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SUCCESSES AND EMERGING ISSUES IN SIMULATING THE MIXING BEHAVIOR OF LIQUID-PARTICLE NUCLEAR WASTE SLURRIES AT THE SAVANNAH RIVER SITE – 211b

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ABSTRACT

Aqueous radioactive high-level waste slurries are combined during processing steps that ultimately produce a stable borosilicate glass waste form. Chemically treated waste slurries are combined with each other and with glass frit-water slurries to produce the melter feed. Understanding the evolution of the rheological properties of the slurries is an important aspect of removing and treating the stored waste. To a first approximation, combinations of colloidal waste slurry with ~0.1-mm mean diameter glass frit or glass beads act in an analogous matter to slurries of spherical beads in Newtonian liquids. The non-Newtonian rheological properties of the waste slurries without frit, however, add complexity to the hydrodynamic analysis. The use of shear rate dependent apparent viscosities with the modified Einstein equation was used to model the rheological properties of aqueous frit-waste slurries.

INTRODUCTION

Legacy radioactive high-level waste (HLW) generated at the Savannah River Site (SRS) during Cold War production of enriched uranium and plutonium is currently being processed into a stable borosilicate glass waste form for long term storage. The majority of the legacy waste is stored as a mixture of hydroxide and hydrous oxide insoluble solids in large cylindrical storage tanks at SRS. Over 90% of the waste solids are non-radioactive chemical byproducts derived from the fuel rod targets and purification chemistry. The 3.5-4.9 thousand cubic meter (900,000-1,300,000 gallon) carbon steel waste storage tanks also contain 5-7M sodium solutions rich in hydroxide, nitrate, and nitrite anions that are contaminated with soluble radioactive isotopes of cesium and strontium. Insoluble solids have been allowed to settle to the bottom of the tanks and have been aging for 25-50 years. These solids must be mobilized and transferred between tanks as the first step in waste treatment.

The list below summarizes some of the tank farm issues:

- Rheological properties of suspended waste solids degrade with time under shear (the slurry becomes more viscous).
- Rheological properties need to be understood as a function of the insoluble solids content, particle size distribution, and composition.
- Slurry pump flow fields in the large, cooling coil filled, tanks have numerous stagnant zones where radioactive waste mounds form creating closure issues.
- Settling times during large tank washing operations are not predictable. Settling times also do not mimic those of small scale radioactive settling test samples.

- Radiolytic hydrogen generation and bubble accumulation during gravity settling constrains washing volumes.
- Addition of glass frit to the slurries prior to the waste glass melter produces a shift in the rheological character of the slurry.

SRNL has a program that produces non-radioactive "simulants" of the tank farm wastes in sufficient volumes, 50 to 5,000 dm^3 (liters), to study multi-phase mixing and transport issues without the radiation hazards of the real waste. Simulant slurries are used in small to intermediate scale equipment to evaluate the potential feasibility of various proposed process operations. Although simulant preparation chemistry generally follows that of the original radioactive wastes, the physical properties (rheology, particle size, cohesiveness, foaming tendency, etc.) often do not adequately match those of the actual wastes. The radioactive and simulant slurries are generally maintained at insoluble solids loadings where they behave like pseudo-homogeneous, thixotropic (shear thinning) fluids. Properties and appearance are similar to those of watered-down clay or the red mud in bauxite refining. Typical particles sizes for the precipitated solids are less than 40 micrometers, including a significant fraction of sub-micron sized particles.

Significant progress has been made in producing rheologically similar simulants. Testing has shown that batch precipitated simulants tend to be more viscous than those produced using continuous stirred tank crystallizers. High-shear mixers have been used to increase the apparent viscosity of simulants as necessary. Unfortunately, this can come at the expense of creating a mismatch in particle size distribution that may impact studies of other phenomena such as foaming or bubble retention. Actual waste rheological properties must be adjusted (by decanting or dilution) into certain ranges for successful tank mixing, solids suspension, and pump inter-tank transfers while retaining sufficient viscosity to minimize segregation of particles during anticipated worst case pump outage scenarios.

A fairly successful method for predicting the Bingham plastic yield stress and consistency of waste slurry blends was developed (Koopman, D., "Successes and Emerging Issues in Simulating the Processing Behavior of Nuclear Waste Blends", *Proceedings of the 2009 AIChE Annual Meeting*, New York, NY: AIChE. 2009). This method involves taking individual slurry rheometer data in the form of shear-rate dependent apparent viscosities, i.e. shear stress/shear rate, and applying empirical mixing rules for viscosity.

Properties of liquid-particle HLW slurries change significantly in the final processing step just prior to the waste melter. Glass frit is added at a mass equivalent to about 2-3 times the mass of the waste solids. The frit provides the chemical backbone that holds the HLW species in a stable glass waste form after processing through the melter. The frit particles are essentially fine shards of ground glass with particles in the 80-200 mesh range (0.07-0.20 mm) based on the Tyler standard screen scale. Figure 1 shows the essentially non-overlapping nature of the particle size distributions of the waste species and the glass frit. The frit peak is centered at about 150 microns, while the waste solids peak is at about two microns.

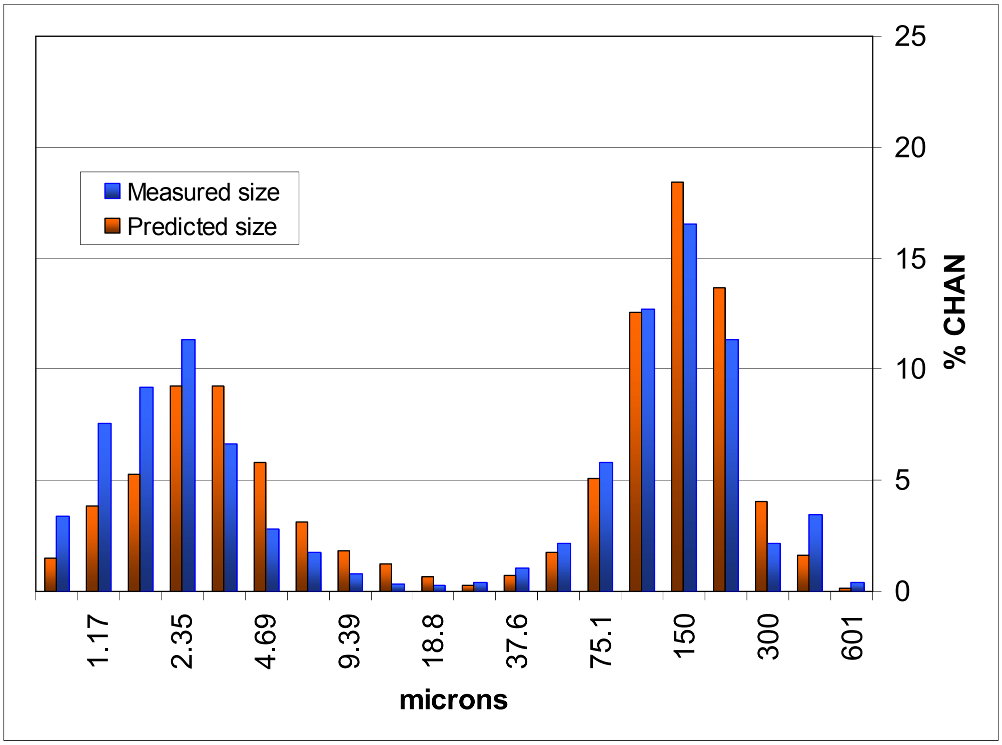

Figure 1. A comparison of the particle size distribution of melter feed with a weighted average of the individual particle size distributions for sludge and frit.

Frit particles are very abrasive, and it may be that the difference between measured and predicted particle size on the low end is partly due to attrition of the waste particles coming into contact with the frit particles under shear.

The impact of the frit particles on rheology is more comparable to adding 0.1 mm glass beads to water than to adding additional fine particles like the precipitated wastes. The bead-water system behaves somewhat like a single-phase Newtonian fluid in certain shear rate ranges even though it is clearly a two-phase medium, that is, the removal of shear would lead immediately to rapid segregation of the beads from the bulk of the water. The viscosity of the bead-water suspension increases with increasing volume fraction of beads. Various models have been proposed, such as the extended Einstein equation. As the volume fraction of beads increases, the models become progressively more complex. Modeling the flow of bead-water mixtures as a single-phase flow subject to certain constraints offers certain advantages over using the equations developed for heterogeneous flows.

A fairly viscous HLW slurry is required to ensure that glass frit particles do not rapidly segregate relative to the waste particles during mixer outages and inter-tank transfers. SRS contractors are required by the U.S. Department of Energy to verify that they are producing a stable homogeneous melter feed slurry with acceptable waste form properties so that direct sampling of the poured glass stream is not required.

EXPERIMENTAL AND MODELING WORK

Progress has been made on modeling the melter feed rheology as a pseudo-homogeneous Bingham plastic fluid (based on the near-colloidal sized fine waste solids) in two-phase flow with the larger frit particles using a variation of the extended Einstein equation. The rheological properties of the frit-free slurry are obtained in the form of an apparent viscosity, μ, (as a function of shear rate, γ) and used with the volume fraction, φ, of the frit particles to calculate the shift in viscosity from the entrained large particles:

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

Frit can occupy 7-14 volume percent of the melter feed slurry. The factor, f, was introduced to the extended Einstein equation to account for deviations from spherical particles. The constant of ten on φ^2 is also semi-empirical (and there are other values of this constant proposed by other researchers, e.g. Guth and Simha proposed 14.1 in 1936). The equation was developed for spheres in a Newtonian fluid, and the constant on the quadratic term was not adjusted during this study. A four term expansion has also been proposed containing the above terms plus an exponential term (Thomas, 1965). The primary use for this equation is in predicting the impact of changing the ratio of frit to waste solids on rheological properties without having to repeat series of rheometer measurements on different compositions of melter feed at different total solids loadings.

The above model was applied to simulated waste rheological data prior to frit addition, Figure 2. A reasonable match was obtained to rheological data following frit addition (11 volume percent frit) with f = 1.8.

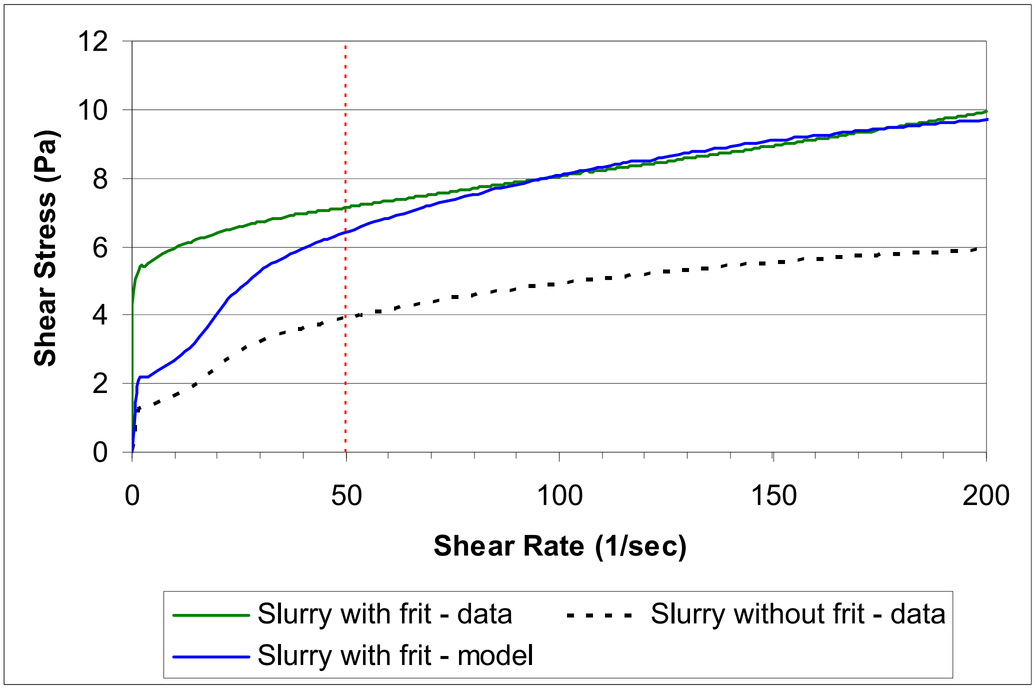

Figure 2. Application of the modified extended Einstein equation corrects rheological data for frit-free slurry to match that for waste slurry with frit at 11 volume percent.

The fit between the model and the slurry-frit data was better at higher shear rates (above 50/s). The shape of the raw flow curve data for the frit-free slurry had some unusual features below shear rates of 50/s. These irregularities were translated into the predicted melter feed flow curve.

Rheological modeling at SRS typically focuses on the region above 50/s shear rates, since most data are fit to the Bingham plastic equation over a range of several hundred reciprocal seconds of shear rate that are typical of site processes. An on-going program is currently evaluating the impact of replacing the glass frit with comparably sized glass beads, Figure 3.

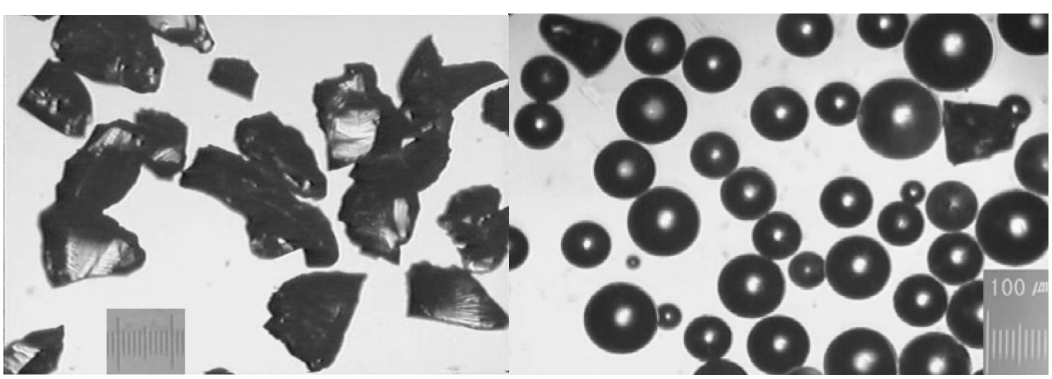

Figure 3. Comparison of glass frit (left) with chemically identical glass beads (right).

Improved rheological properties in the slurries with beads may permit the melter feed to be successfully processed with reduced water content (higher waste content, and less melter energy used for water evaporation).

A test of the modified Einstein equation was possible using flow curves for melter feed slurries with frit and with beads. Data were available for the same volume fractions of frit or beads in the same wt% total solids of HLW particles. The issue was whether or not the two flow curves could be reduced to a reasonably identical baseline flow curve describing the slurry without either particle. In this case an f value of 2.0 was needed for the flow curve with frit to match the result from the flow curve with beads using f equal to 1.0, Figure 4.

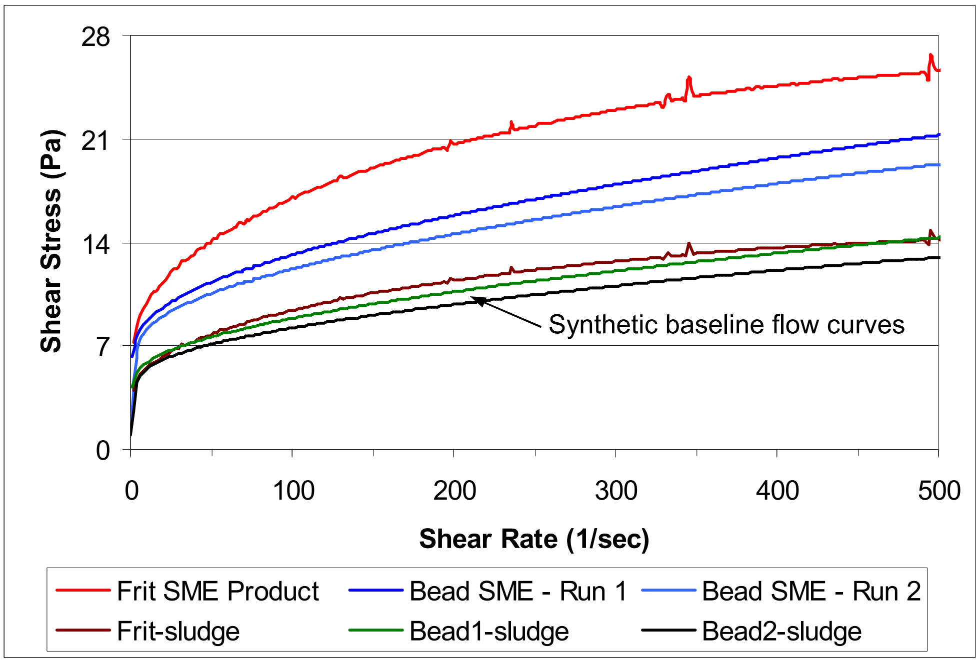

Figure 4. Reduction of the frit-based slurry flow curve data (red) and bead-based slurry data (blue) to a common baseline curve (green-brown-black).

The frit-based slurry was run in duplicate with negligible scatter, so only a single trace is shown in Figure 4. The variation in the bead replicate flow curve data is not unusual and is usually attributed to small variations in the insoluble solids content aliquoted from the sample vessel into the rheometer measuring cup. The spread in the three predicted baseline flow curves derived from the two different slurry systems is of similar magnitude to the general reproducibility of frit-slurry flow curves.

An emerging area of study is an effort to quantify and model the retention of bubbles in the settled solids in the waste tanks. The bubbles are H_2-O_2 mixtures from radiolysis of water. These gas molecules coalesce into bubbles within the settled liquid-particulate mass in the bottom region of the storage tanks. This represents another situation where heterogeneous, or multi-phase, models are likely to be more appropriate then homogeneous models. Molecular diffusion is not able to keep up with the radiolytic generation rate. The settled solid matrix appears to play a key role in retaining the bubbles. Rapid release of trapped bubbles occurs once slurry pumps are inserted and started in a tank containing settled solids. These bubbles can briefly lead to the formation of a flammable or explosive atmosphere over the tank contents, and that is unacceptable for nuclear waste storage.

It is believed that the retention of bubbles in settled HLW solids is not solely due to the more viscous properties that would prevail in the settled slurry due to the higher volume fraction of solids content than when the tank is fully mixed. The particles themselves are thought to try to orient at the bubble-slurry interface in such a manner that the bubbles become anchored to the settled matrix. Fundamental studies are needed to better understand the forces acting to prevent bubble coalescence and release.

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