Investigation of Rheological Impacts on the Defense Waste Processing Facility's Sludge Slurry Feed as Insoluble Solids and Wash Endpoints are Adjusted

T. L. Fellinger, S.J. Howard, M.C. Lee, and R.H. Galloway
Savannah River National Laboratory
Westinghouse Savannah River Company
Aiken, SC 29808

ABSTRACT

The Savannah River Site (SRS) is currently pursuing an aggressive program to empty its High Level Waste (HLW) tanks and immobilize its radioactive waste into a durable borosilicate glass in the Defense Waste Processing Facility (DWPF). To create a batch of feed for the DWPF, several tanks of radioactive sludge slurry are combined into one of the million gallon (i.e. 3.79E06 liters) feed tanks for DWPF. Once these sludge slurries are combined, the soluble sodium and weight percent total solids are adjusted by a “washing” process. The “washing” process involves diluting the soluble sodium of the sludge slurry with inhibited water (0.015 M NaOH and 0.015 M $NaNO_2$) and allowing the sludge slurry to settle into two layers. The two layers in the tank consist of a clear supernate on top and a layer of settled sludge solids on the bottom. The clear supernate layer is then decanted to another hold tank. This “washing” process is repeated until the desired wash endpoint (i.e. sodium concentration in the supernate) and weight percent total solids are achieved. A final washed batch of feed consists of approximately 500,000 gallons (i.e. 1.89E06 liters). DWPF has already processed three batches of feed and is currently processing a fourth.

Prior to processing a batch of feed in the DWPF, it must be well characterized. Samples of the prepared feed batch are sent to the Savannah River National Laboratory (SRNL) for this characterization. As a part of the SRNL characterization for the fourth batch, rheology measurements were performed. Measurements were performed at different weight percent insoluble solids loadings to mimic potential facility processing scenarios (i.e. mixing/pumping of concentrated sludge slurry). In order to determine the influence of the soluble Na on the rheological properties of the sample, the supernate of the “as received” sample was adjusted from 1 M soluble Na to 0.5M soluble Na by using a lab scale version of the “washing” process. Rheology measurements were also completed for the “washed” sample at different weight percent insoluble solids loadings. The flow curves (shear rate vs. shear stress) generated from the “as received” and “washed” samples were modeled to obtain the yield stresses and consistencies. These results were then compared to each other to determine the differences. The results of the SRNL studies showed that increasing the insoluble solids loading typically increased both the plastic viscosity and yield stress for the “as received” and “washed” samples. The studies also showed that the “washed” sample had slightly different physical and rheological properties (i.e. yield stress and plastic viscosity), when compared to the “as received” sample. These differences appear to be a function of sodium concentration and another physical property change. It is assumed that the physical property change was related to an actual shift in the particle size of the insoluble solids of the sample. However, this measurement was not completed as a part of this study due to the radioactivity of the sample. A method is currently being developed for determining particle sizes of radioactive samples.

INTRODUCTION

The DWPF encountered transfer and sampling problems during the processing of the third batch of feed, called Sludge Batch 2 (SB2). These processing problems did not stop production, but did limit the production rate of canisters in the DWPF for a period of time. The processing problems were specifically related to maintaining the suction for the pumps required for sampling and transferring of the sludge slurry from the vessels. These results have been published previously [1]. Since the fourth batch of feed (i.e. called Sludge Batch 3 (SB3)) contained a large heel from SB2, DWPF requested SRNL to perform a rheological study to identify potential processing problems. A three liter sample of SB3 was taken and transported to SRNL in November of 2004. This sample was taken in order to complete chemical and radionuclide analysis required for the Waste Acceptance Product Specification for this sludge batch as well as the rheological studies. 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

In order to accomplish the first objective, a mixed portion of the "as received" 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 then compared. This comparison was completed in order to determine the dependence of yield stress and consistency as a function of insoluble solids and washing. This paper will provide an overview of the test conditions, equipment used for the rheological measurements, and a description of how the data was modeled to obtain the yield stress and plastic viscosity results applicable to the DWPF.

EXPERIMENTAL

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

Description of the Rheological Instrumentation Used for the Rheological Measurements

All of the rheological measurements for the 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 rotor group 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 a previous publication [2]. A National Institute of Standards and Technology (NIST) traceable Newtonian oil standard (~14 mPa·s @ 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 standards viscosity. The MVI rotor and MV cup were used in all of the measurements. Measurements for the samples were performed at 25°C and the weight percent solids were adjusted up (decanting) or down (diluting) by using the 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 [2].

The same programming times and shear rate ranges were used for the oil standard and the SB3 "as received" and "washed" samples. Table I contains the programming times and shear rate ranges for the oil standard and "as received" and "washed" samples.

Table I. Programming Times and Shear Rate Ranges Used for Rheology Measurements

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

The up flow curves (shear rate vs. shear stress) generated from the RV30/M5 for the "as received" and "washed" samples were modeled using the Bingham Plastic model to obtain the yield stresses and plastic viscosities of these samples. Using the up flow curves for the modeling of these samples was conservative, because the down flow curves for these samples were slightly below the up flow curves. The yield stresses and the plastic viscosities were then compared to the operating window for the different DWPF processes 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 ($\tau(Pa) = 0.012\dot{\gamma} + 10$) contained the highest yield stress and plastic viscosity and lower curve ($\tau(Pa) = 0.004\dot{\gamma} + 2.5$) contained the lowest yield stress and plastic viscosity. The Bingham plastic model is defined in Equation 1 as:

$$\tau = \tau_o + \eta\dot{\gamma} \qquad \text{(Eq.1)}$$

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

Analytical Methods Performed in the SRNL Shielded Cells Facility

The pH measurements were performed in the Shielded Cells using an in-cell pH probe. The probe is 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 is completed for the sample.

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 soluble 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 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.

$$wt\%_{is} = (wt\%_{ts} - wt\%_{ds}) / (100\% - wt\%_{ds}) \qquad \text{(Eq.2)}$$

$$wt\%_{ss} = wt\%_{ts} - wt\%_{is} \qquad \text{(Eq.3)}$$

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%)

The densities 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 added mass is measured. The density is then determined by dividing the mass added by the volume of the sealed pipette.

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).

RESULTS

Summary of Data Obtained for the "As Received" Sludge Slurry Sample

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.% 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. The SB3 data in Figure 1 were curve fitted using the Bingham Plastic model from a shear rate range of ~$50s^{-1}$ to $600s^{-1}$. 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 II.

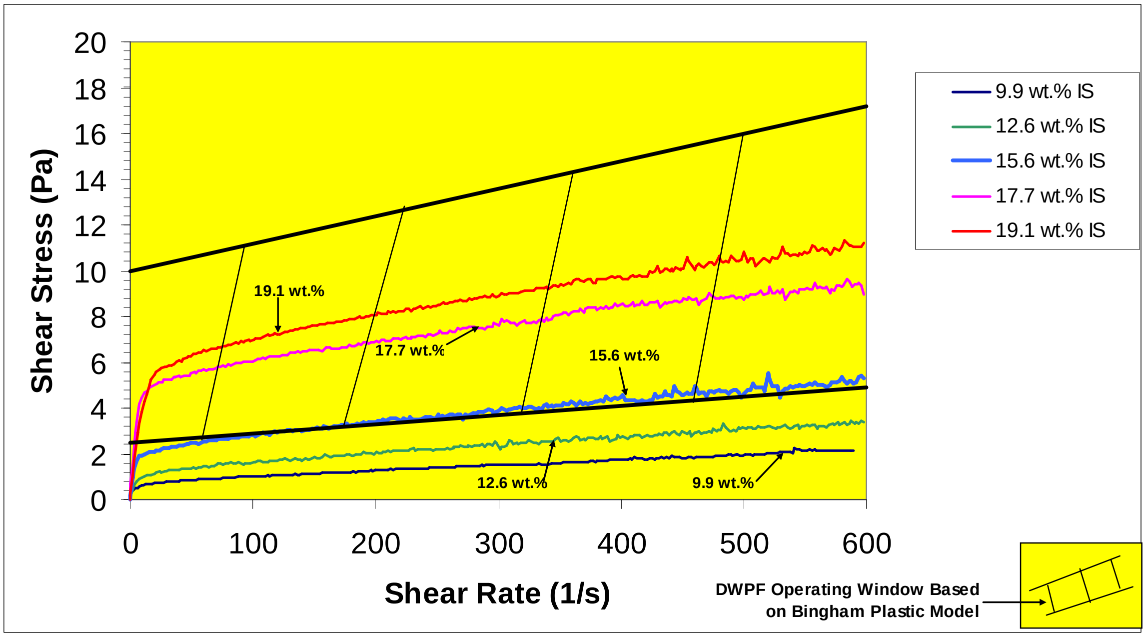

Fig. 1. Up flow curves taken at 25°C for the "as received" sb3 sludge slurry at different weight percent insoluble solids.

Table II. Summary of Weight Percent Solids, Rheology, and pH Data Collected for the "As Received" SB3 Sludge Slurry

Sample ID	Total Solids (wt.%)	Insoluble Solids (wt.%)	Yield Stress (Pa)	Plastic Viscosity (Pa·sec)	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
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
N.M. – Not Measured
N/A – Information Not Available

One conclusion that can be made by studying the data in Figure 1 and Table II is that as the insoluble solids content is increased, the yield stress and plastic viscosity increases. The values that were outside the DWPF operating window were highlighted in Table II. Samples that exceed the upper limit of the DWPF operating window can pose processing problems for DWPF, like the previously mentioned 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.

Summary of Data Obtained for the “Washed” Sludge Slurry Sample

The analyses described in the Experimental section of this paper were completed for both the “as received” and “washed” SB3 samples. Table III presents the IC results for the anions and the ICP-ES results for the Al and Na for the “as received” and the “washed” samples. The majority of the anions and both cations in the “as received” sample have been reduced ~50% by the “washing” process. This reduction was expected. The results for the chloride and fluoride have more variability due to their low concentrations in the supernate. Based on the Na results for the “washed” sample the target Na concentration for the supernate (0.5M) was met.

Table III. Comparison of the Compositions for the Supernate for the “As Received” and “Washed” SB3 Samples

Method	“As Received” SB3 Sample Average of Results (M)[a]	“Washed” SB3 Sample Average of Results (M)[a]
IC Results for Chloride	7.39E-04 (± 2.30E-05, 3.12E+00)	3.01E-04 (± 1.63E-05, 5.41E+00)
IC Results for Fluoride	7.69E-03 (± 1.03E-03, 1.34E+01)	5.53E-03 (± 4.18E-04, 7.56E+00)
IC Results for Formate	<3E-03	<5E-04
IC Results for Nitrate	2.01E-01 (± 9.05E-03, 4.51E+00)	1.03E-01 (± 4.68E-03, 4.54E+00)
IC Results for Nitrite	4.33E-01 (± 1.96E-02, 4.52E+00)	2.31E-01 (± 1.07E-02, 4.64E+00)
IC Results for Sulfate	2.32E-02 (± 1.06E-03, 4.58E+00)	1.28E-02 (± 8.61E-04, 6.74E+00)
IC Results for Oxalate	1.46E-02 (± 1.44E-03, 9.85E+00)	8.77E-03 (± 6.37E-04, 7.26E+00)
ICP-ES Results for Aluminum	2.44E-02 (± 8.97E-05, 3.68E-01)	1.15E-02 (± 1.28E-04, 1.12E+00)
ICP-ES Results for Sodium	9.95E-01 (± 4.59E-03, 4.62E-01)	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.

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 readily entrain air. 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 (thereby diluting the insoluble solids).

The data plotted in Figure 2 are the rheological data (up flow curves only) for the insoluble solids with target concentrations of 9.7, 11.7, 14.1, 16.5, and 19.5 wt.% insoluble solids. All measurements were completed at 25°C. Figure 2 also contains the operating window for the DWPF sludge slurry. The data in Figure 2 were curve fitted using the Bingham Plastic model from a shear rate range of ~50s^{-1} to 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 IV.

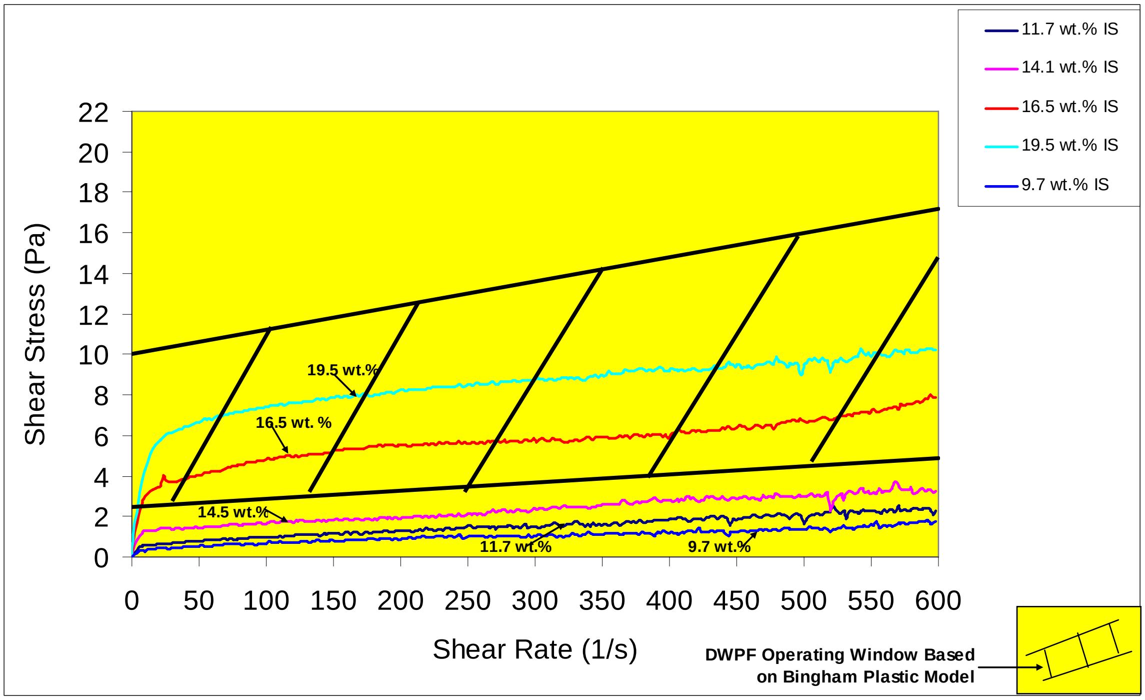

Fig. 2. Up flow curves taken at 25°C for the “washed” sb3 sludge slurry at different weight percent insoluble solids

Table IV. Summary of Weight Percent Solids, Rheology, and pH Data Collected for the “Washed” SB3 Sludge Slurry

Sample ID	Total Solids (wt.%)	Insoluble Solids (wt.%)	Yield Stress (Pa)	Plastic Viscosity (Pa·sec)	Density for the Sludge Slurry (g/mL)	pH
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
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
N.M. – Not Measured
N/A – Information Not Available

One conclusion that can be made by studying the data in Figure 2 and Table IV 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. The density measurements obtained for the 19 wt. % insoluble solids in Table IV appears to be rather low and is considered suspect data. A poorly mixed sample may have been taken from the sample bottle to complete this measurement. Outside of this one data point, the other density data appears to be within the anticipated values for the insoluble solids loading. The values that were outside the DWPF operating window were denoted in Table IV. As mentioned previously, samples that exceed the upper limit can pose processing problems for DWPF and samples below the lower limit for the DWPF operating window have not posed any processing issues to date.

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 II and Table IV were each plotted verses the wt. % insoluble solids content and the data was fitted using an exponential function in Microsoft Office Excel®. This data was then compared to the DWPF operating window. Figure 3 presents the comparison of the yield stress vs. insoluble solids for the "as received" SB3 sample to the "washed" SB3 sample. Figure 4 presents the comparison of the plastic viscosity vs. insoluble solids for the "as received" SB3 sample to "washed" SB3 sample.

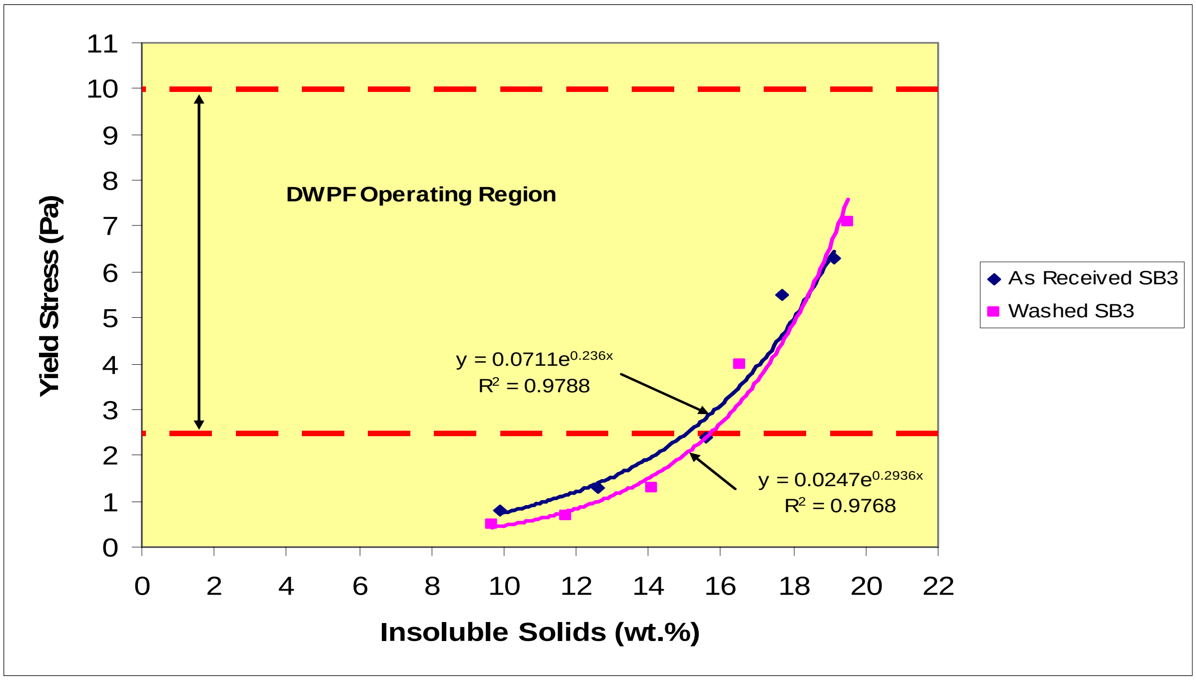

Fig. 3. Comparison of the yield stress vs. insoluble solids for the "as received" sb3 sample to the "washed" sb3 sample

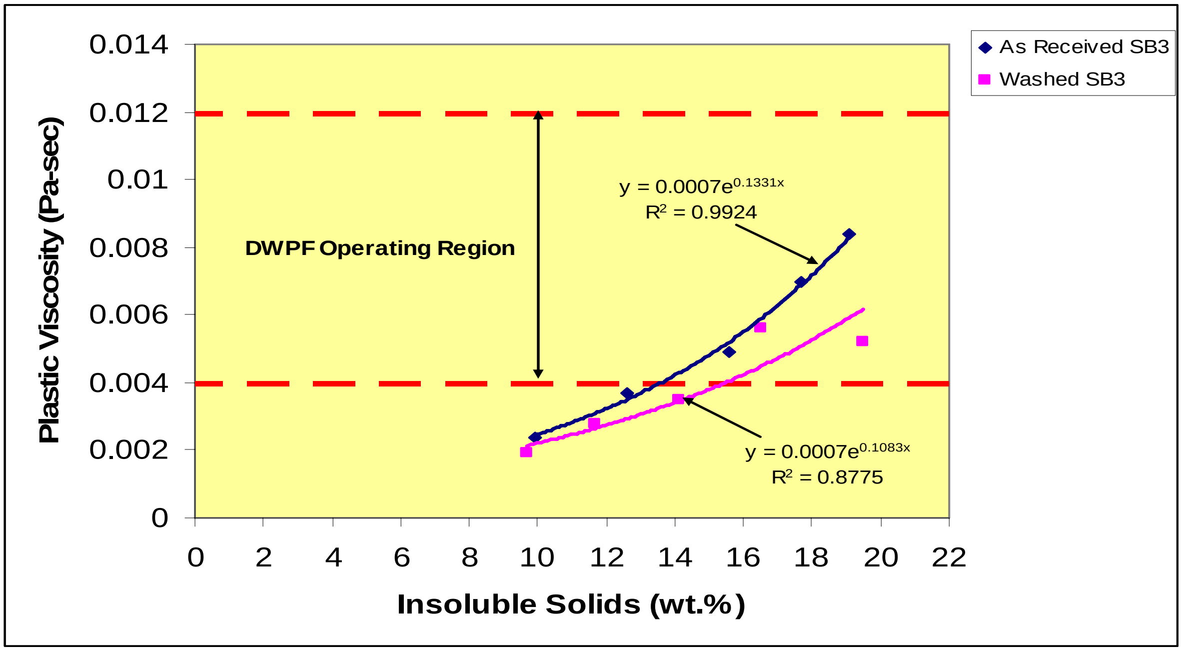

Fig. 4. Comparison of the plastic viscosity vs. insoluble solids for the "as received" sb3 sample to the "washed" sb3 sample

For Figure 3, 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 4, 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. Particle size data could not be obtained at this time, because a technique is currently being developed for determining particle sizes of radioactive samples.

CONCLUSIONS

Several conclusions and observations were made from the data presented in Results section. 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.
- 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. %). 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.

Based on the conclusions above, it was recommended to DWPF that the following activities be pursued to help facilitate the understanding of the rheological differences of prepared sludge batches:

- 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 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.

ACKNOWLEGEMENTS

The authors of the paper would like to thank the SRNL Shielded Cells Facility technicians Analytical Development Section for all of their hard work and dedication to this project.

REFERENCES

1. T. L. Fellinger, E. K. Hansen, and P.M. Patel, *Rheological Properties of Savannah River Site (SRS) Radioactive High Level Wastes and Melter Feeds for Sludge Batch 2*, WSRC-MS-2005-00119, Rev.0, February.
2. HAAKE, *Instruction Manual Rotovisco RV30*.