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CST MELTER FEED CHARACTERIZATION IN SUPPORT OF THE 1999 AND 2000 THERMAL FLUIDS LAB HYDRAGARD TESTING (U)

R. E. EIBLING
D. C. KOOPMAN

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

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Russell E. Eibling
David C. Koopman

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REVIEWS AND APPROVALS

D. C. Koopman, Co-author, Immobilization Technology — Date: 3/7/01

R. E. Eibling, Co-author, Immobilization Technology — Date: 3/7/01

F. G. Smith, III, Design Check — Date: 3/8/01

R. H. Spires, Responsible L4 Manager — Date: 3-16-01

H. H. Elder, Acting Manager, Process Engineering — Date: 3-27-01

J. T. Carter, SWPF Director of Engineering — Date: 3/22/01

D. W. Wester, TFA System Lead for CST — Date: 3/28/01

W. L. Tamosaitis, Manager, Waste Processing Technology — Date: 3/12/01

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LIST OF ACRONYMS

CST	Crystalline Silicotitanate
DWPF	Defense Waste Processing Facility
EDS	Engineering Development Section
ITS	Immobilization Technology Section
SME	Slurry Mix Evaporator Tank
SRAT	Sludge Receipt and Adjustment Tank
TFL	Thermal Fluids Lab (786-A)

EXECUTIVE SUMMARY

The Immobilization Technology Section measured properties of the melter feed simulants used in the 1999 and 2000 Hydragard sample loop tests. These tests used simulated Sludge Batch 1B (Macrobatch 2) melter feeds. The melter feeds were characterized for wt. % total and insoluble solids, pH, composition, particle size distribution, and rheology.

Significant findings from the melter feed samples include:

- The two 1999 melter feeds, Sludge-Frit (35% sludge oxides, 65% frit 200 oxides) and Size-reduced CST-Sludge-Frit (26.7% sludge oxides, 8.3% CST oxides, and 65% frit 202 oxides), had nearly identical rheological characteristics in the range of 39-51 wt. % total solids.

- The two 1999 melter feeds had yield stresses within the DWPF design basis range of 25-150 dynes/cm^2, but had consistencies at or below the lower DWPF design basis limit of 10 cP.

- The two 1999 melter feeds were both about 39-40 wt. % total solids during Hydragard tests.

- Particle size distribution results for the two 1999 melter feeds indicated that size-reduced CST did not significantly interact with either frit or sludge particles to form larger agglomerated structures.

- The two 2000 melter feeds differed significantly from the 1999 melter feeds. The Sludge-Frit melter feed was 26% sludge oxides and 74% frit 200 oxides. The Size-reduced CST-Sludge-Frit melter feed was 25.5% sludge oxides, 7.1% CST oxides, and 67.4% frit 202 and frit 200 oxides. The wt. % frit oxides were constant in 1999, whereas the wt. % sludge oxides were constant in 2000.

- The two 2000 melter feeds had very different rheological properties. The Size-reduced CST-Sludge-Frit melter feed had nearly three times the yield stress of the Sludge-Frit melter feed at about 46 wt. % total solids.

- The 2000 tests with Size-reduced CST-Sludge-Frit at 42.4 wt. % and 45.9 wt. % total solids both occurred with slurries whose yield stress exceeded the DWPF upper design basis limit of 150 dynes/cm^2. The 2000 Sludge-Frit melter feed yield stress and all of the consistency data were within the DWPF design basis limits.

- Problems mixing melter feed slurries in the Hydragard sample loop tank were determined to be primarily due to an insufficient quantity of feed rather than rheological properties.

INTRODUCTION

Engineering Development Section (EDS) Hydragard sampling tests conducted in the fall of 1999 used Sludge-Frit and CST-Sludge-Frit melter feed slurries containing about 40 wt. % total solids [12]. Target waste loading was 35% sludge oxides/65% frit 200 for the Sludge-Frit melter feed and 26% sludge oxides/10% CST oxides/64% frit 202 for the Size-reduced CST-Sludge-Frit melter feed.

The 1999 Hydragard test data [12] suggested that the frit content of the Size-reduced CST-Sludge-Frit melter feed Hydragard samples was lower than in the grab samples, i.e. that Hydragard samples were biased. The 1999 data also suggested that no bias was present for the Sludge-Frit melter feed. Some investigations into the possible causes of Hydragard bias were undertaken by the Immobilization Technology Section (ITS). These investigations were expanded to support future tests. ITS assembled data on various properties of the melter feeds, such as wt. % total and insoluble solids, composition, pH, particle size distribution, and rheology.

A decision was made to have EDS retest the 1999 melter feed materials using a more extensive sampling regimen. One objective was to increase the statistical confidence level for the bias hypotheses being tested. A second objective was to use melter feed slurries with wt. % total solids loadings that were closer to typical DWPF levels. Additional Hydragard testing in 2000 was to use melter feeds at total solids concentrations of 53, 49, and 42 wt. % total solids [13]. These represent the maximum, nominal and minimum total solids concentrations of DWPF melter feeds over the first two macrobatches, as seen in Table I. Data come from DWPF average SME product sample wt. % total solids results for SME batches 19 through 131.

TABLE I – Distribution of DWPF SME Batches Based on Total Solids

Range in Total Solids, wt. %	Total Number of Batches	Cumulative Number of Batches	% of Total
<42	0	0	0.00
42-43	1	1	0.90
43-44	5	6	4.50
44-45	0	6	0.00
45-46	2	8	1.80
46-47	6	14	5.41
47-48	18	32	16.20
48-49	22	54	19.80
49-50	22	76	19.80
50-51	23	99	20.70
51-52	3	102	2.70
52-53	9	111	8.11
>53	0	111	0.00

Note: ~82% of the batches range from 45 to 51 wt. % total solids

The initial ITS objective for the 2000 Hydragard test program was to assist in the preparation of the modified melter feeds. Then ITS was to obtain data on various properties of the melter feeds, such as wt. % total and insoluble solids, composition, pH, and rheology. The discussion below focuses on the ITS work in support of the 1999 and 2000 Hydragard tests.

DISCUSSION

Preparation of Preliminary Melter Feeds

ITS prepared three melter feed simulant slurries for 1999 Hydragard testing using the 1/240th Glass Feed Preparation System in 786-A during the summer of 1999 [8]. One melter feed was Sludge-Frit only. The other two melter feeds contained CST sorbent. These are referred to as As-received CST-Sludge-Frit and Size-reduced CST-Sludge-Frit melter feeds throughout this report. The CST had been caustic treated, then loaded with potassium, cold cesium, and noble metals (palladium, rhodium, and ruthenium) prior to preparation of the melter feed simulants [1].

CST sorbent was added during a simulated DWPF Sludge Receipt and Adjustment Tank (SRAT) cycle at the size it was received from the vendor. The SRAT product slurry was blended with frit in the simulated DWPF Slurry Mix Evaporator (SME) cycle. The slurry product from the SME cycle was the As-received CST-Sludge-Frit melter feed simulant. The preparation of the Size-reduced CST-Sludge-Frit melter feed simulant followed identical processing steps, except that the CST particles had been previously reduced to sizes less than 125 microns in diameter.

EDS constructed a mock-up of a SME tank and Hydragard sample loop in 786-A in 1999. The first generation sample loop pump was only able to move slurries below about 40 wt. % total solids. Consequently, the three melter feeds prepared above were diluted from 45-46 wt. % to 40 wt. % using deionized water. The As-received CST-Sludge-Frit melter feed plugged the Hydragard sampler. That test was discontinued. Tests of the other two melter feeds, Sludge-Frit and Size-reduced CST-Sludge-Frit, were completed successfully [12]. Grab samples of these two slurries were obtained for analysis by ITS. After completion of the Hydragard tests, the melter feeds were drummed and turned over to ITS.

A number of conclusions came out of the 1999 work. Although it appeared that size-reduced CST was introducing a bias into the Hydragard sample results that was not present in the Sludge-Frit melter feed data [12], there was insufficient data to claim that the result was statistically significant. Because of issues with the Hydragard mock-up recirculation pump, the melter feeds had been diluted to about 40 wt. % total solids prior to conducting the respective Hydragard tests. This was below the typical range of DWPF operation of 45-51 wt. %. It was also pointed out that the Sludge-Frit melter feed, which had been prepared for another project, had a non-prototypical ratio of sludge to frit solids. All of the above issues were to be addressed in the follow-up program proposed for 2000.

Preparation of Altered Melter Feeds

A decision was made to retest the 1999 melter feed materials in 2000 using a statistically designed sampling program. It was desired that the solids content of the size-reduced CST melter feed be increased from about 40 wt. % total solids to the DWPF target maximum of 53 wt. % total solids per Table I. ITS assisted in the preparation of two altered melter feeds for the 2000 Hydragard test program using the 1999 Sludge-Frit and Size-reduced CST-Sludge-Frit melter feeds as base materials.

The total solids content of the Size-reduced CST-Sludge-Frit melter feed was increased by allowing the insoluble solids to settle, decanting the aqueous fraction above the settled insoluble solids, concentrating the decanted aqueous phase by boiling, and returning the concentrated solution to the slurry. About 99 lbs. were decanted from 324-325 lbs. of starting melter feed. The 99 lbs. were concentrated until the solution became supersaturated.

Some solids precipitated out upon cooling this solution. Not all of these solids were readily redissolved. The concentrated aqueous fraction was filtered warm to prevent introducing any new particles into the melter feed that might plug the Hydragard. Whatman filter paper was used to retain particles greater than 8 μm. This was well below the size range of frit particles. Filtering led to a loss of about 2 lbs. of solids. The final weight of the Size-reduced CST-Sludge-Frit melter feed was 249 lbs. The estimated solids content was increased to 49.7 wt. % total solids. The contents of the drum were mixed, sampled, and analyzed for total solids by microwave. The result was 50.5 wt. % total solids. The slurry was very thick and difficult to mix in a drum using the TNX drum mixer, which has a pair of 4-inch marine propellers and was operated at about 1200 rpm.

The 50.5 wt. % total solids, Size-reduced CST-Sludge-Frit melter feed slurry was transferred to the Thermal Fluids Laboratory (TFL) and subsequently charged into the SME vessel of the Hydragard test facility. Several issues with mixing were encountered. The agitator was unable to overcome the slurry yield stress and could not produce a homogeneous slurry. The melter feed mass available was not sufficient to cover the simulated SME coils (no flow over the top of the coils). The gap between the mock-up SME coil turns had also been proportionally scaled relative to the actual gaps, and this may have been a contributing factor in retarding slurry circulation (poor flow between the coil gaps). A sample of this slurry from its initial preparation was available to determine its properties.

Dilution of the 50.5 wt. % total solids melter feed with water only would still have left the level of the contents of the TFL mock-up SME vessel below the top of the simulated coils. An alternative dilution scheme was developed. In it, the size-reduced CST melter feed was blended with some of the 1999 Sludge-Frit melter feed plus a small amount of water. The resulting blend was 45.9 wt. % total solids, and contained 25.5% sludge oxides/7.1% CST oxides/12.1% frit 200/55.3% frit 202. (Two frits were present because frit 202 was used in 1999 CST process simulations, while frit 200 was used in 1999 sludge-only conventional process simulations.)

The actual blending was conducted in the SME mock-up vessel in 786-A. This brought the slurry level in the mixing tank to ~2.0 inches above the coils. Good mixing was observed with the increased slurry volume. The EDS sampling test of the Hydragard loop proceeded with the 45.9 wt. % total solids Size-reduced CST-Sludge-Frit melter feed [3]. The sampling program was then repeated with the above melter feed diluted to 42.4 wt. % total solids [4].

EDS repeated the Hydragard test sampling program a third time with Sludge-Frit melter feed. This melter feed had been adjusted through the addition of frit 200 and water to the 1999 Sludge-Frit melter feed to produce a more prototypical waste loading of 26% sludge oxides to 74% frit oxides [5]. The Sludge-Frit melter feed contained 45.5 wt. % total solids. Table II below gives a summary of the oxide loadings in the 1999 and 2000 melter feeds.

TABLE II – Melter Feed Oxide Loadings in 1999 and 2000

	Sludge-Frit (1999)	Size-reduced CST-Sludge-Frit (1999)	Sludge-Frit (2000)	Size-reduced CST-Sludge-Frit (2000)
Sludge oxides	35	26.7	26	25.5
CST oxides	0	8.3	0	7.1
Frit 200	65	0	74	12.1
Frit 202	0	65	0	55.3

The oxide loadings above for the 1999 Size-reduced CST-Sludge-Frit melter feed are felt to be more reliable than those in the 1999 report on hydrogen and foaming studies [8]. The findings of the Hydragard testing program for 2000 were summarized by Z. H. Qureshi et al. [6]. Grab samples for use by ITS were obtained from all three of the 2000 Hydragard tests.

Measuring Methods and Analysis

Slurry samples were analyzed for various physical properties in support of the Hydragard work. These included the wt. % total solids, wt. % insoluble solids, particle size distribution, pH, and rheology.

Solids, Particle Size, and pH Measurements

The weight percent solids were determined by drying known mass samples to constant weight in a microwave oven. Slurry samples were dried to determine the wt. % total solids. A fraction of the slurry was filtered using a 0.45 μm filter to obtain a sample of the supernate. Some of the supernate was then dried to determine the wt. % dissolved solids concentration. Both measurements were performed in duplicate and averaged. Wt. % insoluble solids in the slurry samples were then calculated using equation (1):

$$wt.\%_{is} = \frac{wt.\%_{ts} - wt.\%_{ds}}{100\% - wt.\%_{ds}} \cdot 100\% \qquad (1)$$

Where: $wt.\ \%_{ts}$ = weight percent total solids concentration in the slurry
$wt.\ \%_{ds}$ = weight percent dissolved solids concentration in the supernate
$wt.\ \%_{is}$ = weight percent insoluble solids concentration in the slurry

A Fisher Scientific accumet® model 15 pH meter was used to make pH measurements. The instrument was calibrated using pH 4 and pH 10 buffer solutions, and then checked against a pH 7 buffer. Indicated instrument results were within 0.1 pH unit for the pH 7 buffer. A MicroTrac-SRA150 particle analyzer was used to measure particle size distributions.

Rheology Measurements

Slurry rheology data was obtained using the Haake Rotovisco model RV20 concentric cylinder rheometer employing the Searle technique (rotating inner cylinder). The MV2 stainless steel rotor (36.8 mm outside diameter, 60 mm length) was used because of the presence of frit particles. This provided an annular gap of 2.6 mm between the rotor and the walls of the sample beaker. The torque required to turn the inner cylinder was sensed using the Haake model M5 measuring head. The rheometer was equipped with a rheocontroller which allowed programmable control of the applied shear rate over a range of 0 – 500 sec^{-1}. Details of the controlled shear rate program are given in Appendix A.

The RV20 rheometer was functionally checked using a 102.5 cP silicon oil standard at 25°C on each day that the instrument was used for measurement. Results for the standards were always within ±5%. A slurry sample was placed into a cylindrical stainless steel cup (42 mm inside diameter) and loaded into the heating jacket. The heating jacket controlled the temperature of the rotor, sample and cup. A heating/cooling temperature bath was attached to the heating jacket to provide the heat sink. All measurements were taken at 25°C. A PC running Haake Rotovisco data acquisition software acquired the rheometer data. All rheometer data from this study is included in Appendix A (Figures A-1 to A-10).

The resulting flow curves obtained from the concentric cylindrical data have not been corrected for non-Newtonian behavior, slip, viscous/thermal effects, or end effects. No secondary flow problems, such as Taylor vortices were noted in any of these measurements. Correcting the flow curves would require taking additional rheological measurements using different size rotors and/or cups.

The flow curves were modeled using the Bingham plastic fluid rheological model, equation (2).

$$\tau = \tau_o + \eta\dot{\gamma} \tag{2}$$

Where: τ = shear stress (Pa or dynes/cm^2)

$\dot{\gamma}$ = shear rate (inverse seconds)

τ_o = Bingham plastic yield stress (Pa or dynes/cm^2)

η = Bingham plastic consistency or Bingham plastic viscosity, (Pa-sec or cP)

The flow curves from the RV20 were fit using equation (2) between 75 and 350 sec^{-1}.

Analysis

The DWPF design basis limits for melter feed, using the Bingham plastic model, are 25 to 150 dynes/cm^2 for yield stress and 10-40 centipoise (cP) for the plastic viscosity. Marek [10,11] correlated the two Bingham plastic fluid parameters as a function of both wt. % total and insoluble solids content of the slurry using equations (3) and (4).

$$\tau_o = \frac{\exp^{b_1 * C}}{(1 - C / C_{\max,1})} \tag{3}$$

$$\eta = \frac{\exp^{b_2 * C}}{(1 - C / C_{\max,2})} \qquad (4)$$

Where: τ_o = yield stress from the Bingham plastic model (dynes/cm^2)
η = plastic viscosity (consistency) from the Bingham plastic model (cP)
C = insoluble solids concentration (wt. %)
$C_{\max,i}$ = modeled parameters corresponding to maximum wt. % solids
b_i = modeled parameters (wt. %)$^{-1}$

The original semi-theoretical model correlates the apparent viscosity, or ratio of shear stress to shear rate, of a Newtonian slurry as a function of the volume fraction of insoluble solids. This original equation was modified by Marek to model both the Bingham plastic yield stress and consistency as a function of wt. % solids. Theoretically, $C_{\max,1}$ and $C_{\max,2}$ should be about the same for a given data set.

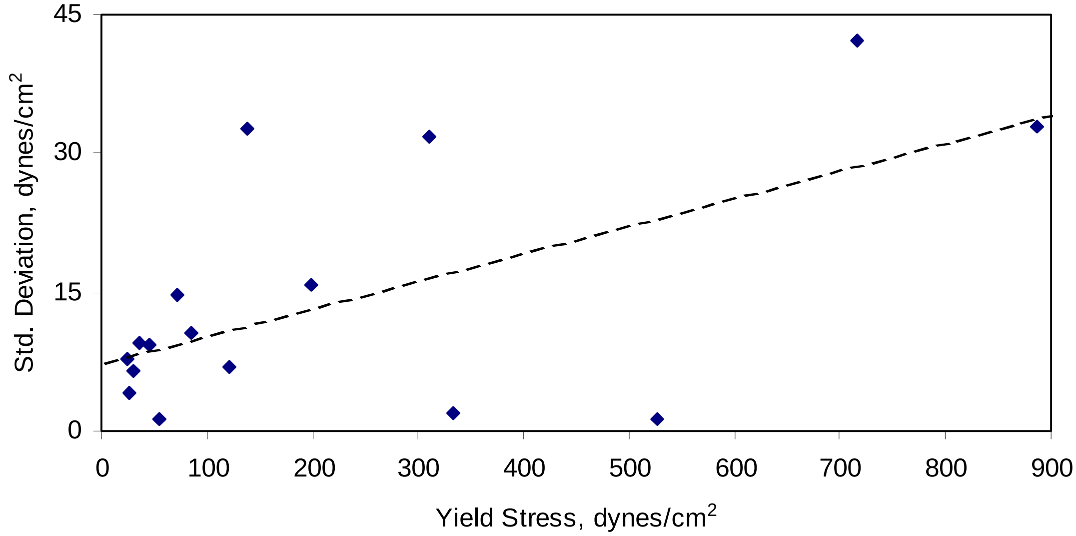
Both equations force the solution at zero wt. % solids to intercept the y-axis at a value of unity. Consequently, consistency was fit using data in cP, since the viscosity of the aqueous phase was close to that of water. A non-zero yield stress at zero solids content was a minor flaw in the model. The larger the units of yield stress used, the smaller the significance of this error. Consequently, dynes/cm^2 were preferred over Pascals. The unknown parameters in equations (3) and (4) were obtained using Table Curve 2D, version 4.06, and verified using SigmaPlot, version 4.01.

Analysis of Historical Variability in Haake RV20 Measurements on Melter Feeds

The experimental uncertainty in determining yield stress and consistency from RV20 rheograms was estimated using historical data obtained by J. C. Marek [9,10] on samples of melter feed simulant (5-9 rheograms per wt. % total/insoluble solids). This data was supplemented by seven other data pairs in his later work [11]. Figure 1 shows the calculated values of standard deviation as a function of yield stress generated from this data (5-9 trial standard deviations were given a weight of two, and pair standard deviations a weight of one, in generating the best fit line).

The data with 5-9 repeated trials was concentrated on the left-hand side of the graph between yield stresses of 20 and 125 dynes/cm^2. There were two pairs of repeated trials where the two calculated yield stresses were nearly identical. These produced the two points at 333 and 526 dynes/cm^2 with the low standard deviations. The values in the other five pairs were significantly different.

Figure 1.
Historical Yield Stress Variability for the TNX Haake



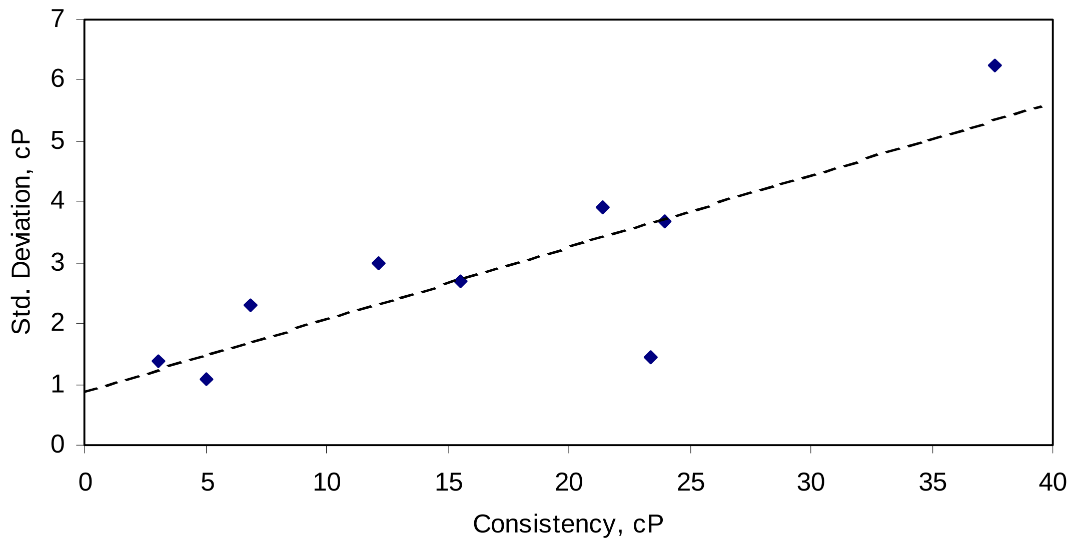
Based on Figure 1, a two-standard-deviation error bar for the yield stress results given later in this report would be on the order of ±20-40 dynes/cm^2. This was equivalent to about 10-20% of the absolute yield stress value. In this context a yield stress of 110 dynes/cm^2 for Sludge-Frit melter feed at 37.4 wt. % insoluble solids could not be distinguished with statistical confidence from a yield stress of 100 dynes/cm^2 for CST-Sludge-Frit melter feed at 37.5 wt. % insoluble solids (even if there was no uncertainty in the wt. % insoluble solids determination).

The TNX wt. % insoluble solids determination required that the wt. % total solids on the entire sample and the wt. % solids on the filtered supernate from the sample be known. Thus there were two measurements where experimental error could be introduced. The calculation of wt. % insoluble solids was based on an average of two results for total solids and an average of two results for filtered supernate total solids. A reasonable value for two-standard-deviations was ±0.30 wt. % (for two analyses of the same sample). This represented the approximate two-standard-deviation range for wt. % total solids (entire sample or filtered supernate). Using algebraic arguments, the value for two standard deviations for the wt. % insoluble solids was about ±0.42 wt. %. (Assuming variances, σ^2, of both measurements were equal, normally distributed, and additive, giving a combined variance of $2\sigma^2$, or a combined standard deviation of $\sqrt{2}\,\sigma$.)

The TNX microwave determinations are biased high compared to oven-dried determinations (or conversely, oven drying produced a biased number on the low side). This bias was seen in waste sludge slurries and SRAT and SME products. It could be related to weakly held waters of hydration of the hydrous ferric oxide in the sludge simulant.

Figure 2 below shows the standard deviations in the consistency data from the sets of 5-9 repeated trials at a given wt. % total solids from Marek's reports [9,10,11].

Figure 2.
Historical Consistency Variability for the TNX Haake



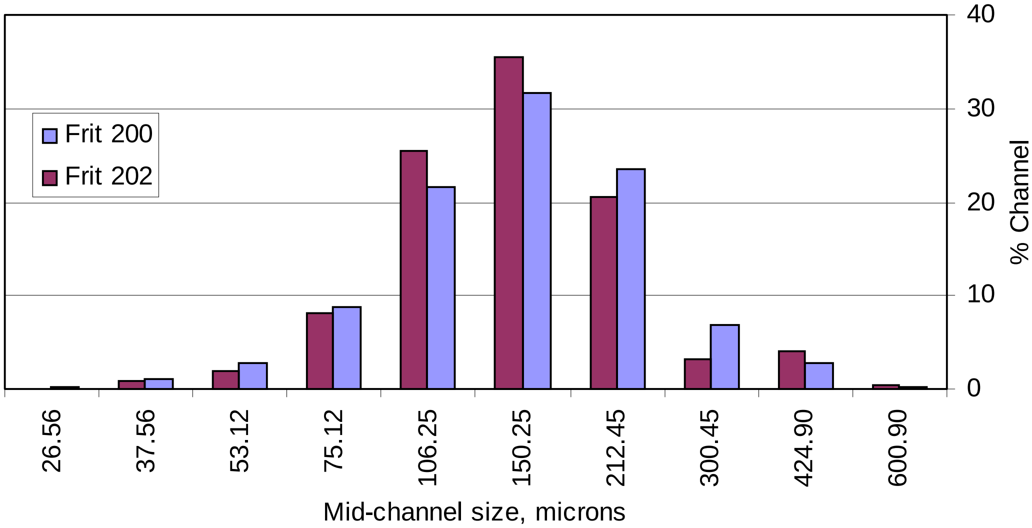
One standard deviation was about 13-20% of the absolute consistency itself for the range of current interest (9 cP - 39 cP). This was comparable to the degree of uncertainty in yield stress. The difference between a consistency of 34 cP and another of 39 cP was marginally significant statistically. In the case of both yield stress and consistency, fitting multiple data points to a realistic model accomplished much the same thing as repeated trials, i.e. an increase in the confidence of a conclusion regarding the hypothesis.

Preliminary Test Results (1999 Melter Feeds)

ITS initiated several investigations, once it was learned that the 1999 Hydragard testing indicated a potential bias in the CST Hydragard sample results. These included studies of the rheological properties of the melter feeds, as well as investigations into the effects of frit and CST particle size on the melter feed slurries.

Figure 3 shows a comparison of the particle size distributions for the frit 200 and frit 202 used in preparing the two melter feeds. Frit 200 was used in preparing the Sludge-Frit melter feed (current DWPF frit). Frit 202 was used in preparing the Size-reduced CST-Sludge-Frit melter feed. All particle size distributions were measured by the Analytical Development Section as described above.

Figure 3.
Comparison of Frit 200 and Frit 202



The mid-channel size is the average of the start size and end size for a given channel of the MicroTrac analyzer, e.g. 300.45-µm is the average of 248.9-µm and 352-µm. The % Channel is the percentage of detected particles found between those two sizes. The two frits had very similar particle size distributions. The chemical compositions of the two frits are given in Table III.

TABLE III – Comparison of Frit 200 and 202 Composition

Component	Frit 200	Frit 202
SiO_2	70%	77%
Na_2O	11%	6%
Li_2O	5%	7%
MgO	2%	2%
B_2O_3	12%	8%

Given the chemical and physical similarities between the two frits, we concluded that the choice of frit was at most a minor factor in the behavior of the melter feed during Hydragard sampling.

Figure 4 shows the particle size distribution for the size-reduced CST. The graph is a composite of data obtained from five measurements. The data is for CST prior to adding it to the SRAT.

Figure 4.
Particle Size Distribution of Size Reduced CST

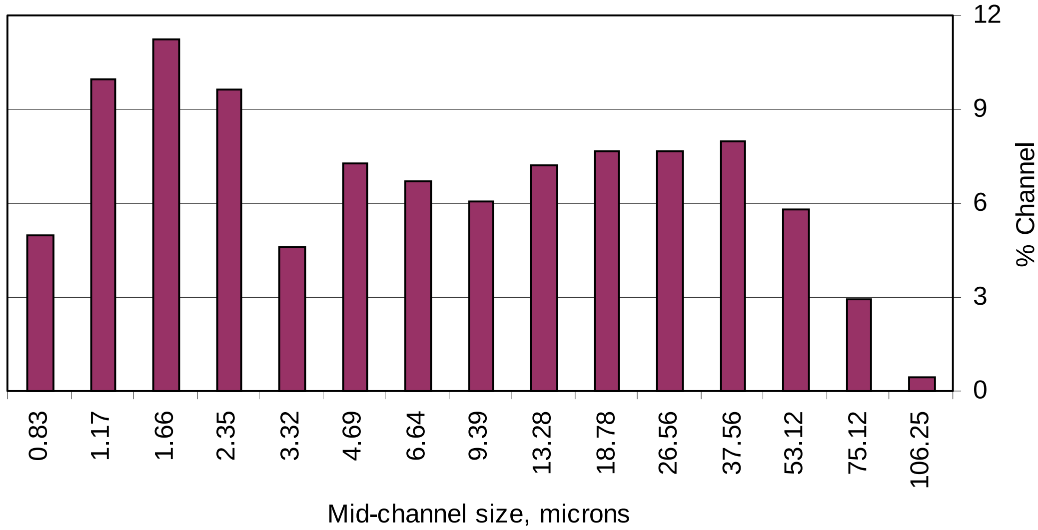
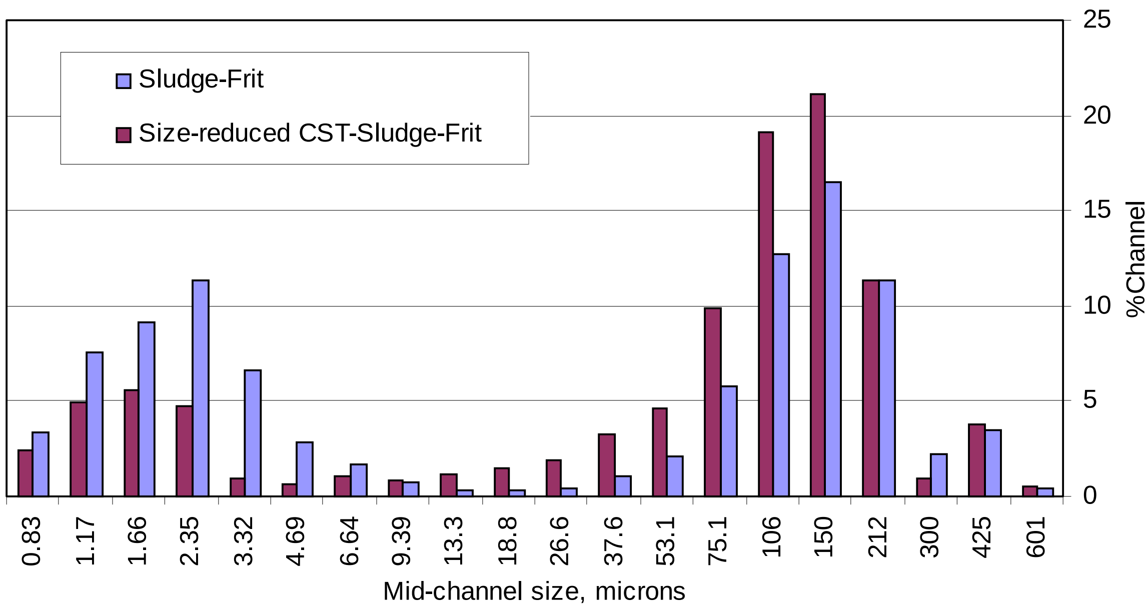


Figure 5 shows a comparison of the particle size distributions of the Size-reduced CST-Sludge-Frit melter feed and the Sludge-Frit melter feed.

Figure 5.
Comparison of 1999 Melter Feeds



The size-reduced CST melter feed had a higher fraction of particles greater than 20 microns. The contribution of size-reduced CST to the melter feed distribution was evident in the channels from 106 microns and smaller according to Figure 4. The relative significance of having 35% sludge oxides in the Sludge-Frit melter feed compared to 26.7% in the CST-Sludge-Frit melter feed was most obvious between 0.83 and 6.64 microns. Although some of the size-reduced CST was being counted with sludge between 0.83 and 6.64 microns, most of the CST contribution was found between 9.39 and 106 microns. The two 1999 melter feeds were very similar based on number and volume mean particle diameters, as seen in Table IV. The bimodal particle size distribution was the reason for the significant differences between the volumetric and number mean particle diameters for a given sample.

TABLE IV – Mean Diameters of Melter Feed Slurry Particles

	Volumetric Mean Diameter, μm	**Number Mean Diameter, μm**
No CST Melter Feed	91.4	1.20
Size-reduced CST Melter Feed	108.3	1.13

Colloidal-sized particles, i.e. those less than roughly ten microns in diameter, are more effective at increasing the apparent viscosity of slurries. Higher apparent viscosities correlate with greater drag forces on particles. These two facts taken together suggest that a higher apparent viscosity due to the presence of colloidal particles might correlate with better Hydragard performance. The mechanism would be superior entraining of frit particles from the sample loop flow streamlines through the right angle change in direction required to enter the Hydragard sample vial. This suggests that the Sludge-Frit melter feed might be expected to perform better in the Hydragard testing than the Size-reduced CST-Sludge-Frit melter feed. The anticipated difference in performance might be small in the case of the 1999 melter feeds, however, given the comparatively minor difference in the relative quantities of colloidal solids.

Rheological data for both melter feeds was obtained over a range of total solids content. Flow curves were fit to equation (2). The rheological results are summarized in Table V in terms of the Bingham plastic fluid parameters.

TABLE V – Rheological Properties of 1999 Melter Feed Simulants at 25°C

Melter Feed Type	Wt. % Total Solids[(a)]	Wt. % Insoluble Solids	Wt. % Soluble Solids	pH	Yield Stress[(b)], dynes/cm^2	Consis-tency, cP
Size-reduced CST	50.6	43.2	7.4	7.3	390	34
Size-reduced CST	47.2	39.9	7.2	7.3	190	24
Size-reduced CST	43.0	37.5	5.5	7.5	100	17
Conventional	50.9	41.2	9.7	7.4	290	39
Conventional	46.3	37.4	9.0	7.6	110	22
Conventional	39.5	31.7	7.8	7.5	60	9

(a) Wt. % data was obtained using the TNX microwave oven.
(b) DWPF Design Bases [14]: Yield Stress, dynes/cm^2 – 150 (max.), 25 (min.)
Consistency, cP – 40 (max.), 10 (min.)

The raw rheogram data for the six melter feeds is given in Appendix A (Figures A-1 to A-6). The yield stress of the initial 50.6 wt. % Size-reduced CST-Sludge-Frit melter feed slurry was found to be 390 dynes/cm^2, about two-and-one-half times greater than the upper DWPF melter feed design basis. Comparing the raw rheogram of this slurry with that of the 50.9 wt. % Sludge-Frit melter feed indicates that the presence of CST has a negative impact on the rheological properties at high wt. % total solids.

Figure 6 below presents correlations between yield stress and total solids data. The two types of melter feed were fit separately to equation (3). A data point of zero yield stress at zero wt. % total solids was included before making the fits. C_{max} is nearly the same wt. % total solids for both data sets (56.4 and 56.5). Taken individually, the differences between the two melter feed yield stresses would not be considered statistically significant per the discussion on historical variability above except at 50.5-50.9 wt. %. R^2 for both fits are greater than 0.99, however fitting four data points with a realistic model containing two adjustable parameters was expected to produce a good fit. The two data sets could have been fit to a common curve. The resulting R^2 for a single fit is 0.93, i.e. still a reasonably good fit. The curve fits, however, indicate that the Sludge-Frit melter feed had a lower yield stress than the Size-reduced CST-Sludge-Frit melter feed at a given wt. % total solids.

Figure 6
Melter Feed Rheology
Weight % Total Solids versus Yield Stress

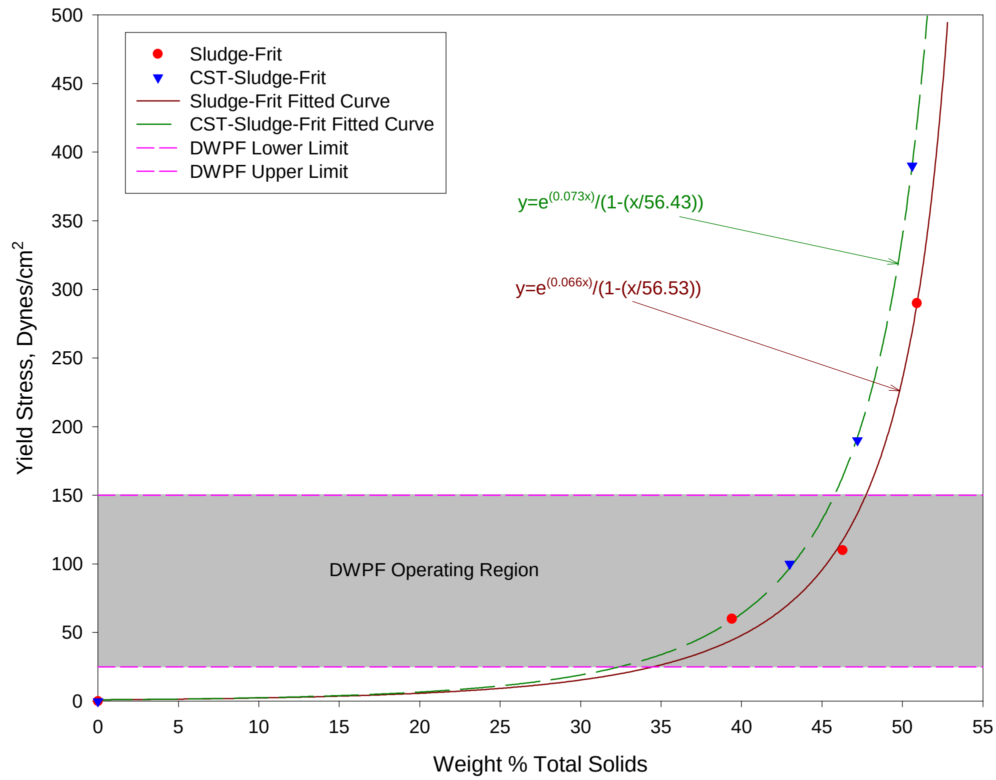
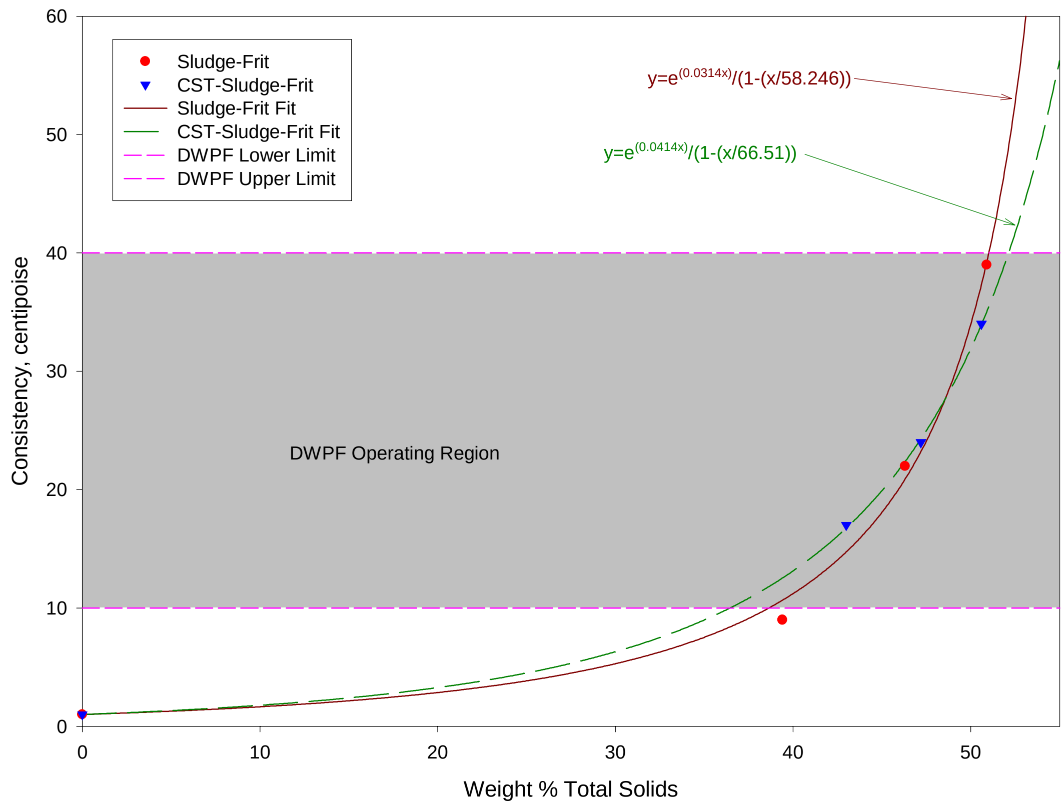


Figure 7 below presents comparable information for the consistency of the six samples. An extra data point of a consistency of one cP at a wt. % total solids of zero was used in making the fits in this figure to equation (4). C_{max} from the consistency data differed from that for the yield stress data, 58.2 wt. % and 66.5 wt. % versus 56.5 wt. % and 56.4 wt. % respectively. The two Sludge-Frit C_{max} values were in fairly close agreement for consistency and yield stress, but the two Size-reduced CST-Sludge-Frit C_{max} values were not. This could have been an artifact of the small sample size.

The R^2 value for a common consistency fit to all the 1999 data was nearly 0.99, while the individual fits had $R^2 > 0.995$. Although the Sludge-Frit melter feed had a lower yield stress, it also had a slightly higher consistency at higher wt. % total solids. Consequently, the apparent viscosities of the two melter feeds at a given wt. % total solids were fairly similar.

Figure 7
Melter Feed Rheology
Weight % Total Solids versus Consistency



Theories for the rheological properties of slurries generally focus on the insoluble solids content of the stream, not the total solids content. Correlations usually use volume fraction of insoluble solids. This variable is presumably directly proportional to weight % insoluble solids in a given melter feed simulant (constant particle geometry). Figures 8-9 plot yield stress and consistency versus wt. % insoluble solids instead of wt. % total solids. The presentation parallels that for Figures 6-7.

Figure 8 was produced by refitting the data in Figure 6 to equation (3) with C_{max} reinterpreted as the maximum bound of wt. % insoluble solids instead of wt. % total solids. Goodness of fit, as measured by R^2, was better when the data was fit against wt. % total solids, but R^2 was still > 0.99 in both cases. Sludge-Frit melter feed had the higher apparent yield stress, but the two melter feeds were within the overall margin of error, i.e. a combination of potential yield stress and wt. % insoluble solids errors. Fitting all yield stress data to a single equation produced a fit with R^2 = 0.979, again indicating the nearly identical yield stress properties of the two 1999 melter feeds.

Figure 8
Melter Feed Rheology
Weight % Insoluble Solids versus Yield Stress

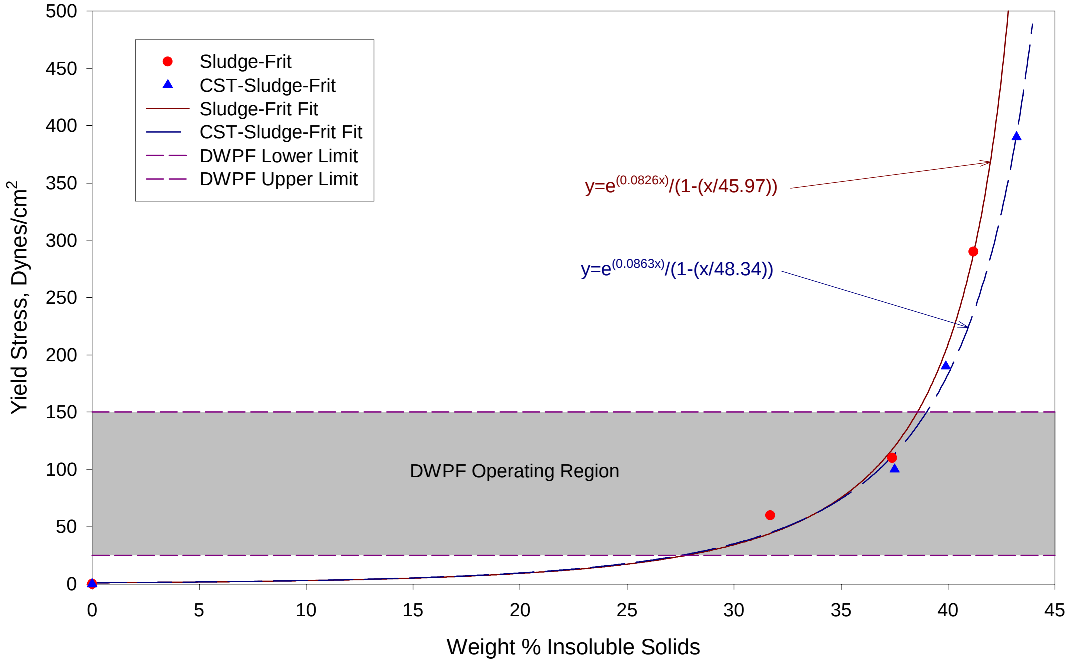
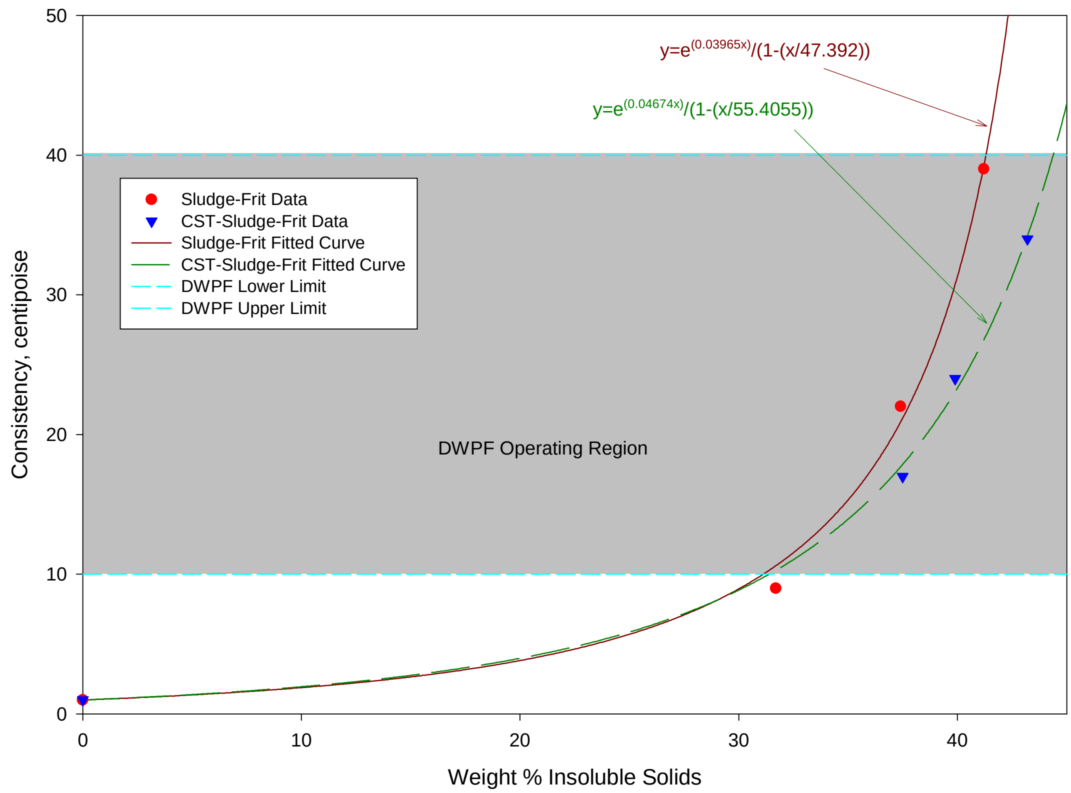


Figure 8 removes the masking effect from different concentrations of soluble solids in the two melter feed types. The ranges of wt. % insoluble solids studied are significantly different for the two melter feeds. Previous experience making model fits of this type indicates that the data point at the highest wt. % dominates the determination of C_{max}.

Figure 9
Melter Feed Rheology
Weight % Insoluble Solids versus Consistency



The wt. % insoluble solid C_{max} values based on consistency in Figure 9, are 55.4 and 47.4. These compare to the yield stress values of 48.3 and 46.0. The R^2 values for the two fits in Figure 9 were both > 0.995. There was statistical confidence that the consistency, at least at higher wt. % insoluble solids, was lower for the CST-Sludge-Frit melter feed than for the Sludge-Frit melter feed. A single fit of equation (4) to all of the data in Figure 9 produced the poorest R^2 value of any of the fits, $R^2 = 0.886$. This was a further indication that the two sets of consistency data were significantly different. The consistency difference was much more pronounced than the yield stress difference.

It was impossible to conclude with any statistical confidence that the two 1999 melter feeds would exhibit different flow characteristics in a typical pipeline or mixing tank environment based on the data above. This conclusion applied strictly to cases where the mass fraction frit in the solids was about equal (CST displaced a fraction of the sludge with frit held constant). Data presented in the next section describe a different case where the mass fraction sludge oxide in the solids was about equal (CST displaced frit with sludge held constant).

Follow-up Test Results (2000 Melter Feeds)

Three additional samples were collected for rheological study. A grab sample was collected from the SME mock-up tank for each of the Hydragard sample loop tests performed in 2000. A rheogram was obtained for each. The fundamental differences between the 1999 and 2000 melter feed solids breakdown were given in Table II above. The raw rheogram data is given in Appendix A (Figures A-7, A-8, and A-9). The wt. % total solids of the slurries were taken from the average grab sample results of the Hydragard loop tests [6]. Table VI summarizes the Bingham plastic fluid parameters obtained from the rheograms and compares them to the predicted values based on the appropriate model equations in Figures 6 and 7.

TABLE VI – Bingham Fluid Parameters for Hydragard Test Samples

Sample	Measured Yield Stress, dynes/cm^2	Predicted Yield Stress, dynes/cm^2	Measured Consistency, cP	Predicted Consistency, cP
45.9 wt. % Total Solids with CST	320	155	12	22
42.4 wt. % Total Solids with CST	160	90	16	16
45.5 wt. % Total Solids, no CST	106	103	17	19

The 45.5 wt. % Sludge-Frit melter feed was expected to have an intermediate yield stress relative to the two melter feeds containing CST. There was a statistically significant difference, however, between the predicted and measured yield stress values for the two melter feeds containing CST. There was also a statistically significant difference in predicted and measured consistency for the 45.9 wt. % CST melter feed. This was in a compensating direction to the yield stress difference.

The principal cause of differences in the rheological properties of the Hydragard test samples containing size-reduced CST was initially attributed to the blending done to prepare them, as described earlier. A small quantity of a similar blend had been prepared and tested rheologically at TNX prior to the blending in the SME mock-up. That sample blend had a yield stress of about 210 dynes/cm^2 and a consistency of 24 cP. It also exceeded the predicted values though not by as much as the actual blend prepared at TFL (the raw rheogram appears in Figure A-10, Appendix A). This was the first suggestion that the material blended for the Hydragard tests might be more viscous than originally expected.

The actual improvement in rheological properties obtained from blending the CST-Sludge-Frit melter feed in the SME vessel from 50.6 to 45.9 wt. % total solids was fairly small (a reduction from 390 dynes/cm^2 and 34 cP to 320 dynes/cm^2 and 12 cP). The blended yield stress and consistency corresponded to ~49 wt. % total solids in the original unblended CST-Sludge-Frit melter feed. Although the net change in rheological properties of the melter feed was small, the mixing in the SME mock-up vessel improved significantly after blending. The region between the coils and the vessel wall went from stagnant to well-mixed. We do not believe that such a dramatic effect would have occurred if the rheological properties were the only thing that changed (no change in slurry volume). It is far more likely that mixing improved when new flow paths were created due to the volume increase. These allowed the slurry to circulate vertically between the coils and the vessel wall (combined with radial flows at the bottom and top of the coils that mixed the region inside the coils with the annular region outside the coils.)

The Sludge-Frit melter feed composition was also adjusted prior to the 2000 Hydragard testing. The ratio of sludge oxides to frit was changed from about 35/65 to about 26/74 by the addition of frit 200. The wt. % total solids was increased from about 39 to 45.5%. No historical data was located on the effect of waste loading on rheology, but first principles suggest that increasing mean particle size at constant wt. % insoluble solids should lead to lower apparent viscosity (lower yield stress and/or consistency). Nevertheless, the frit adjusted Sludge-Frit melter feed did not exhibit appreciably different rheological characteristics.

Data from the three 2000 Hydragard test grab samples show a more significant difference between the rheological properties of the melter feeds with and without CST than was indicated by the 1999 group of samples described in Table IV. The CST and sludge in the 1999 samples comprised about 35 wt. % of the solids on an oxide basis, whether the sample had or lacked CST, i.e. the CST replaced a fraction of the sludge. In the 2000 Hydragard test melter feeds, however, the sludge oxides were present at about 26 wt. %. The size-reduced CST substituted for a fraction of the frit. Because the size-reduced CST was much smaller than frit, it was expected to produce a higher yield stress and/or plastic viscosity. This was observed to be the case, but the present number of data points is small.

CONCLUSIONS

Rheological and other measurements were made of simulated melter feeds with and without CST sorbent. When CST replaced a portion of the sludge in the melter feed (1999 case), the impact on rheology was minor. The two melter feeds, Sludge-Frit and Size-reduced CST-Sludge-Frit, had nearly identical rheological characteristics in the range of 39-51 wt. % total solids. Yield stresses of the two 1999 Hydragard test slurries were within the DWPF design basis range of 25-150 dynes/cm^2, and consistencies were near the lower DWPF design basis limit of 10 cP. Particle size distribution results for the two 1999 melter feeds indicated that size-reduced CST did not significantly interact with either frit or sludge particles to form larger agglomerated structures.

When CST replaced a portion of the frit in the melter feed (2000 case), the impact on rheology was significant and detrimental. The 2000 Sludge-Frit melter feed was 26% sludge oxides and 74% frit 200 oxides. The 2000 Size-reduced CST-Sludge-Frit melter feed was 25.5% sludge oxides, 7.1% CST oxides, and 67.4% frit 202 and frit 200 oxides. The Size-reduced CST-Sludge-Frit melter feed had more than double the yield stress of the Sludge-Frit melter feed at about 46 wt. % total solids. A significant increase in melter feed yield stress in DWPF would probably force the plant to feed the melter at a lower wt. % total solids. This would lead to a lower melt rate and force a longer period of operation to complete the vitrification of the site waste. The 2000 Hydragard tests with Size-reduced CST-Sludge-Frit at 42.4 wt. % and 45.9 wt. % total solids both occurred with slurries whose yield stress exceeded the DWPF upper design basis limit of 150 dynes/cm^2. The 2000 Sludge-Frit melter feed yield stress and all of the consistency data were within the DWPF design basis limits.

Issues related to mixing the 50.5 wt. % total solids Size-reduced CST-Sludge-Frit melter feed slurry in the Hydragard sample loop tank were determined to be primarily due to an insufficient quantity of melter feed rather than to rheological properties.

SUMMARY

The work conducted by ITS in support of the 1999 and 2000 Hydragard testing was successfully completed and adds significant new information to the interpretation of the sampling test results. Unfortunately, the melter feeds had been stored for over eight months before the rheological work and the 2000 Hydragard testing were conducted. The effect of aging on the properties of melter feed is not well understood. This research does suggest several new avenues for future research. Future work should seek to determine answers to some of the following questions.

More data is needed to clarify the impact of CST on melter feed rheology. Current plans call for CST to replace frit rather than sludge in the DWPF melter feed, and the small quantity of data obtained so far have negative implications for the DWPF canister pour rate. The 2000 melter feeds discussed in this report were old and had been manipulated both physically and chemically. During the 1999-2000 time period, it was proposed that at least two new bench-scale process simulations be performed with fresh sludge simulant. These simulations should use identical process operating parameters, but with CST being fed to one of the simulations and not the other. The rheological characteristics of the fresh melter feeds produced would be measured over total solids concentrations ranging from 40 wt. % to 50 wt. %. The melter feeds would target a CST waste loading identical to that currently planned for DWPF. This was seen as the only way to determine if the presence of CST in melter feed will negatively impact DWPF.

(The above testing actually started in November 2000 and completed while this report was being prepared. Three runs were made using Macrobatch 3 starting simulant, which was a blend of Tank 8 and Tank 40 simulants. Consequently, the results will not be directly comparable to the work in this report. Two different size ranges of CST were processed in two of the runs. The third run used no CST. The rheological properties of these three SME products will be characterized and reported in [7]. This data should help to clarify the role of CST on melter feed rheology.)

Table VI shows that the Hydragard experiments were being conducted with material that was outside of the DWPF design basis for yield stress (25-150 dynes/cm^2). It would be desirable to determine whether or not DWPF actually processes within this range. If they do, then findings using fluids with such high yield stresses may have little relevance to the actual plant performance. There is a rheometer with comparable measuring capabilities to the one at TNX within the Shielded Cells. A sample of real DWPF melter feed from a representative SME batch should be submitted for rheological characterization.

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APPENDIX A: RAW HAAKE RHEOGRAM DATA

The following ten figures display the raw (uncorrected) Haake rheograms (flow curves) for the ten samples discussed in this report. The x-axis is the shear rate, and the y-axis is the shear stress. These are derived from the angular speed and torque combined with the assumption that the fluid exhibits Newtonian behavior. Wt. % solids in the figure titles represent total solids on an air-dried at 110-155°C basis or comparable microwave oven dried basis.

The three Size-reduced CST-Sludge-Frit melter feed rheograms, shown in A-1, A-2, and A-3, were obtained by ramping the shear rate linearly from 0 to 350 sec^{-1} over five minutes. The sample was then held at 350 sec^{-1} for six seconds, and then the shear rate was ramped linearly from 350 to 0 sec^{-1} over five minutes. The two Sludge-Frit melter feed rheograms, shown in A-5 and A-6 were run similarly. The Sludge-Frit melter feed rheogram in A-4 was obtained by ramping the shear rate linearly from 0 to 350 sec^{-1} over five minutes, holding at 350 sec^{-1} for five minutes, and then ramping the shear rate linearly from 350 to 0 sec^{-1} over five minutes.

The three Hydragard sample rheograms, shown in A-7, A-8, and A-9, were obtained by ramping the shear rate linearly from 0 to 350 sec^{-1} over five minutes, holding at 350 sec^{-1} for five minutes, and then ramping the shear rate linearly from 350 to 0 sec^{-1} over five minutes. Figure A-10 is the rheogram of a TNX blend of the original Size-reduced CST-Sludge-Frit melter feed, the original Sludge-Frit melter feed, and water that approximated the blend made at Thermal Fluids Lab for the 45.9 wt. % total solids Hydragard Test. (It quite possibly had a slightly lower wt. % total solids than the blend. The sample was run just as a quick check to see what might happen. This rheogram was obtained by ramping the shear rate linearly from 0 to 350 sec^{-1} over five minutes, holding at 350 sec^{-1} for six seconds, and then ramping the shear rate linearly from 350 to 0 sec^{-1} over five minutes.)

Figure A-1
Rheogram for Size-reduced CST-Sludge-Frit
Melter Feed at 50.6 Wt.% Solids

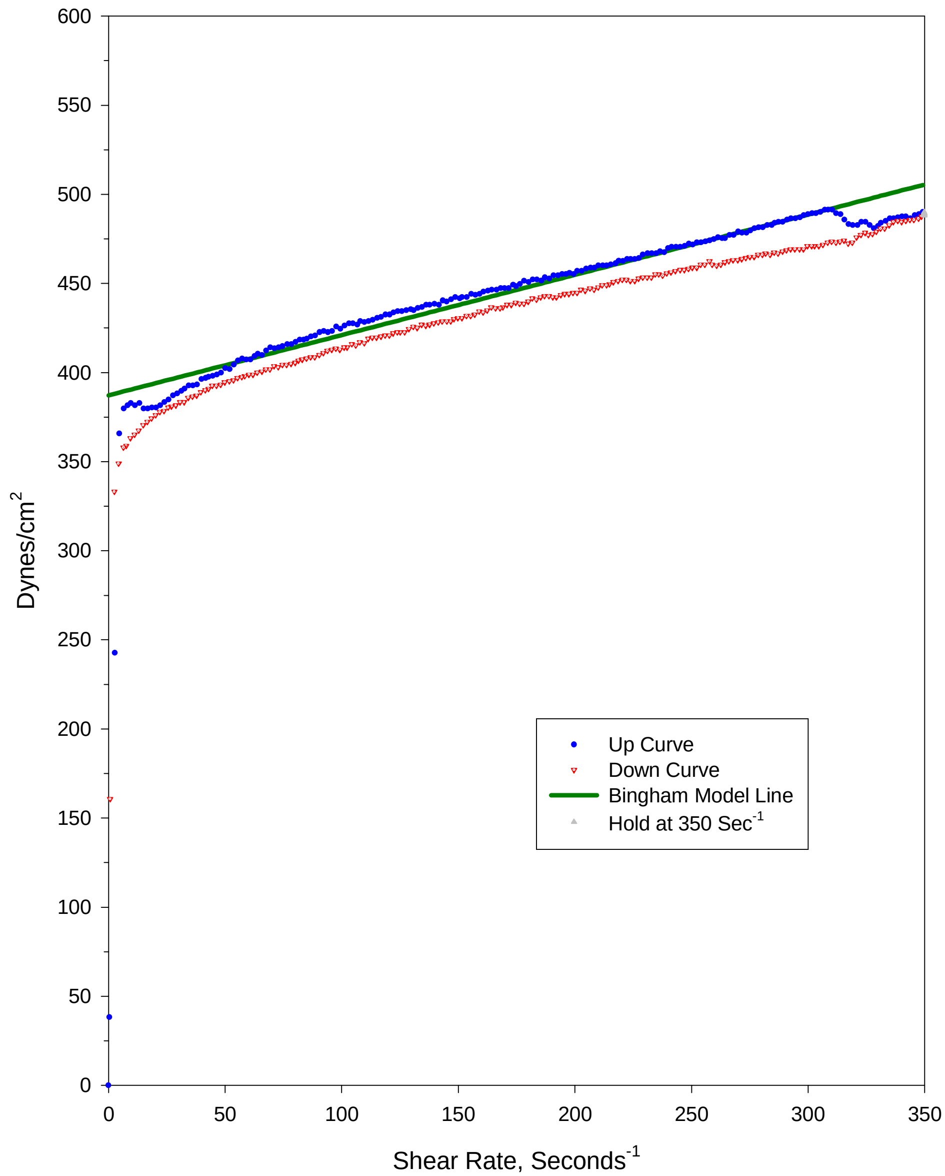


Figure A-2
Rheogram for Size-reduced CST-Sludge-Frit
Melter Feed at 47.2 Wt.% Solids

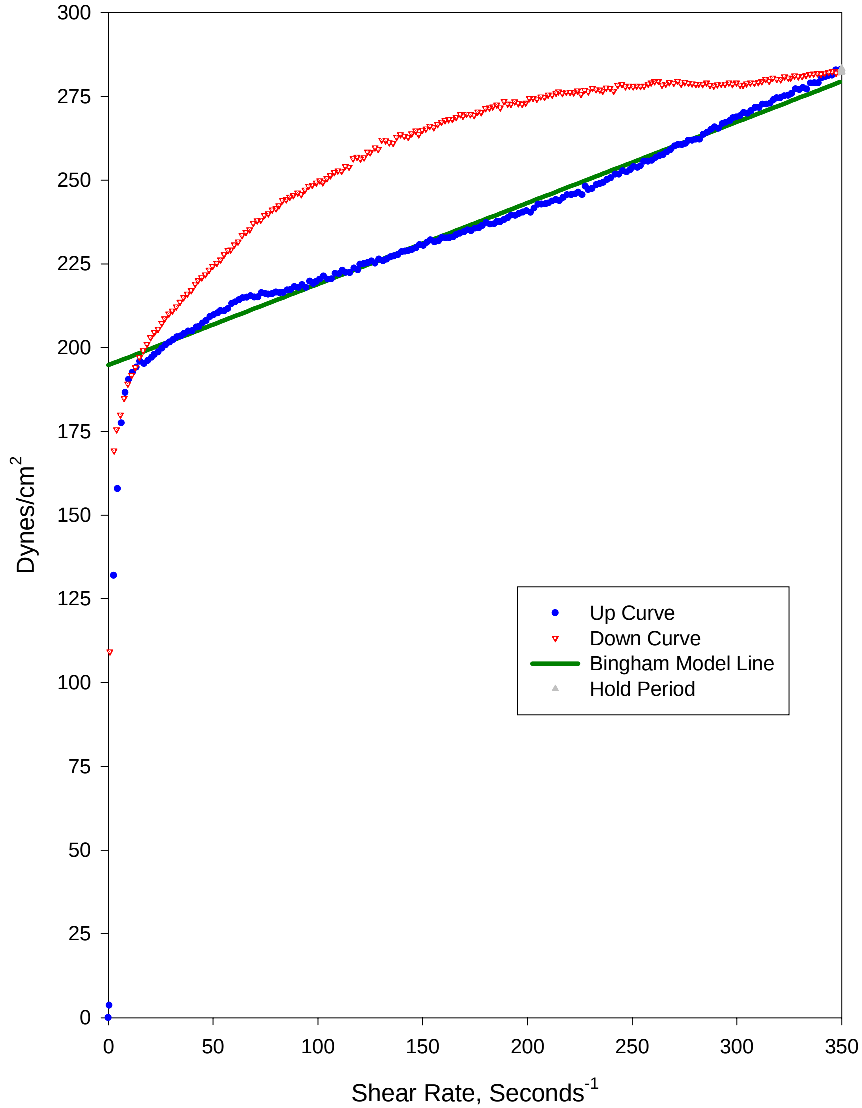


Figure A-3
Rheogram for Size-reduced CST-Sludge-Frit
Melter Feed at 43 Wt.% Solids

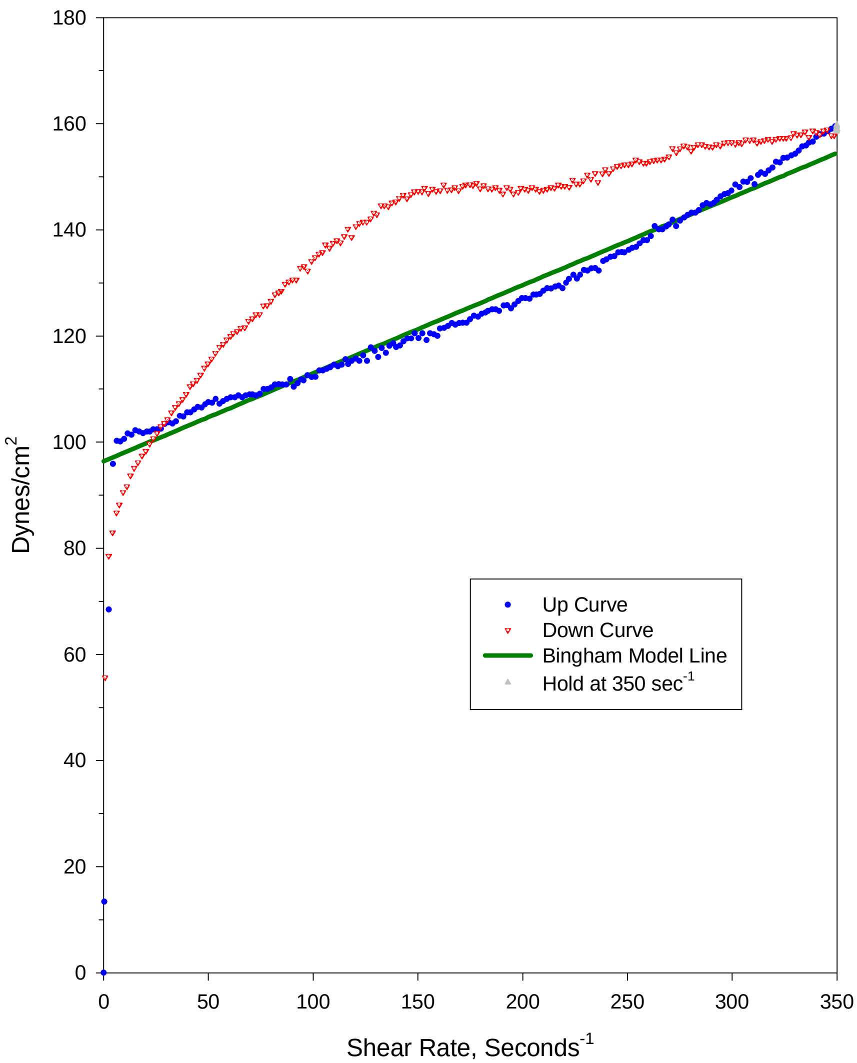


Figure A-4
Rheogram for Conventional
Melter Feed at 50.9 Wt.% Solids

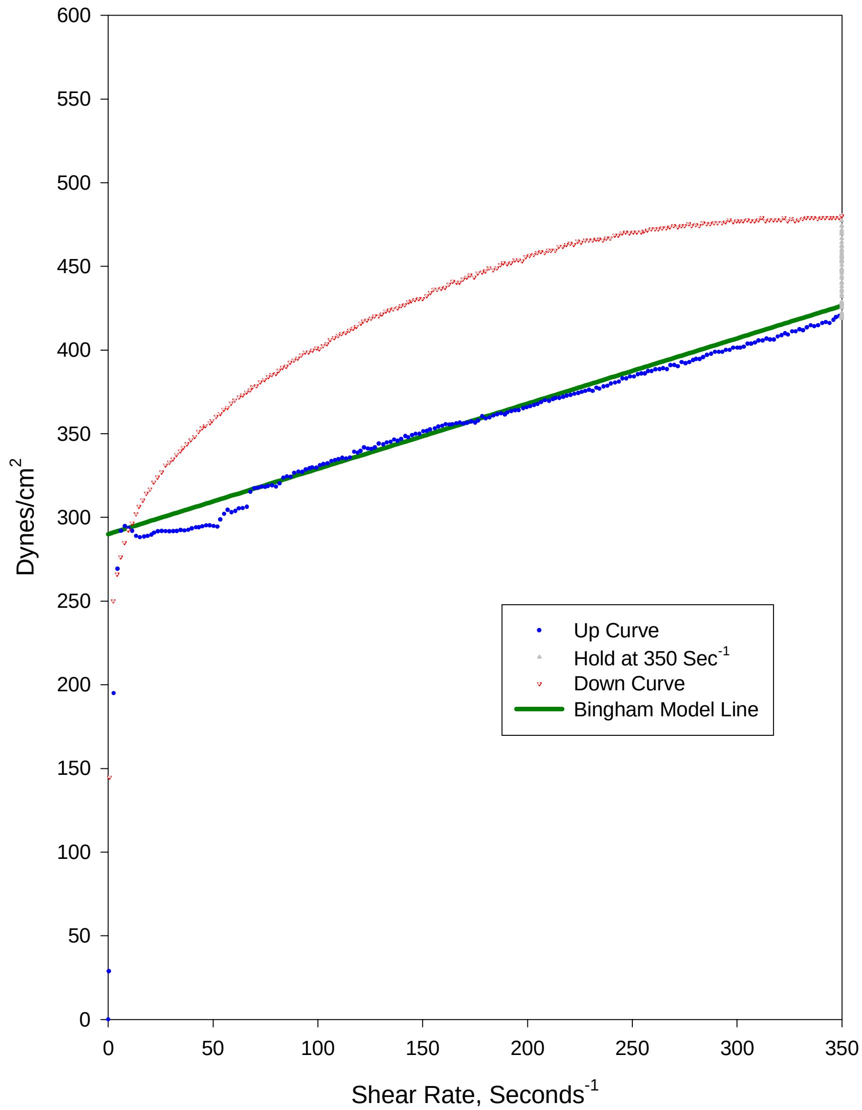


Figure A-5
Rheogram for Conventional
Melter Feed at 46.3 Wt.% Solids

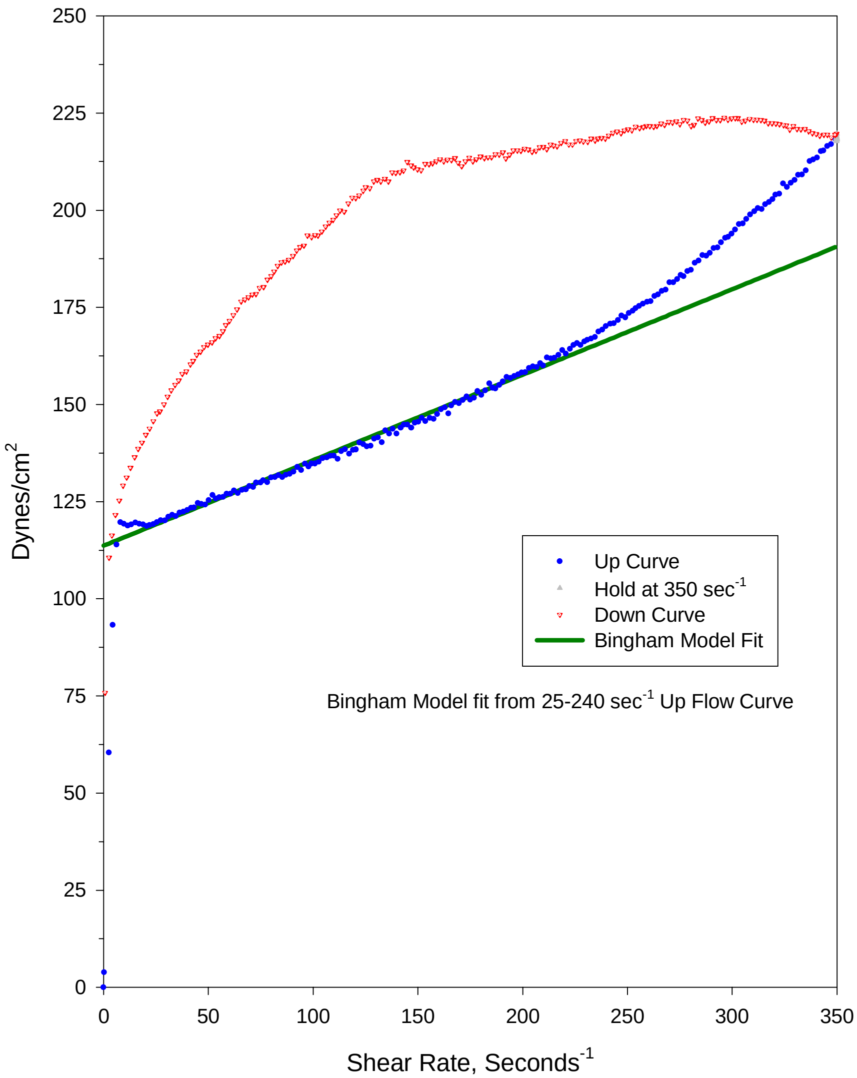


Figure A-6
Rheogram for Conventional
Melter Feed at 39.5 Wt.% Solids

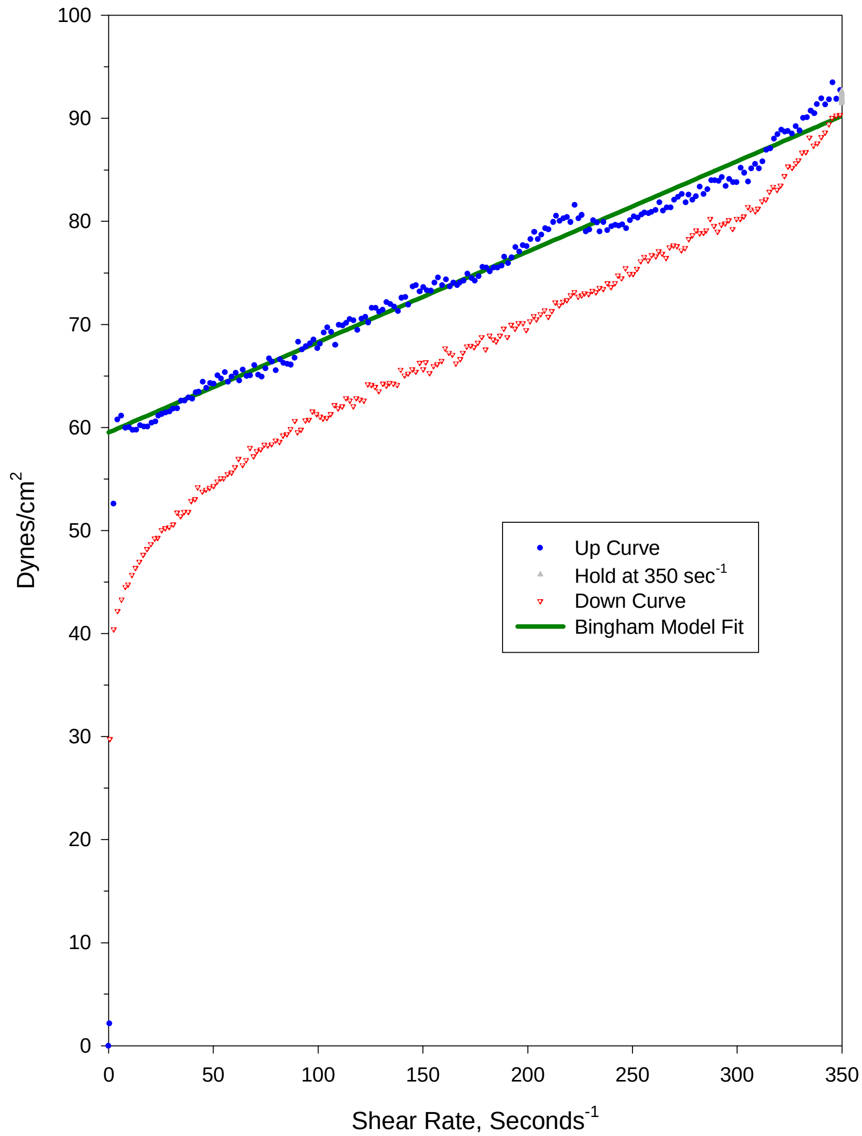


Figure A-7
Rheogram for 42 Wt.% Melter Feed
Hydragard Test with Size-reduced CST

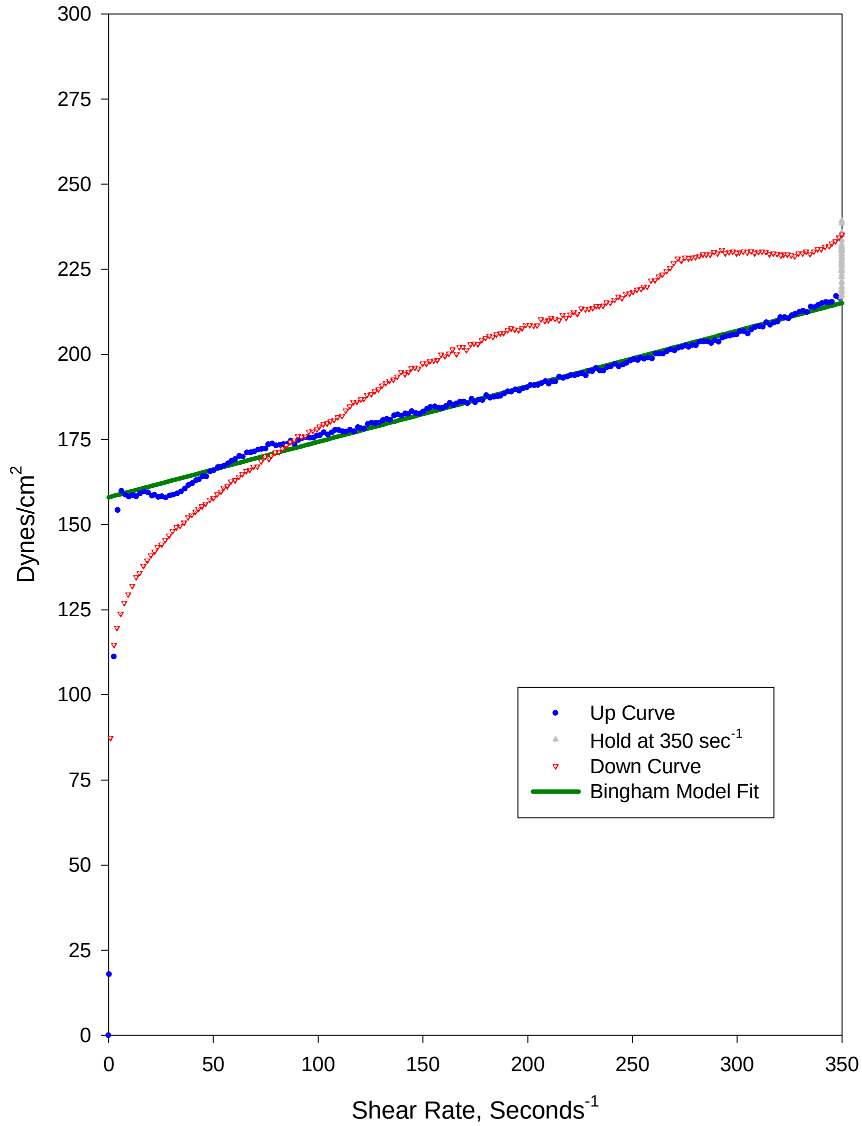


Figure A-8
Rheogram for 46 Wt.% Melter Feed
Hydragard Test with Size-reduced CST

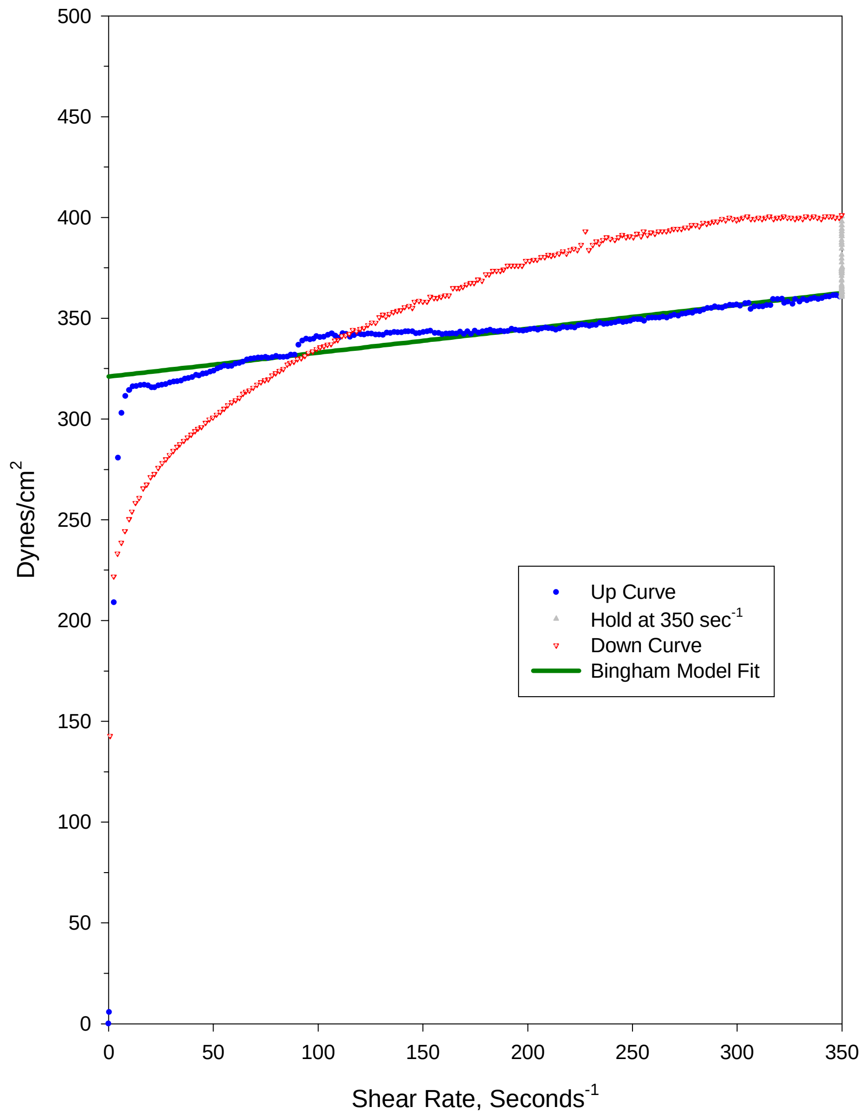


Figure A-9
Rheogram for 45.5 Wt.% Melter Feed
Hydragard Test with No CST

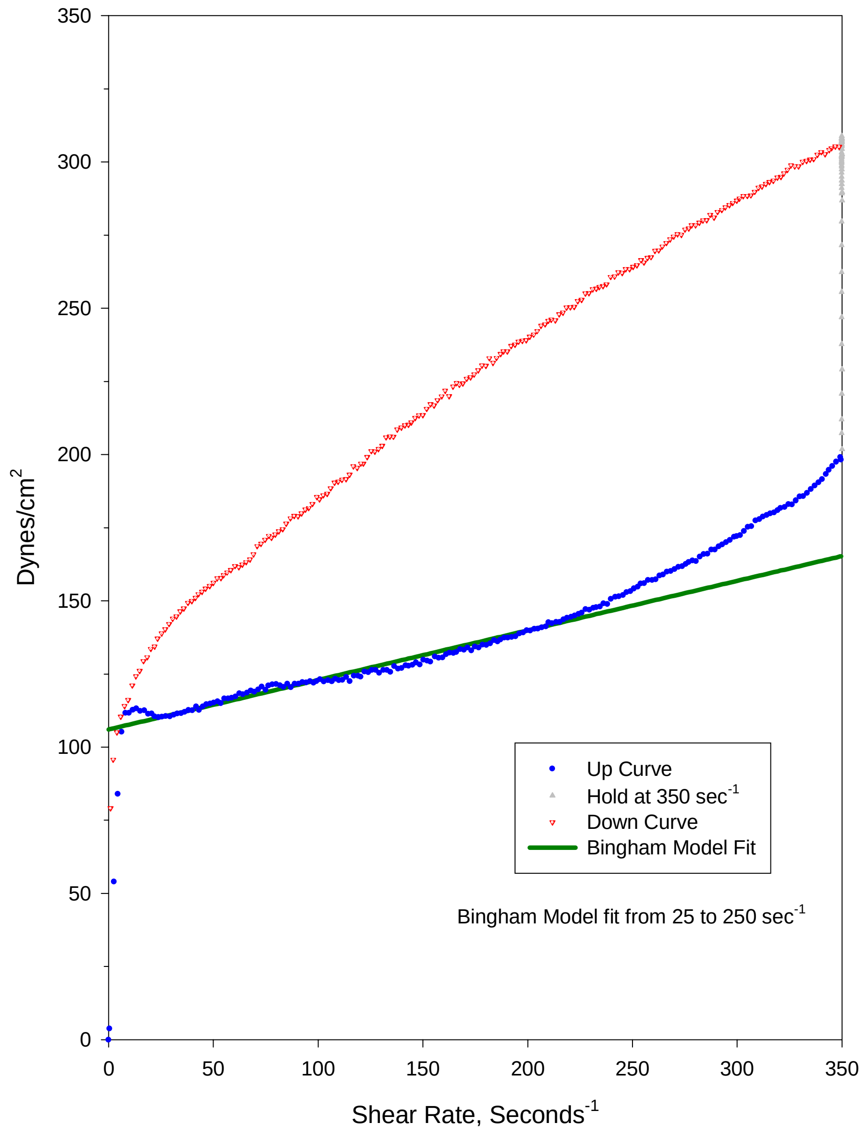
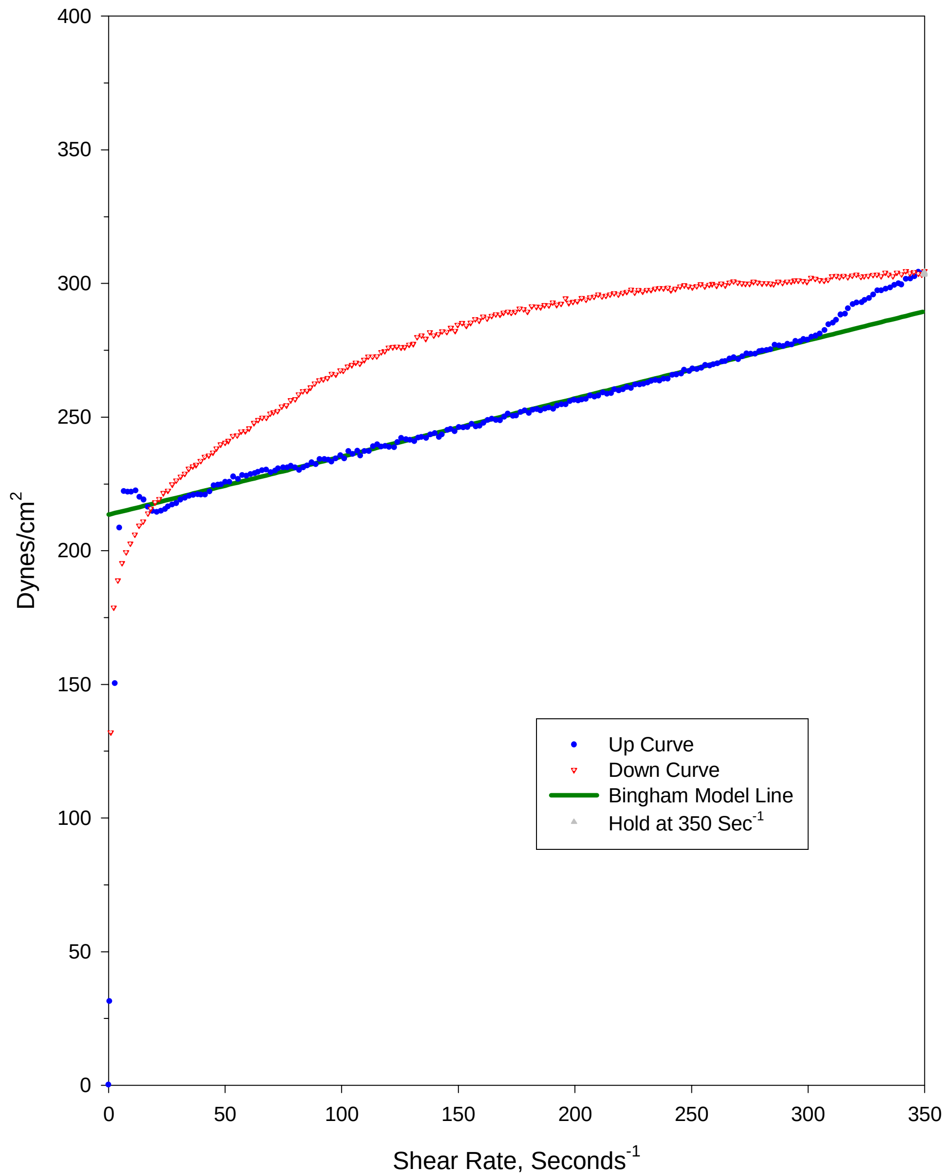


Figure A-10
Rheogram for 46 Wt.% Melter Feed with
Size-reduced CST (TNX Pretest Blend)



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