RHEOLOGICAL PROPERTIES OF SAVANNAH RIVER SITE (SRS) RADIOACTIVE HIGH LEVEL WASTES AND MELTER FEEDS FOR SLUDGE BATCH 2

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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 sludge slurry are combined into one of the million gallon (i.e. 3.79E06 liters) feed tanks for DWPF. A batch of feed nominally consists of 500,000 gallons (i.e. 1.89E06 liters).

After a batch of feed is prepared, a portion of the batch (26,500 liters) is transferred to DWPF. This batch is then chemically adjusted in the Chemical Processing Cell (CPC) prior to being feed to the melter to make the final product; canisters filled with glass. During the processing of the third batch (or Sludge Batch 2) of feed through the DWPF CPC, pumping and transfer problems were noted. These problems hindered the processing of the feed through the CPC, and thus impacted canister production in DWPF. In order to investigate the root cause of these problems, data were collected and evaluated for possible trends. One trend noted was the relationship between the pH, solids loading concentration, and temperature of the feed. As any one of these three variables changed, the rheological properties of the feed appeared to change. To determine the dependency of the rheological property, samples were obtained and shipped to Savannah River National Laboratory’s (SRNL) Shielded Cells Facility. The samples were processed under two sets of conditions and rheological measurements obtained. The results of the SRNL studies showed that the ending pH of the samples impacted the rheological properties of the sample. Lowering the pH of the sludge slurry resulted in lower plastic viscosity and yield stress values, thus alleviating the processing problems. Increasing the solids loading typically increased both the plastic viscosity and yield stress. There was minimal or no dependency on temperature.

INTRODUCTION

The DWPF encountered transfer and sampling problems during the processing of Sludge Batch 2. These processing problems did not stop production, but limited the production rate of canisters in the DWPF for a period of time. The DWPF CPC contains process equipment for chemical adjustment of the sludge slurry, so the feed can be eventually vitrified in the melter. The processing problems were specifically related to maintaining the suction for the pumps required for sampling and transferring of the sludge slurry from the CPC vessels and the Melter Feed Tank (MFT). The two chemical processing vessels in the CPC are the Sludge Receipt and Adjustment Tank (SRAT) and the Slurry Mix Evaporator (SME) tank. The processing that occurs in each tank is considered a cycle (i.e. SRAT cycle or SME cycle depending on which vessel is used).

The issues encountered while transferring and sampling the sludge slurry indicated that there may be problems with the mechanical operation of the pumps or rheological problems with the sludge slurry that caused operational problems for the pumps. The mechanical operation of the pumps was eliminated as a potential cause of the DWPF processing problems. To confirm the cause was related to the rheological properties of the sludge slurry, data were collected from the SRAT, SME, and MFT by transfer number. A transfer number is assigned to a portion of sludge slurry (~26,500 L) that is transferred from the million gallon tank to the SRAT vessel. This transfer number is associated with that portion of sludge slurry as it is processed through the CPC and the MFT. The data sets contained information about the sludge slurry pH, weight percent total solids, temperature, and density measurements.

During the data evaluation it was noted that as the ending pH was lowered in the SRAT vessel, the frequency of transfer and sampling issues were significantly minimized. In order to prove rheological improvements were being obtained by lowering the final SRAT product pH, two studies were completed using actual Sludge Batch 2 feed in the SRNL Shielded Cells Facility. 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

Feed Preparation in the SRNL Shielded Cells Facility

In order to prove that rheological improvements were being made by lowering the final SRAT product pH, two test cases were selected from the DWPF data. DWPF Transfers 213 and 221 were selected and replicated in the SRNL Shielded Cells Facility maintaining all processing conditions as close as possible to the process conditions observed in DWPF. SRAT Transfers 213 and 221 represented the high (6.7) and low (5.5) for the pH range observed during DWPF SRAT processing. To replicate Transfers 213 and 221, samples of the Sludge Batch 2 feed were obtained from the million-gallon feed tank providing the feed for DWPF and sent to SRNL Shielded Cells Facility. The samples were mixed and combined by pouring the samples into a one liter bottle. Approximately 880 mL of sludge slurry was available. To complete the required testing, approximately 150 mL of sludge slurry was used to represent each Transfer case. Figure 1 shows the processing vessel that was used to perform the testing in the SRNL Shielded Cells Facility.

The first step of the SRAT cycle was to heat the sludge to 93°C. After reaching this temperature, nitric and formic acids were added to the sludge to react with carbonates and hydroxides in the sludge to adjust its rheology and to reduce Hg ions in the sludge. At the completion of the acid additions, the sludge was heated to boiling to steam strip mercury and to remove water to obtain the targeted weight percent total solids. During this cycle, the pH was monitored. The product from this cycle was then analyzed for weight percent solids, density, and rheology prior to starting the SME cycle.

The physical properties from the SRAT cycle were considered acceptable, permitting the processing of the sludge slurry through the SME cycle. The acidified sludge was heated to 90°C to start the SME cycle. Upon reaching 90°C, the prescribed amount of glass forming frit was added as a dry powder to the acidified sludge. Dilute formic acid water additions followed the frit addition, which simulated how the frit slurry is added to the SME in the DWPF. After the additions were complete, the acidified sludge/frit mixture was heated to 100°C to boil off the excess water to obtain the correct weight percent total solids. During this cycle, the pH was also monitored. The product of this cycle was then analyzed for weight percent solids, density, and rheology.

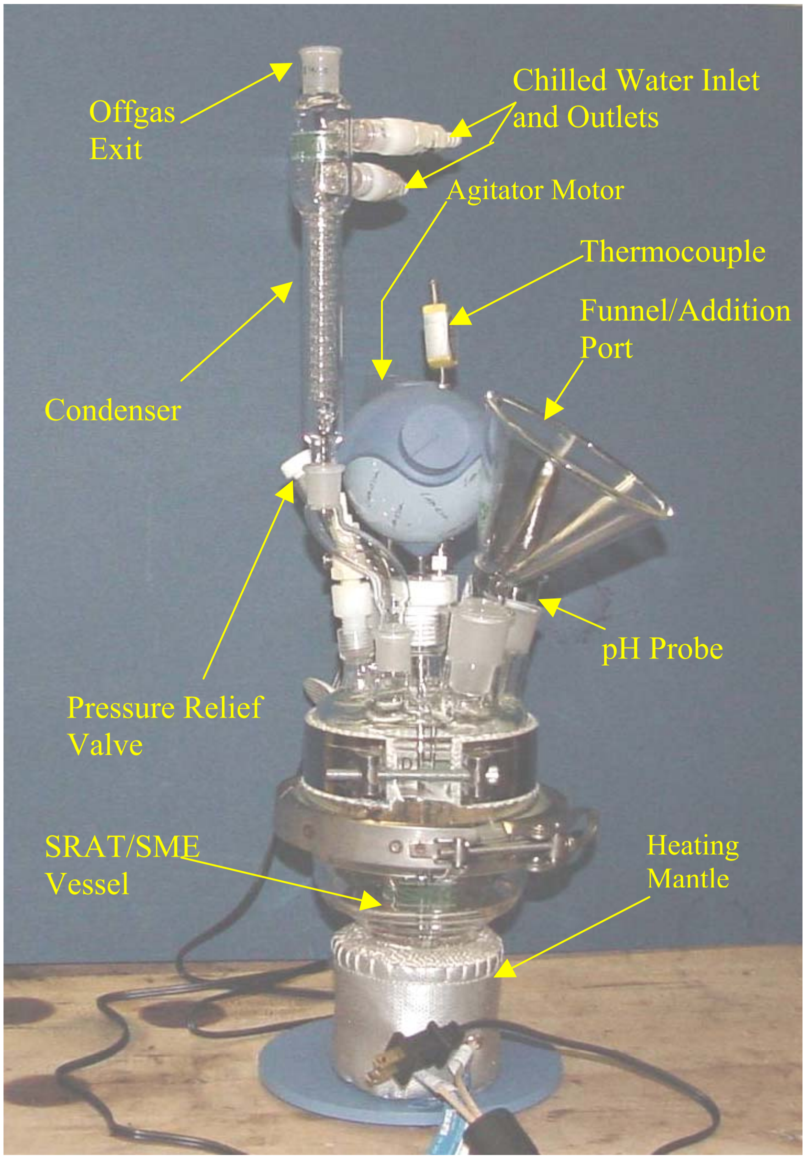

Fig. 1. Picture of the bench top SRAT/SME process vessel prior to being placed into the SRNL Shielded cells facility

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 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 [1]. 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 SRAT and SME product samples were performed at 25°C and the weight percent solids were also 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 [1].

The same programming times and shear rate ranges were used for the oil standard, SRAT product, and SME product samples. Table I contains the programming times and shear rate ranges for the oil standard, SRAT samples, and SME samples.

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

Shear Rate Range and Time		
Up Curve	Hold	Down Curve
0 – 1100s^{-1}, 5 minutes	1100s^{-1}, 1 minute	1100 - 0s^{-1}, 5 minutes

The flow curves (shear rate vs. shear stress) generated from the RV30/M5 for the SRAT and SME products 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 different DWPF processes to determine if the feed may pose potential processing problems. To create the DWPF operating window for the SRAT product, the higher and lower Bingham Plastic parameter of the SRAT process vessel were used to develop two curves. The upper curve ($\tau(Pa) = 0.012\dot{\gamma} + 10$) contained the highest yield stress and the plastic viscosity and lower curve ($\tau(Pa) = 0.004\dot{\gamma} + 2.5$) contained the lowest yield stress and plastic viscosity. The same methodology was applied to create the DWPF operating window for the SME and MFT products, having an upper curve ($\tau(Pa) = 0.040\dot{\gamma} + 15$) and lower curve ($\tau\ (Pa) = 0.010\dot{\gamma} + 2.5$) ranges for consistency and yield stress. 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 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.

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

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

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

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.

RESULTS

Results of the SRAT Processing and Rheology Measurements Completed for Transfers 213 and 221 in the SRNL Shielded Cells Facility

The SRAT cycles for test cases 213 and 223 were completed successfully in the SRNL Shielded Cells. The ending pH of the SRAT products for 213 and 221 were 6.8 and 5.5, respectively. The pH value for the 213 test case was close to the pH of 6.7 achieved in the DWPF for Transfer 213. The pH value for the 221 test case was the same as the pH (5.5) achieved in the DWPF for Transfer 221. Upon confirmation of the pH, the weight percent solids, density and rheology were obtained. The weight percent solids and density for these samples are presented Table II.

Table II. Comparison of the Weight Percent Solids and Density Data Obtained from Transfer 213 and Transfer 221

Physical Properties	SRNL SRAT Transfer 213 Results	SRNL SRAT Transfer 221 Results
Weight Percent Total Solids of the Sludge Slurry	22.0 wt.%[a] (±4.4E-01, 2.0E00%)	18.9 wt.%[a] (±1.0E01, 4.6E00%)
Weight Percent Dissolved Solids of the Supernate	5.44 wt.%[a] (±1.6E-01, 2.9E00%)	4.71 wt.%[a] (±3.7E-01, 8.0E00%)
Density of the Sludge Slurry	1.15 g/mL[b] (±1.4E-02, 1.2E00%)	1.14 g/mL[b] (±1.7E-02, 1.5E00%)
Density of the Supernate	1.06 g/mL[b] (±1.3E-02, 1.2E00%)	1.04 g/mL[b] (±1.2E-02, 1.2E00%)
Weight Percent Insoluble Solids of the Sludge Slurry	17.5 wt.%[c]	14.9 wt.%[c]
Weight Percent Soluble Solids of the Sludge Slurry	4.5 wt.%[c]	4.0 wt.%[c]

[a] Dried in an oven overnight at 115°C. Results are the average of four samples for the slurry and the average of two results for the supernate. The standard deviations and the percent relative standard deviations for the data are also presented in parentheses next to each value, respectively.

[b] Results are the average of six samples for the sludge slurry and three for the supernate samples. The standard deviations and the percent relative standard deviations for the data are also presented in parentheses, respectively.

[c] These values are calculated using the weight percent total solids and dissolved solids for each respective sample in this table.

After the pH, density, and weight percent solids measurements were completed for the samples, the rheology measurements were performed. The SRNL SRAT 213 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 sample was then transferred into two bottles and allowed to settle so that supernate could be removed. The clear supernate was removed and used to dilute the weight percent total solids of the SRNL SRAT 213 sample. The weight percent solids of the SRNL SRAT 213 samples were adjusted up or down by removing/adding supernate. Different weight percent solids concentrations were calculated to determine the quantity of supernate added or removed. After each weight percent solids adjustment, rheology measurements were completed at 25°C for the SRAT Transfer 213 samples. The same protocol was used for SRAT Transfer 221 samples to obtain the rheology at different weight percent total solids.

The data plotted in Figure 2 is the rheological data (up flow curves only) for SRNL Transfers 213 and 221 SRAT products measured at 25°C. Figure 2 also contains the operating window for the DWPF SRAT vessel. The data in Figure 2 were curve fitted using the Bingham Plastic model from a shear rate range of $100s^{-1}$ to $1100s^{-1}$ or a shear rate range of $50s^{-1}$ to $600s^{-1}$ (the upper range was reduced due to Taylor vortices) depending on the flow curve. A summary of the yield stress and plastic viscosity values obtained from the Bingham Plastic Model for the SRNL Transfer 213 and 221 SRAT samples are presented in Table III.

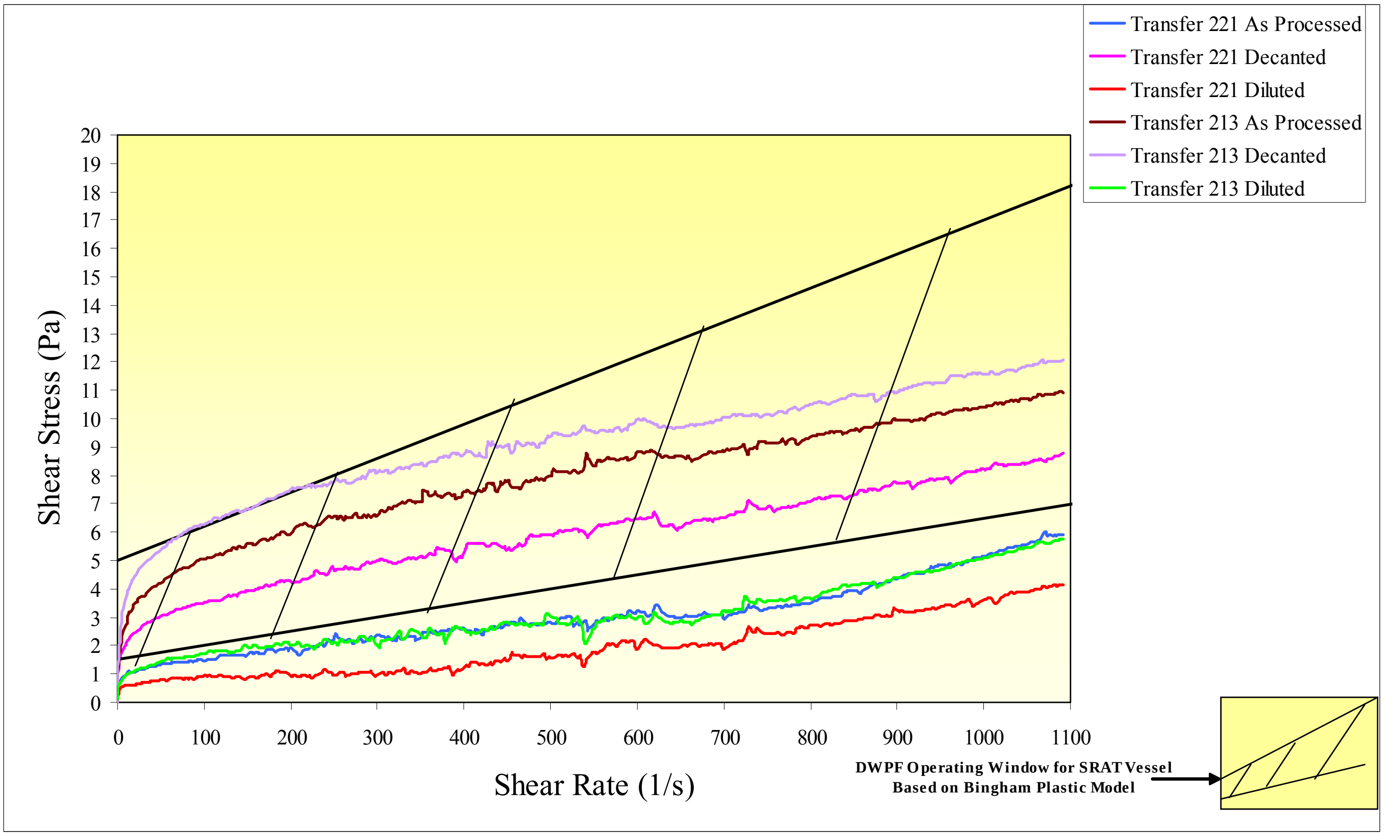

Fig. 2. Uncorrected flow curves taken at 25°C for SRNL transfers 213 and 221 “As Processed”, “Diluted” and “Decanted” SRAT samples

Table III. Summary Weight Percent Solids, Rheology, and pH Data Collected for SRNL Transfer 213 and Transfer 221 SRAT Samples

Sample ID	Total Solids (wt.%)	Insoluble Solids (wt.%)	Yield Stress (Pa)	Plastic Viscosity (Pa·sec)	pH
SRAT Transfer 213 “Decanted” Sample at 25°C	24.3	20.4	6.26[a]	0.0054	6.8
SRAT Transfer 213 “As Processed” Sample at 25°C	20.4	6.0	4.91	0.0057	6.8
SRAT Transfer 213 “Diluted” Sample at 25°C	17.3	12.6	1.48[a]	0.0025[a]	6.8
SRAT Transfer 221 “Decanted” Sample at 25°C	22.3	18.5	2.05	0.0063	5.5
SRAT Transfer 221 “As Processed” Sample at 25°C	18.9	14.9	0.20[a]	0.0043[a]	5.5
SRAT Transfer 221 “Diluted Sample” at 25°C[b]	14.6	10.2	0.53[a]	0.0022[a]	5.5
DWPF Operating Window for the SRAT Vessel	18 – 25	N/A	1.5 – 5.0	0.005 – 0.012	N/A

[a] Data is outside of the DWPF operating window

In Figure 2, there are cases in which the flow curves for the SRAT samples are not within the DWPF operating window for the SRAT vessel. This agrees with the yield stress and plastic viscosity reported in Table III for these particular flow curves, though both the yield stress and plastic viscosity may not necessarily exceed the DWPF Bingham Plastic operating parameters. From the data presented in Table III, it appears that as the weight percent total solids increased for both samples, at a fixed pH, the yield stress and plastic viscosity increased. It also appears that the ending pH of the SRAT sample, impacts the yield stress and plastic viscosity measurements obtained. From the DWPF data evaluation, it was noted that as the ending pH was lowered in the SRAT vessel the frequency of transfer and sampling issues were significantly minimized. The data collected in Table III support the conclusion that was reached from the DWPF data evaluation.

Results of the SME Processing and Rheology Measurements Completed for Transfers 213 and 221 in the SRNL Shielded Cells Facility

The SME cycles for test cases 213 and 223 were completed, but some difficulties were encountered while the samples were in the final concentration step. The final total weight percent solids and ending pH were higher than targeted for test case 213 and the total weight percent solids were higher than targeted for test case 221. In order to recover the material from the vessel, condensate collected from the SME cycle was used. This diluted the total solids for both samples significantly. The ending pH of the SME products for 213 and 221 were 7.3 and 6.8, respectively. The pH value for the 213 test case was higher than the 6.6 achieved in the DWPF for Transfer 213. The pH value for the 221 test case was close to the pH of 6.9 achieved in the DWPF for Transfer 221. Upon confirmation of the pH, the weight percent solids, density and rheology measurements were completed. The weight percent solids measurements and density measurements for these samples are presented Table IV.

Table IV. Comparison of the Weight Percent Solids and Density Data Obtained from Transfer 213 and Transfer 221

Physical Properties	SRNL SME Transfer 213 Results*	SRNL SME Transfer 221 Results*
Weight Percent Total Solids of the Sludge Slurry	43.06 wt.%[a] (± 4.7E-01, 1.1E00%)	38.3 wt.%[a] (±3.5E-01, 9.2E-01%)
Weight Percent Dissolved Solids of the Supernate	2.86 wt.%[a] (± 3.4E-01, 1.2E01%)	4.61 wt.%[a] (±2.2E-02, 4.9E-01%)
Density of the Sludge Slurry	1.38 g/mL[b] (± 1.3E-02, 9.3E-01%)	1.33 g/mL[b] (±6.0E-03, 4.4E-01%)
Density of the Supernate	1.04 g/mL[b] (± 6.0E-03, 5.9E-01%)	1.06 g/mL[b] (±2.3E-02, 2.2E00%)
Weight Percent Insoluble Solids of the Sludge Slurry	41.4 wt.%[c]	35.3 wt.%[c]
Weight Percent Soluble Solids of the Sludge Slurry	1.68 wt.%[c]	2.98 wt.%[c]

* Results of the SME product after recovery with SME supernate from the SME vessel.

[a] Dried in an oven overnight at 115°C. Results are the average of two samples for the slurry and the average of two results for the supernate. The standard deviations and the percent relative standard deviations for the data are also presented in parentheses, respectively.

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

[c] These values are calculated using the wt.% total solids and dissolved solids for each respective sample in this table.

The same protocol used for the SRAT samples was used for the SME samples with one exception, the samples were not diluted to obtain the "diluted" sample rheology measurements. This decision was made in order to preserve the remaining samples. The recovered SME product from the vessels was called the "As Processed" samples for the rheology measurements completed below.

The data plotted in Figure 3 is the rheological data obtained from the rheometer (up flow curves only) for SRNL Transfers 213 and 221 SME products measured at 25°C. The data in Figure 3 also contains the operating window for the DWPF SME vessel. The data in Figure 3 were curve fitted using the Bingham Plastic model from a shear rate range of $100s^{-1}$ to $1100s^{-1}$. The yield stress and plastic viscosity values obtained using the Bingham Plastic Model for the SRNL Transfer 213 and 221 SME samples are presented in Table V.

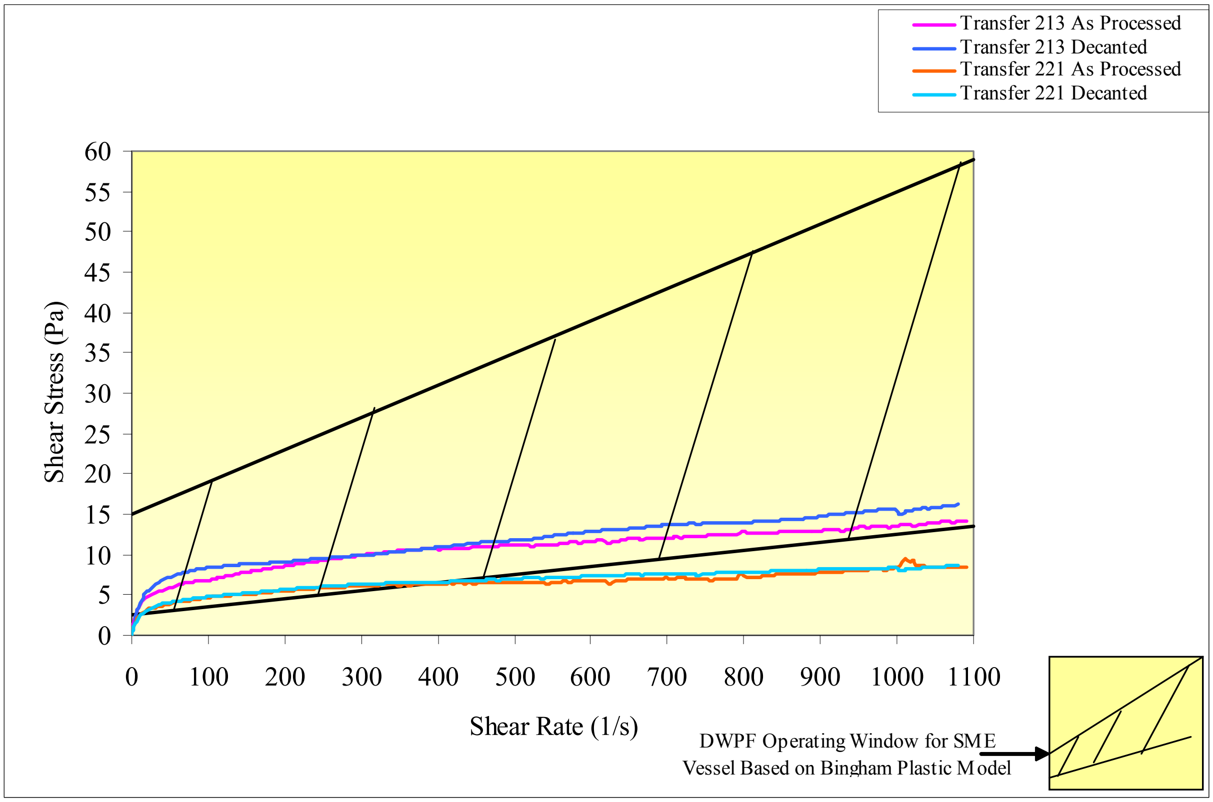

Fig. 3. Uncorrected flow curves taken at 25°C for SRNL transfers 213 and 221 "As Processed" and "Decanted" SME samples

Table V. Summary Weight Percent Solids, Rheology, and pH Data Collected for SRNL Transfer 213 and Transfer 221 SME Samples

Sample ID	Total Solids (wt.%)	Insoluble Solids (wt.%)	Yield Stress (Pa)	Plastic Viscosity (Pa·sec)	pH
SME Transfer 213 "Decanted" Sample at 25°C	46.4	44.8	7.69	0.0080[a]	7.3
SME Transfer 213 "As Processed" Sample at 25°C	43.1	41.4	7.71	0.0061[a]	7.3
SME Transfer 221 "Decanted" Sample at 25°C	46.7	44.2	5.13	0.0034[a]	6.8
SME Transfer 221 "As Processed" Sample at 25°C	38.3[a]	35.2	4.81	0.0034[a]	6.8
DWPF Operating Window	40 - 50	N/A	2.5 – 15.0	0.010 – 0.040	N/A

[a] Data is outside of the DWPF operating window

Comparison of the data in Figure 3 with the data in Table 5, show that only the plastic viscosities are not within the DWPF operating window. Two of the flow curves in Figure 3 show that these samples are within the operating window, due to their higher yield stress and range in which the operating window is shown. The DWP processes are not expected to exceed a shear rate of 600 sec^{-1} in transport or mixing applications (shear rate in the pump may exceed these limits).

The ending pH of the SME sample, impacts both the yield stress and plastic viscosity. This is shown in Table V when comparing the SME Transfer 213 "decanted" sample to the SME Transfer 221 "Decanted" sample. Although both of these samples have the same total solids, the SME Transfer 213 "decanted" sample's yield stress and plastic viscosity is larger. The cause is due to the different ending pH of the samples.

CONCLUSIONS

- The ending pH of the SRAT sample directly impacted the rheological properties. A comparison of the SRAT samples showed that as the pH decreased the plastic viscosity and yield stress of the sample were lower, thus alleviating processing problems.

- The ending pH of the SME sample also directly impacts the rheological properties. Results showed that as the pH was lowered, the yield stress and plastic viscosity were also lower.

- As the weight percent total solids were increased for the SRAT samples, at a fixed pH, the yield stress and consistency increased. The data indicated that this was also true for the yield stress of the SME samples, but not for the plastic viscosity of the SME samples.

Based on the conclusions above, DWPF adjusted process conditions to lower the ending pH of the SRAT product. This improved processing significantly by reducing the rheological properties.

ACKNOWLEGEMENTS

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REFERENCES

1. Instruction Manual Rotovisco RV30, HAAKE.