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Yield Stress Reduction of Radioactive Waste Slurries by Addition of Surfactants

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The Savannah River Site (SRS) and Hanford site are in the process of stabilizing millions of gallons of radioactive waste slurries remaining from production of nuclear materials for the Department of Energy (DOE). The Defense Waste Processing Facility (DWPF) at SRS is currently vitrifying the waste in borosilicate glass while the facilities at the Hanford site are in the design/construction phase. Both processes utilize slurry-fed joule heated melters to vitrify the waste slurries. The rheological properties of the waste slurries limit the total solids content that can be processed by the remote equipment during the pretreatment and melter feed processes. The use of a surface active agent, or surfactant, to increase the solids loading that can be fed to the melters would increase melt rate by reducing the heat load on the melter required to evaporate the water in the feed.

The waste slurries are non-Newtonian fluids with rheological properties that were modeled using the Bingham Plastic model (this model is typically used by SRNL when studying the DWPF process[1]). 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
τ_{BP} = Bingham Plastic Yield Stress
μ_{∞} = Bingham Plastic Viscosity
$\dot{\gamma}$ = Shear Rate

At the shear rates typical of transport and mixing processes, the yield stress of the waste slurries dominates the flow behavior. A small number of tests were conducted by the Savannah River National Laboratory (SRNL) in 2001 which indicated that the use of surfactants to reduce the yield stress of waste slurries was feasible[2]; however, none of the surfactants tested during this study reduced the yield stress of SRS waste simulants.

Additional studies have been completed by SRNL that expanded the original study and utilized various simulants of waste slurries from SRS and Hanford waste tanks[3,4]. The SRS waste simulants were processed through laboratory scale simulations of the DWPF feed pretreatment process. This pretreatment process occurs in two steps, the Sludge Receipt and Adjustment Tank (SRAT) cycle and the Slurry Mix Evaporator (SME) cycle. In the SRAT cycle, the incoming sludge is acidified with nitric and formic acid. This cycle neutralizes the hydroxide and carbonate in the feed, destroys the nitrite and reduces the manganese and mercury. The mercury is removed by reflux boiling the SRAT through a decanter, then the SRAT product is concentrated by boiling to the targeted solids content. After the SRAT cycle, the glass frit is added as a 50 wt% total solids slurry in the SME. The resulting slurry is concentrated to approximately 50 wt% total solids and is transferred to the melter feed tank for subsequent vitrification. The SRAT and SME product slurries were tested during this study. A simulant of the Hanford tank AZ-102 sludge was tested without undergoing the Hanford pretreatment process.

The chemical composition of a simulant for DWPF Sludge Batch 3 is shown in Table 1. Although the composition of the samples tested varied, the chemical species present in all samples are similar to that shown in Table 1. The sludge simulant composition is shown as the sludge is prepared and prior to processing through the pretreatment process. After the pretreatment process, the anions present in the DWPF SRAT and SME samples are primarily nitrate and formate and the pH has been adjusted to approximately 5 – 7.

Table 1. Composition of Typical DPWF SB3 Incoming Sludge Simulant

Component	Result	Units		Component	Result	Units
Al	9.57E+00	wt% total solids		Nitrite	1.91E+04	mg/L
Ba	1.39E-01	wt% total solids		Nitrate	1.42E+04	mg/L
Ca	2.37E+00	wt% total solids		Sulfate	2.22E+03	mg/L
Cr	1.53E-01	wt% total solids		Oxalate	1.20E+03	mg/L
Cu	1.57E-01	wt% total solids		Carbonate	1.20E+03	mg/L
Fe	2.84E+01	wt% total solids				
Gd	7.45E-02	wt% total solids		Total Solids	22.6	wt %
K	1.22E-01	wt% total solids		Insoluble Solids	15.4	wt %
Mg	2.15E+00	wt% total solids		Soluble Solids	7.2	wt %
Mn	4.07E+00	wt% total solids		Calcined Solids	16.3	wt %
Na	1.41E+01	wt% total solids				
Ni	1.06E+00	wt% total solids		Density	1.15	g/ml
Pb	1.00E-02	wt% total solids		pH	12.7	
S	3.50E-01	wt% total solids		Base Equivalents	0.573	molar
Si	1.04E+00	wt% total solids				
Zn	3.23E-01	wt% total solids				
Zr	4.86E-01	wt% total solids				

The surfactants tested were added by weight to each sample to be tested. The samples were then homogenized and the flow curves were measured with a Haake RS600 or Haake RS150 rheometer at 25 degrees Celsius using the concentric cylinder geometry. The flow curve of each sample was measured in the same manner. The rheological properties were determined from the flow curves by regression using the Bingham Plastic model. A baseline sample containing no additive was measured during each set of tests for comparison purposes.

The additives tested were selected based on a review of available literature and conversions with surfactant vendors. The additives tested are shown in Table 2.

Table 2. Surfactants Tested

Additive	Vendor		Additive	Vendor
Sodium Meta-Silicate	Various		Alcosperse® 149	Alco Chemical
Sodium Polyphosphate	Various		Alcosperse® 240	Alco Chemical
Darvan® 7	Vanderbilt Co. Inc.		Alcosperse® 408	Alco Chemical
Duramax® 3005	Rohm and Haas		Alcosperse® 725	Alco Chemical
Dolapix® CE64	Zschimmer and Schwartz		EDAPLAN® 470	Ultra Additives
Disperse-Ayd® W22	Elementis Specialties		EDAPLAN ® 472	Ultra Additives
Disperse-Ayd® W28	Elementis Specialties		Pomosperse® AL36	Piedmont Chemical Co.
Disperse-Ayd® W30	Elementis Specialties		Cyanamer® P-35	Cytec
Disperse-Ayd® W39	Elementis Specialties		Cyanamer® P-70	Cytec
Sugar	Various			

Results and Discussion

Initial tests were conducted with DWPF SME products based on the recommendations from the previous study. The yield stress results for tests with 0.5 grams of surfactant per 100 grams of SME product are shown in Figure 1. The additives planned for the initial tests planned with DWPF SRAT products were adjusted based on the SME product results. Results from these tests, also performed at 0.5 grams of surfactant per 100 grams of sample are shown in Figure 2. No correction was made for active ingredient concentration during initial testing.

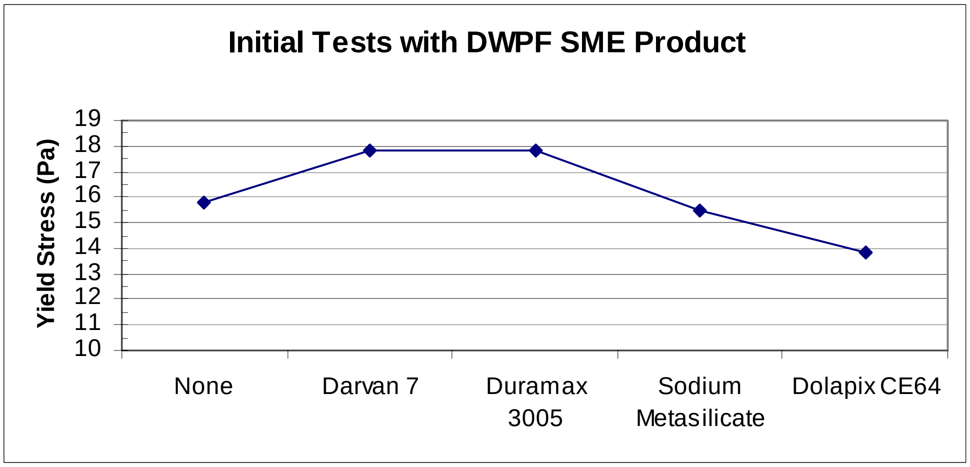

Figure 1. Initial Tests with DWPF SME Product

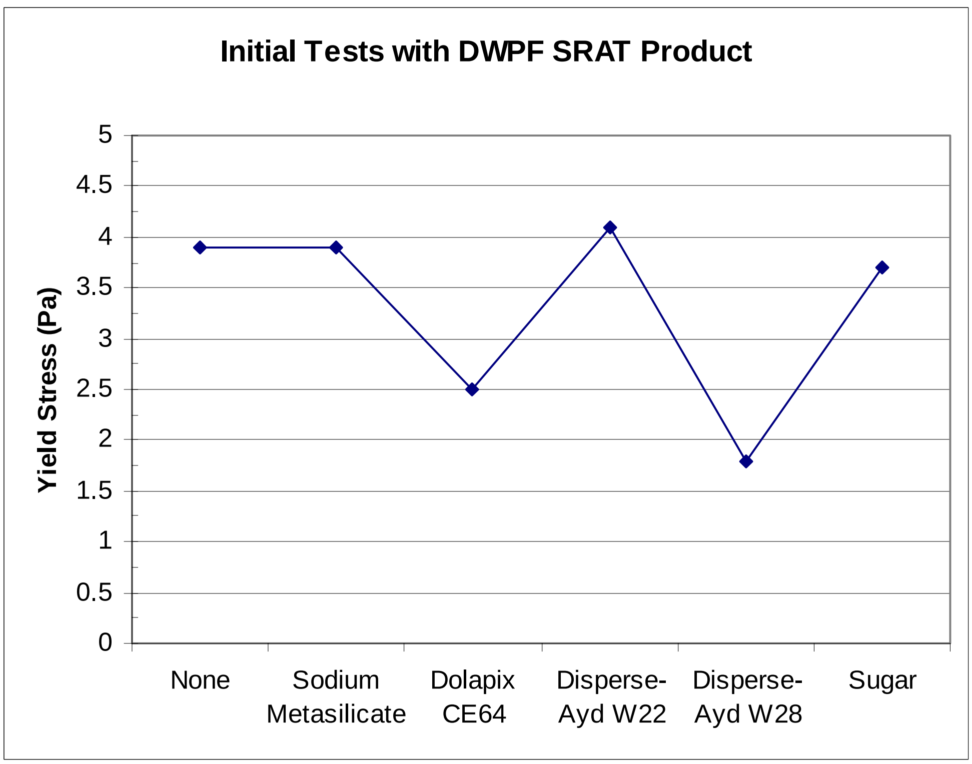

Figure 2. Initial Tests with DWPF SRAT Product

The initial testing identified two additives, Dolapix CE64 and Disperse-Ayd W28, that reduced the yield stress of the SRAT product. Additional additives were selected based on the initial tests and conversations with additional vendors. As shown in Figures 3 and 4, these additional surfactants did not reduce the yield stress of the DWPF process slurries. The performance of Disperse-Ayd W-28 during the additional tests was inconsistent with the initial tests for this sample, but Disperse-Ayd W-28 reduced the yield stress of SRAT product in nearly all other tests.

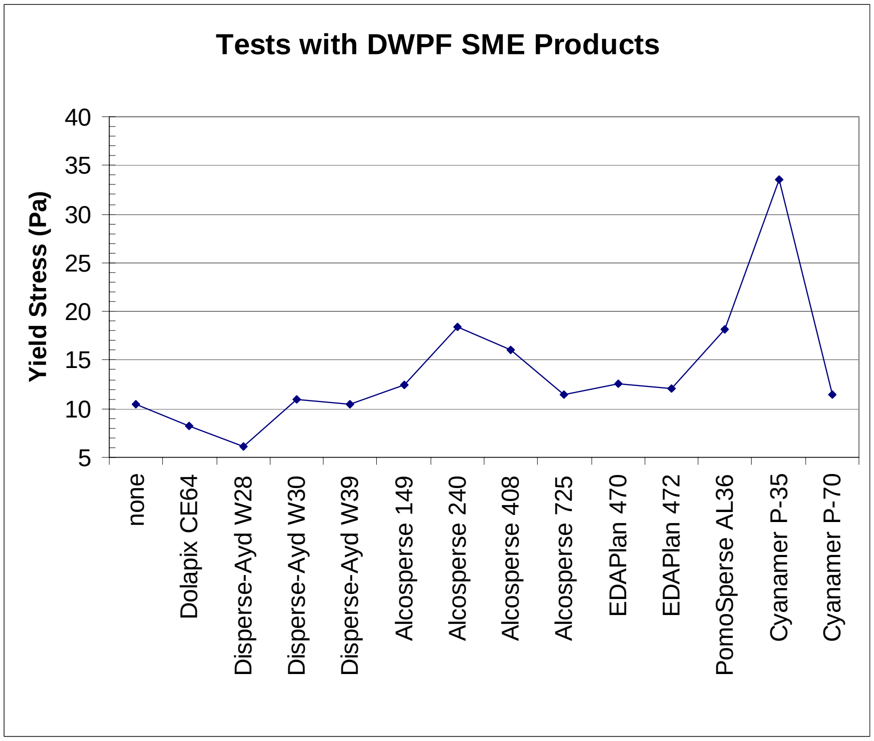

Figure 3. Results for DWPF SME Product

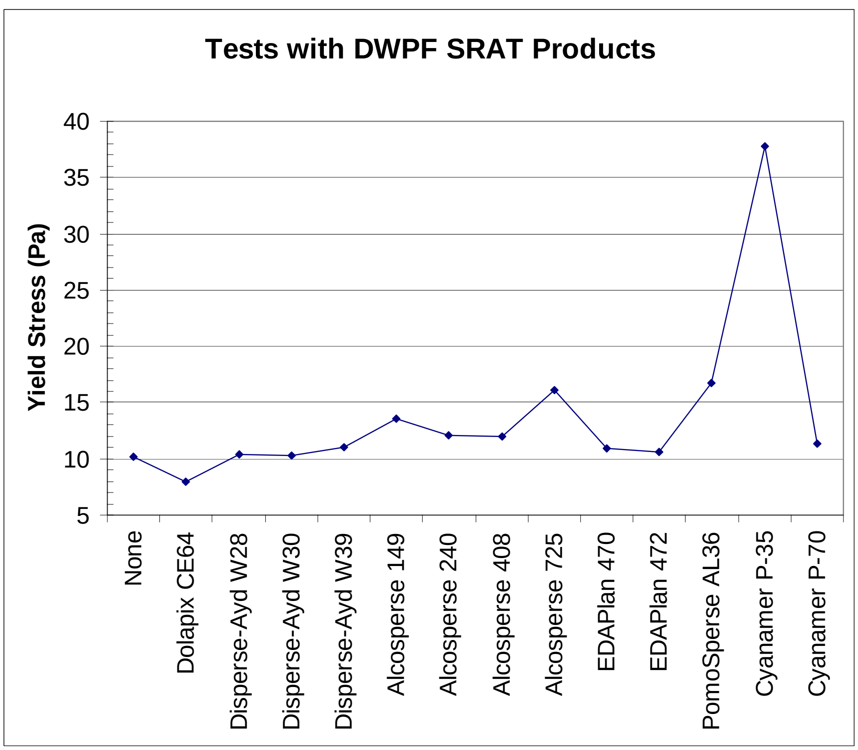

Figure 4. Results for DWPF SRAT Product

The impact of concentration on the performance of Dolapix CE64 and Disperse-Ayd W28 was evaluated. The results for Dolapix CE64 and Disperse-Ayd W-28 were similar, with higher concentrations of the surfactant leading to greater reductions in the yield stress, as shown in Figure 5.

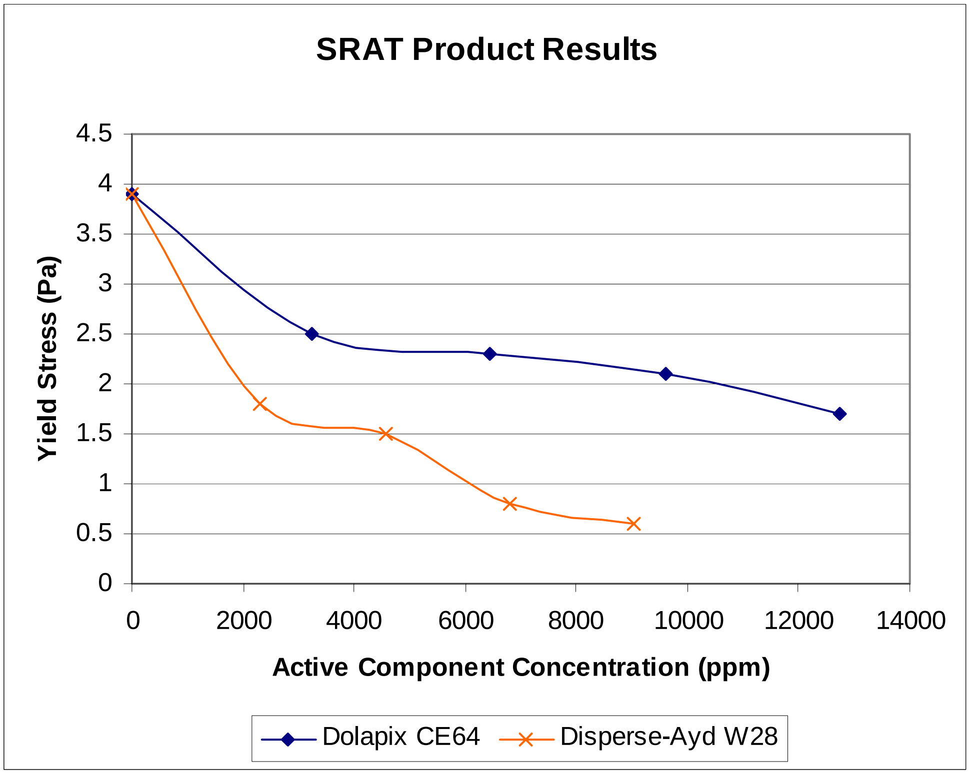

Figure 5. Effect of Surfactant Concentration on Yield Stress

The impact of Dolapix CE64 and Disperse-Ayd W28 on the particle size distribution was determined by laser diffraction. The results, shown in Table 3, indicate that the slurry was flocculated by the surfactants. The laser diffraction technique required a large dilution in order to perform the measurements. All samples were diluted in the same manner to minimize the impact of the dilution on the results.

Table 3. Particle Size of DWPF SRAT Product with Surfactants

	Mean Particle Size (Volume Basis)
Baseline SRAT Product	3.7
0.5 wt% Dolapix CE64	4.0
2.0% Dolapix CE64	7.2
2.0% Disperse-Ayd W-28	4.3

Tests were also performed on two simulants based on the Hanford tank AZ-102. Both simulants tested were based on the same chemical composition, but differed in the final pH. The FIU QARD simulant had a pH of approximately 10 while the QARD-2 had a pH of approximately 12. The final pH of the simulants is affected by the amount of washing performed during makeup. As shown in Figures 6 and 7, all of the surfactants were effective in reducing the yield stress of the FIU QARD simulant and most reduced the yield stress of the QARD-2 simulant. Only one surfactant out-performed Dolapix CE64 for the FUI QARD and no surfactant outperformed Dolapix CE64 in the QARD-2 simulant.

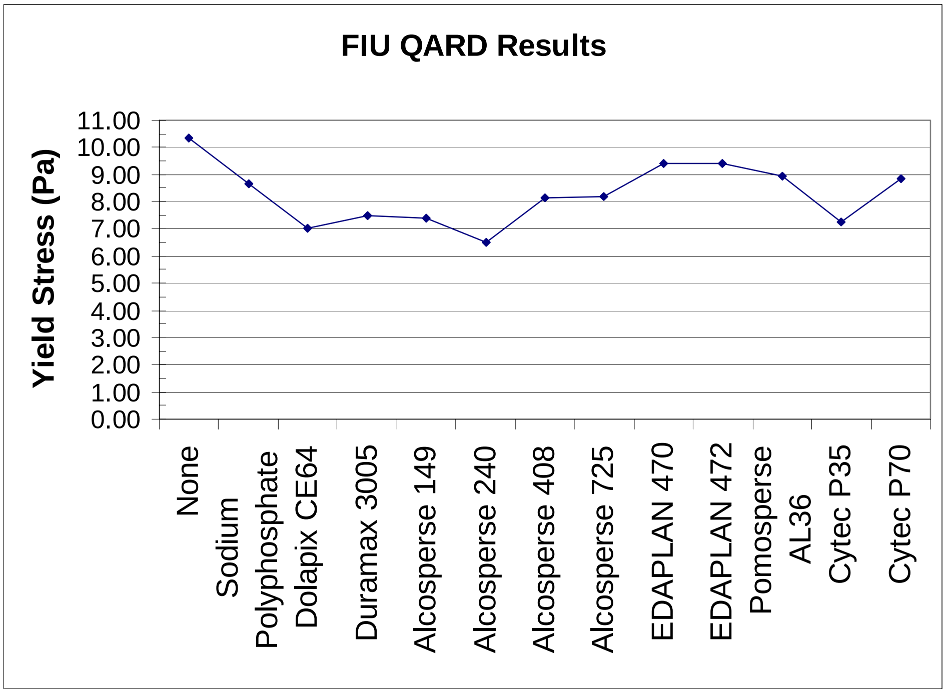

Figure 6. Results for FIU QARD Simulant

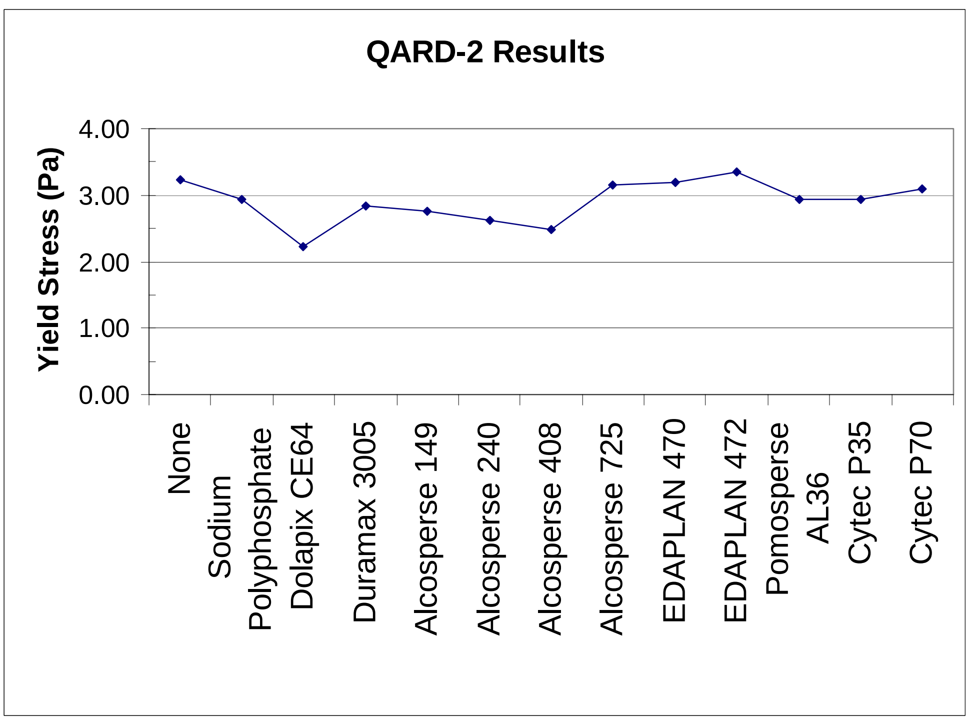

Figure 7. Results for QARD-2 Simulant

The impact of Dolapix CE64 on the particle size distribution of the FIU QARD was determined by laser diffraction. The results, shown in Table 4, indicate that the slurry was dispersed by the surfactant. The laser diffraction technique required a large dilution in order to perform the measurements. All samples were diluted in the same manner to minimize the impact of the dilution on the results.

Table 4. Particle Size of FIU QARD Simulant with Dolapix CE64

Value	FIU QARD	FIU QARD w/ 1000 PPM Dolapix CE64	Units
Volume Based Average	32.400	19.930	microns

The surfactants tested were primary polyacrylate based dispersion agents which typically have proprietary compounds attached to the polyacrylate chain. These compounds are often tailored to provide maximum effectiveness for a given chemical system and are typically effective in a narrow pH range. The effectiveness of nearly all compounds in the AZ-102 simulants at pH values greater than 10 indicates that many of these surfactants were tailored for high pH systems and explains the general ineffectiveness of the agents in the DWPF slurries. The effectiveness of Dolapix CE64 in all the simulants tested is unique among the agents tested and warrants additional evaluation.

The particle size results indicate that the Dolapix CE64 is functioning as a mild flocculation agent in the DWPF process slurries and as a dispersion agent in the AZ-102 simulants. Typically, yield stress reduction by surfactants is characterized by dispersion of the particulates, as seen in AZ-102. Yield stress reduction through flocculation of particles may indicate that the DWPF process slurries are forming large networks of particles (ie. gel-like behavior) that are broken apart by dilution and not detected by the Microtrac particle size analysis. Flocculation of the smaller particles could prevent formation of the larger networks and lead the reduction in yield stress noted. Additional work is warranted to determine the mechanism of the yield stress reduction on the DWPF process slurries.

Conclusions

The results illustrate that altering the surface chemistry of the particulates in the waste slurries can lead to a reduction in the yield stress. Dolapix CE64 is an effective surfactant over a wide range of pH values and was effective for all simulants tested. The effectiveness of the additive increased in DWPF simulants as the concentration of the additive was increased. No maxima in effectiveness was observed. Particle size measurements indicate that the additive acted as a flocculant in the DWPF samples and as a dispersant in the RPP samples.

References

[1] Koopman, D. C., 2004, "A Comparison of Rheology Data for Radioactive and Simulant Savannah River Site Waste", WSRC-TR-2004-00044, Westinghouse Savannah River Company, Aiken, SC.
[2] Kay, E. D. , et al, 2003, "Rheological Modifiers for Radioactive Waste Slurries", WSRC-MS-2003-00136, Westinghouse Savannah River Company, Aiken, SC.
[3] Stone, M. E., 2004, "Rheological Modifier Testing with DWPF Process Slurries", WSRC-TR-2004-00082, Westinghouse Savannah River Company, Aiken, SC.
[4] Stone, M. E., 2004, "Summary of Rheological Modifier Testing on RPP Simulants", SRNL-GPD-2004-00040, Westinghouse Savannah River Company, Aiken, SC.