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SUCCESSES AND EMERGING ISSUES IN SIMULATING THE PROCESSING BEHAVIOR OF LIQUID-PARTICLE NUCLEAR WASTE SLURRIES AT THE SAVANNAH RIVER SITE – 205e

David C. Koopman, Savannah River National Laboratory, Aiken, SC
Daniel P. Lambert, Savannah River National Laboratory, Aiken, SC
Michael E. Stone, Savannah River National Laboratory, Aiken, SC

ABSTRACT

Slurries of inorganic solids, containing both stable and radioactive elements, were produced during the cold war as by-products of the production of plutonium and enriched uranium and stored in large tanks at the Savannah River Site. Some of this high level waste is being processed into a stable glass waste form today. Waste processing involves various large scale operations such as tank mixing, inter-tank transfers, washing, gravity settling and decanting, chemical adjustment, and vitrification. The rheological properties of waste slurries are of particular interest. Methods for modeling flow curve data and predicting the properties of slurry blends are particularly important during certain operational phases. Several methods have been evaluated to predict the rheological properties of sludge slurry blends from the data on the individual slurries. These have been relatively successful.

INTRODUCTION

Legacy radioactive high level waste (HLW), generated at the U. S. Department of Energy's Savannah River Site (SRS) from production of enriched uranium and plutonium during the Cold War, is currently being processed into a stable borosilicate glass waste form for long term storage. The majority of the 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 fuel rod targets and purification chemistry. The 3,500-4,900 cubic meter (~1,000,000 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 settled to the bottom of the tanks and have been aging for 25-50 years. Waste solids must be mobilized and transferred between tanks as the first step in waste treatment. Subsequent steps separate dissolved radionuclides from insoluble radionuclides for separate waste treatment and downstream processing.

A partial summary of processing issues includes:

1) Rheological properties of suspended waste solids degrade with time under shear (slurries becomes more viscous).

2) Slurry pump flow fields in the large, cooling coil filled, tanks have numerous stagnant zones where radioactive waste mounds form creating closure issues.

3) Settling times during tank washing operations cannot be accurately predicted. Settling times also do not always mimic those of small scale radioactive settling test samples.

4)	Radiolytic hydrogen generation and bubble accumulation during gravity settling constrains washing volumes.

5)	Chemical adjustment (pretreatment) of the waste solids upstream of the waste vitrification melter results in various issues such as excessive foaming, catalytic production of hydrogen from formic acid via noble metal fission product catalysis, occasional problems with tackiness or excessive air entrainment, loss of mixing and heat transfer during concentration, etc.

HLW slurry must first be moved from the large waste tanks prior to any processing to stabilize the waste for geologically long term storage. The insoluble sludge solids have settled and packed into a clay-like consistency over time. Local episodes of over-heating have also hardened some of the insoluble solids and formed moderately strong bridges between individual particles. Centrifugal slurry mixing pumps are lowered into the settled sludge layer in order to break down and mobilize insoluble solids for transfer. Four pumps are typically deployed to resuspend the solids, Figure 1.

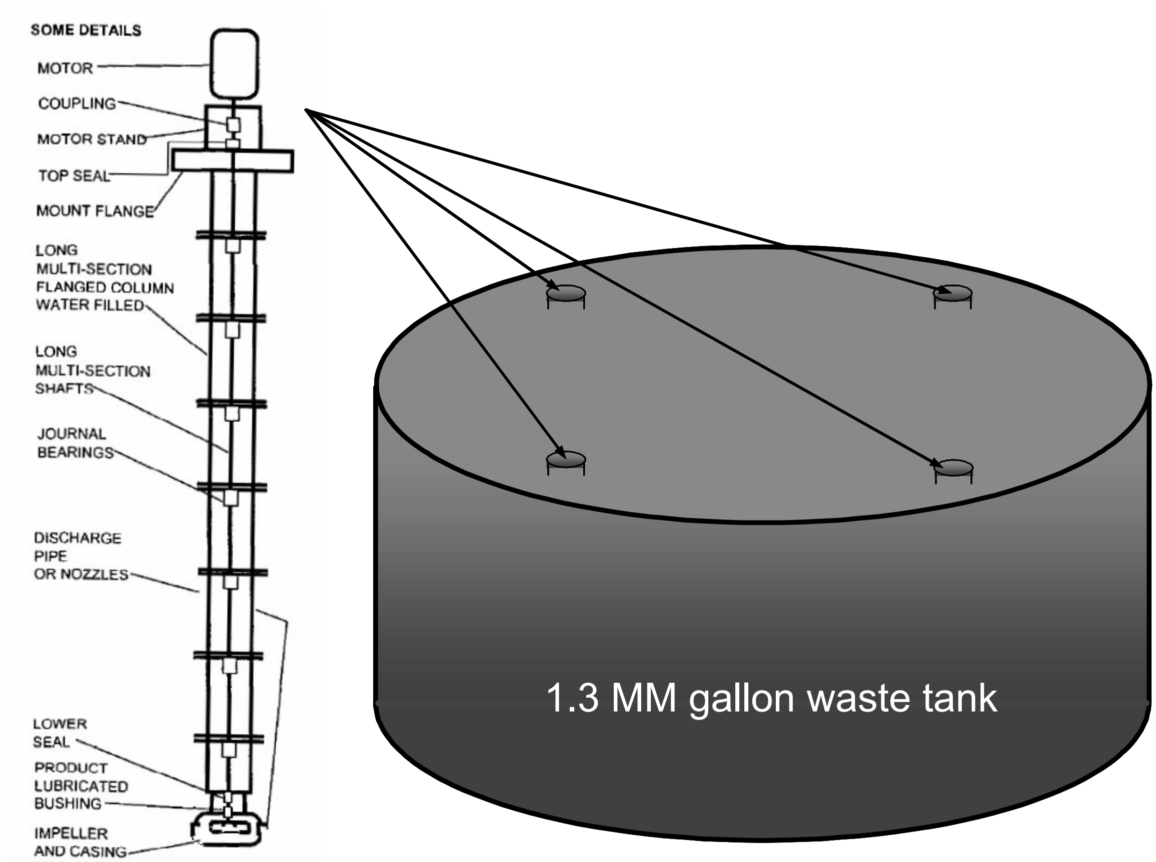

Figure 1. Placement of slurry mixing pumps in large waste storage tanks at SRS.

The Savannah River National Laboratory (SRNL) has a program that produces non-radioactive “simulants” or analogs of the waste slurries in the SRS tank farm. Simulant slurries are used to evaluate the potential feasibility of various proposed 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 generally behave like thixotropic fluids while being mixed or pumped. Typical particles sizes for the precipitated solids are less than 40 micrometers.

RESEARCH PROGRAM

HLW slurries in the SRS tank farm often behave like pseudo-homogeneous fluids. The insoluble solids concentration is kept high enough to keep particles in suspension long enough to perform typical processes such as inter-tank transfers. Significant progress has been made recently 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 (such as the Silverson L4RT-A) have been used to increase the apparent viscosity of simulants that were less viscous than their corresponding radioactive target slurries. This can come at the expense of creating a mismatch in particle size distribution.

The latest advance has been the addition of an ultrasonicator (Vibracell VCX 750) coupled to a flow cell. The ultrasonicator has produced order of magnitude increases in the Bingham plastic yield stress of simulant using a short residence time, whereas the high shear mixers have typically produced factor of 2-3 increases in yield stress in relatively longer times. The continuous stirred tank crystallizer coupled with the ultrasonicator permits low yield stress slurries to be prepared initially. The rheological properties can then be adjusted using the ultrasonicator to match the properties of the corresponding radioactive waste samples. The remaining issue with this approach is to investigate the relative particle size distributions obtained and to determine if any significant processing properties have been lost if the particle size distributions are significantly different. A typical particle size distribution is given in Figure 2. Data were obtained on a MicroTrac instrument.

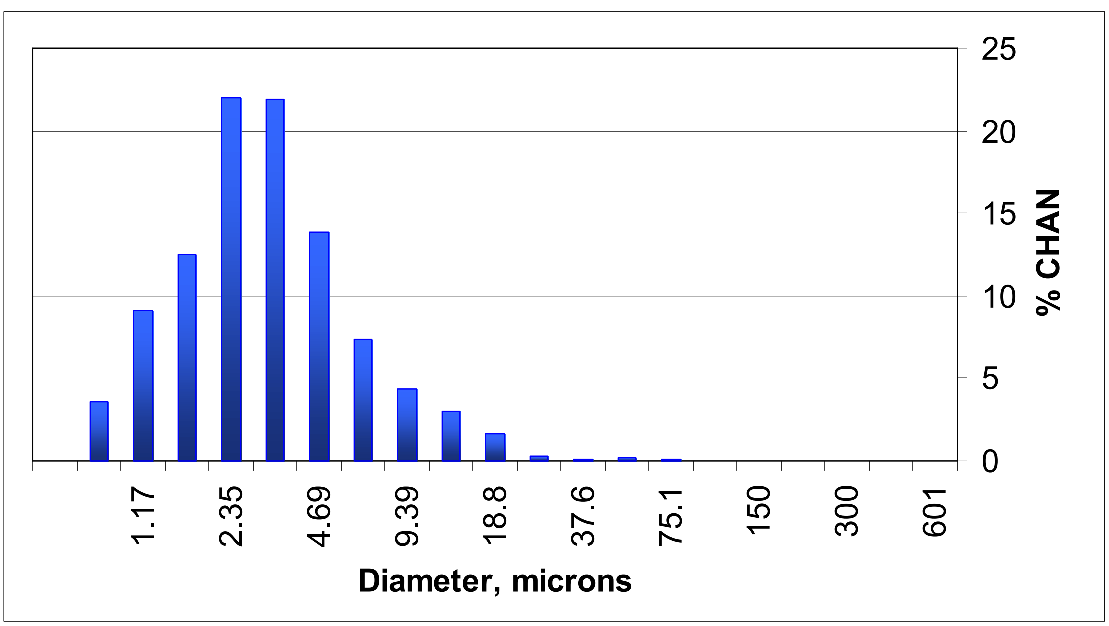

Figure 2. Typical particle size distribution of the insoluble solids in SRS waste slurries.

Often SRNL will receive individual samples of two or more slurries in the tank farm that are ultimately going to be blended together. Due to the difficulty and cost of pulling representative samples from the HLW tanks, there may be insufficient sample mass to characterize the individual slurries and then prepare blend samples for characterization. When this occurs, the properties of the blend often need to be calculated from the individual slurry properties. This is generally not an issue for chemical composition, but presents more of a challenge for certain physical properties such as rheology.

A fairly successful method for predicting the Bingham plastic yield stress and consistency of waste slurry blends has been developed. Rheometric shear stress-shear rate data were obtained for two slurries. Data are obtained using Haake rotational rheometers operated in the Searle mode (a vertical concentric cylinder geometry with a rotating bob in centered inside a fixed cup). SRNL has one Haake rotational rheometer that can be operated remotely inside one of the Shielded Cells where HLW samples can be handled.

The apparent viscosity of a non-Newtonian fluid is a function of shear rate. Apparent viscosity was selected as the mixing parameter rather than the fitted yield stress and consistency. Apparent viscosity, μ_i = shear stress/shear rate of slurry at a selected shear rate. SRS waste sludge feeds for the Defense Waste Processing Facility were expected to be in the range of 2.5-10 Pa in Bingham plastic yield stress and 4-12 cP in Bingham plastic consistency. In apparent viscosity versus shear rate these ranges are equivalent to the following, Figure 3.

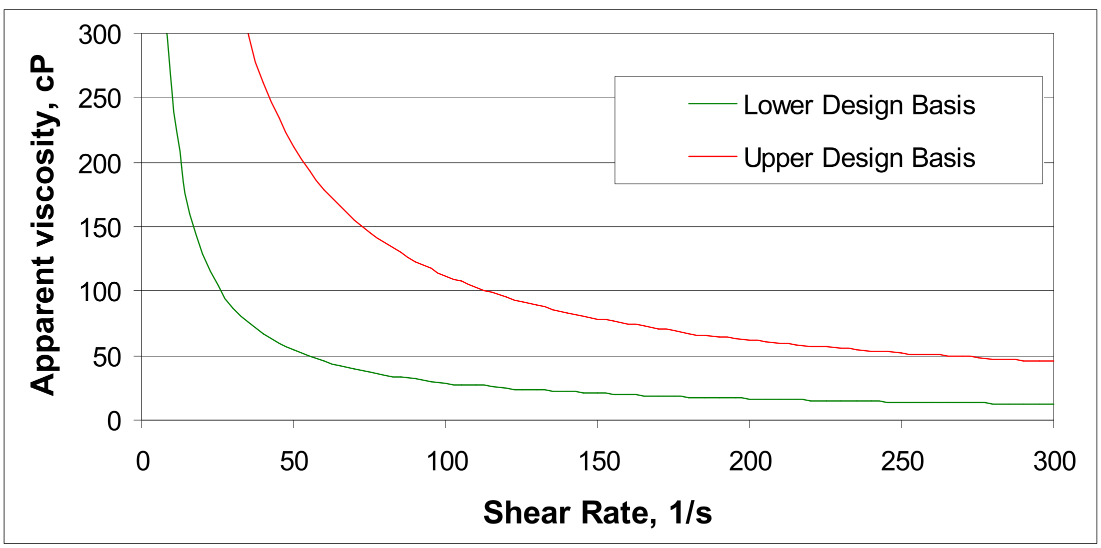

Figure 3. Rheological design bases for sludge slurries.

The empirical Kendall-Monroe rule was used locally on the individual apparent viscosities to produce the apparent mixture viscosity: $\mu_m^{1/3} = x_1\mu_1^{1/3} + x_2\mu_2^{1/3}$. The two x_i were taken as the mass fractions of the two slurries being blended. An example fit of the measured flow curve of a blend of two radioactive waste slurries to that predicted from adaptation of the Kendall-Monroe equation is shown below, Figure 4.

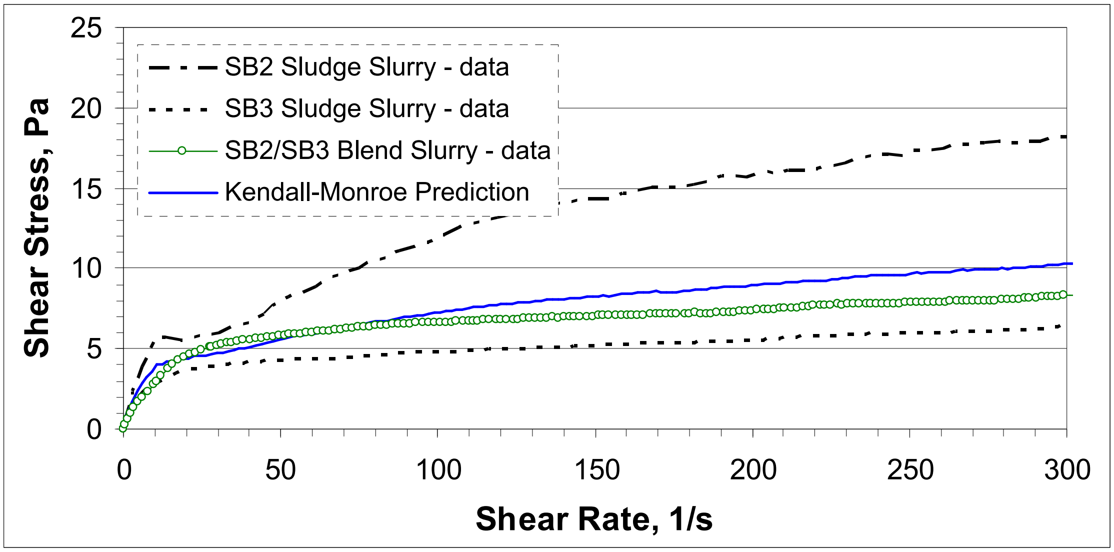

Figure 4. Application of the Kendall-Monroe viscosity blending algorithm to HLW.

The rheological data are obtained as shear rate-shear stress data points (γ, τ). Each curve in Figure 4 contains approximately 300 data points. At each shear rate data point, $\mu_i = \tau_i/\gamma_i$ is found for the two starting slurries and for the mixture. The prediction curve in Figure 3 came from approximately 300 applications of the Kendall-Monroe model, one for each shear rate in the data. The predicted curve was particularly good for shear rates from 0-100/s. The predicted curve from 100-300/s is biased high relative to the measured values, but is not off by much more than the normal reproducibility of flow curve data obtained on radioactive samples using the remotely manipulated equipment in the SRNL Shielded Cells.

The Olney-Carlson model for predicting mixture viscosities was also applied to the apparent viscosities of the waste slurries at each shear rate. The Olney-Carlson model is given by: $\mu_m = \mu_1^{x1} + \mu_2^{x2}$. The results of applying the Olney-Carlson model at each shear rate in a method analogous to that used in the Kendall-Monroe prediction are given in Figure 5.

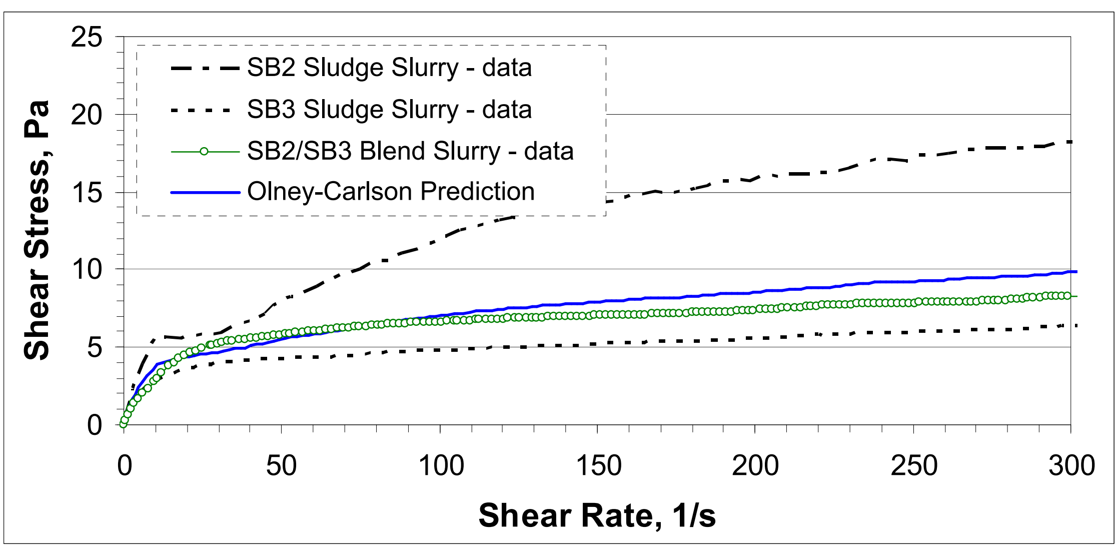

Figure 5. Application of the Olney-Carlson viscosity blending algorithm to HLW.

The Olney-Carlson algorithm was comparable to the Kendall-Monroe equation at low shear rates and slightly better at higher shear rates. Comparable agreements have been obtained on several subsequent slurry blend systems.

An alternative perspective on the model performance in predicting the measured values can be obtained by plotting the apparent viscosity versus the shear rate. Figure 6 shows the values obtained on the blended waste sample compared to the two empirical viscosity mixing models.

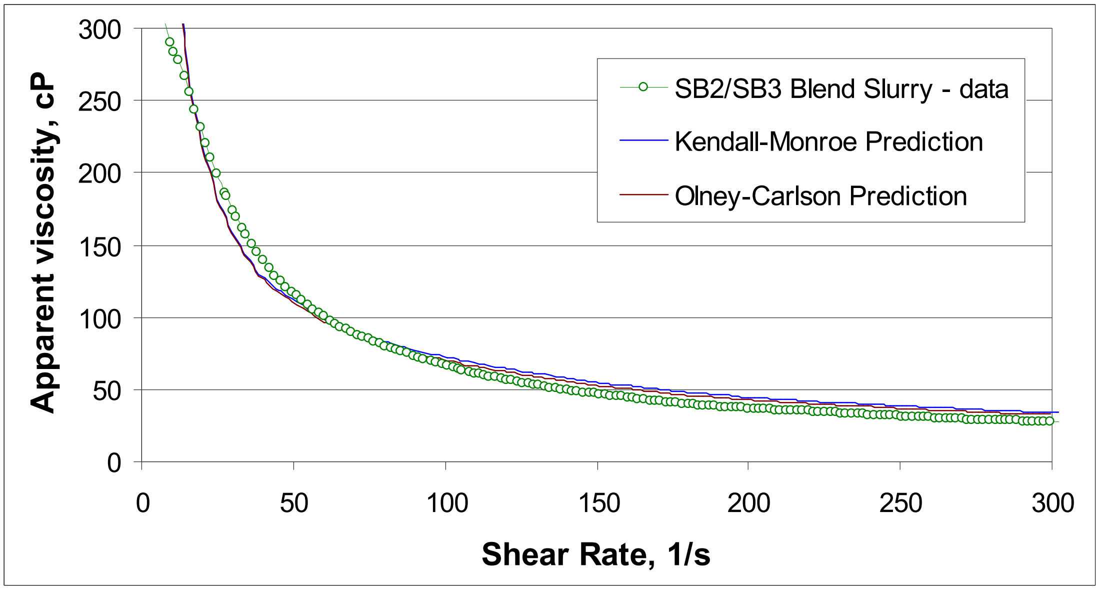

Figure 6. Comparison of predicted to measured apparent viscosity.

The results in Figure 6 indicate that the predicted flow curve data will be adequate for most engineering applications such as predicting pressure drop in pipe flow.

One on-going R&D program is investigating rheology modifiers. Pre-screening and preliminary experiments are all being conducted with non-radioactive simulants of the HLW slurries. Both ionic and non-ionic surfactants are being investigated. The challenges in this task include the variations in the chemical composition of individual waste tanks, the changes in pH during washing and chemical pre-treatment of the waste prior to vitrification, and the impact of adding significantly larger glass frit particles to the waste slurry just prior to the melter. Another issue is the use of high temperature sodium hydroxide treatments to leach much of the aluminum content of the insoluble solids into the aqueous phase for eventual separation from the bulk of the insoluble species.

One final tank farm issue is the preparation of former HLW tanks for ultimate closure. The slurry pumps in Figure 1 do not mobilize all of the insoluble solids in a given tank. Large cooling coil banks inside the tanks create obstructions to flow and local low velocity regions where solids continually settle out. The current program in this area is based on the use of oxalic acid solutions to break down the residual solids through dissolution. Once a tank has been sufficiently cleaned, the tank and internal coil are both to be filled with grout to immobilize any remaining material.

The bulk of the insoluble HLW is processed through the Defense Waste Processing Facility. Chemical pre-treatment is performed there to convert the waste to an acidic condition that permits separation of mercury which is present at concentrations that are not stable in glass. A combination of waste slurry with glass frit is ultimately fed into a cylindrical, joule-heated melter to produce a stable borosilicate glass waste form. The water content of the feed impacts melter throughput, but it is often constrained by processing issues such as loss of mixing and heat transfer during the final concentration by boiling. The impact of glass frit on rheological properties is a separate issue from the pseudo-homogeneous behavior of the waste slurry. The mechanism of rheological properties modification is more like the effect obtained when adding small glass beads to water. These issues were presented in a separate talk at the 2009 AIChE Annual meeting.

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