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Revision 0

A COMPARISON OF RHEOLOGY DATA FOR RADIOACTIVE AND SIMULANT SAVANNAH RIVER SITE WASTE (U)

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March 2004

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EXECUTIVE SUMMARY

The purpose of this study was to review historical rheology data for radioactive Savannah River Site (SRS) wastes from storage tanks through to the melter feeds in the Defense Waste Processing (DWPF) facility. SRS wastes were generated from either the Purex (high iron) or HM (high aluminum) processes. The available rheological data for SRS wastes were then compared to any historical simulant data for equivalent SRS wastes.

The comparisons were accomplished by initially obtaining all available radioactive rheology data for sludge, Sludge Receipt and Adjustment Tank (SRAT) product, and Slurry Mix Evaporator (SME) tank product (equivalent to DWPF melter feed). These data were grouped as sludges, SRAT products, or SME products. The data within each group were then sub-divided to reflect individual waste tanks or DWPF sludge batches, e.g. Tank 8 sludge or Sludge Batch 1B SRAT product.

The comparability of a simulant and a radioactive waste was assessed primarily by the value of the Bingham Plastic model yield stress at equivalent weight % insoluble solids content. Values within 20-30% were considered to be giving “good agreement”. Values different by a factor of two or more were considered to be giving “poor agreement”. Intermediate cases were rated as “fair agreement”.

Rheological data for Purex sludges indicated good to fair agreement between real and simulant waste. The presence of HM sludge mixed with Purex sludge gave fair to poor agreement. Similar results were seen for SME products. There is insufficient SRAT product data to make a comparable conclusion.

The differences between Tank 8 and Tank 40 sludges used to prepare Sludge Batch 2 also manifested as rheological differences. Similarly, Tank 40 simulant had an order-of-magnitude higher yield stress than Tank 8 simulant. Tank 8 simulant had good agreement with Tank 8 waste rheology. The Tank 8/40 blend that became sludge batch 2 (SB2), however, did not have good agreement in rheology. The implication is that real Tank 40 waste was more viscous than simulant Tank 40 waste, even though simulant Tank 40 waste had ten times the yield stress of both real and simulated Tank 8 waste. Large differences in yield stress in real waste tanks were seen in the work of B.A. Hamm. The main difference there was driven by waste type, Purex vs. HM. HM gave the higher yield stresses. Tank 8 was Purex, while Tank 40 contained a blend.

The database for simulant to radioactive waste slurry rheological comparisons is still small. Presumably, more radioactive data will become available over time. It is recommended that sludge, SRAT products, and SME products be routinely characterized for their rheological properties. This will strengthen our ability to deal with more complex processing issues.

Current simulants capture many of the proper chemical and physical features of Purex waste. It has been noted, however, that the properties are dependent on the preparation. For example, trim chemicals are not uniform in size, washing with gravity settling is different from using cross-flow filtration, the influence of shear is variable, etc. The impact of these phenomena on physical properties is not well understood at this time. Current simulants may lack some key feature of HM waste. Sludge Batch 1B simulant was not tacky like the real waste. Sludge Batch 2 simulant (probably through the Tank 40 component) was significantly less viscous than real SB2 waste. Simulant rheology also seems to be very sensitive to the Ni/Fe and/or Mn/Fe ratios in the co-precipitation phase of simulant preparation. This sensitivity is not well understood at this time due to the limited set of data.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

ACTL	Aiken County Technical Laboratory
CETL	Clemson Environmental Technologies Laboratory
CPC	Chemical Processing Cell
CUF	Cross-flow Ultra-Filtration unit
DWPF	Defense Waste Processing Facility
GFPS	Glass Feed Preparation System
IS	Insoluble Solids
SME	Slurry Mix Evaporator
SMRF	Slurry-fed Melt Rate Furnace
SRAT	Sludge Receipt and Adjustment Tank
SB1A	Sludge Batch 1A (first batch processed in DWPF)
SB1B	Sludge Batch 1B (second batch processed in DWPF)
SB2	Sludge Batch 2 (current batch in DWPF)
SB3	Sludge Batch 3 (next batch to be fed to DWPF starting in March 2004)
SRS	Savannah River Site
SRTC	Savannah River Technology Center
TS	Total Solids
USC	University of South Carolina – Columbia

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1.0 INTRODUCTION AND BACKGROUND

This document reviews radioactive and simulant rheology data on SRS waste slurries. Simulant sludge slurries have been prepared at Optima: Tank 51 for Sludge Batch 1A (SB1A) and trimmed for Sludge Batch 1B (SB1B), at USC-Columbia: Tank 8 and Tank 40 for Sludge Batch 2 (SB2), and at Clemson Environmental Technology Laboratory (CETL): SB2, Sludge Batch 3 (SB3), and several generic simulants. Various radioactive waste tank slurry samples have been analyzed for rheology in the SRTC Shielded Cells during the past 25 years. More recently, some rheological measurements have been made on the DWPF qualification samples for new sludge batches or on special samples pulled to help with resolution of processing issues.

This document attempts to make comparisons of rheological data for systems where there were both some radioactive slurry data and some potentially similar simulant slurry data. The Approach section describes the basic data types encountered, e.g. sludges, Sludge Receipt and Adjustment Tank (SRAT) products, and Slurry Mix Evaporator (SME) products. The last are equivalent to melter feeds. This is followed by a discussion of rheometry and the Bingham Plastic fluid model. This model has been used to reduce rheological data on SRS waste slurries over the past twenty years.

The Results section discusses rheological data for particular sludges first, data for SRAT products second, and data for SME products third. The discussion of sludge data starts with SB1A, continues with SB1B, then moves to SB2 and SB3. Finally, some miscellaneous historical data are presented. Each set of applicable reported data on a given sludge batch or waste tank is reviewed and referenced. A comparison of the related data is then made before moving on to the next system. A similar sequence is used when discussing SRAT and SME products.

The data being summarized here have been obtained by many people over about a twenty year period. The rheological data have also been obtained on a number of different rheometers. A reference for the raw data is given along with a brief description of some of the known sample properties. Additional data can often be found in the original source material. Data below are given for results at 25°C, or at room temperature. Data at other temperatures exist, but no elevated temperature data were found that could be used in this comparison study.

Noteworthy points developed in the discussion of the various slurries are reiterated in the Conclusions section. Major points were brought forward into the Executive Summary. Unresolved issues found during the review of the data often led to recommendations for future work. Absences of certain types of data also led to recommendations for future work. These suggestions plus a few others were collected together in the Recommendations section.

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2.0 APPROACH

2.1 HISTORICAL DATA

Site reports were searched for radioactive rheology data. A search was then conducted for any corresponding simulant data. This sequence was selected for reasons of efficiency, since there were considerably more simulant rheological data available in SRS reports than radioactive data.

Rheological data were classified as sludge, SRAT product, or SME product. Sludge meant basic waste slurries such as are found in the SRS waste tanks or the DWPF feed tanks (Tanks 40 and 51). The variation in pH and sodium molarity between washed and unwashed sludge was left for separate discussion within the results for a given waste stream. SRAT product meant a (typically) acidified sludge that had undergone processing by the sludge-only flow sheet used in DWPF. Such processing might have been carried out in smaller scale equipment, e.g. a 1-L glass reactor. SME product meant a mildly acidic to near neutral pH slurry containing processed sludge combined with glass frit for use as a feed to the DWPF melter.

Data were subdivided within each of the three main classes to reflect the specific waste tank of origin, or the specific combination of wastes that formed a distinct feed (sludge batch) to the DWPF. Each significant change of feed to the DWPF has been referred to as "Sludge Batch x" or SBx. DWPF has completed processing Sludge Batches 1A, 1B, and 2 (SB1A, SB1B, and SB2) and is currently processing Sludge Batch 3 (SB3). SB3 is now the blend of new waste material from Tank 51 with the remainder of SB2 from Tank 40 (about 50:50). This combination freed up Tank 51 for the preparation of Sludge Batch 4. Some analyses of SB3 rheology were made that did not include the contribution from the remainder of SB2. Those analyses made on the blend of SB3 with SB2 are referred to as SB2/3.

Sludge batches to date have been blends prepared from several different waste tanks at SRS. Samples of wastes from some of these tanks have been taken in the past. Analyses of some of these samples have included rheological characterization. Not all of these waste tanks have become part of the DWPF sludge batches to date. Rheological data for these yet-to-be-processed wastes are given by the tank number, e.g. Tank 8 or Tank 15, rather than by a sludge batch number. Not all waste tanks samples came from well-mixed tanks. Therefore, some of the historical rheological data may not be representative of the bulk contents of a given tank.

The radioactive waste stored in the SRS waste tanks was generated by either the Purex process or the HM process. Purex waste is typically high in iron and relatively low in aluminum. HM waste is typically higher in aluminum than iron. DWPF SB1B had the most HM content of the batches processed to date. It was characterized as tacky compared to SB1A. A large fraction of SB1B came from Tank 42. This tank was used for the in-tank sludge processing demonstration and the aluminum dissolution demonstration. The In-Tank processing demonstration used 150,000 gallons of Tank 15-H sludge.

SB2, a combination of Tanks 8 and 40, had an intermediate level of HM character through Tank 40 (Tank 8 was entirely Purex waste). SB2 processing has been characterized by air entrainment, pumping, and heat transfer problems. These appear to be symptomatic of operation in an undesirable rheological regime. The insoluble solids content in SB2 is more than twice as high in uranium as either SB1A or SB1B. The noble metal concentrations are also considerably higher in SB2 than in the two prior sludge batches. The Tank 8 solids were allowed to dry out over time, and they had to be re-slurried before the Tank 8 waste could be combined with the contents of Tank 40 to make SB2.

Sludge Batch 3 (SB3) is primarily the waste from Tank 7 combined with the heel from SB2. Tank 7 contained Purex waste. The heel from SB2 may be about half of the final blend. Preliminary indications are that the SB3 blend will be less viscous than SB2 by itself. These indications are derived from a synthesized SB3 waste prepared in the SRTC Shielded Cells. Confirmation awaits an actual sample of the blend prepared in Tank 51.

2.2 Rheometry

Rheology is the science of the deformation and flow of matter. Rheometry is the measurement of the deformation and flow of matter.

2.2.1 Rheometers

The Savannah River Technology Center (SRTC) has measured rheological properties with a series of instruments called rheometers. The vendor for these instruments has been Haake (now Thermo Electron Corp.). The first two instruments were Haake RV-3 rheometers with either an M50 or M500 measuring head. One was set up at TNX for simulant work in the summer of 1979. The SRTC Shielded Cells had the second RV-3 rheometer installed in Cell block A in 1981, where it was used until 1982. In late 1982, a Haake RV-12 rheometer with an M150 measuring head was installed in the Cells. About 1999 a Haake RV-30 rheometer with an M5 measuring head was tested and installed in the Cells. This instrument remains in service today, and it is referred to below simply as the RV-30 rheometer.

SRTC also had Haake rheometers in non-radioactive service. A Haake Rotovisco RV-3 rheometer with MK500 sensor system was still in service in 1992. A Haake RV-20 rheometer with an M5 measuring head was purchased in the fall of 1992 and was in service in 1993. This instrument is referred to simply as the RV-20 rheometer below. This rheometer was relocated to a radioactive hood in 773-A in 2001 (following the preliminary analysis of SB2 simulant slurries). A Haake RS150 research grade rheometer was purchased in 2000, and a Haake RS600 research grade rheometer was purchased in 2003. The RS600 is shown below with the parallel plate sensor mounted. The last two instruments are currently located at the Aiken County Technical Laboratory (ACTL) area of the Savannah River Research Center.

Figure 1. Haake RS600 Rheometer

2.2.2 Rheometer Sensors

The primary measurement mode has been to use the coaxial cylinder geometry. This configuration involves a vertical cylindrical beaker that holds the slurry sample. A solid cylindrical bob is moved into the top of the slurry beaker. The sample in the beaker is forced to flow into the annular region between the walls of the bob and the beaker. The bob is spun over a predetermined range of revolutions per minute, held at the upper speed, and then decelerated back to a stationary position. The rheometers are operated in the Searle mode, in which the rotational speed of the inner cylinder is controlled, and the torque required to turn it is measured.

Torque is converted into shear stress based on the exact measurement geometry. The angular speed is converted into the equivalent shear rate that a Newtonian fluid would have in that measurement geometry. A plot of shear stress versus shear rate data is called a "flow curve". This is the typical graph presented in the historical reports. Valid rheometric data is only obtained in the laminar flow region.

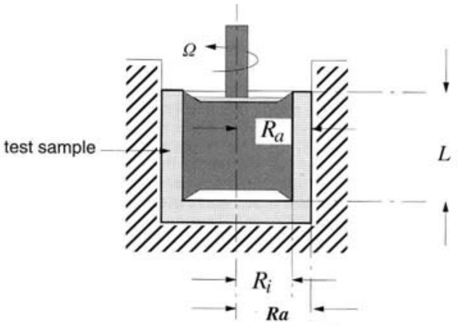
A flow curve is obtained by ramping the rotational speed of the bob to obtain a range of shear rates and by simultaneously recording the shear stress (torque). An *up flow curve* involves ramping the shear rate from 0/second to some upper limit, e.g. 400-500/second. A *down flow curve* involves ramping from the maximum shear rate back to zero. Ramping has historically been done as a linear function of the time, i.e. if the shear rate is to be ramped from 0/s to 500/s over five minutes, then the shear rate is 100/s after one minute, 200/s after two minutes, etc. A fluid at rest is unsheared, i.e. the shear rate is zero. Shear rates in pumping and mixing applications can reach between ten to several hundred per second. Recent SRTC measurements have generally used five minutes for both the up flow curve ramp time and for the down flow curve ramp time.

There is no difference in the torque response (shear stress) of a down flow curve and an up flow curve for a Newtonian liquid. A Newtonian fluid also has a linear response, i.e. a 5% change in shear rate produces a 5% change in shear stress. The onset of non-laminar flow patterns causes an obvious change in the slope of the flow curve. Data in the region of non-laminar flow are ignored, since the precise nature of the flow and the relationship between and angular speed and shear rate are unknown.

There should be no difference between the up and down flow curves for fluids whose properties are independent of time at shear (an example would be a simple polymer solution). These samples can be either Newtonian or *non-Newtonian*. Non-Newtonian samples, however, have a shear stress response that is not linear with shear rate. SRS waste slurries typically exhibit non-Newtonian fluid behavior. SRS waste supernates (free of insoluble solids) are typically Newtonian in behavior. Some materials have properties that depend on time. These are called thixotropic if the shear stress falls with time at a given shear rate, or rheopectic if the shear stress rises with time at a given shear rate.

The underside of the cylindrical measurement bob is hollowed out as shown in Figure 2. An air pocket is trapped there during sample loading. The bob can be rotated over the top of the slurry in the bottom of the beaker with negligible torque. The measured torque then comes from the shear stress in the annular gap between the beaker and the bob. Care is also taken not to overfill the beaker before inserting the bob. Sample fill lines are inscribed on the inside of the beakers to assist in this. Any excess sample is trimmed from the top of the beaker-bob combination. The purpose of these steps is to match the surface area of shear stress as closely as possible to the outside cylindrical area of the side of the bob. A small source of error is introduced by the meniscus of fluid that rises up the beaker wall above the height of the bob. This error is kept small by using a relatively long cylinder (50-60 mm) relative to the typical height of a meniscus.

Figure 2. Layout of the Concentric Cylinder Measurement Geometry



Each rheometer comes with a beaker and a set of bobs. Beakers and bobs for the RV-20 and RV-30 rheometers are interchangeable. The bobs have designations such as MV1, MV2, and MV3 in order of decreasing diameter (or increasing annular gap). Beakers and bobs for the RS150 and RS600 are also interchangeable. These bobs have designations such as Z41, Z38, and Z31 in order of decreasing diameter (2*R_i in Figure 2).

Figure 3. The Z Series Cylindrical Bobs

The Z series bobs and the MV series bobs are not interchangeable. The matching beakers are also not interchangeable between the RV-20/RV-30 and the RS150/RS600. The newer Z series bobs were chosen to preserve as closely as possible the approximate gap widths (R_a-R_i) and ratios of bob to beaker radii (R_i/R_a) found in the MV series. The Z41 bob is the analog to the MV1 bob, the Z38 bob is the analog to the MV2 bob, and the Z31 bob is the analog to the MV3 bob. The Z series bobs are 5 mm shorter in height, L, compared to the MV series. Sample volume requirements are smaller for the Z series cup and bob combinations than for the corresponding MV series due to improved position of the bob in the beaker and the smaller height of the annular gap. The beakers have all been made of stainless steel. The MV bobs are made of stainless steel, but the Z series bobs are made of titanium. The titanium bobs have lower inertia (less mass). This increases their sensitivity and accuracy at small shear rates.

Recent data for sludge and SRAT product slurries have been obtained using either the MV1 or Z41 cylinder/cup configurations. These give the smallest gap width, ~1mm. The smallest feasible gap gives the minimum model error from the assumption that the shear rate is constant across the annular gap. The annular gap, however, should be significantly larger (~10x) than the largest solid particle in the sample. Recent SME product data have been obtained using MV1 for radioactive samples, and MV2, Z41, or Z38 for simulant samples. The larger gaps of MV2 and Z38 are appropriate for the presence of frit particles approaching 0.5mm in diameter. MV2 and Z38 are fairly similar geometries, but are not that similar to MV1. The annular gap widths of the MV2 and Z38 configurations are not as narrow as for the MV1 and Z41. Raw flow curves for a given sample obtained using both MV1 and MV2 bobs are not identical though they are typically similar.

The two new research grade rheometers (RS150 and RS600) can perform numerous measurements in addition to the simple flow curve (controlled on shear rate). These include flow curves controlled on shear stress, as well as fundamentally different measurements involving oscillating shear rates with controlled frequency or shear stress. They are also equipped to perform measurements in geometries other than the concentric cylinder geometry. These additional geometries include horizontal parallel plate and cone-and-plate geometries, as well as vane paddle measurements. There are some data in the 60mm parallel plate geometry for simulants that are similar to radioactive wastes, but they are not included here. A proven method for quantitatively comparing non-Newtonian slurry rheology data between concentric cylinder and parallel plate geometries has not been identified. The rotating vane/paddle geometry has been used on both the RV and RS rheometers. Some vane measurements have been made in the Shielded Cells (the only other geometry than concentric cylinders that the RV-30 is equipped to run), but there are no chemical simulant analogs to this data so these measurements will not be discussed further.

The generation of a flow curve takes about 15 minutes. It is important that the solid particles remain uniformly suspended during this period of time. Slurries where this is true are referred to as “slow settling”, whereas those where this is not true are referred to as “fast settling”. Fast settling slurries are best treated as a two-phase fluid flow problem. An example would be the pneumatic transport of sand particles in compressed air. Another example would be 10 wt. % frit slurry in water or dilute acid solution. Most waste slurries, and SRAT and SME products, are considered to be slow settling slurries. Some, however, are close to the dividing line between the two regimes. This occurs physically when the slurry becomes too thin (insufficiently viscous to adequately suspend the larger solids).

2.2.3 Bingham Plastic Fluid Model

Rheometric data are often analyzed using rheological models, or mathematical relationships between shear stress and shear rate. In many of the reports reviewed during this study, the only “data” were in rheological model form, i.e. the raw flow curves were not given. Because of this, it is necessary to introduce the Bingham Plastic fluid model and discuss a few of its features before continuing.

Slow settling slurries can be modeled as a single phase fluid. This produces certain simplifications over dealing with a two-phase liquid-solid transport model in the analysis of pumps, pipeline flow, and tank mixing. Various empirical and semi-theoretical models have been proposed to relate the shear stress and the shear rate of non-Newtonian slow settling slurries. One of the simplest of these is the Bingham Plastic fluid model. This model is a two parameter relationship between the shear stress and the shear rate (Newtonian fluids have a one parameter relationship through viscosity):

$$shear\ stress = yield\ stress + consistency * shear\ rate$$

The two parameters are the *yield stress* and *consistency*. They are constants for a given sample. This model reduces to the Newtonian fluid when the yield stress is zero. The consistency then becomes equivalent to the Newtonian fluid viscosity. When the yield stress is not zero, however, the consistency is no longer analogous to the viscosity. Instead, the physically analogous quantity to Newtonian viscosity, sometimes referred to as the *apparent viscosity*, is given by the ratio of the shear stress to the shear rate:

$$\frac{shear\ stress}{shear\ rate} = consistency + \frac{yield\ stress}{shear\ rate} = apparent\ viscosity$$

The apparent viscosity of a Bingham plastic fluid decreases with increasing shear rate per the equation above. This type of fluid behavior is called *shear thinning*. SRS waste slurries typically behave like shear thinning fluids. The apparent viscosity goes to infinity as the shear rate goes to zero. This is a common feature of all models that have a yield stress.

The Bingham plastic yield stress and consistency are presumed to be independent of time under shear. Not all slurries possess this property. Time-dependence is a potential issue when dealing with slurries containing colloidal solid particles. Colloidal solids are in the range of 1 micron in diameter (perhaps 100 nm to 10 μm). Colloidal solids can exhibit unusual behavior because the size of the particles is small enough that the interparticle surface forces can become an appreciable fraction of the total force acting on a given particle. SRS waste slurries and corresponding simulants contain particles in this size range. Some simulants have shown signs of time-dependent behavior, but recent radioactive data do not show significant time-dependence. The Bingham plastic model is not appropriate for systems with significant time-dependence. DWPF glass frit is larger than the traditional colloidal size range. The main issue with SME product frit slurries is keeping the frit uniformly suspended, so that the slurry can be classified as slow settling.

Flow curve data, in the form of plots of shear stress versus shear rate, are fit to the Bingham Plastic fluid model. This is a simple linear regression once the range of shear rates to be fit has been selected. The intercept of the linear fit with the shear stress axis at zero shear rate corresponds to the yield stress. The slope of the linear fit through the flow curve data corresponds to the consistency. The data to be discussed below come from many different reports. These reports do not always give the raw flow curve data. Only the yield stress and consistency were reported in many cases. Therefore, comparisons between data from different samples were most readily made using the Bingham Plastic parameters rather than the raw flow curves.

The Bingham Plastic yield stress has always been found to increase with increasing wt. % insoluble solids (IS) for a given SRS waste slurry. The rate of increase is generally non-linear. The rate of yield stress increase can be modeled as anything from a quadratic function of wt. % IS to an exponential dependence of wt. % IS. Even more complicated functions have been tried, depending on the amount of data,. Because of this strong dependence on wt. % IS, the yield stress and consistency data tabulated in section 3 were sorted in order of increasing wt. % IS.

2.3 Rheological Comparisons

One final issue needed to be resolved before proceeding with this investigation. This involved a statement of "what constitutes a reasonable rheological approximation between a simulant and the corresponding real slurry?" A simulant that is suitable for physical processes dominated by rheological properties, such as pipeline flow and pump design, may not be suitable for studying issues with a greater dependence on the particulate chemistry, such as air entrainment, foaming, and settling rate which could be strong functions of the particulate composition, size and shape, the system zeta potential, the supernate surface tension, etc.

Even identical rheological behavior between simulant and radioactive slurry would not guarantee identical performance in these latter areas. A purely rheological simulant could be prepared without using typical DWPF slurry chemicals, for example using Kaolin. It could be suitable for pipeline flow and pump design calculations, but would not process chemically through the SRAT or make good glass. The current simulants do process chemically through the SRAT and can be made into good glass. Potential shortcomings of the current simulants may, however, impact the efforts of SRTC to solve processing problems in the DWPF. This document seeks to summarize how close simulant and radioactive slurries have been in a rheological sense.

The comparability of a simulant and a radioactive waste was assessed primarily by the value of the Bingham Plastic model yield stress at equivalent wt. % insoluble solids content. The yield stress dominates the behavior of waste slurries at low shear rates. Yield stress values within 20-30% were considered to be giving "good agreement". Values different by a factor of two or more were considered to be giving "poor agreement". Intermediate cases were rated as "fair agreement". These ranges may seem unreasonably large. It should be noted, however, that rheometry is not an exact science. There are also issues associated with sample handling that can lead to variability in the measured results. Finally, there has been no systematic study of the measurement variations between instruments.

The Bingham Plastic model consistency has some physical significance. If the yield stress is small, e.g. less than 20 dynes/cm^2, or if the consistency is large, e.g. greater than 30-40 cP, then the consistency may contain as much significant information about the flow properties as the yield stress. It was noted during this review that systems with yield stresses within 20-30% typically also had different consistencies, but that these differences would not alter the conclusions about the qualitative similarities of a pair of samples. Similarly, it was noted that when yield stresses differed by more than 20-30%, the differences in consistency were generally insufficient to claim that the qualitative agreement within the pair was better than fair.

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3.0 RESULTS

This section gives summaries of the available rheological data used in comparisons between radioactive waste slurries and simulants. Data were classified as sludge, SRAT product, or SME product. Washed and unwashed sludges were grouped together. Data within each group were separated into individual sludge batches and waste tanks, e.g. SB2 or Tank 8. The data for simulants were taken under temperature control at 25°C. RV-30 radioactive data were taken at 25°C. Older Shielded Cells data were taken at Cells temperature.

3.1 SLUDGES – WASHED AND UNWASHED

The sub-sections below focus on the Bingham Plastic fluid model rheological properties for washed and unwashed sludges. Data for DWPF sludge batches are given first, followed by data for individual waste tanks.

3.1.1 Sludge Batch 1A

Only radioactive rheology data was found for the first DWPF sludge batch. This was primarily a Purex waste sludge. This was reported in WSRC-MS-92-410. B.C. Ha reported on the rheology of the initial Tank 51 waste blend that ultimately became Sludge Batch 1A in the DWPF in this manuscript. Three different wt. % total solids (TS) were reported:

- Tank 51 at 12 wt. % TS, yield stress = 5 dynes/cm^2
- Tank 51 at 15 wt. % TS, yield stress = 11 dynes/cm^2
- Tank 51 at 18 wt. % TS, yield stress = 14 dynes/cm^2

There does not appear to be any Tank 51 simulant rheology data other than the Tank 42 trimmed variation of the Tank 51 simulant given in 3.1.2.2 below at 17.0 wt. % TS and a yield stress of 15 dynes/cm^2. This is in good agreement with the last result above for the radioactive slurry data, assuming the two can be compared (trimming involved only some minor additions of extra chemicals to the slurry).

3.1.2 Sludge Batch 1B-related (Including Tank 42)

Limited radioactive rheology data was found for SB1B sludge. A single measurement was found for simulant that generally corresponds to SB1B in composition. Tank 42 contained a certain element of HM sludge character as well as containing the product from the aluminum dissolution tests. The data described further below primarily relate to Tank 42 as used for preparing SB1B.

3.1.2.1 WSRC-MS-95-0371 (SB1B radioactive rheology)

B.C. Ha made rheological measurements using the RV-12. See WSRC-RP-97-236 in addition to WSRC-MS-95-0371. These were Shielded Cells measurements on the washed Tank 42 sludge sample. Data were taken at five different wt. % total solids. Insoluble solids were not reported for the individual samples, but the text included a comment that the 17 wt. % TS sample was about 13 wt. % insoluble solids (IS):

- Tank 42-rad-1 – 8% TS, unknown IS
- Tank 42-rad-2 – 17% TS, ~13 wt. % IS
- Tank 42-rad-3 – 23% TS, unknown IS
- Tank 42-rad-4 – 27% TS, unknown IS

- Tank 42-rad-5 – 34% TS, unknown IS

Also noted was a reference by B.C. Ha to old Tank 21 rheology data by B.A. Hamm:

- Tank 21, <14 wt. % IS, yield stress <40 dynes/cm^2

This is mentioned here since Tank 42 waste contained a large fraction of Tank 21 waste.

3.1.2.2 WSRC-TR-2001-00051 (SB1B simulant rheology)

D.C. Koopman reported this result in the SB2 simulant rheology report. Some SB1B simulant had been prepared by trimming a few species in the existing Optima SB1A simulant to better match the measured properties of Tank 42 sludge. A single sample was run to give a basis for comparison with the two new USC simulants for Tank 40 and Tank 8 washed sludge (two halves of SB2):

- Trimmed Tank 51 simulant for SB1B – 17.0 wt. % TS, 13.9 wt. % IS, pH 12.8

The sample was analyzed on the RV-20 rheometer located in 772-T at the time.

3.1.2.3 DPST-84-439 (Tank 42 rheology)

This report by B. A. Hamm covers Shielded Cells rheology of Tanks 15H, 42H, and 8F Sludges. It gives 21 measurements of Tank 42 sludge slurry rheology following the 1982 in-tank processing demonstration (used 125,000 gallons of Tank 15 waste). This was the caustic dissolution test, and it was followed by three water washes. These data are for a different composition than that in Tank 42 in 1995. Tank 42 received major additions from Tanks 18 and 21 during 1986. This was primarily low activity Purex and HM waste respectively. The HLW tank composition data do not indicate that Tank 21 was a high aluminum waste stream, however, which is consistent with the final composition of SB1B. This data was excluded from the comparison to other SB1B sludges.

3.1.2.4 Summary of SB1B Results

Table 1 below compares the rheological parameters for the five radioactive sludge samples and one simulant sludge sample. Sludge sample ID's correspond to those in the bulleted lists above.

Table 1. Sludge Batch 1B (Tank 42) Related Sludge Rheology

Sludge Sample ID	Wt. % Insoluble Solids	Yield Stress, dynes/cm^2	Apparent Viscosity at 300/sec	Consist-ency, cP	Wt. % Total Solids
Tank 42-rad-1-8%	N.R.	10	10	N.R.	8
Tank 42-rad-2-17%	~13	11	20	~16-est.	17
Tank 42-rad-3-23%	N.R.	63	35	N.R.	23
Tank 42-rad-4-27%	N.R.	90	45	N.R.	27
Tank 42-rad-5-34%	N.R.	381	150	N.R.	34
Trimmed Tank 51 simulant for SB1B	13.9	15	10.5	5.6	17

N.R. – not reported.

More descriptive data would have been useful for the radioactive sludge slurries, but they appear to have been at least partially washed, since the soluble solids reported are low. The simulant and radioactive samples may not be directly comparable in target composition (too little information). It would seem that the single simulant results should be compared to the Tank 42-rad-2 sample based on total solids content. These are in fairly good agreement for yield stress (36% higher in simulant, but also slightly higher insoluble solids). The Bingham plastic consistency can be calculated from the yield stress and apparent viscosity at a shear rate of 300/second, or vice versa, using the equations in section 2.2.3. The resulting consistency for Tank 42-rad-2 is about 16 cP, which is in poor agreement with the simulant consistency.

If the raw data were available, the flow curves for the Tank 42-rad-2 sample and the trimmed Tank 51 simulant would presumably cross through each other, since the simulant jumps faster initially than rises more slowly than the Tank 42-rad-2 sample. What is not clear is the extent of washing of the Tank 42 radioactive samples when compared to the simulant. From what little is known about the radioactive samples, the simulant does not appear to be a bad model for the radioactive slurry behavior. It is probably in the fair range, but close to the good range, as laid out in section 2.3. A stronger statement on the suitability of this simulant in a rheological sense cannot be made, given the uncertainties in the sludge history, the preparation of the simulant by modifying an existing simulant, etc.

3.1.3 Sludge Batch 2

Some radioactive rheology data was found for SB2 sludge. Various measurements were found for simulants corresponding to SB2. These are described further below. The earliest SB2 simulants were prepared by blending separate simulants for Tank 8 and Tank 40. These individual simulants were produced at the University of South Carolina (USC). The second generation SB2 simulants were prepared to match the composition of the Tank 8/Tank 40 blend simulant from USC. They were produced at the Clemson Environmental Technology Laboratory (CETL). Preparation of small quantities of a third generation SB2 simulant was performed within SRTC in early 2004.

3.1.3.1 WSRC-TR-2002-00302 (SB2 Rheology Data Comparison)

This report by T.L. Fellinger and D.C. Koopman collected rheology data obtained during the initial SB2 rheology work with USC simulants (WSRC-TR-2001-00051) along with the rheology work done on the initial SB2 qualification sample in the Shielded Cells. In addition, some new simulant data obtained on USC SB2 simulants used in the 1/240th scale Glass Feed Preparation System (GFPS) was incorporated that had not been published elsewhere. "Rad" indicates a Shielded Cells measurement on a radioactive sample. "TNX" indicates a result obtained during the initial SB2 work with USC simulants. "GFPS" indicates the unpublished results.

Table 2. SB2 Radioactive and Simulant Sludges in 2002

	Wt. % Total Solids	Wt. % Insoluble Solids	Density, g/ml
SB2 Rad Qual-sludge	18.4	15.5	1.12
SB2-USC/TNX-sludge	15.9	13.2	1.11
SB2-USC/GFPS-sludge-1	13.5	10.8	~1.1
SB2-USC/GFPS-sludge-2	16.8	14.2	N.R.
SB2-USC/GFPS-sludge-3	17.1	14.5	N.R.
SB2-USC/GFPS-sludge-4	18.5	15.9	N.R.

N.R. – not reported.

Up and down flow curves were generally very similar for a given sample. This is mentioned because later SB2 simulant from CETL did not behave this way. GFPS samples were run on the RS150. The

TNX sample was run on the RV-20, and the radioactive sample was run on the RV-30. The Z41, or corresponding MV1, cylindrical bobs were used.

3.1.3.2 WSRC-TR-2001-00051 (SB2 Simulant Rheology Study)

This report by D.C. Koopman was the preliminary study on SB2 rheology. The primary focus of the report was on SME product rheology. The individual Tank 8 and Tank 40 simulant sludges from USC were analyzed along with a sample of the nominal starting Tank 8/Tank 40 blended sludge:

- SB2 USC/TNX (Tank 8/Tank 40 blend) – 15.9 wt. % TS, 13.2 wt. % IS, pH 10.3

The data was obtained using the RV-20 rheometer.

3.1.3.3 WSRC-TR-2003-00136 and –00253 (Phase I Cells SB2 Rheology)

These two reports by T.L. Fellinger describe follow-up rheological work in the Shielded Cells on a new sample of SB2 washed waste. The sludge rheology was determined on the sample as received:

- SB2 Rad-2003-sludge – 19.9 wt. % TS, 17.5 wt. % IS, 1.14 g/ml

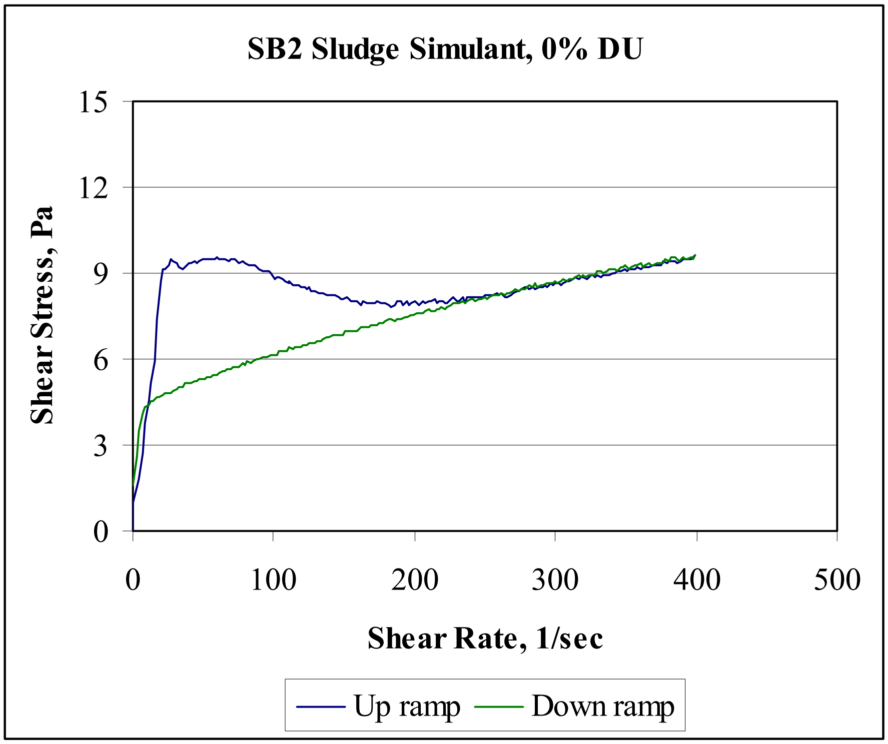
3.1.3.4 WSRC-TR-2003-00402 (SB2 Simulant from CETL)

D.T. Herman and W.R. Wilmarth trimmed some SB2 sludge with sodium nitrite and depleted uranium nitrate. This was treated with caustic to precipitate the depleted uranium (DU). This test used SB2 simulant made at CETL, instead of USC. The sodium nitrite trim was needed because the supernate had been depleted in salts during a remediation of the simulant to raise the wt. % total solids. The CETL sludge did not give the same form of flow curve seen with most past sludge simulants (traditional slurry flow curve). Analysis was made using the RV-20 rheometer. One of the three sludges was a baseline case containing no DU, which should be comparable to the other SB2 sludge data.

- SB2-CETL/773A-sludge – 19.17 wt. % TS, 17.18 wt. % IS, 1.15 g/ml

The up curve had a distinct maximum in the low shear rate range, Figure 4. Therefore, the Bingham plastic model was fit to the down flow curve which lacked this feature.

Figure 4. SB2 CETL-based Simulant Flow Curve



Historically, however, the fit has been made on the up curve, so this model data is less comparable for that reason, in addition to it not acting like real waste in the rheometer.

3.1.3.5 Unpublished SB2 Simulant from CETL

A sample of SB2 simulant from CETL was taken directly from the drum, i.e. not trimmed in the supernate, and run on the RS600 rheometer using the Z41 bob. Sludge was being used for investigations into processing issues with SB2 in DWPF. M.E. Stone was the principal investigator, E.K. Hansen ran the sample, and D.C. Koopman analyzed the data.

- SB2-CETL/ACTL-sludge 19.1 wt. % TS, 17.2 wt. % IS, 1.22 g/ml, pH 12.9

The CETL simulant up flow curve had a distinct maximum in the low shear rate range similar to Figure 4 given in section 3.1.3.4.

3.1.3.6 C.J. Bannochie SB2 Simulant Testing

There is some work with a new SB2 simulant being made at SRTC occurring in early 2004 in parallel with this report. This included a SB2 simulant made at SRTC that was chemically similar to the USC and CETL simulants. There were also four simulants with four levels of uranium targeting essentially constant total solids, i.e. lower levels of the other sludge elements were introduced to offset the presence of uranium. Sludge simulant rheograms were obtained for each of the six sludges. Mean particle sizes were several times larger than had been seen with previous simulants. The flow curves were considerably below those of CETL and USC based simulants. Therefore this data will not be discussed further.

3.1.3.7 SB2 Sludge Rheology Summary

Table 3 below summarizes the various rheological measurements that have been made on SB2 sludges. The sludge sample ID corresponds to the samples given in the individual sections above.

Table 3. Sludge Batch 2 Related Slurry Rheology

Sludge Sample ID	Wt. % Insoluble Solids	Yield Stress, dynes/cm^2	Consist-ency, cP	pH	Wt. % Total Solids
SB2 Rad Qual-sludge	15.5	119	11.1	11.2	18.4
SB2 Rad-2003-sludge	17.5	166	6.0	12.7	19.9
SB2-USC/GFPS-sludge-1	10.8	17	3.6	10.6	13.5
SB2-USC/TNX-sludge	13.2	36	8.5	10.3	15.9
SB2-USC/GFPS-sludge-2	14.2	49	5.8	10.6	16.8
SB2-USC/GFPS-sludge-3	14.5	51	6.0	10.7	17.1
SB2-USC/GFPS-sludge-4	15.9	76	7.9	10.7	18.5
SB2-CETL/773A-sludge	17.18	49[d]	12.4[d]	-	19.17
SB2-CETL/ACTL-sludge	17.4?	73[d]	7.32[d]	-	19.1

d-down curve data used instead of up curve data, because up curve data was ambiguous

Radioactive SB2 washed sludge appeared to be thicker than the USC blended simulant by about a factor of three at similar wt. % insoluble solids, i.e. poor agreement. The higher pH of the radioactive samples was not seen as a potentially mitigating factor. CETL sludge simulant appeared to be potentially less viscous than the USC Tank 8/40 blended simulant for a given wt. % insoluble solids, i.e. a less good rheological simulant than the USC simulant.

CETL simulant gave unusual up flow curves, i.e. time-dependent behavior was indicated during what should be a pseudo-steady state shear rate ramping program. This was not desirable, and indicated that the true steady-state flow curve was not being measured. Down flow curve data were used for the above table, but results should be taken as potentially not representative of the true fluid properties of the CETL simulant.

USC simulants had down flow curves that were slightly above the up curves. This is unexpected for a time-independent fluid. Older sludge simulants were either insensitive to time at shear, or were thixotropic, i.e. thinned with time at shear. The USC simulant data exhibited a more rheopectic behavior (thickened with time at shear), but the effect was very muted for USC simulant. Reproducible results were obtained on sample reruns. USC simulants were analyzed with the RV-20 rheometer. CETL simulants were analyzed with the RS150/RS600 rheometers, except for the sample included in the work with depleted uranium. That one data point may indicate that the potential issues are with the CETL simulant rather than with the rheometer.

3.1.4 Sludge Batch 3 Slurry (prior to blending with SB2)

3.1.4.1 WSRC-TR-2004-00050 (SB3 Shielded Cells Qualification)

A sample of the contents of Tank 51 was received by SRTC in the summer of 2003. The contents of Tank 51 are to be transferred to Tank 40 (currently containing SB2) in late March 2004. This sample was adjusted with plutonium and neptunium wastes to approximate the anticipated composition of the new portions of the next sludge batch, i.e. the portions not already in SB2. This preparation was then put through the SRTC Shielded Cells qualification process.

The rheological analysis was performed in the SRTC Shielded Cells using the RV-30 rheometer and the MV1 bob. The results are given in Appendix B. Sample properties and ID are:

- SB3-rad qual runs, 27.2 wt. % TS, 17.1 wt. % IS, 1.22 g/ml,

Corresponding simulant rheological data has not been obtained on the SB3 CETL simulant at this time. The actual SB3 slurry fed to DWPF will probably not have these properties, since it will include a significant portion of SB2 at the projected time that Tank 51 is transferred to Tank 40.

3.1.5 SB2/3 Blend Sludge Slurry

SRTC prepared a blend of SB2 and SB3 radioactive sludges in the Shielded Cells based on the projected date for the transfer of Tank 51 (SB3) into Tank 40 (SB2). The SB3 portion was described in 3.1.4. The SB2 portion was described in 3.1.3.3. The sample was analyzed on the RV-30 rheometer with the MV1 bob. The rheological results are given in Appendix B, and the sample properties are given below:

- Blend of 19.9 wt. % SB2 and 27.2 wt. % SB3 to give 24.4 wt. % TS, 17.26 wt. % IS

The wt. % IS was calculated from those of the two starting slurries. The calculation assumes no dissolution/precipitation upon blending. It is likely that in the future this blend will be referred to as “SB3” in site reports. Rheological measurements on equivalent simulant slurries have not been made.

3.1.6 Tank 8 Sludge

3.1.6.1 DPST-84-439 (Radioactive Tank 8 data)

B.A. Hamm made some of the earliest rheological measurements on SRS tank farm waste slurries. This report presents radioactive rheology data from three waste tanks, Tanks 15H, 42H, and 8F. Three separate samples of Tank 8 were pulled in 1983. The following list indicates which Tank 8 sample formed the basis for the slurry rheology measurement.

1983A=25-L sample processed in June 1983
1983B=25-L sample processed in July 1983
1983C=25-L sample processed in October 1983
1984A=samples from combined 25L samples
1984B=samples from a sludge settling study

This report does not give individual up or down flow curves, only yield stress and consistency values from fitting the data to the Bingham plastic model. Flow curves were obtained on 0-300/s shear rates using a 12 minute ramping interval, followed by a six minute hold. (This is slower ramping than typically performed today, plus the shear rate range is smaller.) Bingham Plastic fits were apparently made on the interval of 150/s to 300/s. Appreciable shear thinning or thickening during the hold was not observed according to the text. This indicates that the rheograms probably represent equilibrium shear stress-shear rate data. This is good. A considerable amount of data was taken under a variety of conditions.

The Tank 8 samples in Table 4 were characterized using the Shielded Cells rheometers:

Table 4. Description of Tank 8 Radioactive Slurry Samples

Sample ID	Wt. % Total Solids	Wt. % Insoluble Solids	Wt. % Soluble Solids	Density, g/ml
1983A-5-rad	15.0	8.3	6.7	1.07
1983A-6-rad	18.9	10.5	8.4	1.12
1983A-7-rad	25.2	15.5	9.7	1.19
1983B-2-rad	12.4	5.4	7.0	1.10
1983B-3-rad	15.9	7.8	8.1	1.14
1983B-4-rad	24.6	12.9	11.7	1.18
1983C-1-rad	21.5	11.5	10.0	1.18
1983C-2-rad	21.4	12.0	9.4	1.17
1984A-1-rad	16.0	13.2	2.8	1.13
1984A-2-rad	20.2	17.4	2.8	1.14
1984A-3-rad	22.9	19.6	3.3	1.18
1984A-4-rad	27.8	24.4	3.4	1.21
1984A-5-rad	32.7	29.6	3.1	1.25
1984B-1-rad	12.7	12.4	0.3	1.09
1984B-2-rad	31.2	27.9	3.3	1.30

There was quite a range of total solids, insoluble solids, and soluble solids as seen in Table 4. These ranges were obtained by diluting the starting Tank 8 samples in one of three ways. These included dilution with salt-supernate, dilution with de-ionized water, and dilution with a pH 12 solution (0.01M NaOH). The rheometer in the Shielded Cells was changed during this work. An RV-3 was used until late 1982, when it was replaced by an RV-12. The T1 sensor system was used on both rheometers.

3.1.6.2 WSRC-TR-2000-00900 (Radioactive Tank 8 data)

T.L. Fellinger made measurements on a Tank 8 variable depth sample using the RV-30 in the Shielded Cells. These samples may not be representative of the bulk composition of Tank 8 waste. The solids composition indicates that this material has not been washed.

- Tank 8 rad-as received – 38.5 wt. % TS, 19.29 wt. % IS, 1.38 g/ml
- Tank 8 rad-diluted – 27.7 wt. % TS, 11.3 wt. % IS, 1.29 g/ml

Both the as-received and diluted sample gave good flow curves (traditional shape with minimal evidence of time dependent behavior).

3.1.6.3 WSRC-TR-2001-00051 (USC Tank 8 Simulant for SB2)

A rheological measurement was made on the Tank 8 simulant that was combined with Tank 40 simulant to produce the Sludge Batch 2 simulant for flow sheet testing by D.C. Koopman. Tank 8 simulant was prepared in the washed state. The measurement was made on the RV-20 rheometer in 772-T using the MV1 bob.

- USC Simulant for Tank 8-SB2 – 14.9 wt. % TS, 12.5 wt. % IS, pH 9.9

The flow curve was traditional with minimal dependence on time under shear.

3.1.6.4 WSRC-TR-2002-00322 (Pu-Gd Study for SB3 using Tank 8 simulant)

C.C. Herman, D.C. Koopman, et al. considered the impacts of adding a Pu-Gd waste stream into Sludge Batch 3. Only USC Tank 8 simulant was available in sufficient quantity at this time. Some of the simulant was decanted to more closely match anticipated SB3 solids levels in DWPF. A portion of the decanted simulant was combined with NaOH, $NaNO_2$, etc. to more closely resemble unwashed sludge, rather than washed sludge. This was the only reported preparation of a de-washed sludge simulant associated with a rheological measurement. (This material was later combined with an approximate Pu-Gd waste and used in a glove box washing demonstration.) The de-washed simulant was mixed with some sand and coal, since site records indicated the presence of sand and coal in Tank 7 (the main waste component in SB3).

Rheological data were taken on both the de-washed and the decanted sludges using the RS150 rheometer with the Z41 bob.

- USC De-washed Tank 8 – 32.6 wt. % TS, 11.7 wt. % IS, 1.29 g/ml, pH > 13.2
- USC Simulant for Tank 8-SB3 – 18.0 wt. % TS, 15.7 wt. % IS, 1.11 g/ml, pH ~10

The de-washed sludge pH was checked by one probe in 773-A. A pH value over 13 was well outside the calibration range of the instrument. It should be taken as an indication that the sludge was fairly basic. The USC Simulant for Tank 8-SB3 was the decanted simulant with no sand or coal added.

3.1.6.5 SRT-GPS-2001-040 (Radioactive Tank 8 data)

T.L. Fellinger measured rheological properties of some CUF slurries; see also WSRC-TR-2001-00212, by M. Poirier for further details. These reports deal with cross-flow ultra-filtration tests and supporting rheology. The total solids were not measured, but the supernate was a ~5M sodium solution typical of the unwashed HLW tanks at SRS. The insoluble solids were measured.

- Tank 8 2001 Radioactive sludge – 6.0 wt. % IS

The measurement was made on the RV-30 rheometer in the Shielded Cells.

3.1.6.6 Tank 8 Sludge Rheology Summary

The various sources of data for Tank 8 sludge were collected for comparison in Table 5 below. Once again the comparisons are targeted toward the wt. % insoluble solids content of the samples. Sample identifications coincide with those given in the individual Tank 8 sections above.

Table 5. Tank 8 Related Sludge Rheology Results

Tank 8 Sludge Sample ID	Wt. % Insoluble Solids	Yield Stress, dynes/cm^2	Consist-ency, cP	Wt. % Total Solids
Tank 8 rad-as received	19.29	30	10.3	38.5
Tank 8 rad-diluted	11.3	14.4	4.06	27.7
USC Simulant for Tank 8-SB2	12.5	7.4	4.8	14.9
USC De-washed Tank 8	11.7	~15	~10	32.6
USC Simulant for Tank 8-SB3	15.7	23	7.6	18.0
1983A-5-rad	8.3	13	4	15.0
1983A-6-rad	10.5	19	4	18.9
1983A-7-rad	15.5	39	6	25.2
1983B-2-rad	5.4	9	3	12.4
1983B-3-rad	7.8	13	3	15.9
1983B-4-rad	12.9	16	4	24.6
1983C-1-rad	11.5	9	4	21.5
1983C-2-rad	12.0	13	4	21.4
1984A-1-rad	13.2	19	6	16.0
1984A-2-rad	17.4	44	8	20.2
1984A-3-rad	19.6	79	11	22.9
1984A-4-rad	24.4	170	21	27.9
1984A-5-rad	29.6	330	47	32.7
1984B-1-rad	12.4	27	4	12.7
1984B-2-rad	27.9	245	30	31.2
Tank 8 2001 Radioactive sludge	6.0	8.3	3.7	N.R.

The original Tank 8 USC simulant flow curve was obtained at TNX using the RV-20 rheometer and the MV1 bob. The down flow curve was slightly above the up flow curve which is a little unusual. The de-washed and decanted (SB3) flow curves were obtained with the RS150 rheometer, Z41 bob (which is the near analog to MV1). The RS150 up and down flow curves were nearly identical for both samples, indicating little time dependent behavior.

The USC Simulant for Tank 8-SB3 sample compares well with the 1984A-1-rad result. Total solids, insoluble solids, and yield stress are all slightly higher in this simulant than in the radioactive result. This is the expected direction of change in yield stress with insoluble solids at similar soluble solids levels and pH (moderately basic in this case). This point supports the use of this simulant for Tank 8 waste in a rheological sense.

A comparison of 1983A-7-rad and 1983B-4-rad samples to the Tank 8 rad-diluted sample seems to indicate that the drying out and subsequent re-slurrying of Tank 8 did not have much impact on the slurry rheological properties of the unwashed sludge. A less direct comparison of the Tank 8 2001 Radioactive sludge sample from the CUF work to 1983B-2-rad seems to generally confirm this observation.

It is reasonably certain that the Tank 8 rad-as received and Tank 8 rad-diluted samples had a more viscous supernate phase than the USC washed sludge simulant. They also almost certainly had a higher pH, and higher ionic strength. Both of these factors could potentially impact the yield stress. The data for USC simulant for Tank 8-SB2 appear to have been thinner than the ones for the variable depth samples. It is difficult to weigh the competing factors of different wt. % total and insoluble solids, pH, and ionic strength. The USC De-washed Tank 8 simulant sample (supernate salts added) gave a similar rheogram to those of the variable depth samples. De-washing Tank 8 simulant roughly doubled both the yield stress and the consistency relative to the original Tank 8 simulant. De-washing also increased the pH from ~9.9 to >13.2.

3.1.6.6.1 Tank 8 and SB2

The 1983 and 2000 Tank 8 radioactive sample results were much thinner than the SB2 radioactive rheology results given above in Table 3. SB2 was nearly 50% Tank 8. Yield stress was approximately five times lower in Tank 8 results than in SB2 results. Either Tank 40 rheology or the blending/washing process apparently impacted the overall SB2 radioactive rheology very significantly. Tank 40 simulant was also observed to impact the blended 8/40 USC simulant significantly, but apparently not enough to elevate the yield stress to SB2 radioactive levels. This was consistent with historical data that indicates that significant rheological differences can exist between waste tanks. The point is that the separate preparation of Tank 40 simulant without the Tank 8 material also produced a more viscous slurry of Tank 40 waste. This seems to be consistent with the Tank 8 and SB2 radioactive slurry data which show a much thicker Tank 8/40 blend than Tank 8 alone. This indicates that the current simulant preparation methodology is capturing some of the chemical impact on rheological properties.

Tank 40 did receive 160,000 gallons of HM waste from Tank 22 (estimated ~15% of the Fe in Tank 40). Older radioactive slurry data (see 3.1.8 for more detail) indicated that HM slurries were more viscous than Purex slurries {HM data were for Tanks 15, 21, and Tank 42 vs. Tank 8 and 51 for Purex, plus Tank 42 c. 1995 (after blending more wastes into it), see WSRC-TR-2000-00239 for a more detailed summary}. This suggests that current simulants may be more accurately simulating the rheological properties of Purex waste than of either HM slurries or slurries containing a significant amount of HM waste mixed with Purex slurry. This would help to explain why Tank 8 rheology matched well, while SB2 rheology did not.

It would be worthwhile to understand why the Tank 8 simulant apparently compared to radioactive samples better than the SB2 simulant for unprocessed sludge. The recipes for Tank 8 and Tank 40 simulants were fairly similar except for Ni. Tank 40 simulant from USC had a roughly ten times higher yield stress than Tank 8 simulant from USC (at nearly identical insoluble and soluble solids levels). There was no Ni in the Tank 40 simulant recipe (although a small amount of nickel was later found in the Tank 40 real waste sample). Adding Ni and Mn after the fact increased the yield stress further. These were not co-precipitated with iron, however. Visual observations at CETL during the preparation of generic simulants A, B, and C suggest that high Ni simulants are more viscous, settle more slowly, and settle less densely than low Ni simulants. This may provide a clue that can be used to improve simulant formulations in the future.

3.1.7 Other/Miscellaneous Radioactive Sludge Slurry Data

3.1.7.1 SRT-GPS-2001-040 (Tanks 11 and 51)

T.L. Fellinger obtained some data on Tank 11 and Tank 51 sludge rheology in the Shielded Cells in support of the CUF test program; see also WSRC-TR-2001-00212 by M. Poirier for more details. This was apparently an unwashed sludge from a Tank 51 sample (the SB1A feed stock once it was washed).

- Tank 51 – 6.0 wt. % insoluble solids, yield stress 8.7 dynes/cm^2, consistency 1.9 cP

There was also the data for Tank 8, given in section 3.1.6.5 plus data for Tank 11 (mixed Purex and HM waste):

- Tank 11 – 6.0 wt. % IS, yield stress 8.4 dynes/cm^2, consistency 5.8 cP

These samples were comparable to unwashed sludges. Measurements were made with the RV-30 rheometer and the MV1 bob.

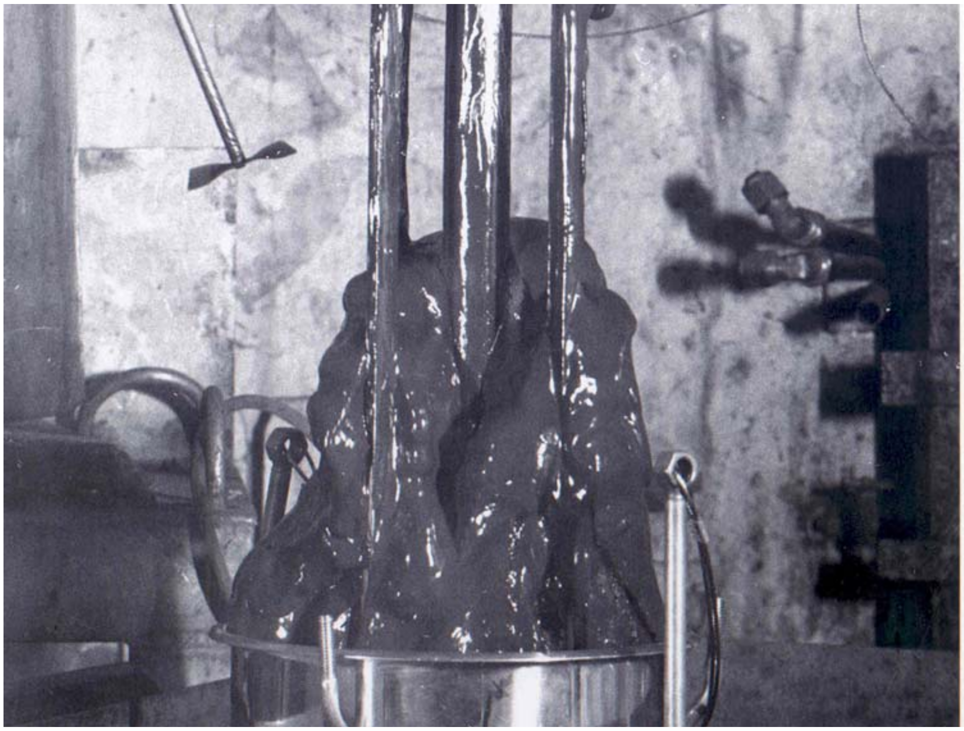
3.1.7.2 DPST-86-206 (Tank 21H)

D. D. Walker obtained some Tank 21H sludge rheological data. This was referenced by B.C. Ha in his Tank 42 report, plus additional Tank 21 data. Most of the Tank 21 sludge was transferred to either Tank 42 or Tank 51 in 1986.

3.1.7.3 DPST-84-439 (Tanks 8F, 15H, & 42H)

B. A. Hamm obtained two additional sets of data comparable to that given in section 3.1.6.1 for Tank 8F and for Tanks 15H and 42H. Tank 15H data is primarily HM High Activity Waste. The Tank 42 data is not comparable to the SB1B composition. Measured Tank 15 and 42 yield stresses rose much more quickly with increasing wt. % insoluble solids than did the Tank 8 yield stress measurements. A yield stress of 100 dynes/cm^2 corresponded to about 10 wt. % insoluble solids for Tanks 15 and 42, but to about 22 wt. % insoluble solids for Tank 8. This suggests that processing HM wastes may be more challenging than processing Purex wastes. The figure below is from a sample of Tank 11 waste received in the Shielded Cells in 1979.

Figure 5. Sample of Tank 11 in 1979



The image is DPSTF-14472-1, identified only as High Level Caves Sludge Sample, dated 10/1/1979. As the quantity of solids increases, a waste sludge loses the ability to flow under the force of gravity alone. Adding water produces a more fluid slurry.

3.1.7.4 WSRC-TR-2002-00070 (Tank 19 mound sample)

This document by T.L. Fellinger & E.K. Hansen reports on testing of the Tank 19F radioactive mound sample, and does not appear to apply to traditional DWPF sludge simulants in any way.

3.1.8 Overall Summary of Sludge Comparisons

The Purex simulant rheology seemed to match fairly well with the actual Purex wastes, but the radioactive samples with an HM component, e.g. SB2, were not always similarly well matched. It would be possible to test this hypothesis further with additional tests. For example, generic simulants could be blended to target Tank 15 and 21 compositions (HM), and then the rheology could be compared to the historical data to see if this trend holds. This could be done as part of the simulant development program. Such a trend could indicate that some Al co-precipitation, or other adjustment, is needed to produce comparable HM simulants in a rheological sense.

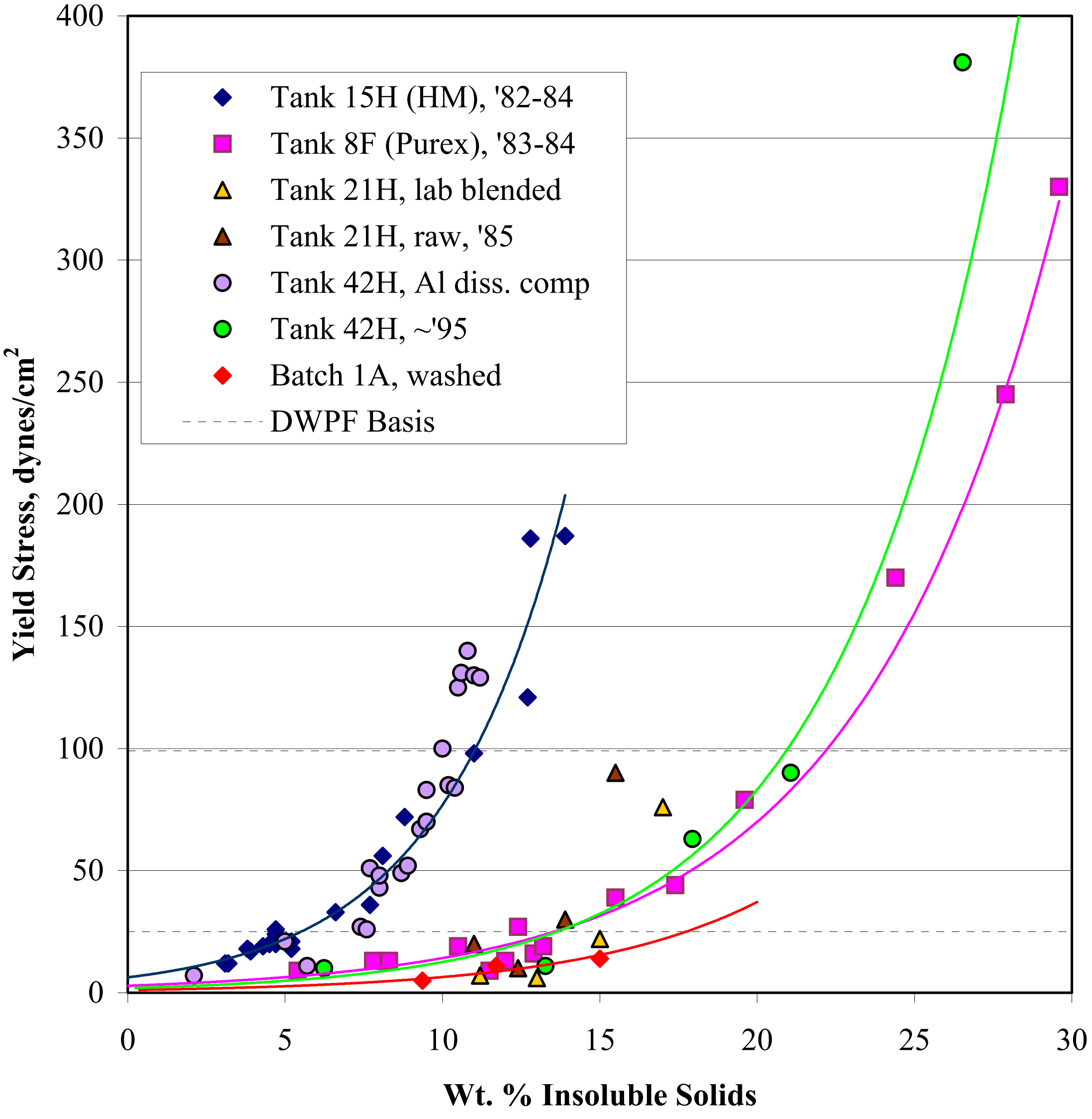
A review of the simulant flow curves shows that the up and down flow curves have generally been very similar and normal in appearance, except for SB2-CETL simulant (up curve has a hump). The down flow curve could either be slightly above or below the up flow curve in the other cases (Tank 8, Tank 40, Tank 8/40 blend, Tank 42, CETL SB3 untrimmed). The typical shear rate range was about 0-400/sec over five minutes. Similar up and down flow curves are consistent with Shielded Cells sludge rheograms.

The CETL SB2 sludge run on the RV-20 during the DU testing had a hump in the up curve. The shear stress at the top of the hump was comparable to the SB2 radioactive sludge rheograms. At this point it was closer than the USC sludges ever got to the radioactive sludge rheograms. Recent data indicate that the hump is a transient phenomenon that does not reappear if the sample is left in the beaker and run through another up ramp measurement.

It was noted during preparation of USC Tank 8 and Tank 40 simulants for SB2 that the nickel-free Tank 40 simulant was much thicker during iron precipitation than the Tank 8 simulant. The final Tank 40 simulant had an order of magnitude greater yield stress than the Tank 8 simulant at approximately the same total and insoluble solids contents. A similar observation was made at CETL during preparation of the generic simulant ("C") that was high Ni/Fe and low Mn/Fe (opposite of USC case), but was not noted during preparation of the generic simulant that was both low in Ni/Fe and Mn/Fe ("A") or the simulant that was high in Mn/Fe and low in Ni/Fe ("B") and similar to the USC Tank 40 case. This suggests that the Mn-Fe-Ni precipitation portion of the simulant recipe has a profound affect on the simulant properties.

Figure 6 below was first published in WSRC-TR-2000-00239 which investigated potential reasons for SB1B being tackier than SB1A.

Figure 6. Composite Plot of Radioactive Slurry Rheology Data



The most noteworthy feature is the relative behavior of HM versus Purex sludge yield stress as a function of wt. % insoluble solids. HM sludge exceeded 100 dynes/cm^2 yield stress at about 9-11 wt. % insoluble solids while Purex sludge exceeded this yield stress at about 20-22 wt. % insoluble solids. (The graph does not include SB2 or SB3 data which did not exist at the time it was prepared.)

T. B. Edwards analyzed the above data from Tanks 15 and 42 using the JMP statistical software package. A quadratic function of wt. % IS was statistically significant in explaining the variation in yield stress and had an R^2 of 0.923 (an exponential function was used to generate the curve in Figure 6). A function that was quadratic in both wt. % IS and wt. % soluble solids (with no cross terms) was statistically significant as well, although the R^2 only increased to 0.935. The five constants in this model were all statistically significant at the 95% confidence level, although the improvement in fit was small. These sample series were really not ideal for assessing the impact of washing on sludge rheology, but they were the only data available that might have done so. The fact that the soluble solids content was varied by three different methods (dilution with supernate, de-ionized water, or 0.01M caustic) may have contributed to masking the effect of washing (pre-planned dilution with a single fluid). A potential rheology study during washing should be considered. This may need to be done with simulants, since the Shielded Cells washing is often done in fewer steps than the Tank Farm washing, i.e. would not give a sufficient number of intermediate compositions to track the effect of washing on rheology.

3.2 SRAT PRODUCTS

The sub-sections below focus on the Bingham Plastic fluid model rheological properties for DWPF SRAT product slurries. No rheological data was found for any of the early Shielded Cells SRAT products (made from samples of Tanks 4, 11, 15, and 51).

3.2.1 SB1A and SB1B SRAT Products

There does not appear to be any radioactive SRAT product data for the first two sludge batches in DWPF. There does not appear to be much, if any, simulant data for the SRAT products for the first two sludge batches either.

3.2.2 SB2 SRAT Product

3.2.2.1 WSRC-TR-2002-00302 (SB2 rheology comparison)

T.L. Fellinger and D.C. Koopman investigated the radioactive and simulant rheological data that were available prior to the replacement of the first DWPF melter. SRAT product made during the SB2 qualification run in the Shielded Cells was analyzed on the RV-30 rheometer using the MV1 bob.

- SB2-Rad-SRAT Product-125% acid-1 – 20.2 wt. % TS, 15.0 wt. % IS, 1.15 g/ml, pH 6.49
- SB2-Rad-SRAT Product-125% acid-2 – 20.2 wt. % TS, 15.0 wt. % IS, 1.15 g/ml, pH 6.49
- SB2-Rad-SRAT Product-125% acid-3 – 20.2 wt. % TS, 15.0 wt. % IS, 1.15 g/ml, pH 6.49
- SB2-Rad-SRAT Product-125% acid-4 – 20.2 wt. % TS, 15.0 wt. % IS, 1.15 g/ml, pH 6.49

The sample was run four times. The results of the last three flow curves differed from that of the first flow curve.

3.2.2.2 WSRC-TR-2003-00136 (Phase I Rheological Work for SB2)

T.L. Fellinger made additional measurements on fresh sample material from SB2 during the DWPF plant outage to replace the first melter. SRAT testing targeted conditions in DWPF SRAT batches 213 and 221, which were relatively low and high in acid stoichiometry respectively. The SRAT product for the batch 221 case was not initially as low in pH as desired. It was remediated after rheological characterization with additional acid that dropped the pH from 6.2 to 5.5. This became the most extensive set of radioactive rheological testing related to SRS waste since the work of B.C. Ha on Tank 42 washed sludge.

The above SRAT cycle testing created a set of three SB2 SRAT products at different pH values. In each case the SRAT product was allowed to settle. Supernates were decanted to create higher wt. % total solids and insoluble solids slurries. Rheological measurements were made. Supernate was then added back to a portion of the solids-rich slurry to create a diluted slurry with lower wt. % total solids and insoluble solids. Rheological measurements were repeated. The supernate and insoluble solids-rich material were then recombined before continuing with processing (two SME cycles were performed on the pH 6.8 and pH 5.5 recombined samples). This decanting/diluting effort led to a set of nine rheological characterizations of SB2 SRAT product. That some of these samples can be called SRAT products is subject to the assumption that direct preparation of such slurries would have produced samples with identical rheological behavior. Even if this assumption does not turn out to be entirely true, the testing would show the qualitative impacts of changing the wt. % insoluble solids and the pH on the rheological properties of the SRAT product slurry.

Table 6. Summary of SB2 Radioactive SRAT Products from 2003

Sample ID	Wt. % Total Solids	Wt. % Insoluble Solids	pH
2003 Rad SRAT-221 Product	21.4	17.5	6.2
Decanted Rad SRAT-221 Product	25.9	22.3	6.2
Diluted Rad SRAT-221 Product	18.4	14.3	6.2
Remediated Rad SRAT Product[1]	18.9	14.9	5.5
Decanted-Remediated Rad SRAT Product	22.3	18.5	5.5
Diluted-Remediated Rad SRAT Product	14.6	10.2	5.5
SRAT Batch 213 Rad Product[2]	20.4	16.0	6.8
Decanted 213 Rad Product	24.3	20.4	6.8
Diluted 213 Rad Product	17.3	12.6	6.8

1 – More acid added to the 221 SRAT product, since the pH target was missed high – this is the “high acid” case.

2 – This is the “low acid” case.

Batch 221 was initially 145% of stoichiometric acid. It was then remediated to 170% of stoichiometric acid following characterization. Batch 213 was at 125% of stoichiometric acid. Rheological data was obtained in the Shielded Cells using the RV-30 rheometer with the MV1 bob.

3.2.2.3 WSRC-TR-2001-00051 (SB2 Rheology with USC Simulants)

D.C. Koopman obtained the first rheological data on SB2 simulant SRAT products. Seven SB2 SRAT products were generated. Two were from essentially identical batching and processing strategies. Various levels of noble metals were used in the SRAT cycle trim chemical additions. This occurred when a sample of Tank 40 (prior to blending with Tank 8) was characterized. The measured noble metal concentrations were much lower than early estimates. “HiHi” noble metals in Table 7 were based on earlier higher estimates for both Tank 8 and Tank 40 noble metal concentrations. “Hi” noble metals were based on measured Tank 40 noble metal concentrations and a conservatively high estimate for Tank 8 noble metal concentrations. They were fairly close to the HM bounding level of noble metals developed during IDMS pilot plant testing. The SB2 flow sheet study program concluded before chemical analyses were obtained on the noble metal concentrations of the final Tank 8/Tank 40 sludge blend that was used in the qualification testing.

Table 7. SB2 Simulant Flow Sheet Study SRAT Products

Sample ID	Noble Metals	Wt. % Total Solids	Wt. % Insoluble Solids	pH
USC-137.5% acid	hi-hi	17.0	~12	6.75
USC-137.5% acid	hi	16.9	~12	6.50
USC-125% acid-1[1]	hi	16.5	11.7	6.50
USC-125% acid-2	hi	16.4	11.2	6.81
USC-125% acid-3	HM[2]	16.5	11.8	7.29
USC-110% acid	hi	16.5	11.4	6.35
USC-290% acid	hi	18.7	11.2	6.33

1 – Suspicious rheology (suspect yield stress).
2 – HM bounding noble metals from IDMS testing.

The 290% acid run simulated a formic acid tank dump. The case labeled USC-125% acid-2 was the nominal baseline case for the SB2 qualification run. This study also generated data for three Tank 40 only SRAT products containing no Tank 8. There is no corresponding radioactive SRAT product data for these.

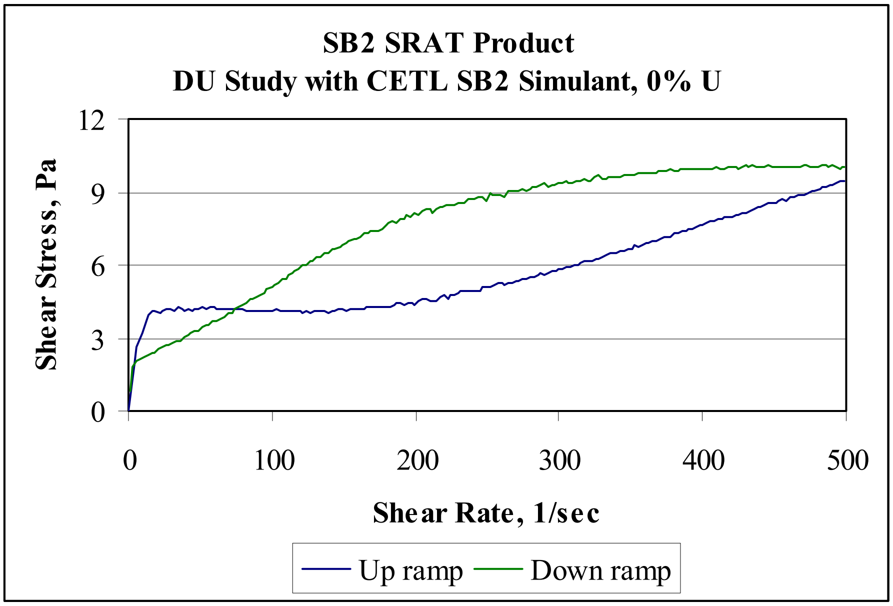
3.2.2.4 WSRC-TR-2003-00402 (DU study with CETL SB2 simulant)

D.T. Herman/W.R. Wilmarth report results for their baseline case SRAT product, which contained no depleted uranium (DU). The samples were run in 773-A on the RV-20 rheometer using the MV1 bob. The acid addition was quite high at 170% compared to preliminary flow sheet studies at 110-137.5%. Noble metals were matched to the SB2 qualification sample results (“normal”).

- CETL DU study, 0%U, 170% acid – 20.7 wt. % TS, 14.9 wt. % IS

The shear stress rose initially during the shear rate ramp up, hit a plateau, then rose some more, as seen in Figure 7.

Figure 7. Unusual SRAT Product Rheogram from CETL SB2 DU Study



This flow curve with plateau may be an intermediate form between a normal flow curve and one with a hump. The shear stress continued to rise during the hold. The down curve was above the up curve until about 50-75/s shear rate, where it crossed over and went below. There were also some data at 7.5% U and 15% U.

- CETL DU study, 7.5% U, 170% acid – 23.2 wt. % TS, 13.1% IS

Data for the 15% U case were not comparable to other data collected.

3.2.2.5 WSRC-TR-2003-00364 (SB2 Processing Issues)

M.E. Stone and P.L. McGrier report some CETL simulant rheological data for SRAT products. There were six SRAT product rheograms from the early part of the SB2 processing issues program. The early data was taken using the 60mm parallel plate geometry, however, instead of the concentric cylinder geometry. It is not clear how comparable this data would be to concentric cylinder geometry data, either for simulant or radioactive SB2 SRAT product. (Parallel plates are horizontal, with approximately a 1-1.5mm gap. Settling of larger particles can be more significant with such a short vertical path compared to the concentric cylinder geometry.)

3.2.2.6 SB2 Testing with Depleted Uranium

C.J. Bannochie and D.T. Herman have recently overseen the preparation of six new SB2 simulants in 773-A. This includes a SB2 simulant similar to the USC and CETL simulants, plus five simulants with four levels of uranium targeting essentially constant total solids, i.e. lower levels of the other sludge elements were introduced to offset the presence of uranium (the mid-point DU simulant is being prepared twice as a control check). SRAT product rheograms were obtained for each SRAT cycle. One unusual feature of this data set was that the SRAT products with DU were thicker than the starting sludge simulants, while in prior simulant and radioactive SB2 work, the SRAT products were thinner than the starting sludges.

3.2.2.7 SB2 SRAT Product Rheology Summary

The various sources of data for SB2 SRAT product were collected for comparison in Table 8 below. Once again the comparisons are targeted toward the wt. % insoluble solids content of the samples. Sample identifications coincide with those given in the individual SB2 SRAT product sections above.

Table 8. SB2 SRAT Product Rheology Comparison

SB2 SRAT Product Sample ID	Noble Metals	Wt. % Insoluble Solids	Yield Stress, dynes/cm^2	Consist-ency, cP	Wt. % Total Solids
SB2-Rad-SRAT Product-125% acid-1	normal	15.0	41	4.7	20.2
SB2-Rad-SRAT Product-125% acid-2,3,4	normal	15.0	30	4.5	20.2
Decanted Rad SRAT-221 Product	normal	22.3	50.6	5.8	25.9
2003 Rad SRAT-221 Product	normal	17.5	35.1	3.8	21.4
Diluted Rad SRAT-221 Product	normal	14.3	18.0	3.4	18.4
Decanted-Remediated Rad Product	normal	18.5	20.5	6.3	22.3
Remediated Rad SRAT Product-high acid	normal	14.9	(2.0[a])	(4.3[a])	18.9
Diluted-Remediated Rad Product	normal	10.2	lost[a]	lost[a]	14.6
Decanted 213 Rad Product	normal	20.4	62.6	5.4	24.3
2003 SRAT 213 Rad Product-low acid	normal	16.0	49.1	5.7	20.4
Diluted 213 Rad Product	normal	12.6	14.8	2.5	17.3
USC-137.5% acid	hi-hi	~12	43	8.4	17.0
USC-137.5% acid	hi	~12	31	12.7	16.9
USC-125% acid-1 (suspect yield stress)	hi	11.7	~55	8.3	16.5
USC-125% acid-2	hi	11.2	35	9.4	16.4
USC-125% acid-3	HM	11.8	33	8.4	16.5
USC-110% acid	hi	11.4	37	8.5	16.5
USC-290% acid	hi	11.2	43	8.6	18.7
CETL-DU study, 0% U, 170% acid	normal	14.9	~25-40	>1	20.7
CETL-DU study, 7.5% U, 170% acid	normal	13.1	~30-40	>3	23.2

a – given the data at 35°C, not shown here, and the fact that one set of data was lost, it still looks to me as though the data for the remediated SRAT product belong with the remediated-diluted SRAT product instead.

One observation worth discussing is that the simulant flow sheet study formic acid dump (USC-290% acid) did not produce an improvement in rheology compared to the nominal flow sheet run (USC-125% acid-2). It also failed to produce much of a pH change, however, due to the actions of the noble metals on the excess formic acid. The high formic acid addition also significantly changed the appearance of the insoluble solids from sort of medium brown to black-brown. Volume mean particle size was also lower in the 290% acid SRAT product, 3.6 vs. 5.6 microns. One hypothesis is that additional SRAT acid could be a less effective rheology modifier than acid addition at the end of the SME cycle when noble metal concentrations get high.

SRAT product rheology has not been extensively studied other than for SB2. The USC-based simulant SRAT products generally gave regular up flow curve shapes with down flow curves that were lower. Not all flow curves were regular, however. One of three measurements of the “nominal SB2 flow sheet case” SRAT product did give a hump in the up flow curve using the RV-20 rheometer. It was similar to those seen on some of the CETL simulant sludge rheograms. The other two measurements, however, showed no sign of a hump.

Some of the CETL-based SB2 SRAT products in the first DU study had down flow curves that ran well above the up flow curves, then crossed over as shear rate decreased. The 0% and 7.5% DU SRAT product did this at 25°C. The effect was subtle for the 15% DU case. At 50°C the 7.5% DU product had a hump in the up flow curve similar to that occasionally seen in SB2 sludge rheograms. Perhaps of note is that, while the three starting sludges and the three SRAT products in the DU study sometimes had "unusual" behavior, the three samples pulled after acid addition (minimum pH) had totally normal rheograms (simple up flow curve, with down flow curve close to up curve). This suggests a possible linkage between pH and time-dependent rheological behavior.

3.2.3 SB3 SRAT Product

At the time of this report, SB3 represents the sludge preparation occurring in Tank 51. This includes the heel of SB1B, a large transfer from Tank 7, plus some minor transfers through Tank 7 of other tanks, along with a Pu waste stream, and, potentially, some fraction of a Np waste stream. Two qualification SRAT runs were made in the Shielded Cells in late 2003. SRAT product from the first of these is available for rheological characterization. There were some issues with the processing of that sludge. It is expected that the term "SB3" will eventually represent the combination of the contents of Tank 51 with the remainder of SB2 in Tank 40, sometimes referred to as SB2/3 in this report (to indicate the blend is being described).

3.2.4 SB2/3 SRAT Product

Radioactive and simulant rheological data may become available on this system in the next three months. The initial test of the SB2/3 blend was completed in the Shielded Cells in December. A rheology sample was pulled to be analyzed at the next opportunity. Per the note above under "SB3 SRAT Product", this SB2/3 blend will likely become known as SB3 in the future.

3.2.5 SRAT Product Comparison Summary

SRAT product is the phase of the DWPF process with both the least rheological data and the least comparable data between radioactive and simulant systems. This observation excludes consideration of additional rheological changes that could occur during processing itself, such as changes during SRAT acid addition as pH changes, changes in the SME cycle between frit additions, etc. There could be an opportunity to improve this by mocking up the Shielded Cells SB3 SRAT product with simulant. This would involve trimming some SB3 simulant and running it through a SRAT cycle. Another opportunity to improve this exists with the blended SB2/3 system that will be processed in DWPF starting in March 2004. Some simulant data has already been taken on SRAT products as a function of excess acid, but the radioactive piece of the comparison is missing.

The SB2 simulant SRAT products appeared to be somewhat more viscous than the radioactive SRAT products. This is the opposite trend observed in the SB2 washed sludge data, i.e. SRAT processing did more to change the radioactive slurry rheology than to change the simulant rheology.

Samples pulled during acid addition in the GFPS runs (WSRC-TR-2003-00179) indicated that yield stress increased during the first part of acid addition, reaching a maximum at pH's near 7, then decreased continuously during the remainder of acid addition. It is unknown at this time whether yield stress falls steadily during real waste processing, or goes through a similar maximum. SB2 data indicate a significant decrease in yield stress from the starting sludge to the SRAT product. There is currently no intermediate data on radioactive sludges as the pH changes.

3.3 SME PRODUCTS

The sub-sections below focus on the Bingham Plastic fluid model rheological properties for DWPF SME product slurries. Radioactive data exist only for the DWPF sludge batches that have been processed to date.

3.3.1 Sludge Batch 1A (SB1A) SME Product

3.3.1.1 WSRC-MS-92-410 (Tank 51 sludge + frit)

B. C. Ha reported on some Tank 51 slurries with frit. These radioactive slurries, however, were *not acidified* in a SRAT/SME cycle (pH>11).

- SB1A-41% - 41 wt. % TS (14.3% Tank 51 sludge, 85.7% Frit 202), yield stress = 5 dynes/cm^2
- SB1A-55% - 55 wt. % TS (31.1% Tank 51 sludge, 68.0% Frit 202), yield stress = 145 dynes/cm^2
- SB1A-57% - 57 wt. % TS (9.3% Tank 51 sludge, 90.7% Frit 202), yield stress = 75 dynes/cm^2

The last two results indicate that lowering the sludge oxide waste loading at roughly constant total solids may produce a significantly less viscous melter feed under these conditions. The insoluble solids content must have increased by more than the 2% that the total solids increased (since the soluble solids come primarily from the sludge), but, in spite of that, the yield stress dropped by a factor of two. The yield stress was reported in the document, but consistency was not reported.

3.3.1.2 WSRC-TR-96-0179 (Batch 1, Run 5)

J. C. Marek reported on the impact of wt. % insoluble solids (IS) on SME product. These simulant melter feeds were run through a SRAT cycle, but not a SME cycle. Frit was added to the SRAT product without further prototypical processing at elevated temperature. The rheology samples are almost certainly based on Optima Tank 51 simulant, i.e. SB1A.

- B1R5-1 - 45.36 wt. % TS, 37.54 wt. % IS
- B1R5-2 - 48.79 wt. % TS, 39.53 wt. % IS
- B1R5-3 - 51.26 wt. % TS, 40.99 wt. % IS
- B1R5-4 - 55.18 wt. % TS, 43.64 wt. % IS
- B1R5-5 - 57.78 wt. % TS, 44.56 wt. % IS
- B1R5-6 - 59.66 wt. % TS, 47.38 wt. % IS
- B1R5-7 - 63.74 wt. % TS, 48.93 wt. % IS

These simulant melter feeds were made from 1419.8 g of frit 200 added to 3838.4 g of SRAT product. The alternative sludge-only flow sheet was used. B1R5 stands for run #5 of batch 1 sludge. Batch 1 was normally associated with the SB1A-Tank 51 sludge simulant recipe. Wt. % total solids were adjusted by concentrating down individual samples of the synthesized SME product by boiling. The pH was most likely less than 7. Any comparison of these simulant melter feeds to the high pH radioactive melter feeds of B. C. Ha above can only be approximate. Simulant data were taken on the RV-20 rheometer in 772-T.

3.3.1.3 SB1A SME Product Rheology Summary

The various sources of data for SB1A SME product were collected for comparison in Table 9 below. Once again the comparisons are targeted toward the wt. % insoluble solids content of the samples. Sample identifications coincide with those given in the individual SB1A SME product sections above.

Table 9. SB1A SME Product Rheology Results

Sample	Wt. % Insoluble Solids	Yield Stress, dynes/cm^2	Consistency, cP	Wt. % Total Solids
SB1A-rad-41%	~37[1]	5	-	41
SB1A-rad-55%	~46[1]	145	-	55
SB1A-rad-57%	~54[1]	75	-	57
B1R5-1	37.54	14.3	6	45.36
B1R5-2	39.53	23	15	48.79
B1R5-3	40.99	48	17	51.26
B1R5-4	43.64	129	38	55.18
B1R5-5	44.56	200	56	57.78
B1R5-6	47.38	333	97	59.66
B1R5-7	48.93	715	210	63.74

1 – Estimated by author, see text.

The wt. % insoluble solids for the radioactive samples are only reasonable estimates based on the sludge solids fraction of the total solids. These estimates have been made here to facilitate comparisons with the simulant data. Sludge was assumed to be about 70% insoluble solids:30% soluble solids. (These estimates were not part of B.C. Ha's original data.) This was a Purex-based waste system.

The 55% radioactive sample was the only one with a reasonable mixture of sludge and frit relative to actual SB1A processing. It was relatively close to the B1R5-4 and B1R5-5 simulant results in solids content. The yield stress was in good agreement for the radioactive and simulant data. The other two radioactive slurries were too frit rich to be directly comparable to the simulant data, but do seem to indicate that decreasing waste loading tends to lower the apparent viscosity of melter feeds (at least under basic conditions).

3.3.2 Sludge Batch 2 (SB2) SME Product

3.3.2.1 WSRC-TR-2002-00302 (Preliminary SB2 Rheology Data Comparison)

T.L. Fellinger and D.C. Koopman compared some of the early simulant and radioactive rheology data for SB2. This included the preliminary SB2 rheology work with simulants, WSRC-TR-2001-00051, some data from the preparation of simulant melter feeds for the Mini-melter using the 1/240th Glass Feed Preparation System (GFPS, a 50 gallon SRAT/SME unit), plus the available Shielded Cells data.

- SB2-Rad-SME Product – 45.3 wt. % TS, 40.8 wt. % IS, 1.36 g/ml, pH 6.3

This was a frit 200 based SME product. It was made from sludge that was washed in the Shielded Cells and then run through a SRAT/SME simulation. The waste loading was about 28.3% sludge oxides in glass. It was analyzed in the Shielded Cells on the RV-30 using the MV2 bob.

3.3.2.2 WSRC-TR-2003-00253 (Shielded Cells Phase I SB2 Rheology Work)

T.L. Fellinger reported on follow-up studies based on new samples of Tank Farm-washed SB2 sludge. These SME products were at about 30% waste loading in glass. This was a frit 320 based series of tests. The SME cycle used the SRAT products characterized in section 3.2.2.2. Two SME products were made. Each was divided into two parts. Some of the supernate from one was added to the other to prepare samples at two different wt. % total solids.

- SME Rad-Batch 221 Diluted – 38.3 wt. % TS, 35.2 wt. % IS, pH 6.8
- SME Rad-Batch 221 Decanted – 46.7 wt. % TS, 44.2 wt. % IS, pH 6.8

- SME Rad-Batch 213 Diluted – 43.1 wt. % TS, 41.4 wt. % IS, pH 7.3
- SME Rad-Batch 213 Decanted – 46.4 wt. % TS, 44.8 wt. % IS, pH 7.3

Batch 213 was at 125% stoichiometric acid in the SRAT cycle. Remediated batch 221 was at 145% stoichiometric acid in the SRAT cycle, and then adjusted to the equivalent of 170% acid before the SME cycle.

3.3.2.3 WSRC-TR-2001-00051 (SB2 USC Simulant Rheology)

D.C. Koopman obtained rheological data for simulant melter feeds prepared during the simulant flow sheet studies that preceded the SB2 qualification run in the Shielded Cells. The selected samples below were from the SME product of the nominal flow sheet run at 125% acid, see section 3.2.2.3. This run used the projected noble metal concentrations ("hi" in the SB2 SRAT product table, Table 8) that were ultimately found to be significantly higher than in the real waste. One goal was to obtain the dependence of the yield stress and consistency on the wt. % solids.

The SME product waste loading target was 25% sludge oxides in glass. Frit 200 was used. The 55 wt. % product was obtained by boiling down a portion of the nominal SME product. The other four wt. % total solids below were obtained by diluting either the nominal SME product or the 55 wt. % product with condensate collected during the final dewatering portion of the SME cycle. Properties of the six SME products are given in Table 10.

Table 10. SB2 Simulant SME Product Properties

Sample ID	Wt. % Total Solids	Wt. % Insoluble Solids	pH
USC SB2-1	37.8	33.7	6.9
USC SB2-2	41.0	36.4	6.8
USC SB2-3	44.2	39.1	6.8
USC SB2-4	48.9	42.8	7.0
USC SB2-5	51.7	45.3	6.9
USC SB2-6	55.0	48.2	7.0

Various rheogram shapes were obtained using the RV-20 with the MV2 bob, but no "humps" were observed. At low wt. % solids, the up flow curves were generally shaped as expected with the down curves below them. At intermediate solids, the up flow curves were generally as expected with the down curves above them. At high solids, the up curves were generally as expected, though sometimes they were a bit bumpy, with the down curves quite close to them. (This was also true for the SME products from the Tank 40 only (no Tank 8) trial that were analyzed at the same time.) Data at 50°C indicate that raising temperature may have increased the % solids range over which the up curve was below the down curve, i.e. made the flow curve more conventional.

3.3.2.4 WSRC-TR-2003-00512 (waste loading impact on SB2 melter feed)

M.E. Smith and T.M. Jones reported some simulant SB2 SME product rheology data. Data were obtained at 40 and 45 wt. % TS, for 31, 35 and 40% waste loadings (sludge oxides in glass) at 25°C in the Z41 concentric cylinder geometry. The RS600 was used. The 40% TS product was made by diluting 45% TS product with SME cycle condensate. The sludge matrix was CETL SB2 simulant processed through the 22-L SRAT for the Slurry-fed Melt Rate Furnace (SMRF). Noble metal concentrations were matched to the actual SB2 measurements. The acid was added to 113% of stoichiometry plus the equivalent of 50 gallons of formic acid added at the end of the SME cycle. Frit 320 was used. Density did not trend as expected. All sample rheological data were obtained in duplicate.

Table 11. SB2 SME Products for Melt Rate Testing

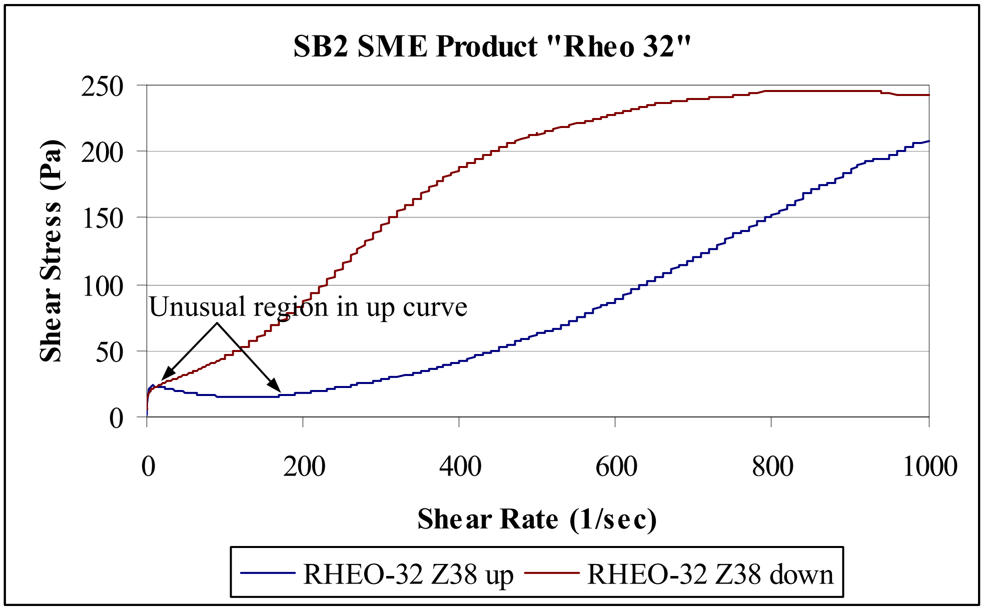
Sample ID	Wt. % Total Solids	Wt. % Insoluble Solids	pH	Density, g/ml
CETL-SMRF-45-31WL	45	38.4	5.1	1.42
CETL-SMRF-45-35WL	44	39.3	5.2	1.46
CETL-SMRF-45-40WL	45	39.6	5.2	1.35
CETL-SMRF-40-31WL	~40	-	-	-
CETL-SMRF-40-35WL	~40	-	-	-
CETL-SMRF-40-40WL	~40	-	-	-

Up flow curves were not the usual shape, except for one run of the 40 wt. % total solids, 31% waste loading sample. The other eleven up flow curves exhibited unusual behavior. This may relate to the CETL starting sludge which has given unusual behavior as sludge and as SRAT product. Bingham plastic parameters were obtained from the down flow curves, since the up flow curve data was not amenable to such an analysis. Nevertheless, the absolute values of the Bingham plastic fluid parameters were not considered reliable. The data were primarily useful in showing relative trends in behavior.

3.3.2.5 WSRC-TR-2003-00364 (SB2 Processing Issues Study)

M.E. Stone and P.L. McGrier obtained rheological data on SB2 simulant melter feeds. The Z38 concentric cylinder bob was used with the RS150/RS600 rheometers to obtain the flow curves. The melter feeds were prepared by running a SRAT/SME simulation on CETL SB2 simulant. The flow curves were not the expected shape. Up and down flow curves were quite separated, with down curves generally well above up curves. Some rheograms had falling shear stress with increasing shear rate during the up flow curve, indicating significant non-steady state measurement conditions. An example is given in Figure 8.

Figure 8. Example SME Product Flow Curve From SB2 Study



Seemingly similar compositions and processing times did not produce flow curves that were as similar as expected. This suggests that some additional variations in properties may have been present that were not identified by the analytical results. A grand average nominal case for 180% acid and 30% waste loading using this data could approximately be described as:

- CETL-Process Issue-50-30WL, 50 wt. % TS, ~43 wt. % IS estimated, pH 4.1-5.0

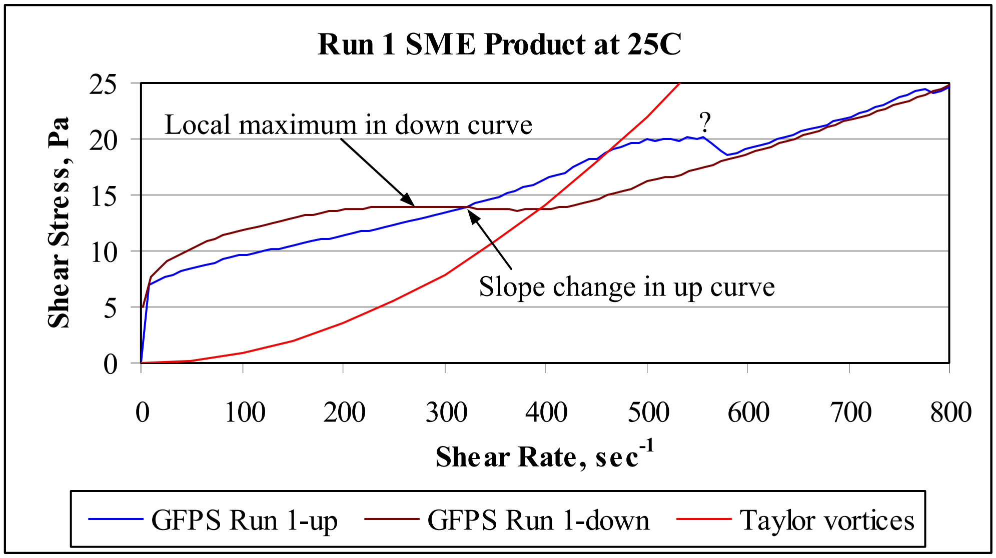
The range in pH was surprisingly large among the six runs with 180% acid and 30% waste loading, as was the range in shear stress observed at low shear rates (roughly taken as yield stress for the table below).

The nominal conditions in this study were 180% of stoichiometric acid, 30% waste loading in glass, and 50 wt. % total solids in the SME product. Reducing the stoichiometric acid appeared to make the SME products thicker. Increasing the waste loading appeared to make the SME products thicker. Both reduced acid and higher waste loading increased separation between the up flow curves and down flow curves, which may indicate increased time dependence of the slurries to shear phenomena. The impacts of lowering iron in glass redox from 0.2 to 0.1 and of varying the SME cycle boiling time were not clearly resolved by the data. Perhaps lower redox and longer boiling times led to the less viscous SME products, but additional research would be needed to test these hypotheses.

3.3.2.6 WSRC-TR-2002-00186 (GFPS SB2 SME products with Frit 320)

D.C. Koopman and D.H. Miller reported some SME product rheological data for the frit 320 based melter feed prepared in the 1/240th Glass Feed Preparation System (GFPS) as feed for the Mini-melter. Two GFPS runs were made with USC-SB2 simulant. The RS150-Z38 bob rheograms formed loops, and were unlike those previously obtained with the USC-SB2 simulant, frit 200-based SME products on the RV-20 with the MV2 bob. An example of an RS150 rheogram is shown in Figure 9.

Figure 9. Example of SB2 SME Product from GFPS Run 1 with Frit 320



Samples were taken to 800/s shear rates, but data appeared to be useless above about 250/s. Taylor vortices were not predicted to affect the data until about 400/s shear rates. Effects were noted there in both the up and down flow curves, but these came after other unexpected behavior was seen. Up flow curves were above the down flow curves at high shear rates, where they broke down into oscillations of shear stress with increasing shear rate. Samples tended to retain small bubbles that migrated to the cylindrical sensor surface during the rheological measurement and partially coated the surface. The bubbles remained attached to the cylinder as it was removed from the cup. Partial centrifugation of frit toward the beaker wall was also proposed as a possible explanation for some of the unusual rheogram characteristics. Additional tests on this slurry indicated that it would not come to steady state at a constant shear rate after twenty minutes. Shear stress increased steadily during this test. Given that frit could be settling, bubbles could be migrating, etc., it was not possible to come to a definitive conclusion as to what was causing the time-dependence in the shear stress response.

No table entries are given below, since the data were problematic and seem to add little to the discussion, but yield stress appeared to be in the 80-150 dynes/cm^2 range. Wt. % total solids were 46.2% and insoluble solids were 41.5 wt. %. This puts the sample around USC-SB2-3 in the table below, i.e. it is generally consistent with the earlier USC-based SME product data.

3.3.2.7 SB2 SME Product Rheology Comparison

Table 12 below provides a direct comparison of the various data that have been obtained on the SB2 SME product. Simulant numbering indicates approximate wt. % total solids followed by approximate waste loading of sludge oxides in glass.

Table 12. SB2 SME Product Rheology Comparison

SB2 SME Product Sample ID	Wt. % Insoluble Solids	Yield Stress, dynes/cm^2	Consist-ency, cP	Wt. % Total Solids
SB2-Rad-SME Product-Qual sample	40.4	200	9.5	45.3
SME Rad-Batch 221 Decanted-30WL	44.2	51.3[a]	3.4[a]	46.7
SME Rad-Batch 221 Diluted-30WL	35.2	48.1[a]	3.4[a]	38.3
SME Rad-Batch 213 Decanted-30WL	44.8	76.9	8	46.4
SME Rad-Batch 213 Diluted-30WL	41.4	77.1	6.1	43.1
USC-SB2-1	33.7	40	13	37.8
USC-SB2-2	36.4	70	18	41.0
USC-SB2-3	39.1	130	17	44.2
USC-SB2-4	42.8	260	34	48.9
USC-SB2-5	45.3	400	41	51.7
USC-SB2-6	48.2	680	67	55.0
CETL-SMRF-45-31WL	38	560	52	45
CETL-SMRF-45-35WL	39	950	93	44
CETL-SMRF-45-40WL	40	1600	170	45
CETL-SMRF-40-31WL	~34	270	27	~40
CETL-SMRF-40-35WL	~35	380	47	~40
CETL-SMRF-40-40WL	~36	760	88	~40
CETL-Process Issue-50-30WL	~43	60-200	-	~50

a – the 221 batch SME product rheograms at 25C were essentially identical, suggesting there was a problem with labeling or file storage; the 35C rheograms were distinctly different.

b – the insoluble solids for the 40 wt. % TS SMRF SME products were estimated from the 45 wt. % insoluble solids data and the understanding gained with the USC tests.

c – the insoluble solids for the Entrainment SME product was estimated from the 45 wt. % insoluble solids SMRF data and the understanding gained with the USC tests.

The CETL simulant SME products seemed to be more viscous than the USC simulant SME products, but the compositional regions in terms of waste loading did not overlap. The comparison is not as quantitative as desired. Nevertheless, the thinnest CETL SME product with comparable acid stoichiometry at 31% waste loading and 40% total solids had four times the yield stress of the USC SME product at 25% waste loading at 41% total solids. (The impact of waste loading within the CETL data does not indicate that such a large drop should be expected to occur between 31 and 25% waste loading.) The USC and CETL SRAT product data did not seem to differ by a factor of four in rheological properties, although the CETL product up flow curves had humps. It might be that whatever caused the humps in the CETL SRAT product flow curves was related to whatever led to higher yield stresses and generally more viscous behavior in the SME.

The CETL SME products in the waste loading study were thicker than the radioactive SME products from the 2003 study or the 2001 qualification sample. The USC SME product series was similar to the SB2-Rad-SME Product Qual sample in that USC-SB2-3 and -4 had similar yield stress and wt. % insoluble solids values. Simulant consistency was ~3 times higher, but this is of less practical consequence when the yield stress is above 100 dynes/cm^2.

3.3.3 SME Product Comparison Summary

The available comparative SME product rheology data were primarily for SB2. Issues were found with CETL SB2 simulant rheology from the starting sludge through the process to the SME cycle product. Rheology data suggest that the slurry has a strong time-dependent component not previously identified in other simulant sludges. Issues were found with USC SB2 simulant made from the Tank 8 and Tank 40 simulants. These do not appear to be as large an issue as for the CETL simulant, with the possible exception of the bubble entrainment issue. The switch from frit 200 to frit 320 in SB2 occurred simultaneously with the switch from the RV-20 to the RS150 rheometer in simulant work. It became more difficult to get good flow curves at this time.

Issues were found with the radioactive SB2 SME data as well. All data in hand with simulants (as well as first principles) indicate that increasing waste loading and increasing wt. % insoluble solids simultaneously should lead to increased yield stress. This apparently was not observed between the qualification sample result in 2001 and the 2003 SB2 results. The qualification sample SME product may potentially have dried out somewhat during preparation for the rheology measurement. This would have caused an increase in the total and insoluble solids contents leading to higher than expected yield stress and consistency, but there is no way to check this now. Another possibility is that the contents of Tank 40/SB2 have significantly changed in rheological properties with time.

SB2 simulant rheograms have often been difficult to interpret due to the shape of the up and down flow curves. Similar general trends of increasing yield stress with increasing insoluble solids were seen in simulant and radioactive systems. The systems would seem to rank by yield stress as 2003 radioactive sample < 2001 radioactive qualification sample < USC simulant < CETL simulant at roughly constant insoluble solids, waste loading, etc.

The SB1A data were more similar between radioactive and simulant SME products, but allowance must be made for the fact that the radioactive samples were not put through SRAT/SME processing.

Getting some SB3 and SB2/3 radioactive SME product rheology data would significantly expand the available comparison database for SME product slurries. There is already a considerable body of simulant work with no corresponding radioactive work.

The SME product slurry should have been relatively easy to simulate historically. The SME product tends to be about pH 6, and the dominant particle has been frit. SRTC has used the same frit as the plant, so there were no issues with particle size or composition between radioactive and simulant melter feed for ~65% of the insoluble solids. As waste loading increases, the significance of the sludge component to the melter feed rheology is expected to increase.

4.0 CONCLUSIONS

The discussion above emphasized the Bingham plastic yield stress and insoluble solids content of sample slurries. Other properties, such as pH and particle size, are also known to effect yield stress. The comparisons that were made above are only semi-quantitative. Below are listed some of the major conclusions and observations that came from the radioactive-simulant rheology comparison discussion above.

- Real washed sludge seems to range from as viscous as simulant to more viscous than simulant. The relative simplicity of the simulant may be one reason for this. It should be noted that simulants as viscous as some of the radioactive sludges would be considerably more difficult to handle in drum-sized quantities. Tank 8 and SB1B radioactive sludge had good agreement with simulant properties, while radioactive SB2 sludge had fair to poor agreement with simulant properties.

- Radioactive Purex sludge is less viscous than radioactive HM sludge based on available data.

- Simulant Purex sludge seemed to match less viscous Purex waste better in a rheological sense. Simulant blends targeting a significant HM component had poor agreement with similar radioactive samples.

- Radioactive sample rheograms have been those of a shear-thinning non-Newtonian fluid with a yield stress and no significant time dependent behavior. Simulant sample rheograms have sometimes been similar, and other times have exhibited time-dependent behavior (USC-Tank 8 with oxalate, SB2-USC&CETL, SB3-CETL). If the cause of this can be traced to the simulant preparation, then it is recommended that corrective steps be taken in future simulant preparations to avoid this phenomenon.

- Simulant rheological data greatly outnumber radioactive rheology data. The majority of simulant data are for SME products/melter feeds. Much of it has no corresponding radioactive SME product data available for comparison. The majority of the radioactive data were for sludges until a few years ago, but there is a slowly growing database of SRAT and SME product rheograms.

- Comparable rheological data for SRAT and SME products are still relatively scarce. Nevertheless, there are radioactive data for which there are no comparable simulant data.

- Simulant data for different SRAT products are still relatively scarce in general.

- The SB2 simulants, particularly the CETL simulant, have not been as well-behaved as desired in the rheometer measurement process. This has impacted the number of good SRAT and SME product comparisons (significant body of radioactive SB2 work with corresponding simulant work that is hard to interpret). CETL SB2 simulants may be exhibiting a time-dependence to shear with a long relaxation time, i.e. the slurry is responded to shear much slower than the rate of change of shear rate in the rheometer.

- Processing in the SRAT had more of an impact on the SB2 radioactive sludge than on the simulant sludge. Both thinned during processing. SB2 radioactive sludge was initially more viscous than SB2 simulant, but SB2 radioactive SRAT product was less viscous than SB2 simulant SRAT product.

- Tank 8 radioactive sludge data from 1983 and 2000 are similar. Tank 8 dried out and was re-slurried in-between these samples. The apparent impact on rheology was minimal.

- SB2 was made from Tank 8 and Tank 40 sludges. The measured rheological properties of SB2 were much thicker than those of Tank 8. This suggests that the properties of Tank 40 would have been thicker than those of SB2, assuming that rheological properties of blends are intermediate to those of the two systems being blended. Continuing this logic, Tank 40 would have been much thicker than Tank 8. This may be due to the HM waste content that was present in Tank 40. The same trend was seen with the two USC simulants of Tank 8 and Tank 40. The two USC simulants differed by a factor of ten in yield stress. The implication in the radioactive data seems to be that real Tank 8 and Tank 40 differed by more than a factor of ten.

- The SB2 simulant formic acid dump (290% acid vs. 125% nominal) did not produce an improvement in rheology, although it significantly changed the appearance (color) of the solids. This dump did not produce a significant pH change, perhaps due to increased acid consumption from noble metal catalyzed reactions.

- Measured Tank 15 and Tank 42 (HM wastes) yield stresses rose much more quickly with increasing wt. % insoluble solids than did Tank 8 and other Purex sludge yield stresses.

- The de-washing of Tank 8 simulant to raise the pH and molarities of the supernate species did not seem to adversely impact the quality of the comparison of the simulant rheology to the radioactive data. The two systems remained relatively comparable throughout.

- Simulant sludge rheology seems to be particularly sensitive to the ratios of Ni/Fe and Mn/Fe in the co-precipitation portion of the recipe.

- Simulant rheograms with humps may be a sign of new chemical or physical interactions between particles that can withstand a small amount of shear. These interactions would form some sort of transient structure in the slurry. The majority of the structure would need to be relatively easy to destroy to explain the hump. The structure would readily reform under minimal shear conditions in just a few minutes, e.g. in the time between vigorously shaking the sample bottle and loading the rheometer to the start of the up flow curve routine.

- The overall cause(s) of differences between simulant and radioactive samples remains difficult to identify. Supporting measurements of pH, wt. % total and insoluble solids, and particle size distribution have generally not been made. Radioactive sample pH is typically being checked now, and this should continue. Radioactive sample particle size distribution has only been estimated a few times (from images of the particles). This is an area where future improvements would allow a better understanding of the differences between simulants and real wastes.

The overall conclusion seems to be that the current simulants made at Optima and USC, and to a lesser extent CETL, give fair to good agreement for Purex waste. They reasonably approximate many of the desired properties of real waste, including rheology and bulk composition. There is room for improvement in the preparation methodology, however. These improvements could be used to support studies on more subtle processing issues such as foaming, heat transfer, and air entrainment.

5.0 RECOMMENDATIONS/PATH FORWARD

Recommended experiments and/or tasks to better define the simulant-radioactive system comparability and to create a better basis for improving simulant properties are listed below:

1. Pull samples during acid addition during a Shielded Cells SRAT cycle and perform rheology measurements on them to determine the rheological response to acid addition. Simulant response (WSRC-TR-2003-00179) indicated that a very significant maximum in yield stress exists at a pH near 7. This could address the following relevant question: If the radioactive and simulant sludge rheological properties are not comparable initially, then does the situation improve or deteriorate during CPC processing? It appears that the rheological similarities may improve with processing, but the SB2 basis for this conclusion is not yet supported by any other work. A glimpse of the phenomena for SB2 in the Shielded Cells suggests there may be a continuous decline in yield stress from starting sludge to the end of acid addition.

2. Always measure sludge, SRAT product, and SME product flow curves on new Shielded Cells samples. Support with simulant work that reflects Shielded Cells' compositions as closely as possible. This will help to add substance to a database that can be used to improve simulants in the future. If urgency is an issue, then request additional waste tank samples for characterization to accelerate the formation of the radioactive slurry database. Adequate waste tank sample volumes must be requested for such characterization work to be effective.

3. Review the Canyon processes that produced the high and low activity HM and Purex wastes and attempt to incorporate the knowledge gained into the simulant recipe. Assess the impact of changes to the recipe strategy singly and/or in combination relative to the existing recipe from a rheological perspective. Use the small-scale simulant preparation apparatus at ACTL to prepare alternative strategies of a given nominal sludge.

4. Assess the impact of washing on rheology. Washing is known to impact rheology. T.B. Edwards has shown that there is a high likelihood of finding a statistically significant effect. Current simulants are made in a highly washed state that permits adding additional supernate salts if a less-washed state is desired. Prepare a less-washed version of an existing simulant, e.g. a pH 13+ version; then wash to various endpoints. Decant samples to various insoluble solid levels at each wash endpoint and assess the evolution of rheology with washing. Compare less-washed simulant after washing to original washed simulant to check whether they have come together on rheological properties. The washing issue should be understood before making any more very-washed simulants, such as the three generic simulants prepared at CETL in 2002. This experiment should be repeated with a similar radioactive sample for comparison.

5. There is conflicting data on the role of Ni/Fe relative to simulant rheology. Low Ni/Fe was observed to give more viscous simulant at USC. High Ni/Fe was observed to give more viscous simulant at CETL. The latter has not been quantified by a rheometer, however. CETL generic simulant "C" could be trimmed to match SB2 simulant supernate, Al, etc. and compared to regular SB2 simulant to quantify initially. The current observations, if valid, suggest an optimum Ni/Fe for minimum yield stress exists in the current recipe. Alternatively, there may be an interaction between Ni/Fe and Mn/Fe during the co-precipitation phase of the simulant preparation recipe. This needs to be better understood before making more simulants.

6. There is radioactive sludge rheology data available for several waste tanks that have not been processed, e.g. Tanks 11 and Tank 15 without Al dissolution. Tank 11 contains mixed high and low activity HM sludge that has not been processed. Tank 11 is projected to be a major component of Sludge Batch 4. Tank 15 rheology data were taken after the addition of Tank 16 sludge to it. That sludge also remains to be processed, and the data would appear to be valid. Simulants for both Tank 11 and 15 could be prepared now from the generic A, B, and C CETL simulants, plus additional trim chemicals, and several additional simulant-radioactive slurry rheological comparisons could be made. (Additional simulants for Tank 21 and for Tank 42 following the in-tank processing demonstration could be made for radioactive-simulant rheology comparisons, as well, but these would have somewhat less value since the waste has already been processed.)

7. One difference between USC and CETL simulants was the use of cross-flow filtration at USC vs. gravity settling at CETL during washing of the Mn-Fe-Ni precipitated solids. Pumping and cross-flow filtration probably modified the particle size distribution in ways that gravity settling did not, leading to potentially different rheological properties. The entire simulant batch went through the pump many times during cross-flow filtration washing. Another difference was in the nature of the final trim chemicals, which represented an entirely new set of purchases of chemical stocks with the associated variations in particle size. While the USC SB2 simulant made from the Tank 8 and Tank 40 simulants was not ideal in a rheological sense, it does appear to have been better behaved than the CETL SB2 simulant. Identifying the cause would seem to provide knowledge of something to avoid in future simulants. One experiment that could be done is to track the particle size distribution and rheology (the latter suitably adjusted by gravity-settled washes to a common endpoint) during continuous washing by cross-flow filtration using the small-scale simulant preparation rig at ACTL. Radioactive slurry for DWPF has been pumped (several transfers), but not run through a cross-flow filter.

8. Determine why the Tank 8 simulant had good agreement with the radioactive data, while the SB2 sludge simulant had poor agreement with the radioactive data.

9. Rheological measurements on sludge, SRAT product, and SRAT slurry samples taken following acid addition (minimum pH) during the SB2 with DU program indicated that good rheograms were obtained at minimum pH, but questionable rheograms were obtained at intermediate pH. The issues with SB2 SME products and new simulants may be dependent on pH more than is realized. The effect of pH on simulant rheology should be investigated as part of the simulant development program.

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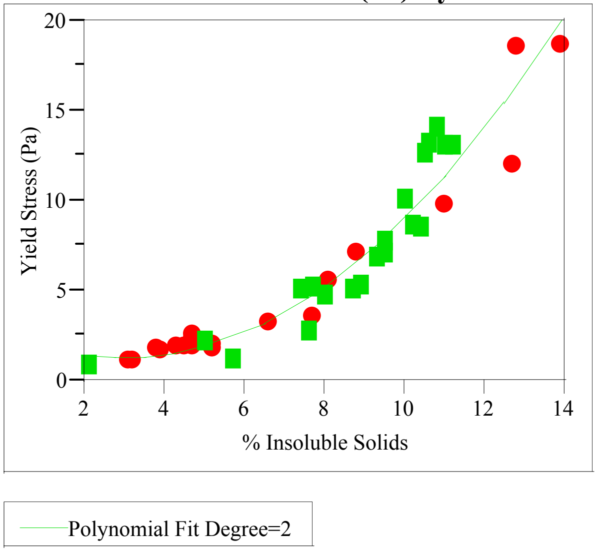
Note: the author also had access to unpublished data on the SB2 and SB3 systems.

APPENDIX A. Statistical Analysis of Tank 15 and 42 Data

This is the JMP analysis of yield stress versus wt. % insoluble solids by T.B. Edwards for Tank 15 (red circles) and Tank 42 (green squares) rheology data by B.A. Hamm.

Bivariate Fit of Yield Stress (Pa) By % Insoluble Solids



Polynomial Fit Degree=2

Yield Stress (Pa) = 2.5266654 - 0.8953052 % Insoluble Solids + 0.1538872 % Insoluble Solids^2

Summary of Fit

RSquare	0.9228
RSquare Adj	0.918511
Root Mean Square Error	1.421246
Mean of Response	6.269231
Observations (or Sum Wgts)	39

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	30	66.061209	2.20204	1.9848
Pure Error	6	6.656667	1.10944	Prob > F
Total Error	36	72.717876		0.1996
				Max RSq
				0.9929

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	2	869.22520	434.613	215.1610
Error	36	72.71788	2.020	Prob > F
C. Total	38	941.94308		<.0001

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	2.5266654	1.429905	1.77	0.0857
% Insoluble Solids	-0.895305	0.398284	-2.25	0.0308
% Insoluble Solids^2	0.1538872	0.025224	6.10	<.0001

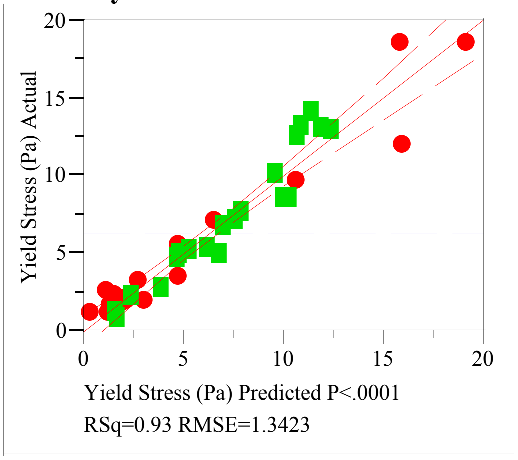
This is the JMP analysis by T.B. Edwards of yield stress vs. both wt. % insoluble solids and wt. % soluble solids for Tanks 15 (red circles) and Tank 42 (red squares) rheological data by B.A. Hamm using first-order and second-order terms in both wt. %'s.

Least Squares Fit

Response Yield Stress (Pa)

Whole Model

Actual by Predicted Plot



Summary of Fit

R-square	0.934963
R-square Adjusted	0.927311
Root Mean Square Error	1.342312
Mean of Response	6.269231
Observations (or Sum Wgts)	39

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	4	880.68183	220.170	122.1946
Error	34	61.26124	1.802	Prob > F
C. Total	38	941.94308		<.0001

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	2.8198719	1.504648	1.87	0.0695
% Soluble Solids	-0.273297	0.110836	-2.47	0.0189
% Soluble Solids*% Soluble Solids	0.0128752	0.005141	2.50	0.0172
% Insoluble Solids	-0.840792	0.386734	-2.17	0.0368
% Insoluble Solids*% Insoluble Solids	0.1518381	0.024036	6.32	<.0001

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
% Soluble Solids	1	1	10.955039	6.0800	0.0189
% Soluble Solids*% Soluble Solids	1	1	11.302256	6.2728	0.0172
% Insoluble Solids	1	1	8.516468	4.7266	0.0368
% Insoluble Solids*% Insoluble Solids	1	1	71.899770	39.9044	<.0001

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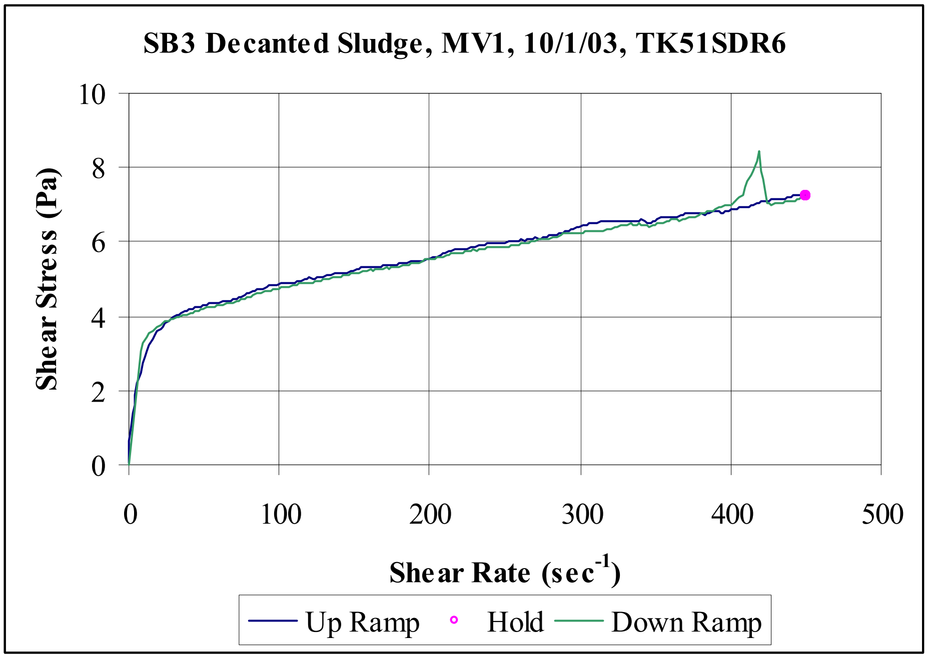
APPENDIX B. Recent Cells Rheology Data

This Appendix presents recent rheology data obtained in the SRTC Shielded Cells for SB3 waste and for a blend of SB2 and SB3 waste.

SB3 sludge was prepared from a sample of Tank 51 (containing primarily waste from Tank 7) for Chemical Process Cell qualification work in SRTC. Pu and Np streams were prepared in the Shielded Cells to simulate the contributions of secondary wastes that were to be added to SB3 prior to processing. Details are available in the report by J.M. Pareizs et al., WSRC-TR-2004-00050. The sample was 27.2 wt. % total solids and 17.1 wt. % insoluble solids. A flow curve for this sludge was measured on the Haake RV-30 rheometer in the Shielded Cells. It is shown in Figure 10.

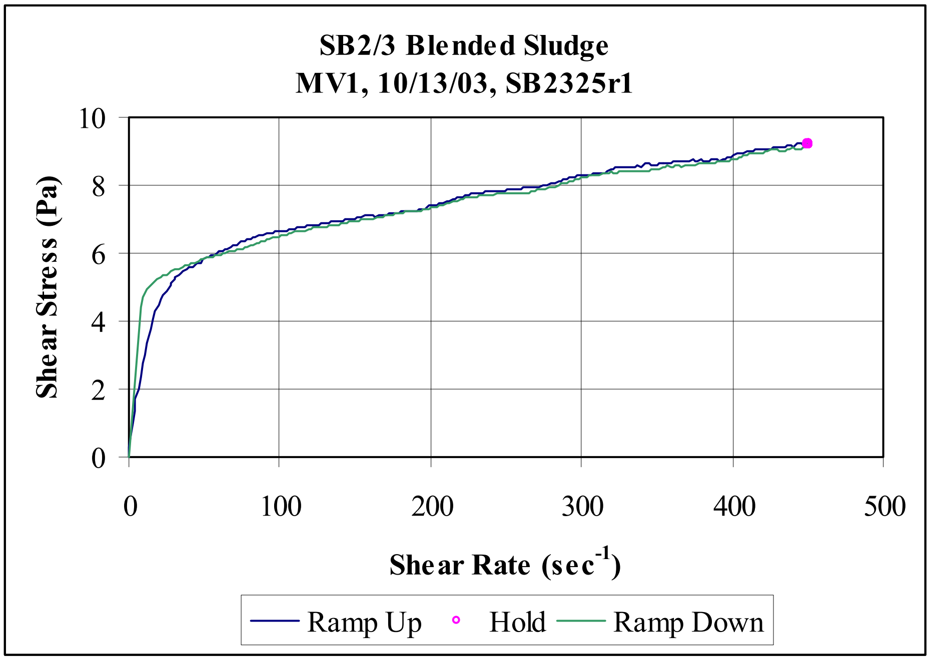
Figure 10: Raw Rheological Data for SB3 Sludge As-trimmed in SRTC



The data was fitted on the shear rate range of 25-450/s to a Bingham Plastic model. The up curve yield stress was 40.6 dynes/cm^2 and the consistency was 7.4 cP. The down curve yield stress was 39.2 dynes/cm^2 and the consistency was 7.8 cP. The up and down flow curves were virtually identical.

A portion of the SB3 waste described above was combined with some of the Tank 40/Sludge Batch 2 sample that was pulled to assist in studies on processing issues in the DWPF. Further information about the SB2 sludge slurry can by found in the report by T.L. Fellinger, WSRC-TR-2003-00253. The blend was 41% SB2 slurry and 59% SB3 slurry by mass. The calculated properties of the blend were 24.2 wt. % total solids and 17.3 wt. % insoluble solids (using the wt. % data of the two starting slurries). Measured properties were 22.8 wt. % total solids and 16.0 wt. % insoluble solids.

Figure 11: Raw Rheological Data for the SB2/3 Blend Prepared in SRTC



The up and down flow curves were nearly identical, indicating minimal time-dependence in the slurry rheological properties. The slurry was shear-thinning (apparent viscosity decreases with increasing shear rate). This is the typical behavior of SRS wastes analyzed to date. A Bingham Plastic model was fitted to the data on the shear rate range of 25-450/s. The up curve yield stress was 56.5 dynes/cm^2 and the consistency was 8.45 cP. The down curve yield stress was 56.2 dynes/cm^2 and the consistency was 8.2 cP.