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SYNTHESIS OF NON-RADIOACTIVE SLURRIES TO SIMULATE THE PROCESSING BEHAVIOR OF PARTICLES IN RADIOACTIVE WASTE SLURRIES – 626g

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ABSTRACT

Process development using non-radioactive analogs to high-level radioactive waste slurries is an established cost effective alternative to working with actual samples of the real waste. Current simulated waste slurries, however, do not capture all of the physical behavior of real waste. New methods of preparing simulants are under investigation along with mechanisms for altering certain properties of finished simulants. These methods have achieved several notable successes recently in the areas of rheology and foaminess. Particle size is also being manipulated more effectively than in the past, though not independently of the rheological properties. The interaction between rheology and foaminess has exhibited counter-intuitive behavior with more viscous slurries being less foamy even though drainage of liquid from the foam lamellae should be inhibited by higher viscosities.

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. A majority of the legacy waste is stored as a mixture of insoluble hydroxides and hydrous oxides 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. Uranium and plutonium are two of the major radionuclides by mass in the balance of insoluble material. 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.

The majority of the laboratory and pilot scale process development work being performed at the Savannah River National Laboratory (SRNL) in support of nuclear waste processing is done with non-radioactive simulated waste slurries, or “simulants”. These simulants match the bulk chemical properties of the non-radioactive components in the insoluble and aqueous phases of the actual radioactive wastes. Following simulant testing, limited proof of concept testing is done in special facilities using radioactive samples from the actual waste tanks. Cost is one of the major factors driving this approach. There is roughly a ten-fold cost advantage to performing the preliminary testing with the non-radioactive analogs to the real waste. The success of this strategy is dictated in part by how well the processing properties of the non-radioactive simulant slurries match those of the actual waste slurries.

Actual waste slurries were produced at SRS from about 1955-1990. Many have sat relatively undisturbed in the storage tanks since they were originally precipitated by adding

caustic to the acidic waste streams. The freshly precipitated slurry particles are not in thermodynamic equilibrium. Atomic scale processes, such as Ostwald ripening, act to change the chemical and physical properties of the particles over time. For example, aluminum precipitates primarily as Gibbsite, $Al(OH)_3$, but a significant fraction converts to Boehmite, AlOOH, over time. Similar changes are likely occurring with the amorphous hydrous ferric oxide precipitate, Fe_2O_3•xH2O. The value of x appears to decline with increasing storage time. The percent crystallinity of the precipitated solids is low when examined by X-ray diffraction, and this is particularly true of the ferric oxide. The waste solids are very difficult to quantify with respect to speciation, crystal forms, etc. due to the presence of over fifty elements. The insoluble solids are believed to include double salts as well as simpler compounds involving single cations. The waste is, however, relatively free of any organic species (there is a small amount of oxalate).

TECHNICAL

Several different approaches have been taken historically toward preparing simulated waste slurries. All of the approaches used in the past dozen years involve some precipitation of the species using similar chemistry to that which formed the radioactive waste solids in the SRS tank farm. All of the approaches add certain chemical species as commercially available insoluble solid compounds. The number of species introduced in this manner, however, has varied widely. All of the simulant preparation approaches make the simulated aqueous phase by adding the appropriate ratios of various sodium salts. The simulant preparation sequence generally starts with an acidic pH and ends up with a caustic pH (typically in the 10-12 range).

Presently, all recipes first precipitate MnO_2 from $Mn(NO_3)_2$ and $KMnO_4$ by combining two aqueous solutions. Reagent grade MnO_2 did not behave prototypically during chemical pre-treatment steps. Following MnO_2 precipitation, hydrous ferric oxide and nickel hydroxide are simultaneously precipitated in the presence of the MnO_2 solids from a solution of their nitrates. Nitrates of many other elements may or may not be present and precipitated at this point including Al, Ba, Ca, Cu, Cr, Gd, La, Mg, Pb, Sn, Zn, and Zr. Alternatively, these species may be added as mixtures of oxides, hydroxides, sulfates, oxalates, carbonates, etc. as indicated by thermodynamic modeling and the bulk chemical distribution of the elements.

Following precipitation of the nitrate salts using sodium hydroxide and sodium carbonate, excess nitrate is removed by repeated additions of inhibited water (0.001 M NaOH, 0.001 M $NaNO_2$) and allowing the insoluble solids to settle, then decanting the aqueous supernate. Typically 3-5 wash cycles are performed. Certain minor species, such as silica and TiO_2, are added as finely-milled insoluble solids based on data indicating that the proper form or speciation would not be obtained from a nitrate precipitation. Finally, soluble sodium salts are added to adjust the composition of the aqueous phase to match that of the HLW slurry.

Significant differences in physical properties of the simulated wastes are observed depending on the preparation route selected. Similar differences are observed with respect to the actual HLW waste slurry being modeled. The rheological properties of the slurries tend to be more viscous when more species are precipitated together. Batch precipitations tend to produce more viscous slurries than continuous precipitations. Batch precipitations occur over a wide range of pH from less than three to about ten. Continuous precipitations occur at the

target pH of the pre-washed final slurry (typically about ten). Continuous precipitations tend to produce a narrower range of particle sizes than batch precipitations, Figure 1:

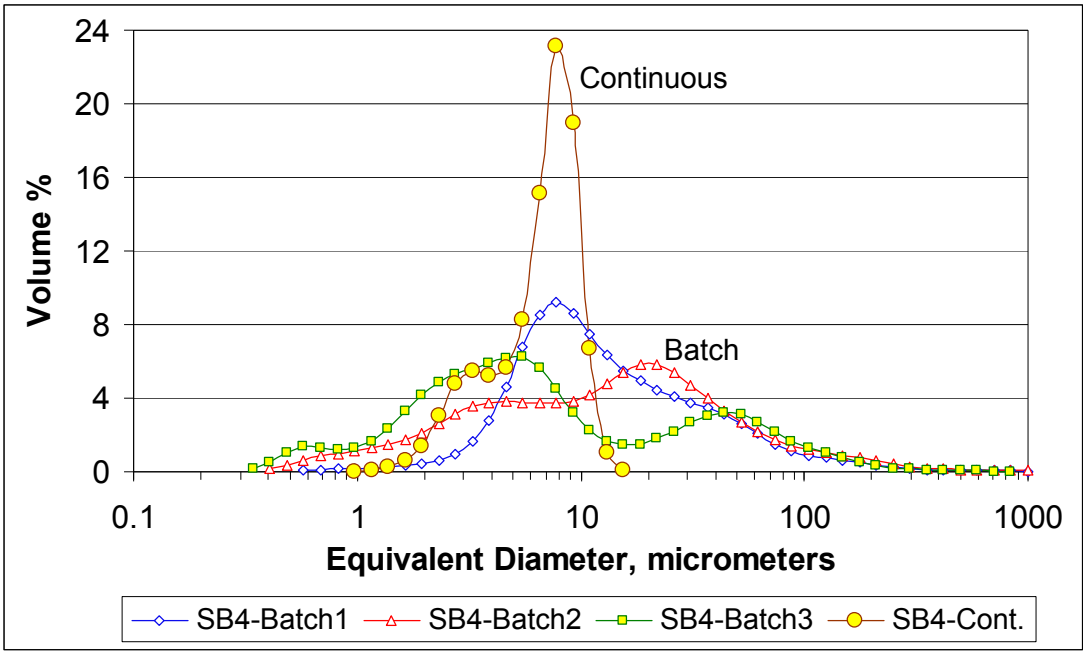

Figure 1. Impact of continuous precipitation geometry on the particle size distribution of the final simulated slurry solids compared to batch precipitation.

Note that while the sodium hydroxide driven precipitations in Figure 1 were either batch or continuous, the subsequent carbonate strike, washing, and trimming steps were performed using equivalent batch processing methods.

The particle size distribution of the MnO_2 in the first precipitation step depends significantly on the presence or absence of the nitrates of the cationic species being formed in the second-step precipitation, Figure 2:

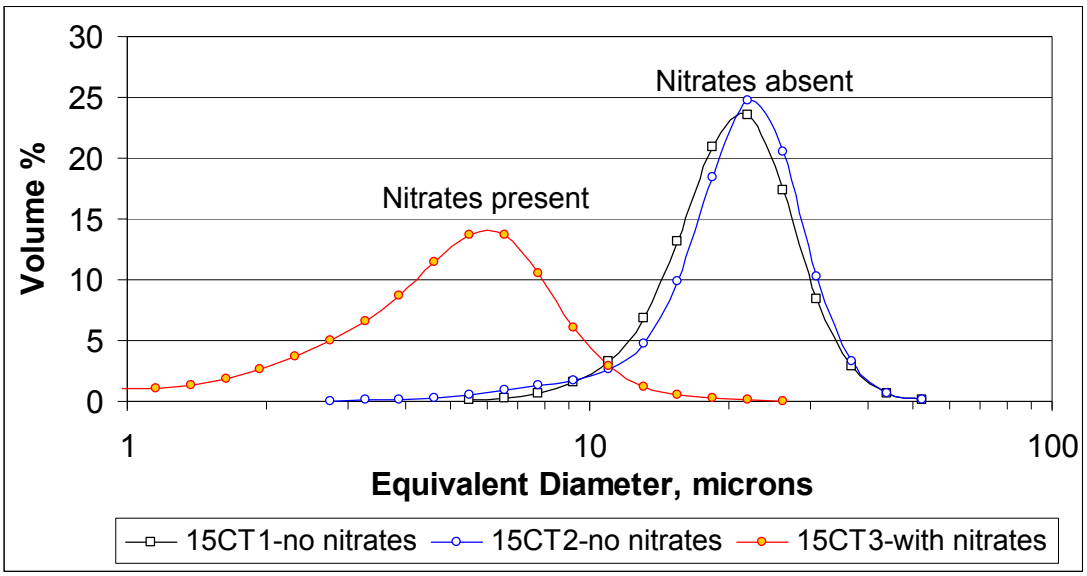

Figure 2. Impact of the presence of additional metal nitrates on the particle size of batch precipitated MnO_2.

Precipitation of iron, aluminum, and other waste hydroxides from the nitrate solution using NaOH proceeded relatively unaffected by the particle size distribution of the MnO_2 particles formed in the first stage precipitation. The conclusion was that the MnO_2 particles were not acting as generic seed crystals for the other precipitated solids. This conclusion was qualitatively supported by visual observations of centrifuged simulant solids which showed a distinct region of darker, denser solids enriched in MnO_2 that segregated from the majority of the other solids near the bottom of the centrifuge tubes.

The sequence of steps involved in producing the final simulant (two precipitations, a carbonate strike, batch washing, and final trimming) typically lasted about three weeks and exhibited a gradually evolving particle size distribution, Figure 3:

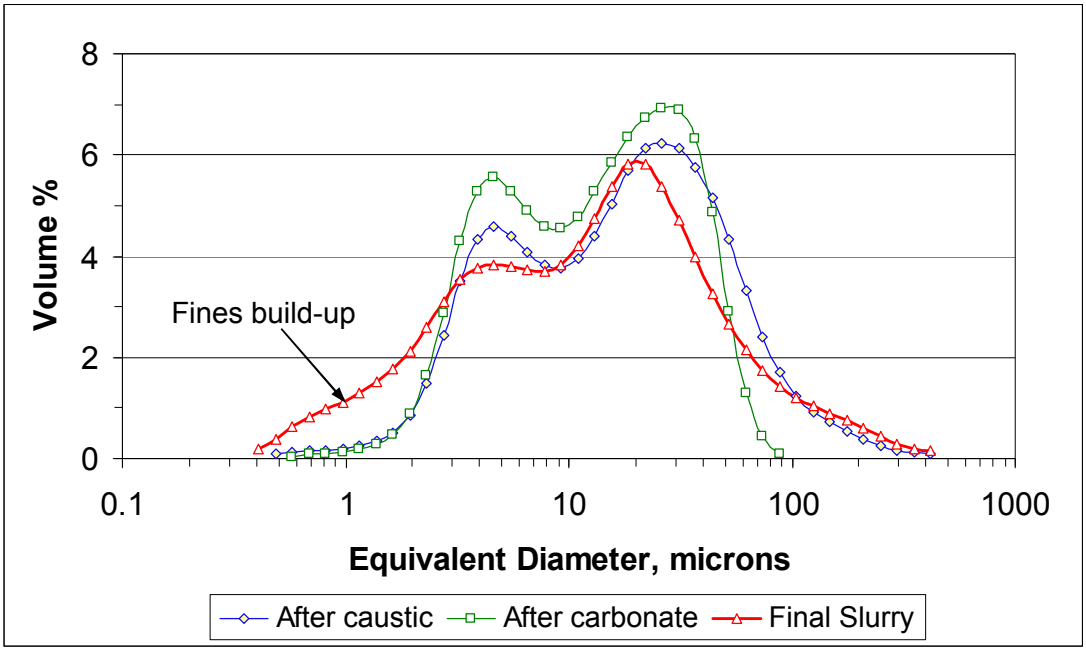

Figure 3. Evolution of particle size distribution during post-precipitation processing.

One trend of particular concern was the gradual accumulation of fines as the number of processing steps increased. There was statistical correlation between increasing fines content (fraction of particles less than 1-2 microns in diameter) and undesirable increases in the apparent viscosity of the final simulants.

Equipment scale was of particular importance in controlling the rheological properties of batch-produced simulants. Although every effort was made to ensure comparably high degrees of mixing intensity at every scale, the final simulant slurry products became progressively more viscous with increasing vessel (batch) size. The Bingham plastic model was fit to flow curve data obtained using a rotational Haake rheometer operating in the Searle mode (concentric cylinder geometry with rotating inner bob with fixed outer cup). Variations in the plastic viscosity (consistency) parameter are relatively minor compared to the differences in the yield stress. Yield stress values obtained from this model are given in Figure 4 covering then range 2-120 dm^3 (L) of precipitation batch size.

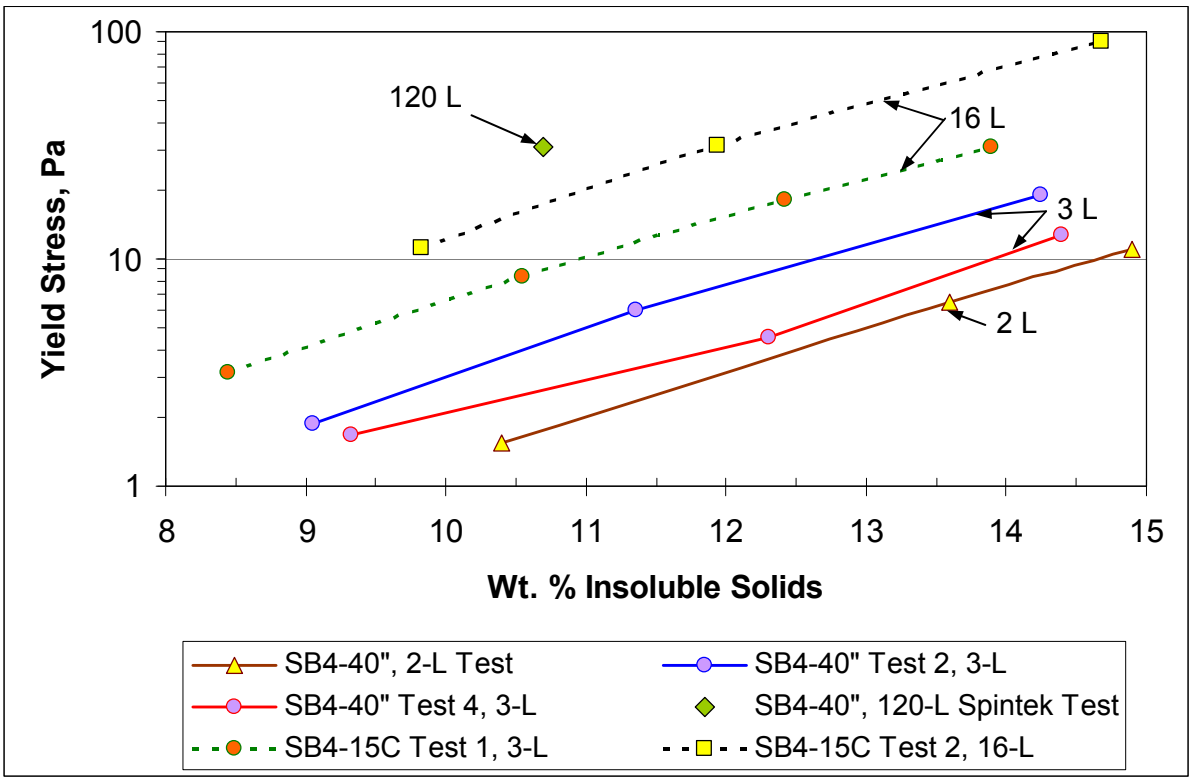

Figure 4. Impact of scale on the Bingham plastic yield stress of batch-produced simulants of high-level waste slurries.

Typically, starting yield stress values in the subsequent pilot plant equipment are desired to be in the 1-10 Pa range. The slurry products prepared at 16 L and 120 L scale were sufficiently difficult to process in the lab-scale pilot plant equipment at the desired wt.% insoluble solids that they had to be blended off with lower viscosity simulants prior to use or put directly into one of the laboratory residue streams.

Switching to a continuously fed stirred precipitator was comparable to about an order of magnitude reduction in vessel size in the batch precipitations. An example of the impact of this change on rheology is shown in Figure 5. Sixteen liters of simulant were prepared by the two different methods with order of magnitude differences in the Bingham plastic yield stress.

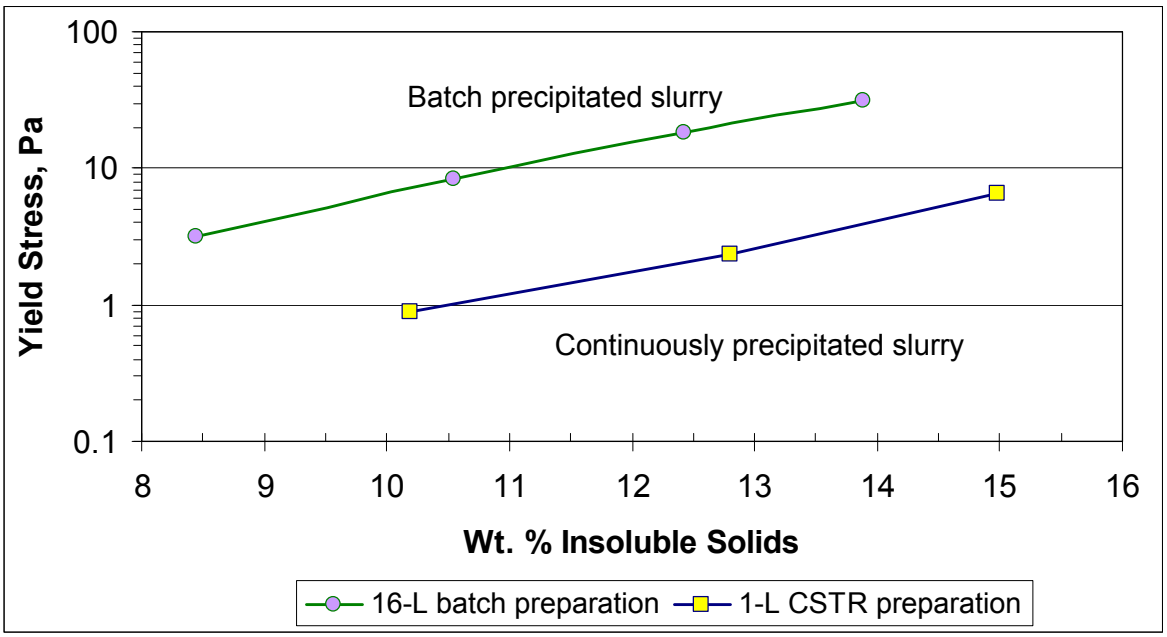

Figure 5. Impact of continuous versus batch precipitation of 16 liters of simulated HLW slurry on the dominant rheological property, Bingham plastic yield stress.

In some simulant preparations, a larger fraction of the insoluble solids were added as reagent chemicals instead of as nitrate salts, for example 50% or more of the insoluble solids. In these simulants, the particle size distributions of the commercial insoluble solids had a significant impact on the rheological properties of the simulants. These simulants were often insufficiently viscous to perform studies on the ability of the slurry to suspend glass frit particles which are added prior to vitrification. Thermal treatments of the freshly precipitated slurries to simulate aging in the waste tanks have only produced minor changes in the physical properties.

High shear mixers have been used to increase the apparent viscosity of simulants that are within a factor of two to three of the target rheological behavior. The high shear mixers seem to increase the Bingham plastic yield stress with increasing time for a while (30-60 minutes) after which the rate of change in yield stress with respect to time becomes nearly zero. It has now been found that ultrasonication can produce nearly a ten-fold increase in the Bingham plastic yield stress in just a few minutes, and that the high shear mixers are not able to achieve the same increases.

The radioactive waste simulants being produced today mimic the chemical processing behavior of real waste essentially as well as can be quantified and with appropriate allowances for the absence of the radioactive species. Differences still remain in physical behavior, however. Currently, a program to improve physical properties of simulants is underway. One goal is to investigate how to produce particles that are foamier under boiling conditions. Real HLW slurries tend to foam when boiled under caustic conditions, while simulants do not (both seem to foam comparably following acidification during chemical pretreatment, but prior to that the two are different). Research at the Illinois Institute of Technology (Bindal et al.) has established that biphyllic particles are stabilizing slurry foams. Simulants form such particles during the acidification phase of waste processing (acidified simulants are foamy during gas

generation and boiling), but apparently do not have enough biphyllic particles as made. Studies on foaminess have been conducted that show that it is possible to alter this characteristic to some extent. Additional studies using the continuous precipitator operated over a designed partial factorial matrix of conditions are underway to determine whether or not certain properties can be adjusted by varying the operational mode of the equipment.

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