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Understanding the Effects of Dispersant Addition to Slurry Rheology using Laser Scanning Confocal Microscopy

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Abstract: The effectiveness of three dispersants to modify slurry rheology was examined using rheology measurements and laser scanning confocal microscopy (LSCM) in simulated waste solutions. All of the dispersants lowered the yield stress of the slurries below the baseline samples. The rheology curves were fitted reasonably to a Bingham Plastic model. The three-dimensional LSCM images of simulants showed distinct aggregates were greatly reduced after the addition of dispersants leading to a lowering of the yield stress of the simulated waste slurry solutions.

Keywords: Dispersants; Laser scanning confocal microscopy; Slurry rheology

INTRODUCTION

Nuclear materials production at the Department of Energy's (DOE) Savannah River Site (SRS) and the Hanford Site yielded radioactive waste that is stored in underground storage tanks with a capacity of up to 1.3 million gallons (1). Efforts are underway to process the radioactive waste contained in 49 tanks at SRS and 177 tanks at the Hanford

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site into solid waste forms suitable for disposal (2). Radioactive waste treatment facilities are in place at SRS and under construction at the Hanford site which involve the transportation, treatment, and immobilization of slurries of insoluble sludge and sodium salt supernates in borosilicate glass. Sludge is primarily comprised of inorganic oxides/hydroxides of aluminum, iron, nickel and manganese formed under alkaline conditions. Sodium salt supernate, containing most of the radioactive Cs-137, is the portion of the waste that is separated from the sludge. The sludge and salt supernates are formed during caustic adjustment of acidic wastes from PUREX (Pu & U solvent extraction plants). The inorganic solids are mixed and transported for treatment, which involves washing and chemical adjustments. Both Hanford and SRS separate the Cs-137 from the sodium salt supernate using either ion exchange or caustic solvent extraction. The separated Cs-137 liquid waste stream is added to the inorganic solids prior to further treatment. Glass frit, created from glass-forming chemicals, is added to the pretreated sludge slurry at SRS in a final step and the mixture is fed to a joule heated glass melter. At Hanford, glass-forming chemicals are added to the waste slurries prior to heating the mixture in the glass melter. Once water is driven off, the molten borosilicate glass containing the sludge is poured into stainless-steel canisters for storage.

Addition of slurry feed to the glass melter is handled by a system of remotely operated equipment including pumps, mixers, and pipes with limits on handling highly viscous fluids. The melter feed displays Bingham plastic rheological behavior that increases yield stress with solids content. The sludge and glass frit solids content in the feed slurry range from 35–50 wt% but is limited by solution handling concerns. Optimally, feed slurries should contain high sludge solids content for efficient waste sludge throughput and have a low yield stress for easy solution handling and transportation.

Dipersants have been used to modify the rheology of radioactive waste slurries (3). Prior to the addition of frit solids, these slurries consist of 1–5 μm irregular shaped particles that form gel-like particle network. Rheology modifiers change the interaction of the suspended particles, such as repulsion and van der Waals attraction, which often leads to lower yield stress. In a previous paper (4), Dolapix CE (Zschimmer and Schwartz) and Disperse-Ayd W28 were identified using rheology as good dispersants for lowering the yield stress of radioactive waste slurries. On some waste simulants, Cyanamer P35 was also identified as effective. The current work uses laser scanning confocal microscopy (LSCM) to examine the particle-particle interactions of two different simulated waste slurries with the rheology modifiers.

EXPERIMENTAL

Chemicals and Materials

Samples of Dolapix CE64 were supplied by Zschimmer & Schwartz. Disperse-Ayd W28 or Nuosperse W28 was obtained from Elementis Specialties. Cytec Industries Inc. supplied the Cyanamer P35. All samples were used as supplied.

Chemicals purchased for the preparation of waste slurries were reagent grade from Alfa Aesar, Sigma-Aldrich or Fisher Chemical. One simulated waste slurry termed High Level Waste (HLW) Hydroxide simulant was prepared to simulate Hanford site waste, mainly AZ-101. A second simulated waste slurry named Sludge Batch Three (SB3) Slurry Mix Evaporator (SME) was prepared to simulate Savannah River Site waste.

Instruments

All weights were determined on an analytical balance accurate to ± 0.2 mg. Rheology measurements were generated on a Haake RS150 using plate-to-plate geometry. Simulated waste slurries were examined using a Zeiss LSCM 510 (Carl Zeiss Inc., Thornwood, NY) using appropriate filter sets (5). The fluorescein (405 nm) and rhodamine (565 nm) worked best in combination with the LSCM argon-helium laser for real-time slurry examination.

Simulated Waste Solutions

Hanford feed is basic slurry with precipitated metal species and soluble sodium salts. The metal species are primarily Fe, Al, Mn, and Zr hydroxides (7). A summary of the solids content is listed in Table 1 and the pH was greater than 12.

SBE SME product is simulated SRS waste that has undergone pretreatment for vitrification. The simulant was prepared as caustic slurry of metal hydroxides precipitants and dissolved sodium salts. The pretreatment process acidifies the sludge with nitric and formic acid additions and concentrates the simulant by boiling. Glass frit is then added to the batch and concentrated further by boiling. The final slurry targets 50 weight percent total solids Sludge batch 3 waste simulant was prepared (8) and an analysis of the final product analyses are listed in Table 2, Table 3, and Table 4. The glass frit contained in SB3 waste simulant was Frit 320 which is 72 wt% SiO_2, 12 wt% Na_2O, 8 wt% Li_2O, and 8 wt% B_2O_3. This frit is created

Table 1. Pretreated high-level waste precipitated hydroxide simulant

Species	Pretreated HLW precipitated hydroxide simulant μg/gram solids
Al	86,659
B	3,573
Ba	1,657
C_2O_4	186
Ca	8,158
Cd	11,265
Ce	3,444
Cl	443
Co	150
Cr	2,344
Cu	609
F	172
Fe	202,384
K	2,508
La	3,755
Mg	1,554
Mn	5,438
Na	42,212
Nd	3,108
Ni	9,970
NO_2	4,623
NO_3	48,686
P	2,564
Rh	546
Ru	947
Si	15,794
Sn	1,554
SO_4	1,997
Ti	341
Zn	337
Zr	61,505

by melting batch chemicals to produce the glass composition required, then grinding the glass to $-80/+200$ mesh.

Rheology Modifier Additions

Waste simulant (35 g) was added to a Corning® 50 mL polypropylene disposable centrifuge tube with a screw top. All rheology modifiers were

Table 2. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of SB3 waste simulant

	Calcined basis	
Element	Wt(%) elemental	Wt(%) oxide
Al	3.31	6.26
B	1.44	4.63
Ba	0.045	0.05
Ca	0.87	1.21
Cr	0.056	0.08
Cu	0.038	0.05
Fe	9.8	14.01
Gd	0.026	0.03
K	0.074	0.09
Li	2.4	5.15
Mg	0.84	1.4
Mn	1.46	1.88
Na	9.03	12.2
Ni	0.33	0.42
P	0.031	0.07
Pb	0.039	0.04
S	0.17	0.52
Si	23.6	50.6
Zn	0.12	0.14
Zr	0.2	0.26
	Sum of oxides	99.09

tested at 3000 ppm based on the percent activity of the product. In addition, Dolapix CE64 and Diperse-ayd W28 were tested at 1000 ppm based on the percent activity of the product. For instance, a simulated waste sample containing 1000 ppm of Dolapix CE64 that has an activity of 65% was prepared by adding 0.054 g (0.035g/0.65) into 35 g of waste simulant. Table 5 summarizes the sample preparations.

Table 3. SB3 waste simulant weight percent solids

Solids	Wt (%)
Soluble	11.6
Insoluble	38.3
Total	49.9
Calcine	41

Table 4. Ion chromatography analysis of SB3 waste simulant

Anion	Wt (%)
Cl	156
NO_3	31,400
SO_4	3,760
HCO_2	53,200

Rheology Protocol

All measurements were obtained on a Haake RS150 rheometer using the plate to plate technique. The measurement geometry used 60 mm plates with a 0.5 mm gap for the Hanford simulant and a 1.5 mm gap for the SRS simulant. The larger gap was required to measure the SRS slurry due to the presence of the hard glass frit particles. All samples were analyzed in duplicate at 25°C over a shear rate of 0 to 600 sec^{-1}. The resulting data was fit to flow curves using the Bingham Plastic model over the range 50 to 600 sec^{-1} for both the up and down portion of the flow curves. This model is a two-parameter relationship between the shear stress and the shear rate:

$$\tau = \tau_{BP} + \mu_{\infty}\dot{\gamma}$$

Where:

τ = Shear Stress (s^{-1})
τ_{BP} = Bingham Plastic Yield Stress (Pa)
μ_{∞} = Bingham Plastic Consistency
$\dot{\gamma}$ = Shear Rate

Table 5. Simulant and rheology modifier formulation

Simulant	Description	% Activity
HLW Hydroxide	Baseline	0
HLW Hydroxide	1000 ppm Dolapix CE64	65
HLW Hydroxide	3000 ppm Dolapix CE64	65
HLW Hydroxide	3000 ppm Diperse-Ayd W28	46
HLW Hydroxide	3000 ppm Cyanamer P35	50
SB3 SME	Baseline	
SB3 SME	1000 ppm Disperse-Ayd W28	46
SB3 SME	3000 ppm Disperse-Ayd W28	46

Confocal Laser Scanning Microscope Protocol

Samples were prepared for imaging by two methods. The SB3 SME set of samples were prepared by placing a drop between two microscope slides. The HLW hydroxide simulant samples were prepared differently, using a Sedgewick Rafter slide (Model P-0042, Phycotech, Inc). The Sedgewick Rafter slide contains a chamber constructed as a flat slide (76 mm × 40 mm) onto which is cemented a 'wall' to form a chamber or cell in the middle. This glass chamber is 50 mm long × 20 mm wide and 1 mm deep and its base is marked with a grid of 100 × 1 mm squares. The chamber was filled with slurry and closed with a cover glass carefully placed over the liquid at an angle to eliminate bubble formation. The slurry sample was then examined under a low (100X) magnification with LSCM. Z-contrast LSCM was used to detail the unique three-dimensional structural information of the slurry composition (6). The Z-contrast image is formed by repeatedly scanning at designated depths (i.e., 40 images at 10 μm intervals) in the Z-plane. The Z-contrast images are collected at the designated depths and the images over the entire scan are (i.e., 400 μm) are collated and analyzed.

RESULTS AND DISCUSSION

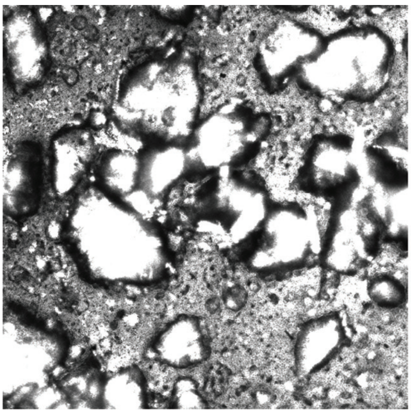
The three dispersants tested were previously (4) found to be effective at lowering the yield stress of the high-level waste hydroxide simulant and one of the three dispersants was considered effective at lowering the yield stress of SB3 SME waste simulant. A number of dispersant formulations were added (0.5 g per 100 g sample) to the waste simulant and rheology was used to compare the dispersant containing sample with a baseline sample. The most promising deflocculants from the previous study are listed in Table 6 and Table 7. Dolapix CE64 and Disperse-Ayd W28, polyacrylate based dispersants, and Cyanamer P35, a polyacrylamide based dispersant, were used in this study to modify interparticle forces and thus lower yield stress (9,10). The desired end result is for the polymer to adsorb onto the sludge particles and disrupt aggregation (11).

For SB3 SME waste simulant, the dispersant lowered the yield stress relative to the baseline simulant at 1000 ppm and at the more optimal 3000 ppm (Table 6). Figure 1 shows laser scanning confocal microscopy (LSCM) images of a baseline sample (Figs. 1A & C) and a sample containing 3000 ppm of Disperse-Ayd W28 (Figs. 1B & D). Figures 1a and c are regular LSCM micrographs while Figs. 1B & D are Z-scans showing results with depth of fields from 200 μm (Fig. 1C) to 450 μm (Fig. 1D). All images show the large particles which are glass frit while flocs are seen

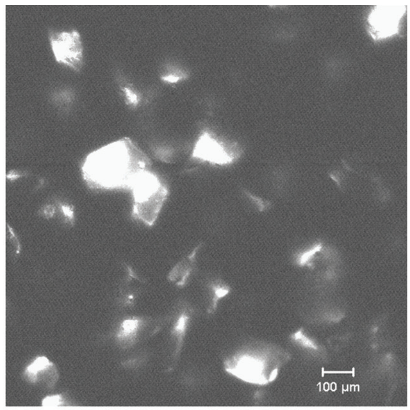
Table 6. Rheology data in duplicate for rheology modifiers in simulated waste

		Rheology data, stress yield, Pa							
Sample #	Description	Up run 1	Up run 2	Average	% diff	Down run 3	Down run 4	Average	% diff
HLW-1	Baseline	13.0	15.0	14.0	N/A	9.68	16.8	13.2	N/A
HLW-2	1000 ppm Dolapix CE64	10.1	10.1	10.1	27.8	7.94	7.77	7.86	40.5
HLW-3	3000 ppm Dolapix CE64	7.91	7.67	7.79	44.2	6.00	5.93	5.97	54.8
HLW-4	3000 ppm Diperse-Ayd W28	8.83	8.83	8.83	36.7	7.99	7.3	7.65	42.1
HLW-5	3000 ppm Cyanamer P35	9.67	9.32	9.5	31.9	8.53	9.03	8.78	33.6
SB3 SME-1	Baseline	12.1	18.4	15.3	N/A	12.0	19.7	15.8	N/A
SB3 SME-2	1000 ppm Disperse-Ayd W28	15.5	12.6	14.0	7.9	16.1	13.1	14.6	7.6
SB3 SME-3	3000 ppm Disperse-Ayd W28	9.89	12.6	11.2	26.3	10.4	13.7	12.1	23.8

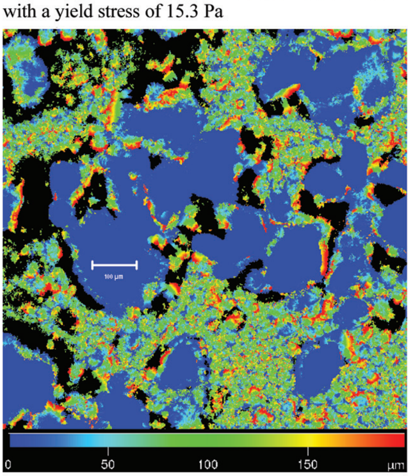
in the baseline sample in the gaps between glass frit particles. The images on the right show that once dispersant is added the flocculants are disrupted and the particles become well dispersed leading to lower yield stress values (9,10). These images demonstrate that the chemical changes in the slurry were accompanied by a physical shift in the sample matrix. These physical-chemical changes would be similar on a variety of scales and environments.



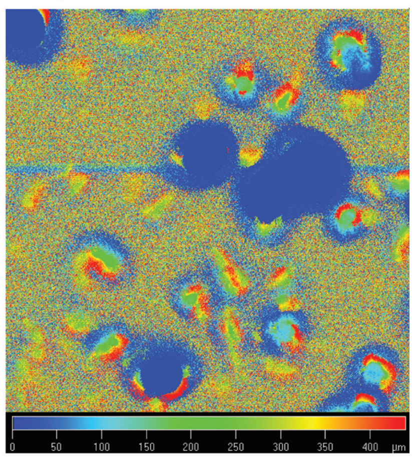
A. Baseline SB3 SME-1 – Sludge Batch 3 SME with a yield stress of 15.3 Pa



B. SB3 SME-3 – 3000 ppm Dysperse-Ayd W28 with a yield stress of 11.2 Pa



C. Baseline SB3 SME-1 – 3D with a yield stress of 15.3 Pa

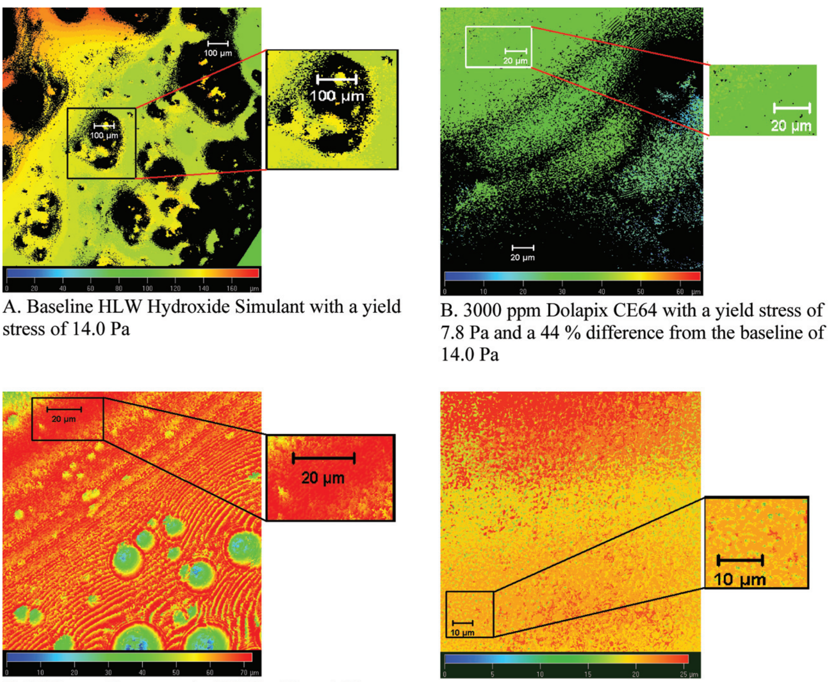


D. SB3 SME-3 – 3000 ppm Dysperse-Ayd W28 with a yield stress of 11.2 Pa

Figure 1. SB3 SME Simulated Waste before A. & C. (left) and after the addition of Dysperse-Ayd B. & D. W28. Note the transition from flocculants between the glass frit particles in images A and C to smaller dispersed particles in images B and D.

Table 7. Rheology modifiers used

Name	Type	Use	Source
Dolapix CE64	Proprietary polyacrylic acid-based polyelec trolyte	Deflocculant	Zschimmer & Schwartz
Disperse-Ayd W28 or Nuosperse W-28	Proprietary anionic and nonionic surfactant, polyacrylate	Pigment, wetting agent	Elementis specialties
Cyanamer P35	Acrylic Acid/ Acrylamide	Antiprecipitant	Cytec Industries Inc.



A. Baseline HLW Hydroxide Simulant with a yield stress of 14.0 Pa

B. 3000 ppm Dolapix CE64 with a yield stress of 7.8 Pa and a 44 % difference from the baseline of 14.0 Pa

C. 3000 ppm Dysperse-Ayd W28 with a yield stress of 8.8 Pa and a 37 % difference from the baseline of 14 Pa

D. 3000 ppm Cyanamer P35 with a yield stress of 9.5 Pa and a 32 % difference from the baseline of 14 Pa

Figure 2. HLW Hydroxide Simulant LSCM images without (A.) and with (B., C., & D.) dispersants. Note the transition from large flocculants in image A to dispersed particles in image B, C, and D.

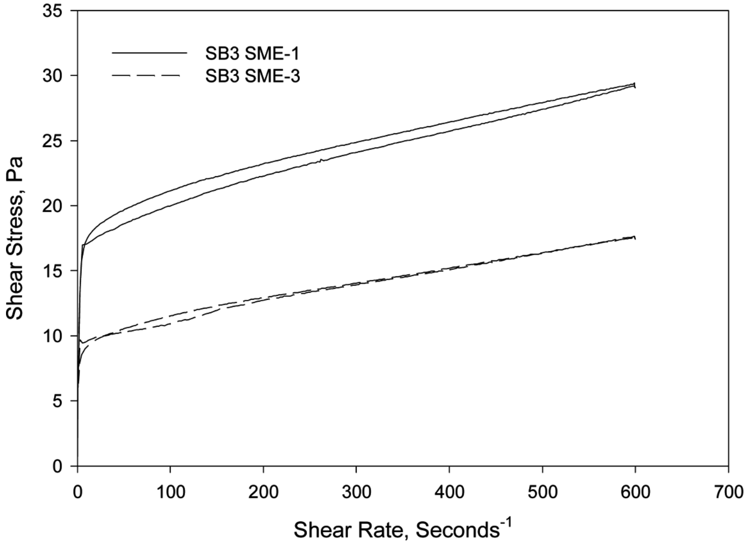


Figure 3. Typical Rheology for HLW Hydroxide Simulant with 3000 ppm Dolapix CE 64 (dashed line) and HLW Hydroxide Simulant with no dispersant (solid line). These curves are typical of a Bingham Plastic model.

A decrease in yield stress and the size of flocs was also observed for the HLW hydroxide simulant. Table 6 summarizes the up and the down rheology curves for samples containing Disperse-Ayd W28, Dolapix CE64, and Cyanamer P35. All samples had a lower yield stress value than the baseline with Dolapix CE64 performing slightly better than Disperse-Ayd W28. Again the LSCM images (Fig. 2A) show aggregation in the baseline material which is largely not present in the evidently more uniform samples containing dispersant (Figs. 2B, C, & D).

CONCLUSION

The rheological properties of two different simulated waste solutions were examined with and without previously selected effective dispersants (4). All of the dispersants lowered the yield stress of the slurries below the baseline samples. The rheology curves were fitted reasonably to a Bingham Plastic model (Fig. 3). LSCM images of the simulants showed distinct flocs which were greatly reduced after the addition of dispersants (Figs. 1 & 2). This physical and chemical reduction of aggregated particles is thought to disrupt solution entrapment within the aggregates and lower the effective solid volume and solution viscosity

(9). Microscopic examination of the dispersant and non-dispersant simulated waste treatments here demonstrates this activity. For the HLW hydroxide waste simulant, Dolapix CE64, Disperse-Ayd W28, and Cyanamer P35 all lowered the yield stress of the waste simulant when compared to the untreated waste simulant. Dolapix CE64 was the most effective, with a 44% drop in the yield stress. Disperse-Ayd W28 was the effective at lowering the yield stress SB3 SME waste simulant. This result is similar to a previous example (4) of Dolapix CE64 with this same simulated waste.

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