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Simulant Development for Savannah River Site High Level Waste

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The Defense Waste Processing Facility (DWPF) at the Savannah River Site vitrifies High Level Waste (HLW) for repository internment. The process consists of three major steps: waste pretreatment, vitrification, and canister decontamination/sealing. The HLW consists of insoluble metal hydroxides (primarily iron, aluminum, magnesium, manganese, and uranium) and soluble sodium salts (carbonate, hydroxide, nitrite, nitrate, and sulfate). The HLW is processed in large batches through DWPF; DWPF has recently completed processing Sludge Batch 3 (SB3) and is currently processing Sludge Batch 4 (SB4). The composition of metal species in SB4 is shown in Table 1 as a function of the ratio of a metal to iron. Simulants remove radioactive species and renormalize the remaining species. Supernate composition is shown in Table 2.

Table 1. Metal species in SB4 as Ratios to Fe

	40-inch Heel Case	**15C, Blend 1**	15C, Batch 1
Al	1.057	0.707	1.874
Ba	0.0088	0.0059	0.0067
Ca	0.0920	0.0919	0.0946
Ce	0.0108	0.0070	0.000
Cr	0.0115	0.0081	0.0109
Cu	0.0041	0.0027	0.00033
Fe	1.000	1.000	1.000
K	0.0953	0.0156	0.0410
La	0.0047	0.0048	0.0075
Mg	0.0433	0.0811	0.0385
Mn	0.249	0.228	0.238
Na	1.170	0.881	1.394
Ni	0.183	0.0666	0.0870
Pb	0.0122	0.00430	0.00033
Si	0.0859	0.104	0.237
Th	0.0027	0.0032	0.0092
Ti	0.0007	0.0011	0.0008
U	0.402	0.349	0.244
Zn	0.0061	0.0043	0.0003
Zr	0.0135	0.0097	0.0117

Table 2. Supernate Species and Solids Content of SB4

	40-inch heel case	**15C, Blend 1**	15C, Batch 1
SpGr, kg/L	1.0585	1.0410	1.0403
Na^+, M	1.3363	0.9180	0.9606
NO_2^-, M	0.5073	0.3970	0.4124
NO_3^-, M	0.2445	0.1910	0.2426
OH^-, M	0.3369	0.1770	0.1389
Cl^-, M	0.0013	0.0010	0.0007
SO_4^{2-}, M	0.0208	0.0220	0.0235
F^-, M	0.0019	0.0040	0.0004
CO_3^{2-}, M	0.0763	0.0510	0.0490
AlO_2^-, M	0.0598	0.0190	0.0178
$C_2O_4^{2-}$, M	0.0033	0.0080	0.0015
PO_4^{3-}, M	0.0012	0.0010	0.0005
K^+, M	0.0034	0.0040	0.0017
wt% Insoluble Solids	14.90	12.20	10.29
wt% Total Solids	21.82	17.41	15.90

Simulants are utilized to perform tests of the DWPF process. The sludge is non-Newtonian and is typically described as a Bingham Plastic. The yield stress of actual waste is typically higher than the simulants prepared by the current preparation technique. Improvement of the simulant was desired to allow more accurate representations of plant processes to allow optimization studies and to incorporate techniques developed during preparation of simulants for the Hanford vitrification process.

The original simulant preparation process is performed in four steps: 1) Manganese nitrate precipitation by addition of potassium permanganate 2) Ferric and nickel nitrate addition to the MnO_2 slurry followed by precipitation by addition of sodium hydroxide 3) Solids washing to remove soluble sodium and potassium nitrate 4) Trim chemical addition to add remaining metals (Al, Ba, Ca, Cr, Mg, Na, etc.) and anions (nitrite, sulfate, oxalate). Solids washing can be performed by gravity settling, decanting the supernate, and addition of dilution water; repeating as required to hit the targeted nitrate level. Continuous washing using a cross-flow or rotary microfilter can also be utilized. Small batches can be washed using a centrifuge to aid gravity settling.

The simulant testing proceeded in phases, based on available funding and need dates for process simulants. During Phase 1, the original preparation method was compared to revised processes to determine if the process was sensitive to changes and could be tuned to match the actual waste properties. Phase 2 consisted of testing the simulants through the DWPF Chemical Process Cell (CPC) process to ensure that the changes noted persisted through the process and additional refinement of the revised methods. Phase III was performed after scaling issues were identified during Phase II testing. Phase IV involved testing and implementation of a CSTR process for simulant production.

During Phase I, testing was conducted using a SB3 composition (similar to SB4, but with less Al and more Fe). A revised process was developed that added all species as metal nitrates prior to the manganese strike[1]. Trim chemical additions were limited to base-reactive species (silica and titanium oxide). Different washing techniques were evaluated during the development of the revised process, as well as inclusion of post treatment processes such as heat treatment at boiling and high shear mixing[2]. As shown in Figures 1 and 2, the revised recipe resulted in yield stresses above the actual waste samples (SB2/3 sample results). The baseline case for this testing was the precipitation of all metals except aluminum during the hydroxide addition. As shown in Figure 1, addition of aluminum to the precipitation process (Tests 7 and 8) lowered the yield stress while the application of shear during washing (Test 2 and Test 3) increased yield stress. Heat treatment provided a small benefit.

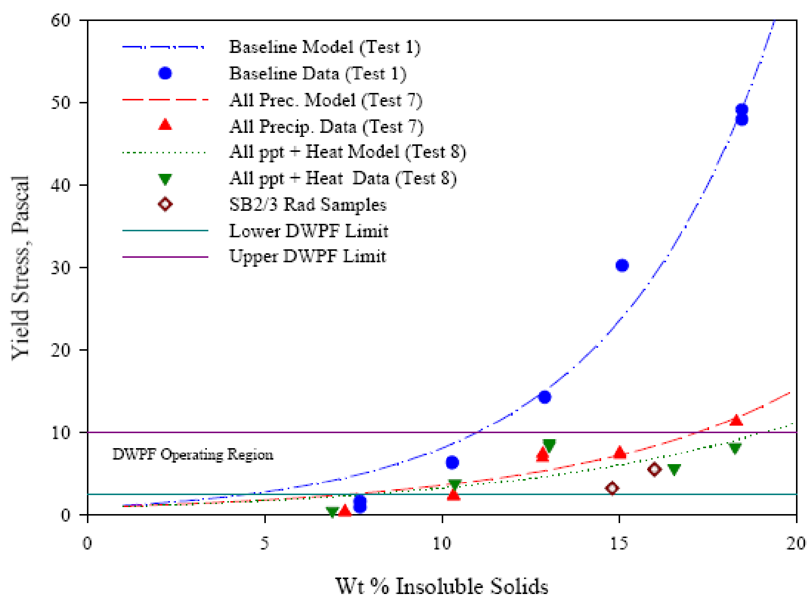

Figure 1. Phase I Test Results for Al Precipitation

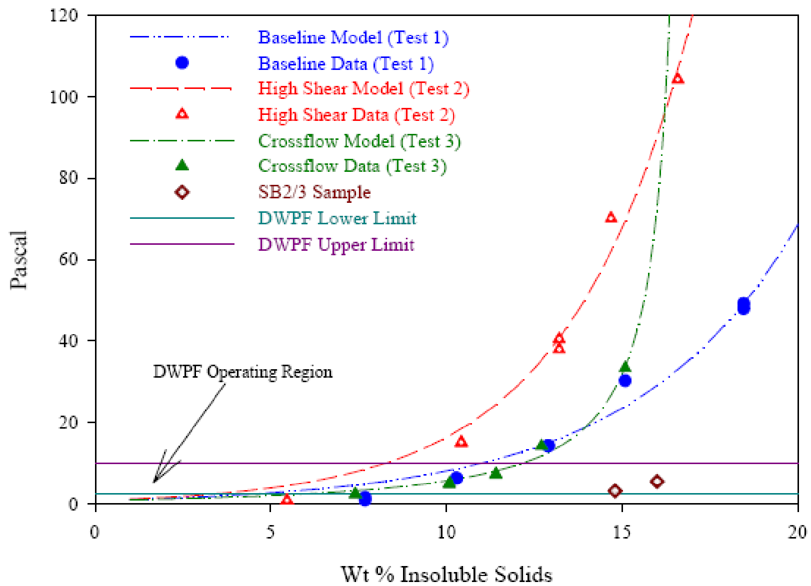

Figure 2. Phase I Test Results: Application of Shear

During Phase II testing, the physical property differences were shown to persist through the DWPF pretreatment process[3]. In addition, irradiation and thermal treatment processes were performed on the simulants to evaluate the impact of these treatments on physical properties. Irradiation did not impact the yield stress, particle size, or crystalline composition of the simulants. The thermal treatment that was performed in an attempt to accelerate any aging processes did impact the yield stress and crystalline makeup of the simulant. The impacts on yield stress were much smaller than the impacts of varying makeup and washing methods, but small benefits were noted as shown in Figure 3.

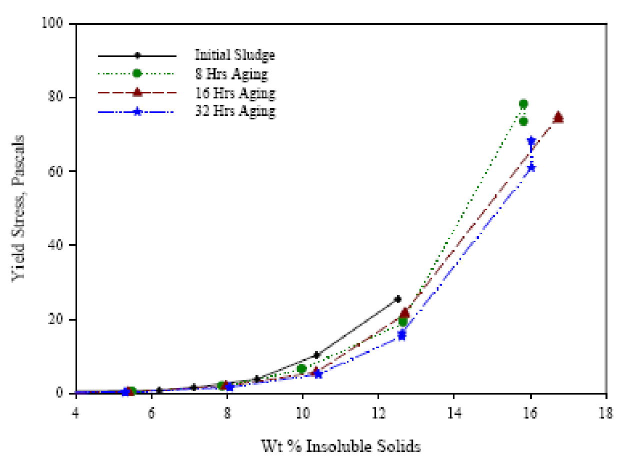

Figure 3. Impact of Thermal Treatment at 90°C on Yield Stress of SB3 Sludge Simulant

During the Phase II testing, a large batch of Sludge Batch 4 simulant was needed. Simulants produced by the original recipe were performing in a marginal manner; therefore, the revised recipe where all species were precipitated together was chosen to produce the needed simulant. The large batch exhibited extremely viscous behavior, likely due to scaling issues with mixing during the precipitation process. The precipitated slurry thickens considerably when the pH reaches ~4, and then thins as the pH exceeds 8. Mixing during the time period with high yield stress was difficult to maintain in the large scale batch.

Phase III testing was performed to evaluate the scaling issues, but efforts were hampered by the requirements to produce batches of SB4 simulant for testing. Modifications were made to the mixing protocols, addition rates of reagents, and the manganese strike prior to metal nitrate additions was reinstated. These changes led to improvements in yield stress as the batch size increased, but all batches greater than 2 liters were significantly higher in yield stress than the 2 liter batches[4,5,6,7], as shown in Figure 4.

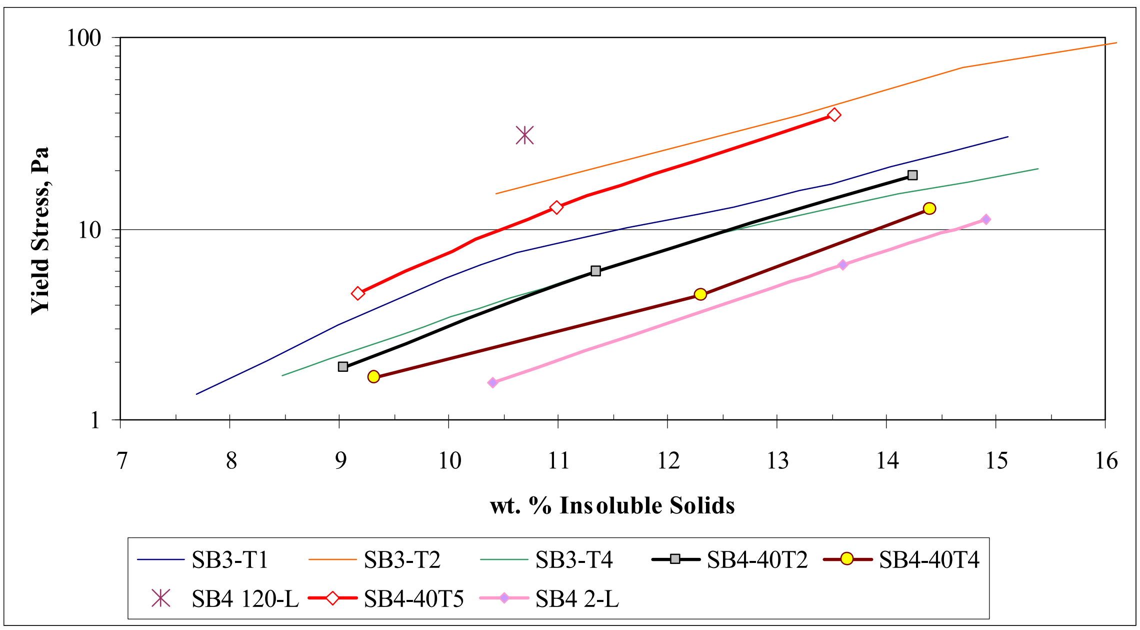

Figure 4. Yield Stress from Batches of SB4 Simulant

A small-scale continuous process was proposed and developed to allow large batches to be produced without the scale-up issues noted during the batch process. The continuous process consisted of a small (2L) CSTR as shown in Figure 5. The automated control system is not shown.

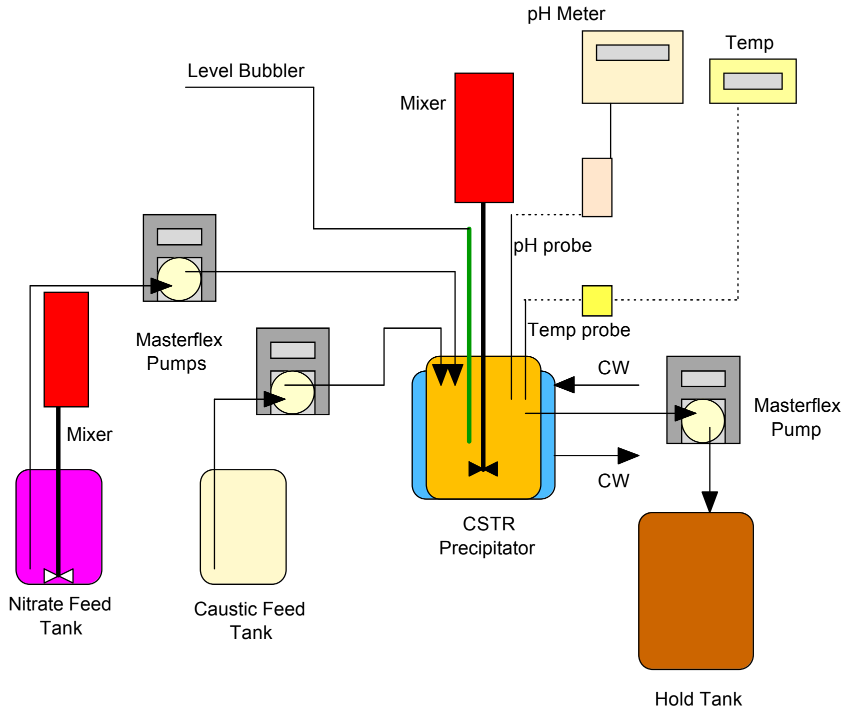

Figure 5. Diagram of CSTR Precipitation Apparatus

The manganese strike is performed in a batch manner in the nitrate feed tank, similar to the original preparation process. Metal nitrates are added to the manganese slurry and a small batch precipitation is then performed and used as the precharge to the CSTR vessel. The remaining metal nitrate slurry is fed to the CSTR concurrently with 50% NaOH to perform the hydroxide precipitation. An automated control system was implemented to maintain a constant level and pH in the CSTR. The CSTR is water-jacketed to maintain a constant temperature. The precipitated slurry is collected in an unmixed container without temperature control.

The CSTR process was utilized to produce large scale batches (20 to 100 liters) with yield stresses typical of those seen with the lab-scale batches (2 liters)[8], as shown in Figure 6 (line SB4-15C-MS2). The process has been successful utilized to prepare simulants of SB4 and SB5 composition and has been adopted as the baseline process.

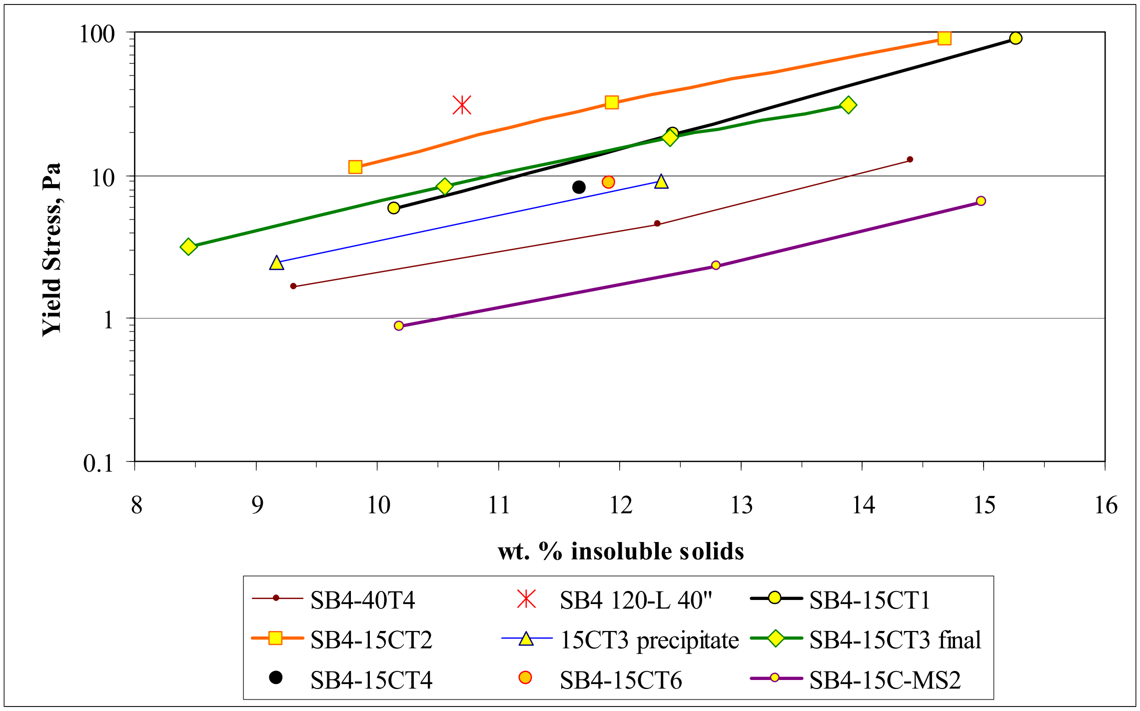

Figure 6. Yield Stress Results from CSTR Testing

Particle size measurements were made throughout the testing. General trends were seen in the data that shearing produced more fines while heat treatment removed some of the fines. The particle size distribution of the simulants was generally similar, with the exception of the CSTR runs. As shown in Figure 7, the particle size distribution was narrower for the CSTR than the batch process. Particle size measurements of actual waste indicate a peak at 3 microns, few fines below 0.8 microns, and a maximum particle size of 50 microns.

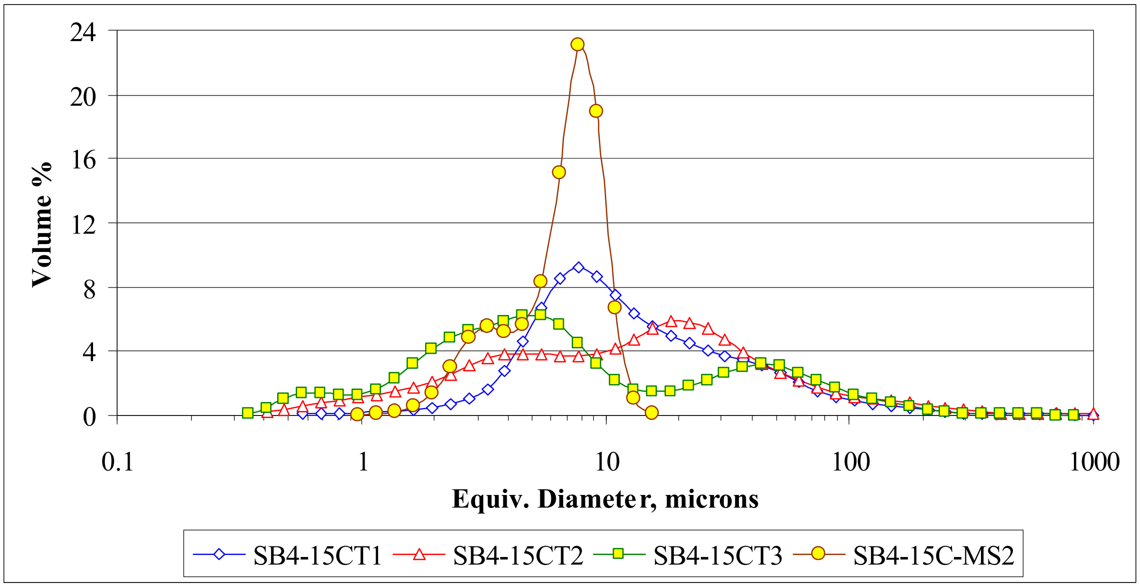

Figure 7. Impact of CSTR Process on Simulant Particle Size

Future testing will prepare a matrix of sludge compositions to determine the impact of varying the sludge composition on the simulant preparation process as well as the DWPF pretreatment and vitrification processes. Additional testing to refine the parameters for the CSTR operation and to scale-up the process to a 20L vessel is under consideration.

References

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