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Review of Rheology Models for Hanford Waste Blending

D. C. Koopman

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EXECUTIVE SUMMARY

The area of rheological property prediction was identified as a technology need in the Hanford Tank Waste – waste feed acceptance initiative area during a series of technical meetings among the national laboratories, Department of Energy-Office of River Protection, and Hanford site contractors. Meacham et al. delivered a technical report in June 2012, RPP-RPT-51652 "One System Evaluation of Waste Transferred to the Waste Treatment Plant" that included estimating of single shell tank waste Bingham plastic rheological model constants along with a discussion of the issues inherent in predicting the rheological properties of blended wastes. This report was selected as the basis for moving forward during the technical meetings. The report does not provide an equation for predicting rheological properties of blended waste slurries.

The attached technical report gives an independent review of the provided Hanford rheological data, Hanford rheological models for single tank wastes, and Hanford rheology after blending provided in the Meacham report. The attached report also compares Hanford to SRS waste rheology and discusses some SRS rheological model equations for single tank wastes, as well as discussing SRS experience with the blending of waste sludges with aqueous material, other waste sludges, and frit slurries.

Some observations of note:

Savannah River Site (SRS) waste samples from slurried tanks typically have yield stress >1 Pa at 10 wt.% undissolved solids (UDS), while core samples largely have little or no yield stress at 10 wt.% UDS. This could be due to how the waste has been processed, stored, retrieved, and sampled or simply in the differences in the speciation of the wastes..

The equations described in Meacham's report are not recommended for extrapolation to wt.% UDS beyond the available data for several reasons; weak technical basis, insufficient data, and large data scatter. When limited data are available, for example two to three points, the equations are not necessarily satisfactory (justified) for interpolations, due to the number of unknown variables equal the number of known data points, resulting in a coefficient of determination of one.

SRS has had some success predicting the rheology of waste blends for similar waste types using rheological properties of the individual wastes and empirical blending viscosity equations. Both the Kendall-Monroe and Olney-Carlson equations were used. High accuracy was not obtained, but predictions were reasonable compared to measured flow curves.

Blending SRS processed waste with frit slurry (much larger particles and the source of SRS glass formers) is a different sort of problem than that of two similar slurries of precipitated waste particles. A different approach to rheology prediction has had some success describing the incorporation of large frit particles into waste than the one used for blending two wastes. In this case, the Guth-Simha equation was used. If Hanford waste is found to have significant particles in the >100 µm diameter range, then it might be necessary to handle those particles differently from broadly distributed waste particles that are primarily <30 µm in diameter.

The following are recommendations for the Hanford tank farms:

- Investigate the impact of large-scale mixing operations on yield stress for one or more Hanford tanks to see if Hanford waste rheological properties change to become more like SRS waste during both tank retrieval and tank qualification operations.
- Determine rheological properties of mobilized waste slurries by direct measurement rather than by prediction

- Collect and characterize samples during the waste feed qualification process for each campaign.
    - From single source tanks that feed the qualification tanks
    - Blends from the qualification tanks
- Predictive rheological models must be used with caution, due to the lack of data to support such models and the utilization of the results that come from these models in making process decisions (e.g. the lack of actual operation experience). As experience is gained, the use of blending models that have been validated with real waste may become useful to predict future blends.
- Obtain more data measurements to check the validity of unknown coefficients for a given blending equation.

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LIST OF ACRONYMS

DWPF	Defense Waste Processing Facility
HM	H canyon Modified (Purex process)
PNNL	Pacific Northwest National Laboratory
SME	Slurry Mix Evaporator (process tank in DWPF)
SRAT	Sludge Receipt and Adjustment Tank (process tank in DWPF)
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
TTQAP	Task Technical and Quality Assurance Plan
UDS	Undissolved solids
WTP	Hanford Tank Waste Treatment and Immobilization Plant

LIST OF SYMBOLS

A-H	Rheological property model constants
f	Adjustable parameter for particle shape effects on viscosity
x	Mass fraction (of UDS or of slurries being blended)
x_{max}	Model-based maximum practical mass fraction of UDS
$\dot{\gamma}$	Shear rate
μ_{app}	Equivalent Newtonian fluid viscosity at a given shear rate
μ_m	Viscosity of mixture of fluid 1 and fluid 2
μ_B	Bingham plastic viscosity (consistency)
τ	Shear stress (a function of shear rate)
τ_y	Bingham plastic yield stress
ϕ	Volume fraction (of UDS)

1.0 Introduction

As a result of a series of technical meetings among the national laboratories, Department of Energy – Office of River Protection, and Hanford site contractors, a set of four initiative areas for to the Hanford Tank Waste program were identified for national laboratory evaluation. Subsequent discussions in the waste feed acceptance area identified the need for knowledge of rheological properties. Meacham et al. delivered a technical report in June 2012, RPP-RPT-51652 "One System Evaluation of Waste Transferred to the Waste Treatment Plant" that included estimating of single shell tank waste Bingham plastic rheological model constants along with a discussion of the issues inherent in predicting the rheological properties of blended wastes.[1] This report rightly concluded "it is difficult or impossible with the current data to draw deterministic conclusions on the effect of tank blending on rheology" (p. 161). Savannah River National Laboratory (SRNL) was requested to review the rheological content of this report and make recommendations for improvements based on past success with predictive models and known Savannah River Site (SRS) rheological properties. A Task Technical and Quality Assurance Plan (TTQAP) was issued to cover SRNL work on the four needs related to the waste feed acceptance initiative areas.[2]

The TTQAP calls for an evaluation of the Meacham Report rheology estimates as applicable to blend prediction to explain the poor performance of predictive tools and provide recommendations for potential improvements. The Executive Summary of RPP-RPT-51652 stated "No good predictive tool exists for estimating yield stress and viscosity in mixed/blended wastes." and "It is likely that the ranges of yield stress and viscosity for all feed batches will be greater than the data ranges presented in this document." Depending on the definition of "good predictive tool", SRS data is likely to confirm the validity of these two statements. SRS real waste data covers washed and unwashed sludges coming from the waste storage tanks, as well as some data for processed sludge after the Sludge Receipt and Adjustment Tank (SRAT) of the Defense Waste Processing Facility (DWPF) and for the combination of processed waste sludge with frit (i.e. glass formers) slurry to make the melter feed slurry for the DWPF glass melter.

This technical report is focused entirely on rheology, or item 2.c of the Task Deliverables in the TTQAP. The body of this report will cover the reported Hanford rheological data, Hanford models for single shell tank wastes, Hanford blending experience as discussed by Meacham, a comparison of Hanford to SRS wastes, discussion of some SRS models for single tank wastes, and a discussion of SRS experience with the blending of waste sludges with aqueous material, other waste sludges, and frit slurries.

2.0 Discussion

2.1 Rheological Behavior of Tank Wastes

The Meacham report discusses liquid waste viscosity data for Hanford tanks. A broad correlation was attempted to unify all viscosity data as a function of temperature and liquid density. The correlation assuming constant density (in other words, for a single liquid in the available data) did generally well at modeling the temperature dependence of viscosity. Single liquid modeling produced 24 separate two constant models covering temperature dependence. The constants from these models were fit to simple functions of liquid density. Unfortunately, as graphs of the constants versus liquid density showed, the constants were not well correlated to liquid density. Consequently, the broad correlation of all liquid waste viscosity data to a function of temperature and liquid density had a mediocre R^2 less than 0.8, nor was there any reason to expect much improvement in this model while it was constrained to depend solely on temperature and liquid density.

As Meacham indicated, liquid phase compositions would have been the preferred inputs to a general predictive viscosity model, not liquid density. This interpretation appears to be valid. Consequently, this portion of the report was given only a limited review. It was noted that Figure B-3 in Appendix B of RPP-RPT-51652 was either incorrectly titled, "Plot of Arrhenius Equation A Coefficients for the Various Tank-Liquid Density Combinations in Table B-1", or had an incorrect y-axis label "Intercept" (the pre-exponential constants, A, of the individual tank sample viscosity fits must be positive numbers (to give positive viscosities), while the graph contains negative numbers; it is speculated that these might be logarithms of the A's).

There is a limited amount of rheological data obtained from slurried core samples for fewer than twenty waste tanks at the Hanford site (see for example PNNL-16857 for a review[3]). Samples were sometimes analyzed directly as received, but it was more common that they were diluted with process water to obtain mobile slurries. Rheological studies were then performed at various wt. % undissolved solids (UDS) concentrations and temperatures. In a few instances a sample was also subjected to some simulated processing before measuring the rheological properties.

The Bingham plastic yield stress, τ_y, and Bingham viscosity, μ_B, were calculated from the measured Hanford sample flow curves. The two parameters were fit to a pair of model functions of the UDS (converted to a mass fraction, x) for a given tank sample.[1,3]

$$\tau_y = Ex^F \tag{1}$$

$$\mu_B = Ge^{Hx} \tag{2}$$

The four parameters, E, F, G, and H, are fitting constants. This pair of functions has desirable properties in the limit as UDS goes to zero in that τ_y goes to zero (as expected for a UDS-free salt solution) and μ_B goes to non-zero G (so G should be roughly in the 1-4 cP range for well fit data under the assumption that all Hanford wastes have an aqueous phase supernate containing some dissolved salts). These two equations, however, are empirical and their use for extrapolation is not recommended. In addition, their use for interpolation is limited if the original data are sparse (only two to three flow curves available to fit the model function parameters) or if the original data were highly scattered.

In the 1990's, SRS used the following equations to fit slurry yield stress and Bingham viscosity:

$$\tau_y = \frac{e^{Ax}}{1-(x/x_{max})} \tag{3}$$

$$\mu_B = \frac{e^{Bx}}{1-(x/x_{max})} \tag{4}$$

The A and B constants were empirical; while x_{max} represented the maximum mass fraction UDS that could be achieved before the slurry became a virtual solid. The two SRS parameter equations were usually fit independently resulting in two different values for x_{max} (often similar, but not identical). These equations were first presented in this form in a memorandum that subsequently became part of the preliminary melter feed rheology study technical report.[4] The equations "were selected by analogy" to a set that appeared in the technical literature in terms of volume fractions instead of mass fractions.[5] The term x_{max} was often near 0.4 for processed sludge and near 0.6 for melter feed (processed sludge plus glass frit; about 1/4 of the UDS in melter feed was sludge and 3/4 frit when these studies were done; on average, frit is typically at least an order of magnitude larger in particle diameter than sludge). These rheological studies were done over ranges of x that ended with a sample that was nearly impossible to mix or to transfer by pouring. Values of τ_y reaching the 25-130 Pa range were measured and reported. Under these conditions, however, the maximum practical x was always less than x_{max} from the model equation fit to the data, given the capabilities of the equipment at SRS.

The SRS equations approach infinite yield stress and Bingham viscosity as x goes to x_{max}. In the region of x_{max}, just a few hundredths of a change in x can cause orders of magnitude changes in the parameters. This has some semi-quantitative appeal; since this is presumably the region of settled solids compacted to varying degrees with interstitial supernate that is typically studied using vane rheometry. One interpretation is that any x above x_{max} implies the material exhibits solid-like behavior rather than liquid-like behavior. It is also known that most settled sludges (that have not dried out) contain significant liquid within the settled matrix, in other words that there is an x_{max} between zero and one.

SRS rheological data being fit typically were not near the Newtonian (zero yield stress) range of x values. These two equations give τ_y and μ_B equal to one as the mass fraction UDS goes to zero, and these are clearly not the correct asymptotic limits for small x. Potentially improved versions of these equations were considered but not implemented, for example [equations 5 through 7] :

$$\tau_y = \frac{e^{Ax} - 1}{1 - (x/x_{max})} \qquad [5]$$

or

$$\tau_y = \frac{e^{Ax}}{1 - (x/x_{max})} - 1 \qquad [6]$$

and

$$\mu_B = \frac{\mu_0 e^{Bx}}{1 - (x/x_{max})} \qquad [7]$$

where μ_0 in equation [7] is the supernate viscosity. It was also noted that the equation [3] performed better in the limit of small x when the units for yield stress were chosen that gave larger numbers, e.g. dynes/cm^2 instead of Pa, since 1 dyne/cm^2 is only one-tenth the size error of 1 Pa at x = 0, where the actual value of the yield stress at x = 0 is zero. The PNNL equation [1] and SRS equation [3] for yield stress could be combined to give:

$$\tau_y = \frac{Ex^F}{1 - (x/x_{max})} \qquad [8]$$

This equation appears to have reasonable behavior in the limits of both large and small x, but would require fitting three parameters instead of the two in either of the original equations. This would require more data before fitting the model.

In any case, the equations presented above for yield stress and Bingham viscosity are only semi-theoretical. They are still best used only to interpolate between available data. Extrapolation to higher values of x than measured in the original data using these equations is not recommended.

All of the equations have the potential to change rapidly with a small increase in x, and potentially not in the same way that the actual slurry would change.

Rheological results in PNNL-16857 were compared to the same results in RPP-RPT-51652. It was noted that the number of data points for a given tank increased in RPP-RPT-51652 versus PNNL-16857 for a number of tanks. Location (or range) of the UDS values (that gave the matching τ_y and μ_B values) for several tanks shifted significantly between the two reports, e.g. B-203, T-110, and T-203. Some values of yield stress appeared to have been adjusted between the two reports. For example τ_y at 0% UDS dropped from one in PNNL-16857 to zero in RPP-RPT-51652 (which probably corrected a minor error in the earlier report). A value from the data for C-104 (x=22% UDS, τ_y =21 Pa) was excluded from the fit in RPP-RPT-51652 and described as washed and run through the Cells Unit Filter (CUF). The earlier PNNL-16857 showed this point, but it was not the one point in the C-104 data set marked as having undergone additional processing prior to the rheology measurements. A zero yield stress result for BX-107 at 6.5% UDS in RPP-RPT-51652 was approximately 0.5 Pa in PNNL-16857. The two points for AZ-101 in Appendix B of PNNL-16857 did not appear to be consistent with the much more numerous data in RPP-RPT-51652. The above issues are flagged for further investigation (as necessary) as work continues in the waste feed acceptance area supporting the Hanford Tank Waste Treatment and Immobilization Plant (WTP).

There are also issues with the fitting of the yield stress and viscosity data to the UDS model equations, [1] and [2]. The most significant observation is that many of the fits have low coefficients of determination (low R^2). Generally if there are four or more data points, the G constant is physically reasonable. The Bingham viscosity fit for C-109 (two data points) of

$$\mu_B(Pa \cdot sec) = 0.0078e^{107.0491x} \tag{9}$$

which has an R^2 of one due to zero degrees of freedom, however, is likely no better than a straight line for interpolation between the two data points. This equation would be highly suspect if used for extrapolation. The above fit suggests that the viscosity of the supernate (diluted with water) is 0.0078 cP (a reasonable viscosity for a gas, not a salt solution). This equation could be refit to the two data points forcing the leading constant to be one (as a first approximation to the supernate viscosity, or some other predicted value for the aqueous phase viscosity) and likely yield a better match to reality. T-102 (90 ºC) was a lesser example of this same issue.

Data for SY-101 (Meacham, p. 132) show flow curve fits giving a Bingham viscosity as high as 44 cP at 2 wt.% UDS (yield stress less than 1 Pa), and five of the six models (six temperatures) have Bingham viscosity leading constants (G's) over 10 cP. This is very unusual behavior compared to SRS wastes (which would have low viscosities under these conditions). Without seeing the original flow curve data, it is pointless to speculate on what might be happening in this system. This material is salt cake slurry which might dissolve in any event during retrieval operations.

The available Hanford data were used to prepare a table of predicted rheological properties at 10 wt.% UDS (Table 6-4 in RPP-RPT-51652). Out of 35 predictions for yield stress, twenty were <0.1 Pa and only nine were ≥ 1 Pa. Some comparable values from SRS sludges are provided in Table 2-1 for comparison to the Hanford predictions at 10 wt.% UDS. The SRS tank samples are from slurried tanks (using jet mixers) during early stages of sludge batch preparation. Sludge batch samples are also from slurried tanks but are typically obtained at or near the end of sludge batch preparation.

Table 2-1. Selected SRS Sludge Rheology at ~10% UDS

Tank/Batch	Wt.% UDS	Bingham Yield Stress Pa	Bingham viscosity cP
Tank 8	10.5	1.9	4
Tank 15	8.8	7.3	7
Sludge Batch 1A	~11	1.1	Not reported
Sludge Batch 2	15.5	12	11
Sludge Batch 3 (Purex)	9.9	0.8	2.4
Sludge Batch 4-unwashed	6.4	2.9	7
Sludge Batch 5 (SC-8 run)	11	5.2	7
2008 Tank 12	10	45	Not reported

References (top to bottom): 6 (first two), 7, 8, 9, 10, 11, and 12

The 2008 Tank 12 sample was after aluminum dissolution (which had a very significant impact on the yield stress). The Tank 8 and 15 samples were obtained in the 1980’s. The early sludge batches (1A, 2) were in the 1990’s. The later ones are from 2000-2010. Sludge batches include both types of SRS waste (Purex waste and HM, or “high aluminum”, waste). All of the sludge batch samples and the Tank 12 sample were taken after the tank contents had been mixed using a set of slurry mixer pumps (submerged centrifugal pump jets that rotate through 360º at adjustable depths and rotational speeds). The DWPF is designed to receive washed slurries with yield stress values in the 1-10 Pa range (basis for the mixing design of the Sludge Receipt and Adjustment Tank).

Yield stress tends to be more important to the fluid dynamics in the mixing and pumping applications of interest at SRS, i.e. applications with moderate shear rates, while the Bingham viscosity tends to have only a mild modifying impact on the apparent viscosity at a given shear rate. The apparent viscosity for a Bingham plastic fluid is given by:

$$\mu_{app} = \frac{\tau}{\dot{\gamma}} = \frac{\tau_y + \mu_B \dot{\gamma}}{\dot{\gamma}} \qquad [10]$$

For a 5 Pa, 5 cP Bingham plastic at a shear rate of 100 $\sec^{-1}$, the apparent viscosity is 55 cP of which the contribution from the yield stress is 50 cP while the contribution from the Bingham viscosity is 5 cP. At extremely large shear rates, the apparent viscosity approaches the Bingham viscosity, while at extremely low shear rates, the apparent viscosity approaches infinity (the low shear rate limit, however, is considered a weak point of the Bingham plastic model, although the model yield stress tends to bound the actual behavior).

2.2 Rheological Behavior of Waste Blends

2.2.1 *Blending Waste Slurries with Liquids*

RPP-RPT-51652 summarizes existing data on the impact of wt.% UDS on rheological properties. This is actually one type of blend model for rheological properties, the blend being between the waste slurry at some initial wt.% UDS and the diluent added (or removed) to change wt.% UDS. Modeling of this phenomenon was discussed in Section 2.1. Some SRS actual waste data are given below.

The first studies at SRS related to blending were for different blends of the same sludge at different wt.% UDS rather than for blends of two different slurries. Data from the original report[6] on rheological characterization of three SRS tank wastes have been updated to incorporate additional measurements made between 1984 and Sludge Batch 6 (c. 2010), Figure 1. Some blend dilutions were made with water and some with supernatant liquid.

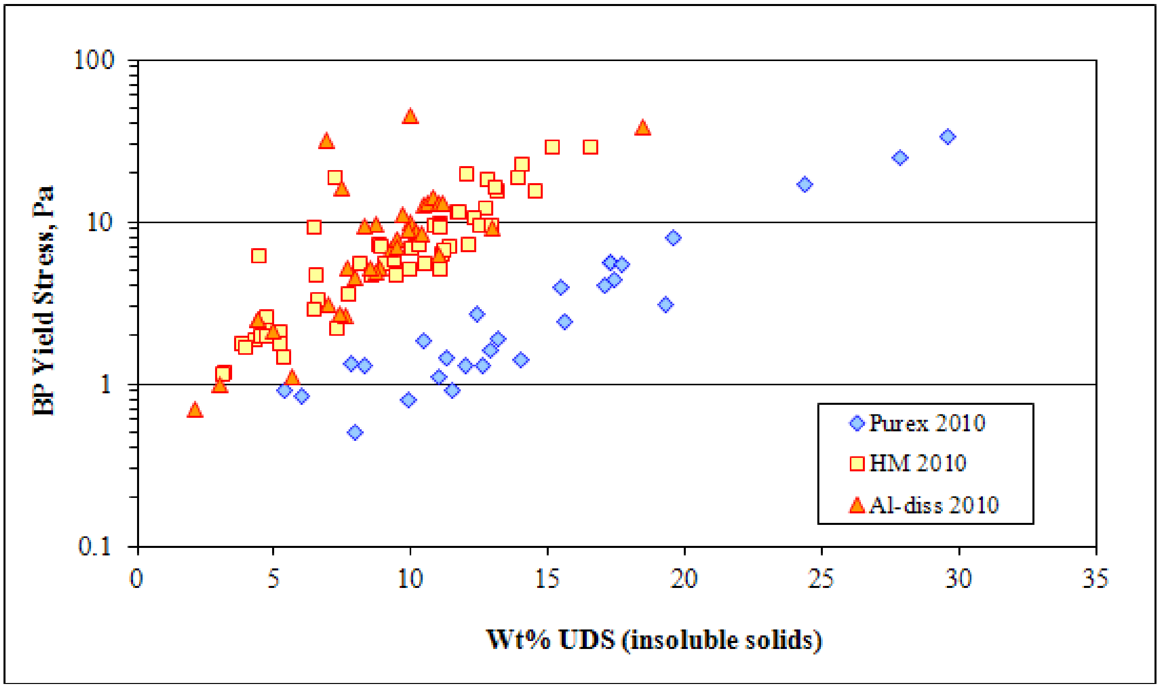

Figure 1. Yield stress of SRS Purex and HM sludges

In rough terms, SRS data show that HM solids (high Al) are about twice as significant in increasing yield stress as Purex solids (high Fe), Figure 1, on a mass basis. For example, if a 5 Pa yield stress is obtained at 7 wt.% UDS with HM waste, it might take 14 wt.% UDS Purex waste to get the same yield stress. This has been speculated to be related to the lower intrinsic density of HM solids relative to Purex solids, or, in other words, the volume fractions of UDS are more similar for HM and Purex wastes than the mass fractions. Literature models have often chosen to use volume fraction over weight fraction, . The use of volume fraction describes solids to solids interactions and the interactions of the solids with the liquid. In these models, other forces, such as electrostatic are typically not considered or specifically modeled. Equation [11] shows the relationship between solid volume fraction ($\emptyset_S$), solids mass fraction (X_S), liquid density (ρ_L), and average solids density (ρ_S). The primary issue with this equation is the determination of the average solids density of actual waste, which can lead to large errors in predicting the volume fraction. Correcting the mass fraction for volume fraction (note, $\rho_S > \rho_L$) will always result in compressing the data along the x-axis, resulting in a curve fit that has more curvature as compared to the mass fraction fit. The issues associated with converting easily measurable mass fractions into calculated volume fractions for SRS slurries does little but add another level of uncertainty to the model using volumetric solids fraction. In reality, the use of mass fraction to understand the behavior of rheological properties has been used extensively throughout SRS and HNF reports and has been used by SRS tank farm operations to assess the fluid properties for operating conditions.

$$\emptyset_S = \frac{\frac{X_S}{\rho_S}}{\frac{X_S}{\rho_S}+\frac{1-X_S}{\rho_L}}) \qquad [11]$$

.

The contrast between the Hanford core samples and SRS rheological data is striking with respect to slurry yield stress by the Bingham plastic model fits. SRS slurried tanks almost never fall below 1 Pa at 10 wt.% UDS or above. The use of core samples at HTF in obtaining physical and chemical properties for a specific vessel in the HTF raises questions on what the analysis of these samples mean with respect to the overall composition of the waste tank, given the large variability of the composition within a waste tank. At SRS, slurries are mobilized (sheared) using slurry mixer pumps in tank retrieval activities, where the blended sludge in the tank is mixed with a much larger volume of material within the tank and samples are pulled from this region where active mixing is observed,. Based on what has been observed (rheological properties versus wt% solids) at SRS, assuming that these rheological measured values will be maintained during waste mobilization at Hanford would not seem prudent.

SRS long-term settled waste may possess some inter-particle bridging or other weak structure created by atomic scale processes such as Ostwald ripening which tie up a significant fraction of the sub-micron particles (which have been seen to contribute the most to yield stress) with larger particles. Such hypothetical SRS waste structure may be mostly destroyed during the SRS tank mobilization process, which involves a series of lowerings of the slurry mixer pumps to greater and greater depths over an extended period of time (days). The sludge particles in the tank pass through the centrifugal impeller chamber many times during mobilization giving the particles many opportunities to shed weakly held smaller particles.

Trending of the two primary types of SRS waste sludges is generally observed indicating a major role for wt.% UDS on yield stress. Aluminum dissolution is carried out on HM sludges, and results for sludges post-Al dissolution still generally fall near the bulk of the HM data. Crude predictability of yield stress is likely possible simply by correctly identifying the waste type when results accurate to within a factor of 2-3 are acceptable.

Data in Figure 1 have been used with more success, however, to predict a yield stress at a new wt.% UDS using a single measured rheological data point for the same waste system (specifically, using the best fit slope from Figure 1 to move up or down in wt.% UDS from the measured yield stress value to a new yield stress value; Purex and HM wastes have different slopes). This approach was done most recently for Sludge Batch 8 and came within about 2% of the subsequently measured value.[13] (The predicted value was sufficient to decide to make a certain decant of supernate, and a post-decant sample was pulled to confirm that the system was still within the prescribed range for transfer.)

By comparison, plots of accumulated historical melter feed rheology (sludge plus frit) show almost no trends. Figure 2 shows data for melter feeds (Slurry Mix Evaporator (SME) products) for HM based sludge batches and blend (Purex-HM blend) based sludge batches. No data were at hand for a Purex only melter feed. When a series of measurements are made on one melter feed over a range of wt.% UDS there is a strong correlation.

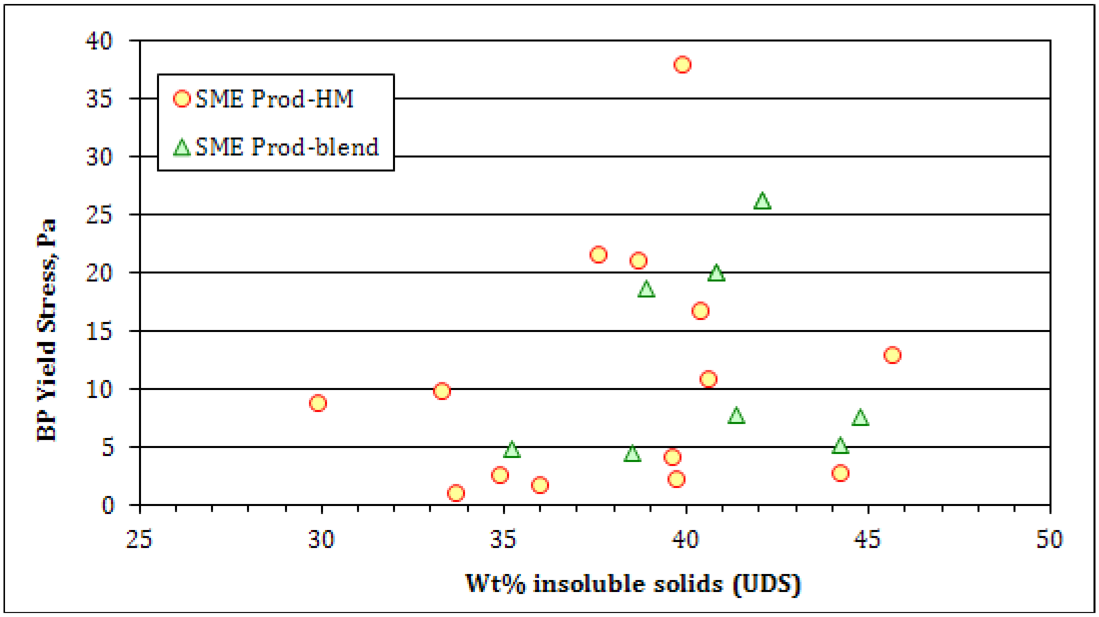

Figure 2. Melter feed rheology based on Shielded Cells measurements

Neither HM nor blend yield stress show a strongly correlated trend with wt.% UDS. One likely explanation for the scatter in melter feed yield stress data compared to sludge data is that processing changes have been made over the life cycle of the Defense Waste Processing Facility, and in particular, the sludge waste fraction of the melter feed has increased over time from about 28% on a waste oxide in glass basis to about 36%. Another potential source for the scatter in Figure 2 is the preparation chemistry (pH has been shown to be statistically significant in some simulant studies of melter feed rheology in explaining differences observed from a series of tests with somewhat different processing chemistry, all starting with the same simulant waste[14]).

As discussed below, it appears that wt.% UDS from frit are not comparable to wt.% UDS from sludge waste particles. Sludge waste particles are much finer than frit particles. While WTP engineers have been concerned about larger waste particles (in the frit size range) from the standpoint of suspension in pulse jet mixed tanks, it is also likely that different blending models may be required to understand the effects of larger particles and how they differ from the finer particles to understand the rheological behavior of Hanford waste slurries.

2.2.2 *Blending Together Two Waste Slurries*

RPP-RPT-51652 discusses rheological (and related) data for three blends of Hanford wastes: a Group 1/Group 2 blend, a Group 3/Group 4 blend, and a Group 5/Group 6 blend. The Group 1/Group 2 blend contains bismuth phosphate sludge and bismuth phosphate saltcake.[15] The Group 3/Group 4 blend contains Purex cladding sludge and REDOX cladding sludge.[16] The Group 5/Group 6 blend contains REDOX sludge and S-saltcake wastes.[17]

When two different waste slurries are blended together, the rheological properties change along with the other physical and chemical properties (density, wt.% UDS, chemical composition,…). Properties such as chemical composition change linearly in proportion to the masses of the slurries being combined. Other properties, however, do not have a linear dependence on the proportions of the slurries being blended. The prediction of the rheological properties of a blend of two systems is complicated by various factors.

Limited work at SRNL has suggested that slurry blending falls into at least two categories. The rheological behavior of a blend of two sludges appears to be different from the behavior of a processed sludge slurry blended with a frit slurry. There has been some degree of success in modeling sludge blend rheology using the flow curves of the two individual sludges and the relative mass fractions of the slurries making up the blend. Testing has used both the Kendall-Monroe equation and the Olney-Carlson equation. Both equations were developed for miscible liquid blends and are in terms of the Newtonian viscosities of the two starting liquids and that of the blend. Application assumes that there are no strong interactions between the species being blended (including dissolution).

The Kendall-Monroe equation is given by[18]

$$\mu_m^{1/3} = x_1\mu_1^{1/3} + x_2\mu_2^{1/3} \qquad [12]$$

And the Olney-Carlson equation is given by[19]

$$\mu_m = (\mu_1)^{x_1}(\mu_2)^{x_2} \qquad [13]$$

Where subscript m is for the blend, and subscripts 1 and 2 are for the two liquids being blended. The references for the two equations are partly transcribed from the 5th edition of the Chemical Engineers' Handbook (Perry and Chilton, 1973). SRNL used the x_i as mass fractions of slurry 1 and slurry 2 in the blend. The original work was on a volumetric basis. The use of mass fraction of the blended slurries is consistent in how previous physical data has been presented and utilized, such as those described in equations [5], [6], and [7]. There was no effort by SRNL in relating the mass fraction to a volume fraction basis when utilizing any of the equations in this report. SRNL has not pursued any effort in determining if volume fraction basis would have yielded better results as compared to a mass fraction basis.

To apply either of these equations to non-Newtonian slurries, it was necessary to eliminate the Newtonian viscosity. The assumption was made that the apparent Newtonian viscosity, μ_{app}, at a given shear rate, $\dot{\gamma}$, could be substituted into either equation (one apparent Newtonian viscosity for each of the two slurries being blended taken at the same shear rate from the flow curves) to calculate the apparent Newtonian viscosity of the blend at that shear rate.

For example, if one had two flow curves from 0 to 300 sec^{-1} shear rate with data every inverse second (301 data points per flow curve), then the above equations would be used 301 times (once at each shear rate) to generate a flow curve for the blend based on the specified (x_1, x_2). The resulting synthetic flow curve for the blend would then be fit to the Bingham plastic model to give the predicted yield stress and Bingham plastic viscosity of the blended slurry.

The procedure just described has been applied at least once to real waste slurries at SRNL. Rheological data was obtained on Sludge Batch 2 (SB2) slurry, Sludge Batch 3 (SB3) slurry before blending into SB2, and the SB2-SB3 blend (SB2/3). The mass fractions of SB2 and SB3 were 0.41 and 0.59 respectively.[20]

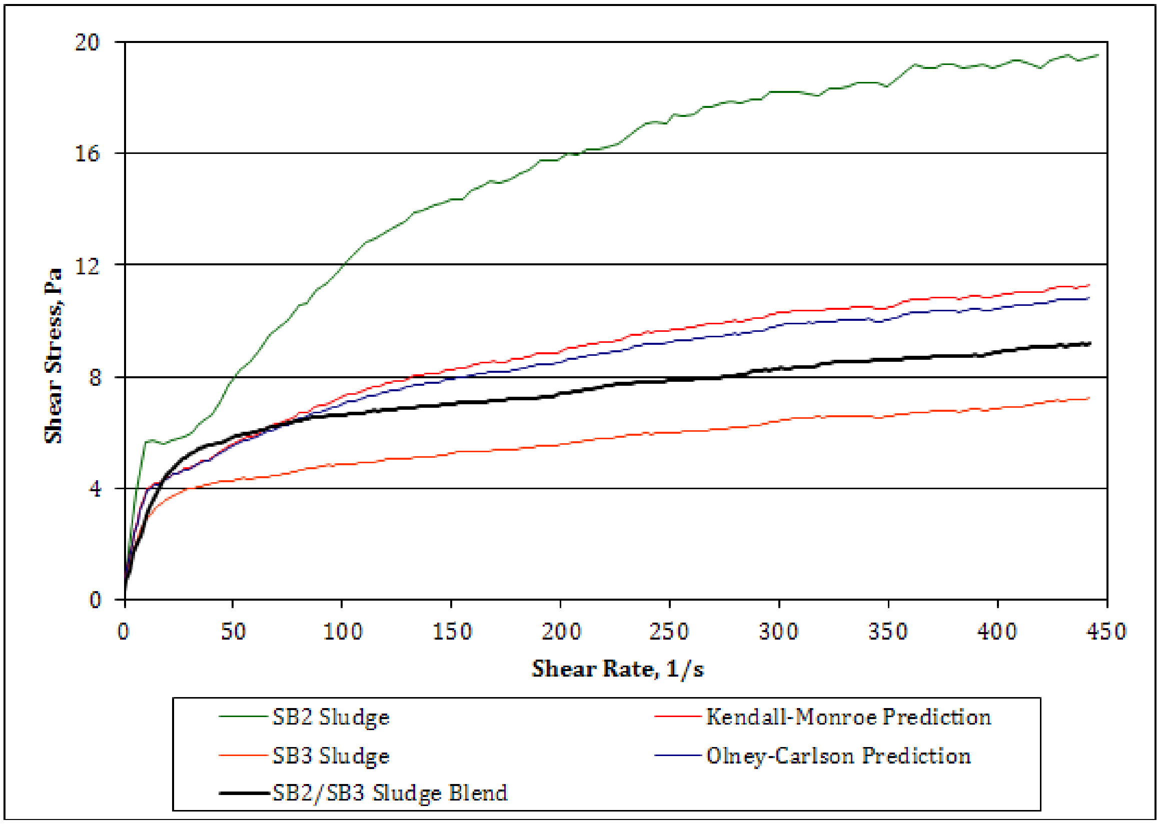

Figure 3. Prediction of SB2/3 Sludge Rheology

The results of the two flow curve predictions were fair, matching fairly well from 0-100 sec^{-1} shear rate, and then diverging as shear rate increased. The predicted shear rates were within 25% of the measured values as the shear rates increased above shear rates of 100 sec^{-1}. The predicted rheological properties were perhaps acceptable for the applications that would utilize the rheometric data. An example would be the prediction for the feasibility of transferring the blend with the existing equipment (pumps and transfer lines). We have not yet attempted to use the Kendall-Monroe or Olney-Carlson equations to predict a flow curve for a rheologically known slurry blended with a known liquid (slurry dilution), although such tests might be worth pursuing for cases where UDS dissolution is unlikely or minimal.

As a random trial, the reported Group 5/Group 6 blend was synthesized in two steps using the Kendall-Monroe equation and data in RPP-RPT-51652 and PNNL-17965. In step one, mass fraction 0..623 Group 5 was blended with 0.377 Group 6 to form an undiluted blend at about 17.1 wt. % UDS. In step two, mass fraction 0.774 undiluted blend was blended with liquid of viscosity 1.5 cP (chosen arbitrarily) with mass fraction 0.226 to form 13.2 wt.% UDS slurry. The resulting flow curve was compared to the reported result for the Group 5/Group 6 blend, Figure 4. All of the flow curves are "synthetic", meaning that they are merely graphical representations of the Bingham plastic model fits and/or Kendall-Monroe models rather than using the raw rheological data. The diluting liquid viscosity for step two is not shown in Figure 4 to reduce clutter (it would lie just off the x-axis).

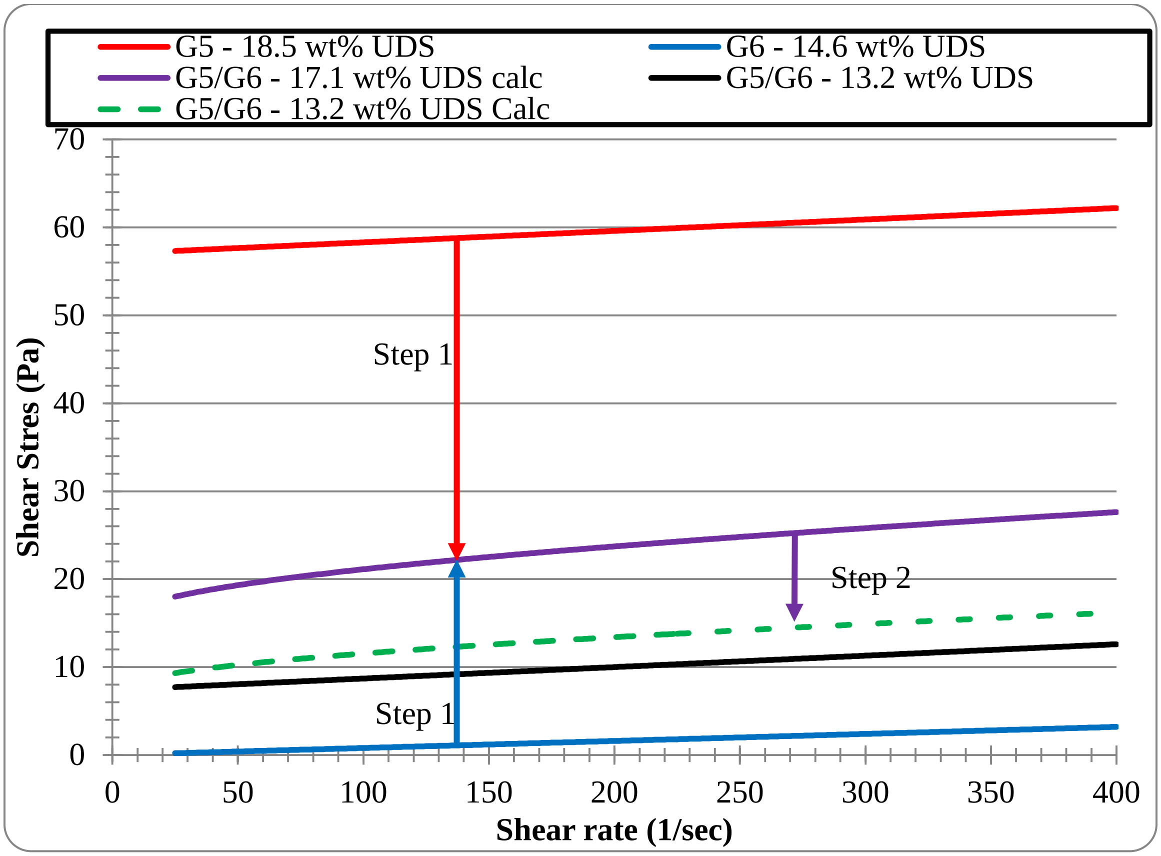

Figure 4. Synthesis of the Group 5/Group 6 flow curve

This is a fairly challenging application of Kendall-Monroe, since Group 5 had yield stress 57 Pa, while Group 6 was Newtonian at 8 cP, and these are two extremely different fluids rheologically. A sweeping assumption was made that the addition of water (or supernate) as well as the combination of the two original wastes did not change any of the UDS into dissolved solids (or form new UDS). In spite of these assumptions, the agreement between the predicted and reported blend flow curves, though not outstanding, appeared to give a plausible ballpark estimate of the final blend flow curve. Numerically the predicted shear stress values are about 20-30% higher than those corresponding to the Bingham plastic fit of the measured flow curve. This equates to a difference of about 1.6-3.6 Pa on a problem spanning over 60 Pa in fluid shear response behavior.

Furthermore, modeling error was able to compound in this numerical experiment, since the Kendall-Monroe equation had to be applied twice to make the 5/6 blend (modeling error 1) and then to dilute it to the reported wt.% UDS (modeling error 2). Someone with a better understanding of the 5/6 blend preparation and chemistry might make some different assumptions, and end up with a fairly different result. Part of the intention was to illustrate how an attempt to make such a prediction could be done (show the thought process). The assumption that there was no interaction between the REDOX sludge and S-saltcake wastes may also have been a poor one.

Choices need to be made if knowing blend rheology is critical to Hanford WTP or Tank Farm operation. It would be easier to pull samples from two slurried tanks, blend them in the lab, and then measure the rheology directly, than to try and deal with particle size distribution effects, particle zeta potentials (in a multi-component system), supernate viscosity, dielectric constants, inverse Debye lengths, and mean particle separations (none of which are known *a priori* for

Hanford tank wastes) that might only feed a model equation (Scales/Zhou) that is accurate to an order of magnitude or to a factor of two for complex systems like Hanford tank waste. It certainly seems like direct measurement would be the more robust approach, and this is the approach taken at SRS.

2.2.3 *Blending Processed Waste and Frit Slurries*

Frit slurry-sludge slurry blends appeared to follow different behavior from sludge-sludge slurry blends.[21] See also Figure 2 above. The research in this area has been limited by the fact that most of the pre-frit addition slurries are at lower sludge UDS contents than the concentrated melter feed with added frit (on a frit-free basis). Nevertheless, two investigations were performed using simulated melter feeds. One looked at predicting melter feed rheology from processed sludge rheology. The second looked at the variability due to normal frit (irregular shards) versus beaded frit (nearly spherical).

These studies used the equation below (ϕ is volume fraction of frit, f is a factor to correct for non-spherical particles), authored by Guth-Simha[22]:

$$\mu_{melter\ feed} = \mu_{processed\ sludge} * (1 + 2.5 * f * \phi + 10 * \phi^2) \qquad [14]$$

The coefficient of 10 on ϕ^2 is semi-empirical, and other coefficients have been proposed in the literature[22], but were not studied at SRS. Models with higher order terms have also been proposed. It was found that a value of f = 1.8 brought most of the melter feed flow curve into agreement with a prediction from the processed sludge (only a single case was found where the processed sludge rheology had been measured at a high enough wt.% UDS to correspond to melter feed wt.% UDS on a frit-free basis).

As in the case of sludge blending, the above equation was applied to each point on the flow curve for the processed sludge to convert the apparent viscosity of the sludge to the apparent viscosity of the melter feed. The apparent viscosity of the melter feed was then multiplied by the shear rate to give the shear stress. The frit volume fraction of the melter feed was not trivial at 11%. Sludge particles were generally less than 35 µm in size, while frit was primarily in the 75-300 µm range (not much > 177 µm, about 50 times larger on average than sludge particles).

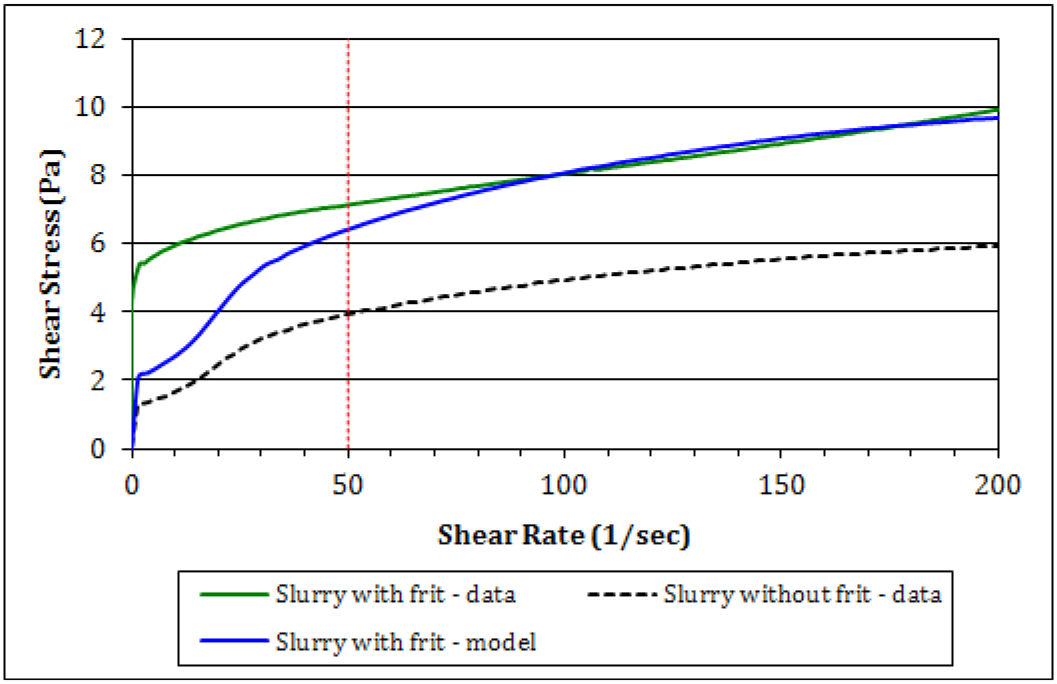

Figure 5. Impact of frit on processed sludge

The flow curve of the processed sludge was a bit unusual in the range of 1-30 sec^{-1} shear rate, and this behavior was translated to the model prediction. Fitting a Bingham plastic model on the range of 50-200 sec^{-1} shear rate gave a slightly lower result than the measured flow curve for the melter feed.

The effect of frit shape was examined in an unrelated experimental program.[21] The hypothesis was made that a common intrinsic flow curve for processed sludge should be derivable from the flow curves for melter feeds with either shard frit or beaded frit. The factor f would need to be determined after the fact for the shard frit. In this case it was assumed that f for a spherical bead, i.e. beaded frit, was one. This is the literature value of f for spheres in suspension. A reasonable match of predicted flow curves for processed sludge was obtained with f=2 for the shard frit (vs. f=1.8 above in an independent study).

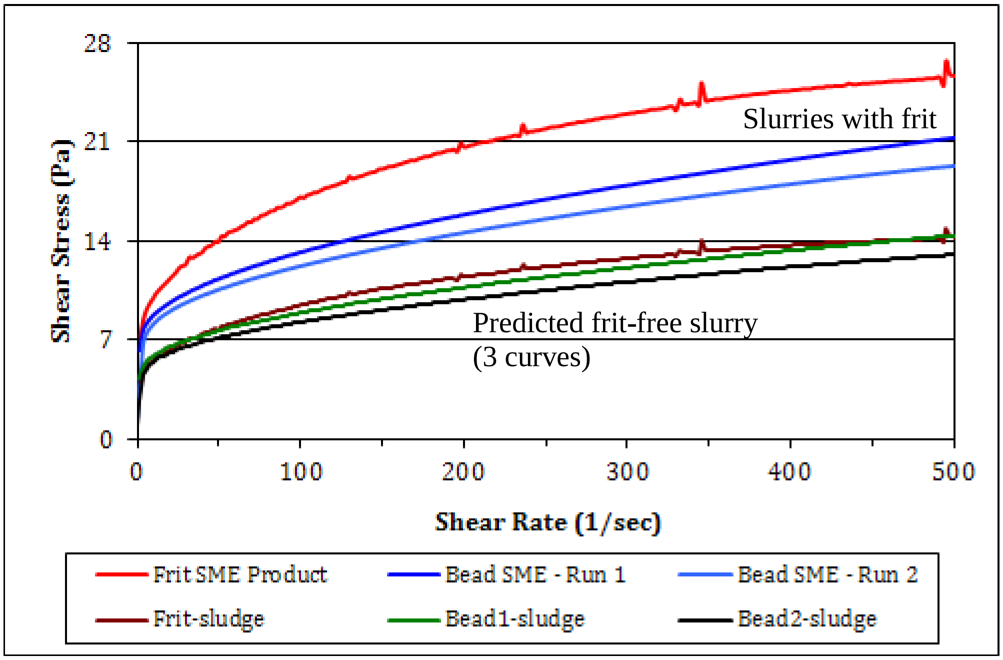

Figure 6. Common frit-free basis for shard vs. beaded frit

The selected value of f=2 put the flow curve derived from the shard frit melter feed (green curve derived from red curve) between the two curves derived from replicate measurements of the bead frit melter feed with f=1 (brown, black curves derived from blue, light blue curves respectively). Unfortunately there was no actual processed sludge flow curve at the wt.% UDS corresponding to the two melter feeds on a frit-free basis for comparison/confirmation.

Inherent in the rheology studies of blends made to date at SRS is that different sized particles have different impacts on blend rheology. Small particle size slurries act like pseudo-homogeneous non-Newtonian liquids, while large particle size slurries act like heterogeneous suspensions with a modified viscosity dependent on volume fraction. There is likely a transition region somewhere in between that has not been studied at SRS. Blend rheology prediction at SRNL is still, essentially, in its infancy. One of the major reasons for this is that it tends to be easier to make the measurement than to make a prediction with a poorly understood uncertainty.

Another factor at SRS that has kept emphasis on direct rheological measurement of samples rather than on prediction is that there have been instances where samples from full-scale processing have been characterized and found to be significantly different from those produced during lab-scale processing. For example, the DWPF was having problems with line plugging in the Sludge Batch 5 (SB5) melter feed system. The plant concluded that the melter feed was too viscous, but the problem turned out to be over-dilution (insufficient viscosity). Yield stress measured from a plant sample was on the order of 2-4 Pa at 48 wt.% total solids, while the melter feed that had been produced by lab-scale processing demonstrations with the same sludge was 38 Pa. (The plant was actually running even more dilute, and their sample had to be concentrated to compare it to the lab-scale result.) The design basis for DWPF melter feed is a Bingham yield stress in the 2.5-15 Pa range to keep frit suspended, and this would indicate that DWPF was actually operating at or below the lower limit. While there were a number of mitigating factors, processing differences, chemistry, etc. in the rheological comparison between the two samples, the bottom line was that lab-scale processing cannot be assumed to mimic full-scale processing in every respect. The focus at SRNL has been to mimic the critical processing chemistry in lab-scale studies (nitrite destruction, Mn reduction, Hg reduction and stripping, catalytic hydrogen generation, etc.). Rheological properties are studied to obtain benchmarks and to understand how the properties change with changing wt.% UDS.

3.0 Conclusions

RPP-RPT-51652 was reviewed to evaluate its rheological modeling content. There was no specific sludge blending model provided in this report. While reviewing this report, it appears that some of the Hanford rheological property-wt.% UDS data had shifted on the UDS axis between PNNL-16857 and RPP-RPT-51652. The data need to be reconciled. A more in-depth review of the rheological data may be warranted due to these conflicts. The review may need to consider how the samples were managed.

The empirical models (Equations [1] and [2]) chosen for Bingham yield stress and viscosity for Hanford waste work well at low wt.% UDS, but they could have fit issues at higher wt.% UDS. The equations are not recommended for extrapolation to wt.% UDS beyond available data for several reasons (weak technical basis, insufficient data, unreasonable results, and data scatter). When limited data are available, the equations are not necessarily satisfactory (justified) for interpolations. Equations [7] and [8] are recommended for fitting the Bingham Plastic rheological parameters as function of UDS concentration. These equations have three parameters, hence at least four data points of actual samples are recommended when fitting these equations.
SRS has had some success predicting the rheology of waste blends for similar waste types using rheological properties of the individual wastes and an empirical blend viscosity equation. High accuracy was not obtained, but predictions were reasonable compared to measured flow curves. Given the limited amount of data analyzed, including the HTF data in this report, the use of equation [12] seems to over-predict the rheology of blended sludges. The relative percent differences can be as high as 30%, given the assessed data.

SRS processed waste blended with frit (much larger in size) is a different sort of blending problem than that of two similar slurries of precipitated waste particles. A different approach to rheology prediction has had some success describing the incorporation of large frit particles into waste than the one used for blending two wastes. If Hanford waste is found to have a significant mass fraction of particles in the >100 μm diameter range, then it might be necessary to handle those particles differently from broadly distributed waste particles that are primarily <30 μm in diameter. This mass faction will depend on the waste stream and its composition (size, shape, morphology) of the UDS. Given the efforts required to make this assessment using actual waste may not be beneficial in the long run, since it would be sensitive to each waste stream.

SRS waste samples from slurried tanks typically have yield stress >1 Pa at 10 wt.% UDS, while Hanford core samples largely have little or no yield stress at 10 wt.% UDS. It would be worthwhile investigating the impact of large-scale mixing operations on yield stress for one or more Hanford tanks to see if Hanford waste rheological properties change to become more like SRS waste under retrieval and transfer conditions.

It is recommended that actual measurements be made of slurried tank samples and tank blends rather than pursuing rheological property modeling. This is the approach currently adopted at SRS. Rheological property modeling contains too many parameters with unknown uncertainties with respect to the model predictions. Once a general data base has been developed for each waste type, it may be possible to identify common features in the rheological data that can be exploited to reduce the number of samples that need to be measured by the rheometer. This data base at a minimum would require rheological and UDS mass fractions at multiple UDS mass fractions, and density of the liquid and average density of the UDS. This would be for both single and batched slurries. Other factors that may have to be characterized are the chemical composition of the solids and liquids. Given the blending models to be tested, the list of measurements (particle size distribution, morphology of the solids, zeta potential, etc.) could expand. Such efforts could be costly and provide no benefit; hence sampling and blending actual waste could be the most cost effectives and direct method in obtaining useful process data.

Liquid phase rheology predictions may be possible using compositional information instead of density. Such a database could largely be developed initially with non-radioactive simulant systems (to determine relative impacts of hydroxide, nitrite, nitrate, carbonate, and other soluble salts.). Again, though, it might be ultimately more practical to just take a radioactive liquid and run a flow curve measurement on it, since that is simpler than determining all of the necessary analytical information to feed a model, and since effects from trace dissolved metals could be problematic to prediction models.

The inconsistencies in the physical properties in waste characterization and waste summary reports on the same waste stream add further confusion into what are the properties of the waste. The rheological data needs to be reconciled taking into account the collection and handling of corresponding samples.

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