recommended that particle size data for the “as received” and “washed” samples be obtained to determine if the particle size changed during the washing process and caused the air entrainment observed.
- Continue to collect rheological and particle size data for future sludge batches to build an understanding of the impact of these parameters on air entrainment and other DWPF processing considerations.

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LIST OF ACRONYMS

DWPF – Defense Waste Processing Facility
IC – Ion Chromatography
ICP-ES - Inductively Coupled Plasma Emission Spectrometer
IS – Insoluble Solids
ITS - Immobilization Technology Section
NIST – National Institute of Standards
SB2 – Sludge Batch 2
SB3 – Sludge Batch 3
SRNL – Savannah River National Laboratory

1.0 INTRODUCTION AND BACKGROUND

A three liter sample of Sludge Batch 3 (SB3) was taken from Tank 40 and transported to Savannah River National Laboratory (SRNL) in November 2004. This sample was taken in order to complete chemical and radionuclide analysis required for the Waste Acceptance Product Specification for this sludge batch, and the rheological measurements requested in the Technical Task Requests (TTRs).[1, 4] Task plans were written in response to the TTRs[2, 5] and summarized below are the main objectives of the rheology work:

- Obtain rheology data in order to gain insight into potential processing problems that may occur as the insoluble solids are adjusted up or down (by concentration or dilution) during the DWPF process.
- Determine the effect of changing the dissolved solids (i.e. washing) of the SB3 sludge slurry on rheological behavior
- Compare the radioactive “as received” SB3 rheology data to the nonradioactive SB3 rheology data for DWPF Simulant Development Program.

In order to accomplish the first objective, a mixed portion of the SB3 sample was taken and measured at different insoluble solids loadings. The different insoluble solids loadings of the SB3 sample were achieved by concentrating the sample (by decanting) or diluting the sample with supernate. To accomplish the second objective, the “as received” SB3 sample was re-combined and washed with inhibited water (0.015 M NaOH and 0.015 M $NaNO_2$) to adjust the Na molarity from 1M to 0.5M Na in the supernate. The insoluble solids for the washed sample were also adjusted and rheological measurements completed. The “as received” and the “washed” SB3 data were compared to previous radioactive rheological data[3] and were then compared to each other. This comparison was completed in order to determine the dependence of yield stress and consistency as a function of insoluble solids and washing. To meet the third objective, the “as received” SB3 rheology data were compared to the rheological data collected from the Simulant Development Program[6]. This comparison was used to determine which simulant preparation method matched the yield stress and consistency of the radioactive SB3 sample. This report documents the results of this rheological study.

2.0 APPROACH

Presented below are brief descriptions of the analytical methods and procedures used to prepare the samples for the rheological study.

2.1 Description of the Rheological Instrumentation Used for the Rheological Measurements

All of the rheological measurements for the SB3 radioactive sludge slurry sample were obtained using a Haake RV30/M5 system located in the SRNL Shielded Cells Facility. The Haake RV30/M5 system is a controlled shear rate rheometer that is operated remotely in the Shielded Cells environment. A water bath/circulator supplies water to maintain the temperature of the water jacket used to keep the sample at a specified temperature. The M5 measuring head can be equipped with different rotors, with each group of rotors having a specified measuring cup. The selection of the rotor/cup combination depends on the sample to be analyzed. The specifications for the instrument can be found in the previous publication[3, 7]. A National Institute of Standards and Technology (NIST) traceable Newtonian oil standard (~14 mPa·s @ 25°C or (~14 cP @ 25°C) was used to verify the operability of the RV30/M5 system prior to the start and at the completion of a set of samples. All measurements for the Newtonian oil standard were within ± 10% of the nominal value. The MVI rotor and MV cup were used in all of the measurements. Measurements for the SB3 samples were performed at 25°C and the weight percent solids were also adjusted up (decanting) or down (diluting) by removing/adding supernate. The supernate used for dilution was obtained from a sample that was allowed to settle and separate. Specifications for the MVI rotor and cup have been published previously.[7]

The same programming times and shear rate ranges were used for the oil standard and the SB3 samples. Table 1 contains the programming times and shear rate ranges for the oil standard and SB3 samples.

Table 1 - Programming Times and Shear Rate Ranges Used to Complete Rheology Measurements

Shear Rate Range and Time		
Up Curve	Hold	Down Curve
0 – 600s^{-1}, 5 minutes	600s^{-1}, 1 minute	600 - 0s^{-1}, 5 minutes

The flow curves (shear rate vs. shear stress) generated from the RV30/M5 for the SB3 samples were modeled using the Bingham Plastic model to obtain the yield stresses and plastic viscosities of these samples. The yield stresses and the plastic viscosities were then compared to the operating window for the DWPF process to determine if the feed may pose potential processing problems. To create the DWPF operating window for the sludge slurry, the higher and lower Bingham Plastic parameter of the sludge slurry were used to develop two curves. The upper curve ($\tau(\text{Pa}) = 0.012\dot{\gamma} + 10$) contained the highest yield stress and the plastic viscosity and lower curve ($\tau(\text{Pa}) = 0.004\dot{\gamma} + 2.5$) contained the lowest yield stress and plastic viscosity. The Bingham plastic model is defined in Equation 1 as:

Equation 1: $$\tau = \tau_o + \eta\dot{\gamma}$$

Where:
τ = Shear stress {Pa}
τ_o= Bingham Plastic yield stress {Pa}
η = Plastic viscosity {Pa·sec}
$\dot{\gamma}$ = shear rate {sec^{-1}}

2.2 Analytical Methods Performed in the SRNL Shielded Cells Facility

2.2.1 pH Measurements

The pH measurements were performed using an in-cell pH probe. The probe was first standardized with buffer solutions at a pH of 10 and 4, and checked with a pH 7 buffer solution. After the standardization of the pH probe, a pH measurement was completed for the sample.

2.2.2 Weight Percent Solids Measurements

The weight percent (wt%) total solids (TS) of a sludge slurry is determined by first weighing out a sample and placing it into a drying oven at 115°C. The sample is dried until a constant dry weight is obtained. The wt% TS is then determined by dividing the dry weight by the total weight of the sample. The dissolved solids in the supernate is determined by filtering a sample through a 0.45 μm Nalgene® filter, weighing the collected supernate and then drying it in the same process as described above. The wt% dissolved solids in the supernate is then determined by dividing the dry weight by the total weight of the supernate. Once the average for the total weight percent solids of the sludge slurry and the average weight percent dissolved solids in the supernate values are determined, the soluble and insoluble weight percent solids were calculated. These values are calculated by using Equations 2 and 3.

Equation 2: $wt\%_{is} = (wt\%_{ts} - wt\%_{ds}) / (100 - wt\%_{ds})*100$

Equation 3: $wt\%_{ss} = wt\%_{ts} - wt\%_{is}$

Where:

$wt\%_{ds}$ = wt% of dissolved solids in the supernate (weight of dissolved solids/weight of supernate times 100)
$wt\%_{ts}$ = wt% of total solids (weight of total solids/weight of sludge slurry times 100)
$wt\%_{is}$ = wt% of insoluble solids (weight of insoluble solids/weight of sludge slurry times 100)
$wt\%_{ss}$ = wt% of soluble solids (weight dissolved solids/weight of sludge slurry times 100)

2.2.3 Density Measurements

The density of the sludge slurry and supernate were measured using sealed pipette tips that were calibrated with water. The sealed pipette is filled with sludge slurry or supernate and the mass added is measured. The density is then determined by dividing the mass added by the volume of the sealed pipette.

2.2.4 Adjustment of Insoluble Solids

Different weight percent insoluble solids concentrations (10, 13, 15, 17, and 19) were calculated to determine the quantity of supernate to be added or removed. The SB3 sample was then split into two parts and allowed to settle so that supernate could be removed or added based on the insoluble solids target. After each weight percent solids adjustment, rheology measurements at 25°C and weight percent total solids measurements were completed for each of samples.

2.3 Washing of SB3 Sludge Slurry with Inhibited Water

In order to study the effect of dissolved solids loading on sludge slurry, a sample of SB3 (currently ~1M Na in the supernate) was taken, analyzed, and then washed with inhibited water (0.015M $NaNO_2$ and 0.015M $NaNO_3$) to target a wash end point of 0.5 M (+/- 0.06M) Na concentration in the supernate. Approximately 250 mL of the SB3 was washed with inhibited water for this portion of the study. The resulting supernate was analyzed by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and Ion Chromatography (IC) to determine the Na concentration and anion concentration. This washing step was completed in order to determine if the rheological conditions deteriorated with washing as observed during Sludge Batch 2 (SB2).

3.0 RESULTS OF THE “AS RECEIVED” AND “WASHED” SB3 SAMPLE

3.1 Summary of Data Obtained for the “As Received” Sludge Slurry Sample

The analyses described in Sections 2.1and 2.2 were completed for the SB3 samples. After the pH and weight percent solids measurements were completed for the samples, the rheology measurements were performed. Each sample was prepared for measurement in the rheometer by mixing and pouring a portion of the sample into the measuring cup. The measuring cup was then loaded into the instrument and the measurements were completed at 25°C. Upon the completion of the rheology measurements, the insoluble solids of the sample were adjusted and the same protocol was followed for the adjusted sample to obtain the remaining data.

The data plotted in Figure 1 is the rheological data (up flow curves only) for the insoluble solids target concentrations of 10, 13, 15, 17, and 19 wt.% compared to the rheological data collected for Sludge Batch 2

(SB2) at 17.5 wt.% insoluble solids. All measurements were completed in duplicate at 25°C. The down curves were on top or slightly below the up curves. The gap between the up and down curve was more pronounced at the lower insoluble solids loadings (10 and 13 wt. %). This was probably due to the insoluble solids settling out during the measurements. Figure 1 also contains the operating window for the DWPF sludge slurry[8]. The SB3 data in Figure 1 were curve fitted using the Bingham Plastic model from a shear rate range of ~50s^{-1} to 600s^{-1}. The SB2 rheological data was fit from 252s^{-1} to 1100s^{-1}. For Figure 1, the SB2 flow curve was truncated at 600s^{-1}. A summary of the yield stress and plastic viscosity values obtained from the Bingham Plastic Model for these sludge slurry samples are presented in Table 2.

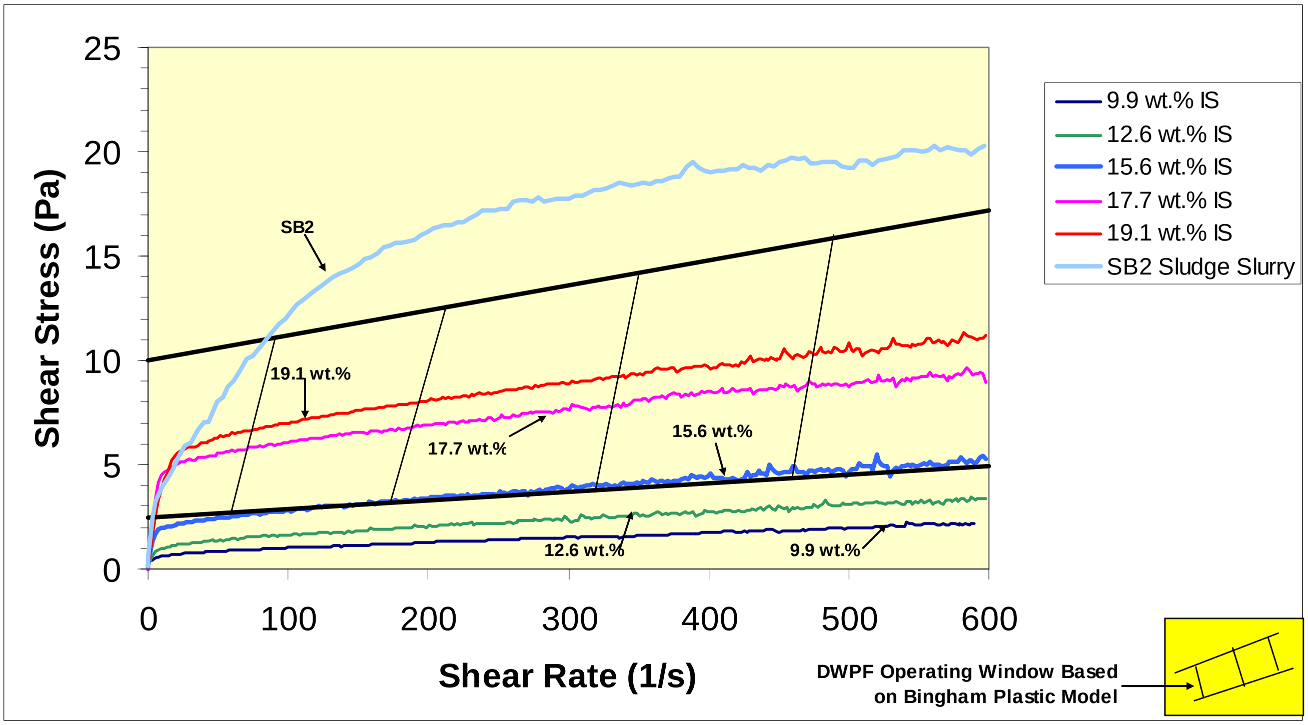

Figure 1 – Flow Curves for the "As Received" SB3 Sludge Slurry Compared to SB2

Table 2 - Summary of Weight Percent Solids, Rheology, and pH Data Collected for the SB3 Sludge Slurry Compared to SB2 Data

Sample ID	Total Solids (wt.%)	Insoluble Solids (wt.%)	Yield Stress (Pa)[b]	Plastic Viscosity (Pa·sec)[c]	Density for the Sludge Slurry (g/mL)	pH
SB3 Sludge Slurry - 19 wt.% I.S. at 25°C	24.4[a]	19.1	6.3	0.0084	N.M.	13.2
SB3 Sludge Slurry – 17 wt.% I.S. at 25°C	23.1[a]	17.7	5.5	0.0070	N.M.	13.2
SB3 Sludge Slurry – 15 wt.% I.S. at 25°C	21.1[a]	15.6	2.4[a]	0.0049	N.M.	13.2
SB3 Sludge Slurry – 13 wt.% I.S. at 25°C	18.3	12.6	1.3[a]	0.0037[a]	1.13	13.2
SB3 Sludge Slurry – 10 wt.% I.S. at 25°C	15.8	9.9	0.8[a]	0.0024[a]	N.M.	13.2
SB2 Sludge Slurry – 18 wt.% I.S. at 25°C	19.9[a]	17.5	16.6[a]	0.006	1.14	12.7
DWPF Operating Window	13-19	N/A	2.5 – 10.0	0.004 – 0.012	N/A	N/A

[a] Data is outside of the DWPF operating window per specifications in document DPST-80-38-2
[b] Pa can be converted to dynes/cm^2 by multiplying by 10
[c] Pa-sec can be converted to cP by multiplying by 1000
N.M. – Not Measured
N/A – Information Not Available

One conclusion that can be made by studying the data in Figure 1 and Table 2 is that as the insoluble solids content is increased, the yield stress and plastic viscosity increases. These data are consistent with previous work completed on nonradioactive and radioactive sludge slurries[3, 6]. The other observation made from looking at the data presented in Figure 1 and Table 2 is that for the same insoluble solids loading, the yield stress for the SB2 samples is approximately a factor of three higher than the SB3 sample. There also appears to be small difference in the plastic viscosity when comparing the SB3 sample at 17.7 wt. % insoluble solids to the SB2 sample at 17.5 wt. % insoluble solids. To explain the differences seen for the yield stress and consistency for the two samples, the chemical compositions (See APPENDIX A, Table A- 1), the wt. % total solids, and wt. % insoluble solids were compared. The differences in the chemical composition for these two samples can be explained by the different wash end points or Na concentration in the supernate for each sludge batch. The “as received” SB3 sample should have a higher consistency value at the same insoluble solids loading due to the higher soluble solids (concentration of Na in the supernate) in the sample and the results in Table 2 confirm this conclusion. The differences in the yield stress could be attributed to the SB2 having a higher Fe to Na ratio (i.e. higher insoluble solids to total solids ratio) than the “as received” SB3 sample. The ionic strength of the “as received” SB3 supernate may help suspend the insoluble solids more readily. The particles size of these slurries could also be a factor influencing the rheological behavior of the sludge slurry. Since the particle size of these slurries has not been determined, the impact of this factor can not be evaluated. The values that were outside the DWPF operating window were highlighted in Table 2. Samples that exceed the upper limit of the DWPF operating window can pose processing problems for DWPF, like the Sludge Batch 2 sample. Samples that have been below the lower limit for the DWPF operating window have not posed any processing issues to date.

3.2 Comparison of the Yield Stress and Plastic Viscosity Data for the "As Received" Sludge Slurry Sample to SB3 Simulants from the Simulant Development Program

The yield stress and plastic viscosity results presented in Table 2, were each plotted verses the wt. % insoluble solids content and the data was fitted using an exponential function in Excel. This data was then compared to the DWPF operating region[8] and the Simulant Development Program's Simulant Preparation yield stress and plastic viscosity equations developed for the down curves for Test 1 through Test 8[6]. Based on the comparison of the results for the yield stress and consistency values obtained at 9.9, 12.6, 15.6, 17.7, 19.1 wt. % insoluble solids, the simulant preparation data that was the closest to the measured yield stresses and plastic viscosities for the "as received" SB3 sample were selected. Figure 2 presents the comparison of the yield stress vs. insoluble solids for the "as received" SB3 sample to Test 7 and Test 8 from the Simulant Development Program[6]. The equations and the R^2 values obtained for the original data sets are also presented in Figure 2. Figure 3 presents the comparison of the plastic viscosity vs. insoluble solids for the "as received" SB3 sample to Test 4, Test 5, and Test 8 from the Simulant Development Program[6]. The equations and the R^2 values obtained for the original data sets are also presented in Figure 3. Table 3 provides a brief description of the Simulant Development Program's Simulant Preparation Methods taken verbatim from WSRC-TR-2004-00578[6]. It should be noted that data presented in Figure 2 and Figure 3 for the Simulant Development Program have been extrapolated beyond the highest insoluble solids loading tested.

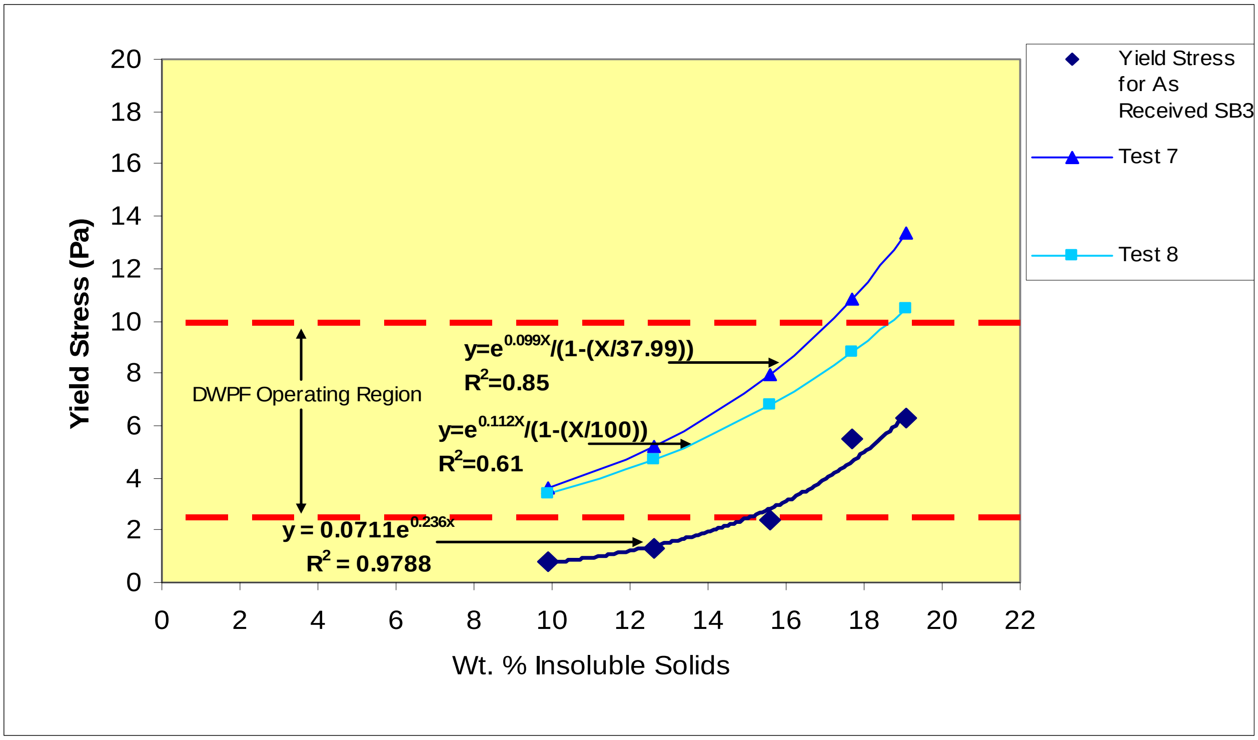

Figure 2 – Comparison of the Yield Stress vs. Insoluble Solids for the "As Received" SB3 Sample to Test 7 and Test 8 from the Simulant Development Program

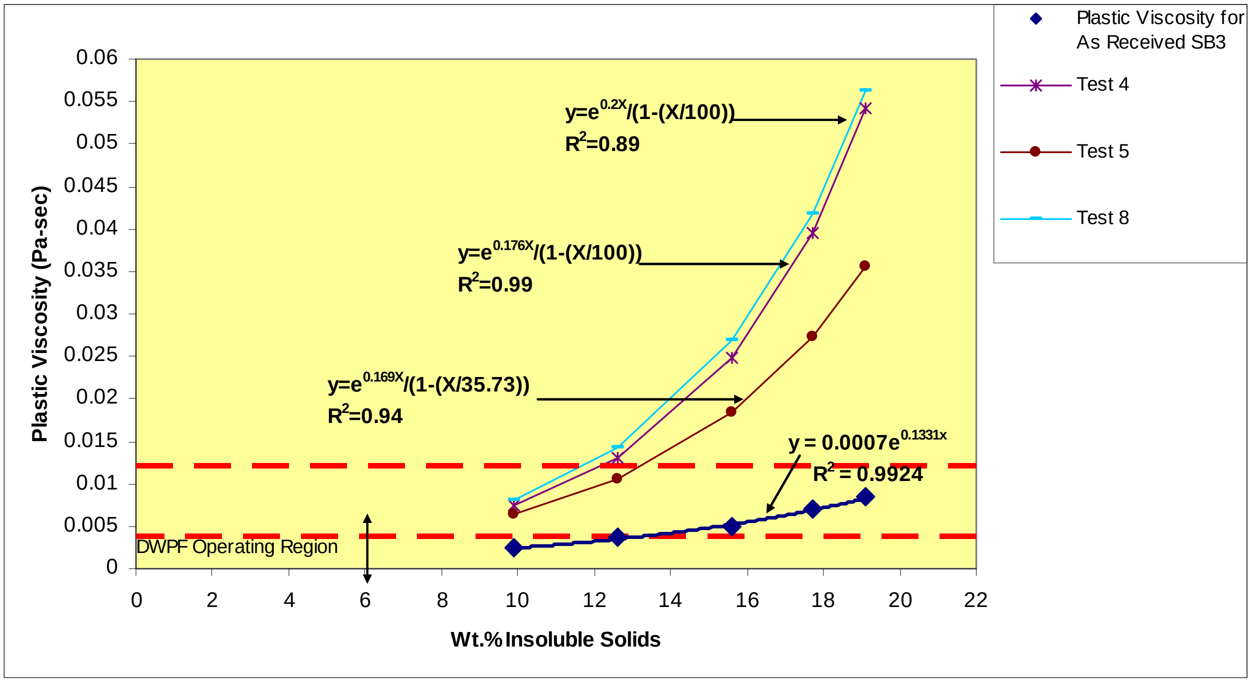

Figure 3 - Comparison of the Plastic Viscosity vs. Insoluble Solids for the "As Received" SB3 Sample to Test 4, Test 5, and Test 8 from the Simulant Development Program

Table 3 – Description of the Simulant Development Program's Sludge Preparation Methods[6]

Test Number	Preparation Method
4	Current preparation method – normal agitation with a thermal treatment before washing
5	Current preparation method – normal agitation with a thermal treatment after washing
7	Preparation including all metals in the MnO_2 generation step followed by caustic precipitation at pH<10 without a thermal treatment
8	Preparation including all metals in the MnO_2 generation step followed by caustic precipitation at pH<10 with thermal treatment step after sludge washing.

From Figure 2, Test 8 appears to be the best simulant for reproducing the yield stress values observed for the SB3 sample. However, the Test 8 data is ~ 1.6 times higher for the 19.1 wt.% insoluble solids loading and ~ 4.2 times higher for the 9.9 wt.% insoluble solids loading. The R^2 value for the Test 8 data indicates that the fit of this data set is poor. Upon examination of the actual data set for Test 8[6], it appears the reason for the poor fit of the data is due to the yield stress data collected at 13.03 wt. % insoluble solids loading. The yield stress data collected for 13.03 wt. % insoluble solids sample exceeded the yield stress data reported for 16.55 wt. % insoluble solids sample by a factor of 1.5. If this data point were removed from the Test 8 simulant data, the data would more than likely be closer to the radioactive data. The reason for this high yield stress value at 13.03 wt.% insoluble solids sample is unknown at this time. For the plastic viscosity results in Figure 2, it appears that Test 5 is the best simulant for reproducing the plastic viscosity values observed for the SB3 sample. However, the Test 5 data is off by a factor of 4 for the 19.1 wt. % insoluble solids loading and a factor of 2.6 for the 9.9 wt.% insoluble solids loading. The differences noted for Figure 3 could be due to several factors including particle size, thermal treatment (i.e. aging of the sludge), shear history, etc. Based on the results from Figure 2 and Figure 3, the next step in understanding the rheological differences between the radioactive sludge and these simulants is to obtain the particle size information for the radioactive SB3 sample. This information coupled with rheological data will provide the necessary basis for developing a simulant that more closely mimics the rheological properties of the radioactive sludge.

3.3 Summary of Data Obtained for the "Washed" Sludge Slurry Sample

The analyses described in Sections 2.1, 2.2, and 2.3 were completed for the SB3 sample. The target Na concentration for the supernate (0.5M) was met and the results for the washed supernate are presented in APPENDIX A, Table A- 2. After the pH, density, and weight percent solids measurements were completed for the samples, the rheology measurements were performed. Each sample was prepared for measurement in the rheometer by mixing and pouring a portion of the sample into the measuring cup. The measuring cup was then loaded into the instrument and the measurements were completed at 25°C. Upon the completion of the rheology measurements, the insoluble solids of the sample were adjusted and the same protocol was followed for the adjusted sample to obtain the remaining data. For the samples containing a higher insoluble solids loading (14.1, 16.5, and 19.5 wt.% insoluble solids), the samples appeared to entrain air readily as it did for SB2. However, as the insoluble solids were lowered the air entrainment issue appeared to dissipate (9.7 and 11.7 wt.% insoluble solids loadings). Based on this observation, the air entrainment was resolved by increasing the soluble solid content (hence diluting the insoluble solids).

The data plotted in Figure 4 are the rheological data (up flow curves only) for the insoluble solids target concentrations of 9.7, 11.7, 14.1, 16.5, and 19.5 wt.% compared to the rheological data collected for Sludge Batch 2 (SB2) at 17.5 wt.% insoluble solids. All measurements were completed at 25°C. Figure 4 also contains the operating window for the DWPF sludge slurry. The data in Figure 4 were curve fitted using the Bingham Plastic model from a shear rate range of ~50s^{-1} to 600s^{-1}. The SB2 rheological data was fit from 252s^{-1} to 1100s^{-1}. For Figure 4, the SB2 flow curve was truncated at 600s^{-1}. A summary of the yield stress and plastic viscosity values obtained from the Bingham Plastic Model for these sludge slurry samples are presented in Table 4.

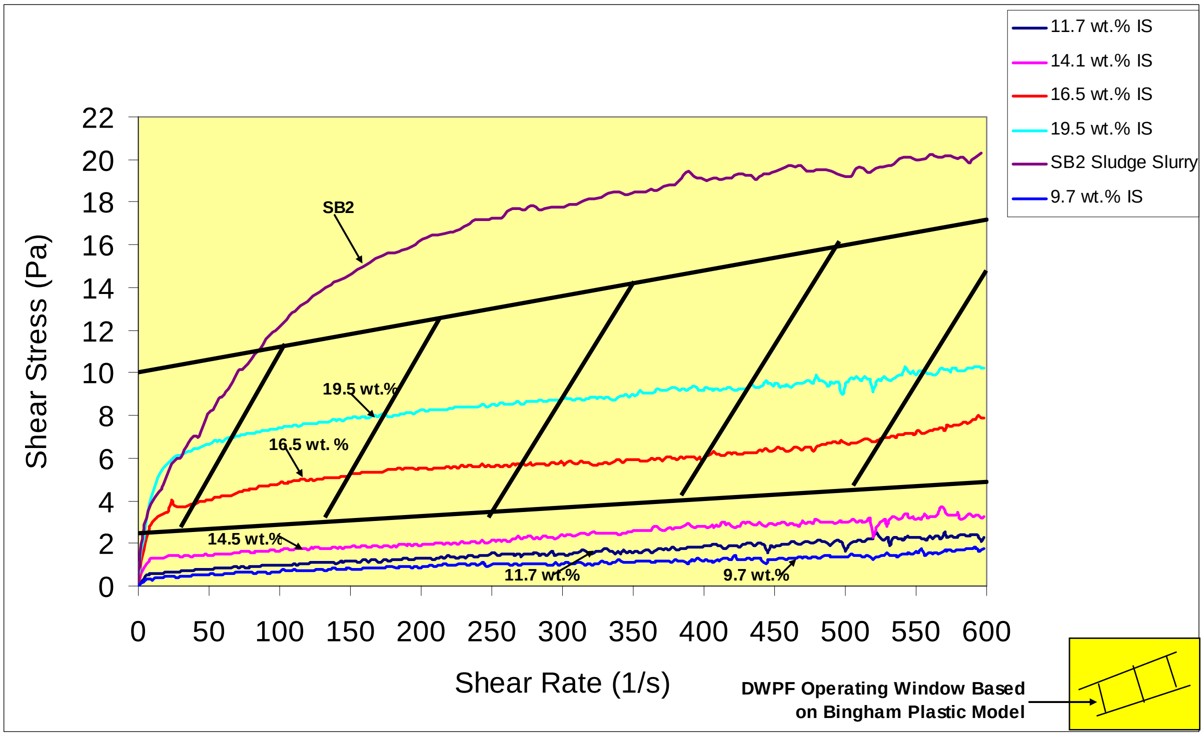

Figure 4 - Flow Curves for the "Washed" SB3 Sludge Slurry Compared to SB2

Table 4 - Summary of Weight Percent Solids, Rheology, and pH Data Collected for the SB3 Sludge Slurry Compared to SB2 Data

Sample ID	Total Solids (wt.%)	Insoluble Solids (wt.%)	Yield Stress (Pa)[b]	Plastic Viscosity (Pa·sec)[c]	Density for the Sludge Slurry (g/mL)	pH
Washed SB3 Sludge Slurry - 19 wt.% I.S. at 25°C	22.4[a]	19.5	7.1	0.0052	1.06	12.8
SB3 Sludge Slurry – 17 wt.% I.S. at 25°C	19.5[a]	16.5	4.0	0.0056	1.10	12.8
SB3 Sludge Slurry – 15 wt.% I.S. at 25°C	17.2	14.1	1.3[a]	0.0035[a]	1.13	12.8
SB3 Sludge Slurry – 12 wt.% I.S. at 25°C	14.9	11.7	0.68[a]	0.0028[a]	1.09	12.8
SB3 Sludge Slurry – 10 wt.% I.S. at 25°C	13.0	9.7	0.48[a]	0.0019[a]	1.09	12.8
SB2 Sludge Slurry – 18 wt.% I.S. at 25°C	19.9[a]	17.5	16.6[a]	0.006	1.14	12.7
DWPF Operating Window	13-19	N/A	2.5 – 10.0	0.004 – 0.012	N/A	N/A

[a] Data is outside of the DWPF operating window per specifications in document DPST-80-38-2
[b] Pa can be converted to dynes/cm^2 by multiplying by 10
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N.M. – Not Measured
N/A – Information Not Available

One conclusion that can be made by studying the data in Figure 4 and Table 4 is that as the insoluble solids content is increased, the yield stress and plastic viscosity increased. These data are consistent with "as received" SB3 data and previous work completed on nonradioactive and radioactive sludge slurries[3, 6]. The density measurements obtained for the 19 wt. % insoluble solids in Table 4 appears to be rather low and is considered suspect data. Outside of this one data point, the other density data appears to be within reason for the insoluble solids loading. The other observation made from looking at the data presented in Figure 4 and Table 4 is that for the same insoluble solids loading, the yield stress for the SB2 samples is approximately a factor of three higher than the "washed" SB3 sample. However, there appears to be a small difference in the plastic viscosity when comparing the "washed" SB3 sample at 16.5 wt.% insoluble solids to the SB2 sample at 17.5 wt.% insoluble solids. Two of the main differences between these two washed samples would be the Fe and Na content of the sludge slurry and the anion concentrations of the resulting supernate. The Fe to Na ratio for "washed" SB3 sample is still projected to be lower than that of the SB2 sample, even though the removal of Na during the SB3 washing step increased the insoluble solids content (i.e. Fe, Mg, Ni, etc.). Also, the concentration of the nitrite is approximately 1.5 times higher and the concentration of the nitrate is approximately 1.7 times higher for the "washed" SB3 sample. This results in a lower hydroxide ion concentration for the "washed" SB3 sample versus the SB2 sample when performing an anion/cation balance for the supernate. These differences in chemical composition could explain the differences seen in the yield stress for these samples. However, the yield stress difference could also be due to several other factors including particle size, thermal treatment (i.e. aging of the sludge), shear history, etc. The values that were outside the DWPF operating window were highlighted in Table 4. Samples that exceed the upper limit of the

DWPF operating window can pose processing problems for DWPF, like the Sludge Batch 2 sample. Samples that have been below the lower limit for the DWPF operating window have not posed any processing issues to date.

3.4 Comparison of the Data Obtained for the "As Received" SB3 Sample to the "Washed" SB3 Sample

The yield stress and plastic viscosity results presented in Table 2 and Table 4, were each plotted verses the wt. % insoluble solids content and the data was fitted using an exponential function in Excel. This data was then compared to the DWPF operating window. Figure 5 presents the comparison of the yield stress vs. insoluble solids for the "as received" SB3 sample to "washed" SB3 sample. Figure 6 presents the comparison of the plastic viscosity vs. insoluble solids for the "as received" SB3 sample to "washed" SB3 sample.

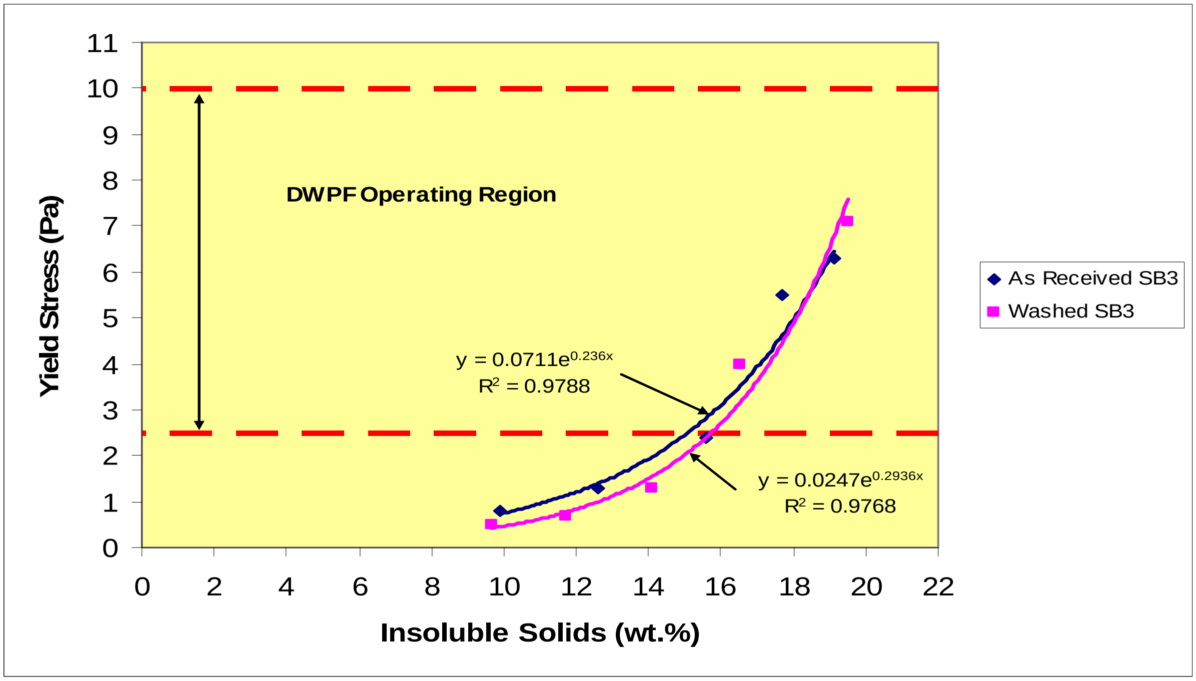

Figure 5 - Comparison of the Yield Stress vs. Insoluble Solids for the "As Received" SB3 Sample to the "Washed" SB3 Sample

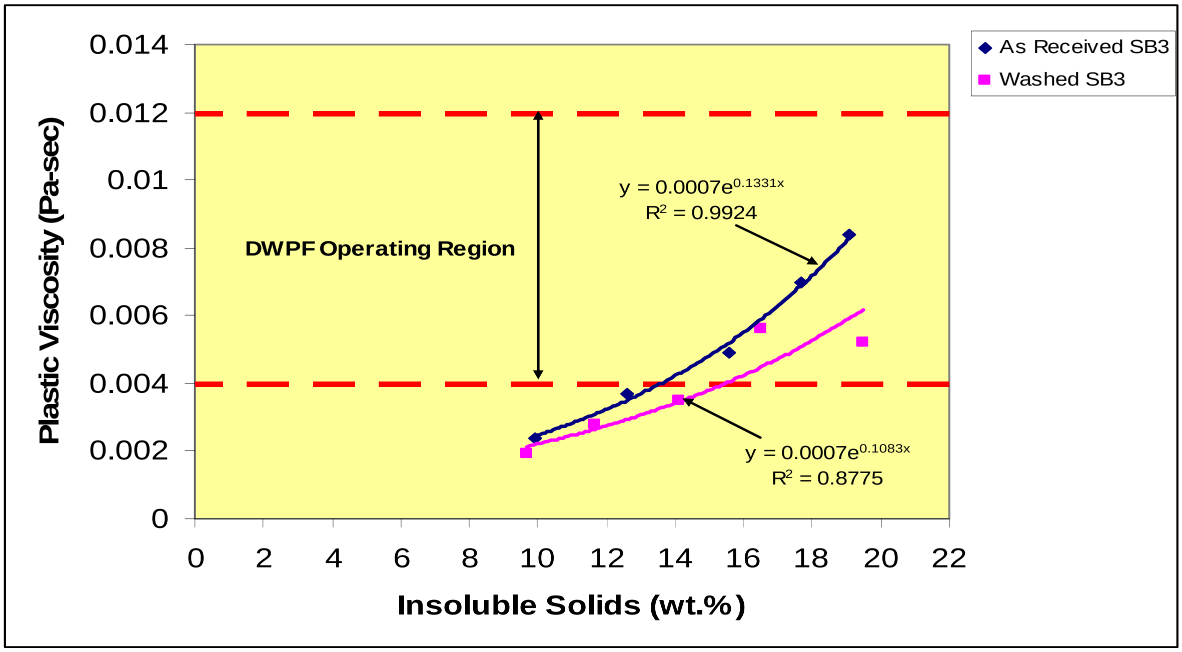

Figure 6 - Comparison of the Plastic Viscosity vs. Insoluble Solids for the "As Received" SB3 Sample to the "Washed" SB3 Sample

For Figure 5, the yield stress curves appear to be very similar although one sample has been washed. The two curves appear to cross one another at the higher insoluble solids loading, with the washed sample slightly exceeding the yield stress of the "as received" sample. For Figure 6, the plastic viscosity curves are also similar. The "as received" sample appears to have a higher plastic viscosity than the "washed" sample. This is probably due to the carrier fluid or the supernate for these samples. The Na molarity of the supernate for the "as received" sample is higher (1 M) than the Na molarity (0.5 M) of the supernate for the "washed" sample. Although the rheological properties for these samples seem very similar, the physical behavior that was observed for each sample at the higher insoluble solids loading was very different. The "as received" sample appeared to be thick, but still fluid. The "washed" sample entrained air readily, and stuck to the sides of bottle. This type of behavior can not be predicted by rheology measurements alone. The cause of the air entrainment is unknown at this time. In order to investigate the air entrainment issue, it is recommended that particle size data for the "as received" and "washed" samples be obtained to determine if the particle size changed during the washing process and caused the air entrainment.

4.0 CONCLUSIONS

Several conclusions and observations were made from the data presented in Section 3.0. A list of these conclusions and observations are presented below.

- The yield stress and plastic viscosity increased as the weight insoluble solids were increased for the "as received" and "washed" SB3 samples, at a fixed pH.
- For the same insoluble solids loading, the yield stress for the SB2 sample is approximately a factor of three higher than the "as received" SB3 sample. There also appears to be small difference in the plastic viscosity. This difference is probably due to the different Na concentrations of the slurries.
- The yield stress for the SB2 sample at 17.5 wt. % insoluble solids loading is four times higher than the "washed" SB3 sample at 16.5 wt. % insoluble solids. There also appears to be small difference in

the plastic viscosity. The differences for the yield stress and consistency can be explained by the differences in the Fe and Na concentrations of the sludge slurry and the anion concentrations of the resulting supernates.

- The rheological properties (i.e. yield stress and plastic viscosity), as the insoluble solids are adjusted, for the “as received” and “washed” SB3 samples are different. The plastic viscosity curve for the “as received” SB3 sample was higher than the plastic viscosity curve for SB3 “washed” sample. The yield stress curve for the “washed” SB3 sample is slightly lower than the “as received” SB3 sample up until ~19 wt.% insoluble solids. The “washed” SB3 sample then exceeds the yield stress curve for the “as received” SB3 sample. This rheological behavior is probably due to the difference in the Na concentration of the supernate for the samples.
- No unusual behavior, such as air entrainment, was noted for the “as received” SB3 sample.
- The observed physical properties of the SB3 sample changed after washing. The “washed” SB3 sample entrained air readily at higher insoluble solids loadings (i.e. 14.1, 16.5, 19.5 wt. %) as it did for SB2. The air entrainment appeared to dissipate for the SB3 sample at the lower insoluble solids loadings (i.e. 9.7 and 11.7 wt.%).
- The physical behavior of SB3 can be influenced by controlling the Na concentration in the supernate and the wt. % insoluble solids. The cause for the air entrainment in the “washed” SB3 sample could be due to a change in the particle size during the washing step.
- The SB3 simulants prepared for the Simulant Development Program were approximately a factor of 1.6 to 4 times higher for yield stress and 2.6 to 4 times higher for the plastic viscosity over a similar range of insoluble solids loadings. The difference noted between the radioactive and simulant samples could be due to several factors including particle size, thermal treatment (i.e. aging of the sludge), shear history, etc.

5.0 RECOMMENDATIONS/PATH FORWARD

- In order to facilitate the understanding of the rheological differences between the radioactive SB3 sludge and the SB3 simulants, it is recommended that the particle size information for the radioactive SB3 sample be obtained and compared to the particle size information obtained for the simulants. This information coupled with rheological data will provide the necessary basis for developing a simulant that more closely mimics the rheological properties of the radioactive sludge.

- In order to investigate the air entrainment issue observed for the “washed” sample, it is recommended that particle size data for the “as received” and “washed” samples be obtained to determine if the particle size changed during the washing process and caused the air entrainment observed.

- Continue to collect rheological and particle size data for future sludge batches to build an understanding of the impact of these parameters on air entrainment and other DWPF processing considerations.

6.0 ACKNOWLEDGEMENTS

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APPENDIX A

Table A- 1– Comparison of the Major Elements for SB2 and SB3 Sludge Slurries

Element	SB2 Sample Weight Percent *,[a]	SB3 Sample Weight Percent *,[b]
Al	5.44E00 (± 6.0E-02, 1.1E00)	5.14E00 (± 8.0E-02, 1.6E00)
Ca	2.3E00 (± 1.2E-02, 5.0E-01)	1.61E00 (± 2.0E-02, 1.5E00)
Fe	2.39E01 (± 1.5E-01, 6.4E-01)	1.64E01 (± 7.0E-01, 4.2E00)
Hg[c]	1.66E-01 (± 3.6E-02, 2.2E+01)	1.46E-01 (± 8.0E-03, 5.9E00)
Mg	1.92E00 (± 1.0E-02, 5.2E-01)	1.52E00 (± 9.0E-02, 5.9E00)
Mn	3.19E00 (± 2.0E-02, 6.3E-01)	3.56E00 (± 1.6E-01, 4.6E00)
Na	6.80E00 (± 1.6E-01, 2.3E00)	1.31E01 (± 1.0E-01, 9.0E-01)
Ni	1.88E00 (±5.8E-03, 4.9E-01)	9.83E-01 (±3.7E-02, 3.8E00)
Si	5.67E-01 (± 4.2E-02, 7.3E00)[d]	1.06E00[e] (± 2.0E-02, 1.6E00)
U	8.12E00 (± 5.9E-02, 7.2E-01)	6.77E00 (± 3.2E-01, 4.7E00)

* The sludge slurry sample was dried overnight at 115°C in a drying oven. Results are present on a dry total solids basis.

[a] Majority of the results are determined by ICP-ES unless otherwise indicated and are the average of three sample results. The standard deviations and the percent relative standard deviations for the data are also presented in parentheses next to each value. See WSRC-TR-2003-00253.

[b] Majority of the results are determined by ICP-ES unless otherwise indicated and are the average of eight sample results. The standard deviations and the percent relative standard deviations for the data are also presented in parentheses next to each value. See WSRC-TR-2005-00049.

[c] Results determined by Cold Vapor Mercury method.

[d] Dissolved by Aqua Regia dissolution method

[e] Dissolved by Peroxide Fusion dissolution method

Table A- 2 – Comparison of SB2 and the "Washed" SB3 Compositions for the Supernate

Method	SB2 Sample Average of Results (M)[a]	SB3 Sample Average of Results (M)[a]
IC Results for Chloride	2.4E-04 (± 2.7E-07, 1.1E-01)	3.01E-04 (1.63E-05, 5.41E+00)
IC Results for Fluoride	3.5E-03 (±8.7E-05, 2.5E00)	5.53E-03 (4.18E-04, 7.56E+00)
IC Results for Formate	8.3E-04 (± 6.3E-05, 7.6E00)	5.11E-04 (4.44E-05, 8.70E+00)
IC Results for Nitrate	6.1E-02 (± 1.2E-03, 1.9E00)	1.03E-01 (4.68E-03, 4.54E+00)
IC Results for Nitrite	1.5E-01 (± 1.8E-03, 1.2E00)	2.31E-01 (1.07E-02, 4.64E+00)
IC Results for Sulfate	1.1E-02 (± 1.5E-04, 1.4E00)	1.28E-02 (8.61E-04, 6.74E+00)
IC Results for Oxalate	5.4E-03 (± 7.0E-05, 1.3E00)	8.77E-03 (6.37E-04, 7.26E+00)
ICP-ES Results for Aluminum	1.7E-02 (± 4.4E-04, 2.6E-01)	1.15E-02 (1.28E-04, 1.12E+00)
ICP-ES Results for Sodium	4.98E-01 (± 2.87E-04, 5.77E-02)	5.02E-01 ((± 2.51E-03, 5.0E-01)

[a] Results are the average of three samples. The standard deviations and the percent relative standard deviations for the data are presented in parentheses next to each value.

Distribution:

E. W. Holtzscheiter, 773-A
D. A. Crowley, 999-W
S. L. Marra, 999-W
T. B. Calloway, 999-W
N. E. Bibler, 773-A
C. M. Jantzen, 773-A
J. R. Harbour, 773-42A
G. C. Wicks, 773-A
T. B. Edwards, 773-42A
D. K. Peeler, 999-W
M. E. Stone, 999-W
R.E. Eibling, 999-W
C. C. Herman, 773-42A
W. E. Daniel, 999-W
J. M. Pareizs, 773-A
D. C. Koopman, 773-42A
C. J. Bannochie, 773-42A
M. A. Baich, 999-W

M. S. Miller, 704-S
J. E. Occhipinti, 704-S
R. M. Hoeppel, 704-27S
H. H. Elder, 766-H
J. F. Iaukea, 704-30S
J. W. Ray, 704-S
F.A. Washburn, 704-28S
P. M. Patel, 704-27S
S.G. Phillips, 704-27S
A. V. Staub, 704-28S
W. B. Van-Pelt, 704-S
W. L. Melton, 704-28S
R. N. Mahannah, 704-28S