This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

WSRC-MS-2003-00136, Rev.0

Proceedings of ASME 2003 Fluid Engineering Division Summer Meeting
July 6th-10th, 2003

FEDSM2003-4549

RHEOLOGY MODIFIERS FOR RADIOACTIVE WASTE SLURRIES

Elizabeth D. Kay*, Westinghouse Electric Company, LLC, Drawer R, Columbia, SC USA 803647-3197, kayld@westinghouse.com *formerly with Westinghouse Savannah River Company

T. Bond Calloway, Jr.** Westinghouse Savannah River Company, Savannah River Technology Center, 999-W Aiken South Carolina 29808 USA 803-819-8416, bond.calloway@srs.gov **Primary Contact

David C. Koopman, Westinghouse Savannah River Company, Savannah River Technology Center, 773-43A Aiken South Carolina 29808 USA 803-725-3737, david.koopman@srs.gov

Robin L. Brigmon, Westinghouse Savannah River Company Savannah River Technology Center, 999-W Aiken South Carolina 29808 USA 803-819-8405, ro3.brigmon@srs.gov

Russell E. Eibling, Westinghouse Savannah River Company Savannah River Technology Center, 999-W Aiken South Carolina 29808, 803-819-8411 russell.eibling@srs.gov

ABSTRACT

One factor limiting the production rate of radioactive waste immobilization processes is the rheological limitations imposed by the design of remotely maintained slurry process equipment (i.e. pumps, piping). Rheology modifiers (dispersants/flocculants) that could potentially decrease the yield stress and/or plastic viscosity of radioactive waste slurries were tested on simulated waste to determine which provided the largest decrease in yield stress and plastic viscosity. The goals of this study were to: 1) determine if trace levels of chemical additives could be used to reduce the rheological characteristics of radioactive waste slurries, 2) identify potential chemical additives for this work and future testing, 3) test a limited set of chemical additive candidates on simulated radioactive wastes, and 4) develop advanced techniques to visualize the internal slurry structure and particle-particle interaction within the slurry.

Radioactive wastes slurries generated from the production of plutonium and tritium during the Cold War are being (and will be) immobilized in a borosilicate glass matrix using joule heated glass melters at various Department of Energy (DOE) facilities located across the United States. The maximum insoluble solids content of the waste slurries is limited by the design-basis rheological properties (e.g. the Bingham plastic yield stress and plastic viscosity) used to design the slurry handling systems. It is possible to modify the equipment used to mix, sample, and transport the waste slurry. However, the design and construction cost for any such modifications is very high due to the constraints (radiation, non-visible remote operation) imposed on the design and operation of radioactive waste processes.

The rheology of two slurries with various rheology modifiers was evaluated using a conventional concentric cylinder rheometer (Haake Rheometer RS150). Only one rheology modifier of those tested was found to decrease the apparent viscosity of the waste slurry by any significant amount and several of the modifiers tested produced the opposite effect. Duramax D-3005 was found to decrease the Bingham Plastic yield stress of simulated radioactive waste slurries by approximately 18%. Selected slurries were further analyzed by a laser scanning confocal microscope. This technique allows the slurry to be analyzed in an unaltered condition. The microscope has the ability to make both two-dimensional pictures and three-dimensional representations of the slurry's internal structure. The microscope allows the user to understand how particles are flocculated or dispersed throughout a concentrated suspension of heterogeneous simulated nuclear waste slurries.

INTRODUCTION

Radioactive wastes slurries generated from the production of plutonium and tritium during the Cold War are currently being immobilized in a borosilicate glass matrix using joule heated glass melters at the Savannah River Site (SRS) in the Defense Waste Processing Facility (DWPF). A similar facility in West Valley, New York also immobilized waste generated from the reprocessing of spent nuclear fuel. The West Valley vitrification plant has completed its mission to safely immobilize the High Level radioactive tank waste. Larger immobilization (vitrification) facilities are planned as part of the Hanford River Protection Project-Waste Treatment Plant (RPP-WTP). High Activity waste is transferred to these facilities from underground tank farms. The insoluble solids content of the waste is limited by the design-basis rheological properties (e.g. the Bingham plastic yield stress and plastic viscosity) used to design the slurry transfer systems.

These facilities have used or will use slurry fed melters to safely immobilize the waste in a glass matrix. Glass forming chemicals or glass frit fabricated from glass formers is added to either the radioactive waste solutions or slurries. The resulting slurries (≈ 35 - 65 wt. % total solids) are sampled, analyzed, and then pumped to the melters. Although the DWPF process is currently operating successfully, the capability to increase production and waste loading is limited by certain bounds (slurry rheology, glass property constraints) of the design and operating envelope that was originally used to build this plant.

The solids loadings in the DWPF and future RPP-WTP melter feed slurries are limited by the rheological design bases of the mixing, sampling, and transport systems. It is desirable to increase the production rate and waste loading of the glass and therefore decrease the total quantity of waste glass produced from a total plant life cycle and cost perspective. Increasing the solids content of the melter feed would decrease the energy required to evaporate the water in the slurry, and would, therefore, increase the overall production (melt) rate of the immobilization process.

It is possible to modify the equipment used to mix, sample, and transport the waste slurry to the melter. The design and construction cost for any such modifications is very high due to the constraints (radiation, non-visible remote operation) imposed on the design and operation of radioactive waste immobilization processes. Therefore, adjustment of the rheological properties by trace chemical addition is being explored as one option to improve the overall production rate of radioactive waste vitrification processes.

The viscous nature of the radioactive waste slurries is also linked to operational problems in the DWPF that require the use of increased flush water. This further reduces melt rate and waste loading. Additionally, the viscous nature of these slurries causes air to be entrained in the slurry, which results in a foamy consistency making the slurries difficult to pump. Similar problems will likely develop in the Hanford RPP-WTP.

The goals of this study were to: 1) determine if trace levels of chemical additives could be used to reduce the rheological characteristics of radioactive waste slurries, 2) identify potential chemical additives for this work and future testing, 3) test a limited set of chemical additive candidates on simulated radioactive wastes, and 4) develop advanced techniques to visualize the internal slurry structure and particle-particle interaction within the slurry.

Experimental Methods

A brief literature search of potential rheology modifiers was conducted using DOE internal documents as well as the open literature. The results of literature search are discussed later in this paper.

Shear measurements were performed using a Haake RS150 Rheometer. The concentric cylinder geometry with cup (Z43) and bob (Z38) was used for DWPF melter feed simulant samples, see Table 1. The slurry contains a mixture of inorganic oxides and hydroxides combined with a ground borosilicate glass frit. A cone-and-plate geometry using a 60mm diameter cone with a 2° angle and matching plate (MP60) was used for the RPP-WTP HLW sludge simulant (AZ-102). The AZ102 designation refers to Hanford waste tank 241-AZ102. The temperature was maintained at 25°C using a constant temperature during the measurements.

The samples measured in the concentric cylinder geometry were prepared by the addition of 1000 ppm by volume (ppmV) surfactant to stirred melter feed simulant. The sample was mixed thoroughly. Then 33 ml was poured into the rheometer cup. Flow curves (shear stress vs. shear rate) were produced for each sample. Samples were ramped from a shear rate of 0 to 400 sec^{-1} over 200 seconds, held at 400 sec^{-1} for 30 seconds, and then sheared down from 400 to 0 sec^{-1} over 200 seconds.

The samples measured in the cone-and-plate geometry were prepared by adding 1000 ppmV surfactant to AZ-102 waste simulant and then mixing vigorously. Three milliliters of this slurry were placed on the MP60 rheometer plate. The samples were ramped from a shear rate of 0 to 1000 sec^{-1} for 300 seconds, held at 1000 sec^{-1} for 120 seconds, and then ramped from 1000 to 0 sec^{-1} over 300 seconds. The Haake software was used to interpret the rheograms and the curves were fitted using a Bingham Plastic model. Yield stress and plastic viscosity were calculated by the Haake software from the fitted rheograms.

Table 1 lists the major components of the two waste simulants on a glass oxide basis. The DWPF melter feed simulant tested was 47 wt. % total solids (i.e. 53 % not water), 41 wt. % insoluble solids and 6 wt. % soluble solids. The soluble solids consist primarily of sodium formate and sodium nitrate. The density was approximately 1.45 g/ml. The solid particles range from about $5*10^{-4}$m in diameter down to sub-micron (colloidal) size. The pH ranges from 6-7. The RPP-WTP AZ-102 simulant was 12.6 wt. % total solids (i.e. 87.4 % not water), 12.1 wt. % insoluble solids and 0.5 wt. % soluble solids. The density was approximately 1.08 g/ml.

Table 1. Waste Simulant Compositions

Component (based on glass oxide)	Wt. % in DWPF Melter Feed Simulant	Wt. % in RPP-WTP AZ-102 Simulant
Ag_2O	0.01	0.06
Al_2O_3	5.1	26.28
B_2O_3	8.5	-
BaO	0.10	0.14
CaO	1.2	0.18
CdO	-	4.77
CeO_2	-	0.25
CoO	-	0.02
Cr_2O_3	0.10	0.30
CuO	0.05	0.001
Fe_2O_3	11.7	40.99
K_2O	0.18	-
La_2O_3	-	1.08
Li_2O	3.3	-
MgO	1.6	0.42
MnO	1.1	0.90
Na_2O	11.5	13.16
Nd_2O_3	-	0.04
NiO	0.56	2.68
P_2O_5	0.01	0.83
PbO	0.07	0.01
SiO_2	56.1	1.97
SrO	0.13	0.0006
TiO_2	0.06	0.03
ZnO	0.14	0.15
ZrO_2	0.30	5.73

The actual chemical compounds in HLW produced at Hanford and SRS during the Cold War vary widely depending mostly on the type of separation process used to recover the weapons material (U, Pu). Table 1 shows the slurry on an oxide basis, but the actual chemical composition is quite complex and is a separate field of study currently being pursued at Hanford and SRS. The melter feed simulant is composed of glass frit (Frit 320, SiO_2-72 wt. %, Na_2O-12 wt. %, Li_2O-8 wt. %, B_2O_3-8 wt. %) and sludge slurry. The glass frit was created by melting glass former chemicals to match the specified composition listed above[19]. The slurry was created by precipitating a metal nitrates solution with a sodium hydroxide solution. The basic procedure for creating simulated HLW sludge slurries of this type is discussed in reference 18. The chemical composition of the slurry was analyzed by x-ray diffraction (XRD) to determine the major crystalline forms in the slurry and the results are shown in Figure 1. The pattern contains a large amorphous pattern which is unidentified but is most likely the glass frit and/or amorphous components (e.g. Mn) of the sludge slurry.

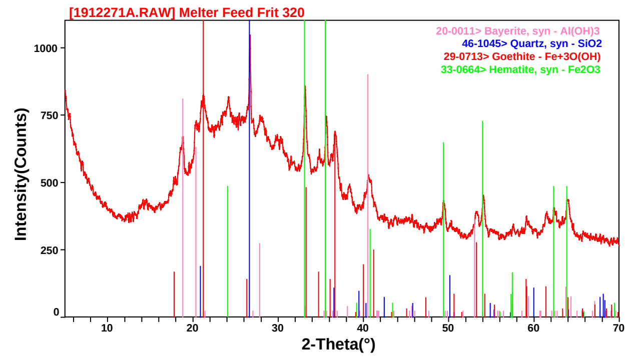


Figure 1 – X-Ray Diffraction Analysis of DWPF Melter Feed Simulant.

The RPP-WTP AZ102 simulant was also analyzed by XRD to determine the major crystalline forms in the slurry. The major crystalline forms were SiO_2, Corundum (AL_2O_3) and Goethite FeO(OH). Silica and Corundum were added to the sludge as raw batch chemicals. Goethite was formed as a result of the slurry preparation method (precipitation of metal nitrate slurry with NaOH) as described in reference 18.

Selected slurries were further analyzed using a laser-scanning confocal microscope. This technique allows the slurry to be analyzed in an as-made condition. The microscope has the ability to make both two-dimensional pictures and three-dimensional representations of a sample. Three-dimensional representations were made by scanning two-dimensional images at 1-micron increments. Image analysis software provided by Carl Zeiss, Inc. was used to stack the images together in a two dimensional image that provides a color gradient corresponding to the depth of the sample. These three-dimensional representations were used to understand the actual physical structure of the slurries. The slides with simulated waste (wet) samples were mounted using 2 drops of the material on a glass slide covered with a coverslip. A drop of oil was added to the top of the coverslip to view through oil immersion at 1300X. Slides were then examined and select images saved with a Laser Scanning Confocal Microscope (Model 310 Carl Zeiss, Inc., Thornwood, NY).

RESULTS AND DISCUSION

Literature Survey

Surfactants, or surface-active agents, are substances that lower or raise the interfacial tension at the boundary surface between two phases[1]. The most common applications of surfactants are found in cement manufacturing, textiles, pigmentation/dying applications, ceramic-processing industry[13] and in the food and drug industries[2]. There are hundreds of specialized commercial surfactants. The properties of the system requiring modification must be considered when selecting potential surfactant candidates. Particle size distribution, surface charge, composition, and solution pH must be identified to obtain the most effective surfactants[2,3,4,14]. It is also very important to add the proper (optimum) amount of surfactant[5].

Particle size distribution has a direct effect on the rheological behavior of real and simulated waste sludges. The size, shape, and concentration of solid particles, as well as the colloidal stability of the particles, help one to determine the flow properties of a system[4].

The pH of the system becomes important when related to the surface charge density. For example, anionic acrylic-type polyelectrolytes were added by Laarz[5] to an aqueous silicon nitride suspension. At a steady shear rate of 50 sec^{-1} using 20 vol. % suspensions containing 0.4 wt. % polyacrylic acid (PAA), the apparent viscosity was lowest at around pH 10. Laarz reported the suspension electrostatically stabilized at pH 10. Electrostatic stabilization occurs when enough polyelectrolyte has adsorbed on the surface to saturate it. As the pH decreased, the surface charge density of the silicon nitride was reduced leading to flocculation. A maximum apparent viscosity was reached at around pH 8.5. A local minimum was reached at pH 7. Further reductions of the pH led to minor increases in the apparent viscosity. Clearly, the pH of this system was directly correlated to the effectiveness of the dispersant[5].

Laarz also discovered that adding too much PAA caused flocculation of the particles. This also led to an increase in the apparent viscosity of the suspension. Small amounts (approximately 1 wt. % or less PAA) resulted in a decrease in the apparent viscosity by 2-3 orders of magnitude. The viscosity increased by 100% of the minimum value, as excess PAA was added (2 wt. %)[5].

A study by Stein[6], using cetyltrimethyl ammonium bromide (CTAB) as a rheology modifier for aqueous sodium kaolinite (ceramics), showed that CTAB initially resulted in a decrease in the slurry yield stress. Adding slightly more CTAB increased the yield stress. Stein suggested that yield stress variability was related to the surface charge of the kaolinite in agreement with Laarz's conclusion[6].

Table 2 - Rheology Modifiers Tested/Not Tested.

Name	Type	Use	Industry	Manufacturer	Tested in This Study	Future Testing Recommended
Antifoam 747	Organo-modified siloxane	Wetting agent	DOE Nuclear Waste Evaporation	DeBourg Corporation	Yes	Yes
Antifoam B52	Sodiumdioctyl sulfosuccinate in polyethylene	Wetting agent	DOE Nuclear Waste Pretreatment	Cytec	Yes	No
D-3005[7]	Polyglycol	Wetting agent	Ceramics	Duramax	Yes	Yes
Sodium metasilicate[7]	Crystalized silicate	Wetting agent, Detergent	Clay processing, De-inking paper	Aldrich	No	Yes
Darvan C[9]	Polymethacrylate, anionic	Dispersant	Ceramics	Vanderbilt Co. Inc.	Yes	Yes
Lomar A22-Na[9]	Anionic, Napthalene sulfonate	Dispersant	Ceramics	Cogniz Corp.	No	Yes
Lomar A23-NH_3[9]	Anionic, Napthalene sulfonate	Dispersant	Ceramics	Cogniz Corp	No	Yes
SDS[6]	Anionic surfactant	Wetting agent, Detergent	Textiles	Aldrich	No	Yes
CTAB[6]	Cationic surfactant	Surfactant	Semiconductors	Aldrich	Yes	No
Disperse-Ayd W22[10]	Proprietary anionic/nonionic surfactant, Polyacrylate	Pigment wetting agent	Paint & Coatings	Elementis Specialties	Yes	No
Disperse-Ayd W28	Proprietary anionic and nonionic surfactant, Polyacrylate	Pigment wetting agent	Paint & Coatings	Elementis Specialties	Yes	No
Dolapix CE64[10]	Ammonium polyacrylate	Deflocculant	Ceramics	Zschimmer & Schwartz	No	Yes
Surfynol	Ionic Surfactant	Wetting agent	Ink	Dow Chemical	No	Yes

Rheology studies have been performed on simulated radioactive waste products at West Valley Nuclear Services Company in West Valley, New York. Deflocculants, such as sodium metasilicate and acrylic acid-based polyglycols, were tested for their affect on the rheological behavior of the simulant waste slurry. The polyglycols used for this study were two Rohm & Haas products, Duramax-3005 (D-3005) and CER-3019. The three deflocculants tested produced decreases in the apparent viscosity by a factor of three. D-3005 gave the lowest apparent viscosity at a shear rate of 256 s^{-1} for all samples tested. An increase of over 10% in the waste slurry, solids concentration was made possible using deflocculants[7].

Two rheology studies of potassium tetraphenylborate (TPB) waste simulants at SRS established that the addition of antifoam agents was beneficial in reducing the yield stress of the waste. The Bingham plastic yield stress was reduced by a factor of approximately five in one study when the slurry contained antifoam agent.[8]

In a previously unpublished DOE study conducted by T. Spatz at the SRS Savannah River Technology Center, Aiken SC, rheological flow curves of TPB simulant with and without a wetting agent were produced. The antifoam Surfynol was added to TPB slurries at a concentration of 1000 ppm. It was found to reduce the yield stress by an order of magnitude over that of the waste simulant without antifoam.

Table 2 gives the potential rheology modifiers identified for use in this and future studies. Resources are currently being directed toward testing some of the rheology modifiers identified for future testing.

Rheology Modifiers Tested

Four different SRS melter feed simulant samples were tested using the Haake RS150 rheometer. These included a control sample with no chemical addition, a sample with 1000 ppmV Antifoam 747, a sample with 1000 ppmV B52 Antifoam, and a sample with 1000 ppmV Duramax D-3005. The Bingham plastic yield stress was determined using the software provided with the rheometer. The yield stresses of each of these samples are given in Table 3. The control sample yield stress was measured in quadruplicate (standard deviation = 1.8 Pa, standard error of the mean = 0.9 Pa).

Table 3. Yield Stress (Pa) of SRS Simulated Melter Feed Samples Using Haake RS150

Sample	Yield Stress (Pa)
Control	10.3
1000 ppmV Antifoam 747	12.9
1000ppmV B52 antifoam	30.3
1000 ppmV Duramax D-3005	14.6

None of the surfactants decreased the modeled yield stress below that of the control sample. Therefore, duplicate measurements of yield stress were not completed as originally planned and none of these surfactants was successful by this measure. The data does show, however, that the yield stress can be changed by the addition of surfactants. B52 antifoam clearly thickened the slurry. The B52 sample was also visually thicker than the control sample. Further tests are planned to ascertain whether the surfactants may have affected other properties of the slurry, such as the amount of air entrained during mixing.

Eight samples of the RPP-WTP AZ102 simulant were prepared. These included a control sample with no chemical addition. The control sample yield stress/plastic viscosity was measured in triplicate (standard deviation = 0.4 Pa, standard error of the mean = 0.1 Pa). Duplicate AZ102 slurry samples, spiked with 1000ppmV of IIT Antifoam 747, IIT Antifoam B52, Duramax D-3005, CTAB, Darvan C, Disperse-Ayd W-22, and Disperse-Ayd W-28 were prepared and analyzed using the Haake RS150 rheometer. The yield stresses and plastic viscosities of these samples are given in Table 4. The duplicate yield stress values for the control sample and samples spiked with Darvan C, B52 antifoam and D-3005 were averaged. The calculated standard deviation for the slurry samples spiked with Darvan C, B52 Antifoam and D-3005 were less than the control sample (range = 0.0-0.3 Pa). Yield stress values reported in Table 5 for samples spiked with IIT Antifoam 747, CTAB, and Disperse-Ayd W-22 are the minimum values measured by the Haake since these surfactants had very little effect or were observed to be thicker.

Some improvement was seen with the D-3005 as seen in Figure 2. The calculated standard deviation and standard error of the mean for the D-3005 sample was 0.0 and 0.0, respectively. Applying the error analysis of the control sample to the D-3005 sample indicates that this surfactant did lower the yield stress of the RPP-WTP AZ102 slurry.

Table 4. Yield Stress and Plastic Viscosity of RPP HLW AZ102 Washed Sludge Envelope D Samples by RS150

Sample	Yield Stress (Pa)	Plastic Viscosity (mPa·s)	% Difference in Yield Stress from Control
Control	4.6	42.3	-
1000 ppm Antifoam 747	4.5	41.3	3.4%
1000 ppm B52 antifoam	5.6	49.0	-20.2%
1000 ppm D-3005	3.8	42.3	18.2%
1000 ppm CTAB	7.0	51.0	-41.1%
1000 ppm Darvan C	4.4	43.6	5.9%
1000 ppm DA W-22	4.6	54.0	0.1%
1000 ppm DA W-28	4.9	59.0	-6.4%

The Antifoam 747 and Darvan C flow curves were quite similar to that of the control sample. The rest of the samples exhibited substantially higher apparent viscosities. This gain was distributed between similar to higher yield stresses and similar to higher plastic viscosities. The plastic viscosity of the D-3005, Darvan C, and Antifoam 747 slurries were the lowest of the surfactants tested. The addition of surfactants that increased the shear stress created visibly thicker slurries. Disperse-Ayd W-22, W-28 and CTAB wetting agents increased the yield stress and plastic viscosity most dramatically. Therefore, only one rheogram for the W-28 wetting agent was completed.

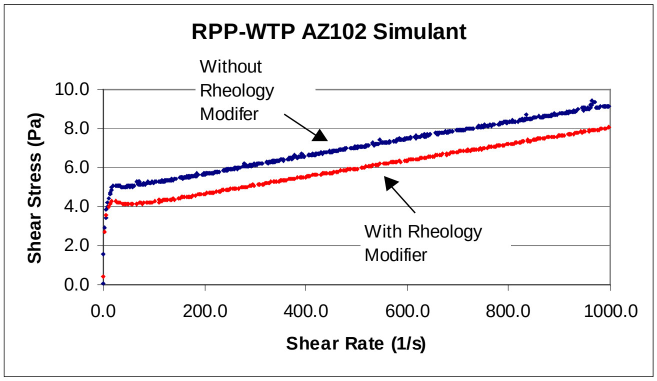


Figure 2. Flow Curve for RPP HLW Simulated AZ102 Washed Sludge Envelope D Samples with and without Duramax D-3005 Added

Figure 3 shows a three-dimensional representation of the RPP-WTP AZ102 slurry (Control) using a laser confocal microscope. The scale in the upper left-hand corner shows the depth of the image. The scale in the lower portion of the image shows the horizontal scale. The red, green, and blue colors correspond to a depth of 0, 7.5, and 15 microns in the slurry sample. The AZ102 slurry particles shown in Figure 3 appear to be flocculated into larger (> 5 micron) size flocs. These flocs are suspended by smaller particles. Figure 3 appears to indicate the slurry is a flocculated, touching network of particles as described in Reference 14.

Figure 4 shows a three-dimensional representation of the AZ102 slurry with 1000 ppm of CTAB added. The image clearly show CTAB dispersed the AZ102 particles into fine particles that appear to be smaller than 1 micron. Analysis of Figure 3 and 4 together appears to indicate that AZ102 slurry is actually composed of particles that are much smaller than 0.5 micron. The smaller particles (< 1 micron) shown in Figure 4 are dispersed and not flocculated together like the particles shown in Figure 3.

Figure 5 and 6 show the RPP-WTP simulated AZ102 slurry with and without a rheology modifier added to the slurry. Analysis of the pictures under various settings of brightness and contrast appears to show the particles in the slurry with D-3005 added are flocculating into larger (25 micron and greater) particles. The slurry with the D-3005 was shown to have an 18 % reduction in the measured yield stress.

The level of yield stress reduction that would be considered valuable from an engineering point of view depends on how close to the edge of the design basis the radioactive waste treatment plant is being operated. Figure 7 shows the original rheological slurry transfer equipment design criteria and operating region for typical SRS HLW slurries that were expected to be immobilized into glass at the DWPF[16]. Since the goal is to maximize the quantity of waste processed (& minimize the water content fed to the melter), the operating point for the process is typically close to the maximum point of slurry weight percent solids and yield stress (shown in Figure 7 – upper right hand corner of dashed box). Therefore, even a small reduction in the yield stress at this point would be deemed to be acceptable from an engineering standpoint.

DWPF and RPP-WTP Melter Feed slurries show a similar relationship between yield stress and weight % total solids. Figure 8 shows a typical melter feed slurry used for testing prior to establishment of the DWPF slurry rheological design basis[17]. Typically, the desired operating point is at the minimum water content and maximum yield stress (upper left hand corner of Figure 8 dashed box, in this case 46 wt.% and 25 Pa). Figure 8 also illustrates the DWPF design basis criterion for melter feeds[16]. At the time the design criterion was established, two criteria were cited in the design basis: 1) Normal Operating range of 2.5 - 15 Pa 2) Off-specification Slurry maximum yield stress of 25 Pa. If the process is being operated just outside the design envelop even a small adjustment in the slurry yield stress would be deemed acceptable from an engineering standpoint.

It is important to point out that each waste composition, simulated or radioactive will have different relationships between rheology and total weight percent solids. Therefore, the final rheology modifier selected for plant use must undergo testing with radioactive slurries prior to introduction in the plant. Thus, an acceptable level of yield stress reduction established for one waste composition might not be acceptable for future waste compositions. Since the waste composition and physical property relationships (wt. % solids vs. rheology) vary with each new batch of HLW, robust criteria for final rheology modifier selection should be developed in future studies. A target yield stress reduction between 30 – 50% would be desirable starting point for future studies. An understanding of the rheological properties as a function of rheology modifier concentration should be developed so the addition of these chemicals can be minimized.

CONCLUSIONS

None of the wetting agents provided a dramatic decrease in apparent viscosity of either the SRS melter feed slurry or the RPP-WTP sludge, based on the rheometer measurement. It was shown, however, that the yield stress is subject to modification by the addition of surfactant materials. The slurry with the Duramax D-3005 was shown to have an 18 % reduction in the measured yield stress which indicates that it is possible to decrease the yield stress of simulated HLW slurry.

Figure 3 – Three Dimensional Representation of Simulated AZ102 Envelope D slurry - Dashed Circle Shows Examples of Large Flocculated Particles.

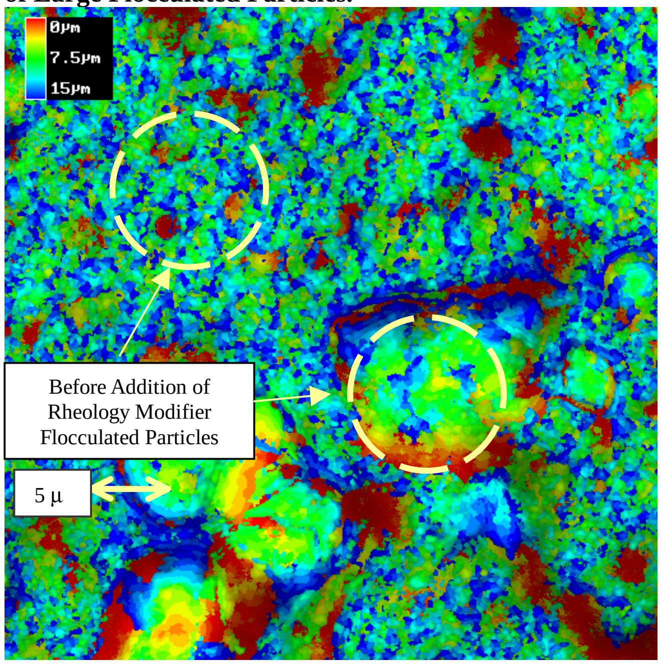


Figure 4 - Three Dimensional Representation of Simulated AZ102 Envelope D Slurry with 1000ppm CTAB – Dashed Circle shows dispersal of AZ102 sludge into fine particle suspension.

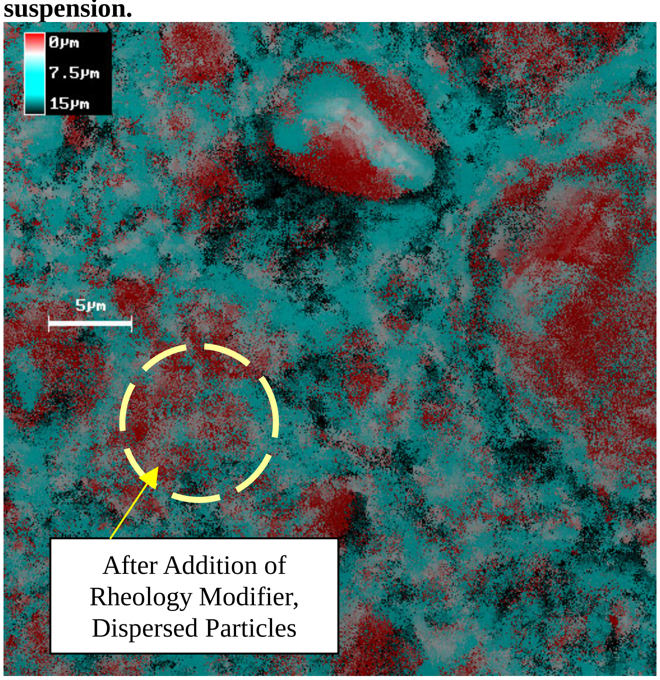


Figure 5 – Two-Dimensional View of Simulated Envelope D Slurry AZ102 – Dashed Circle shows example of particle that are well less than 25 micron in size.

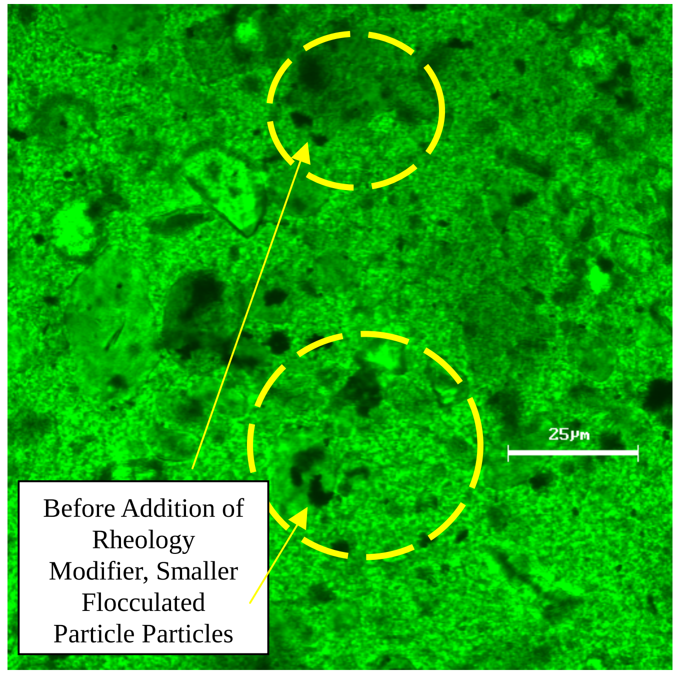


Figure 6 - Two-Dimensional View Simulated Envelope D Slurry AZ102 with Duramax 3005 – Dash Circle shows flocculated particle greater than 25 microns.

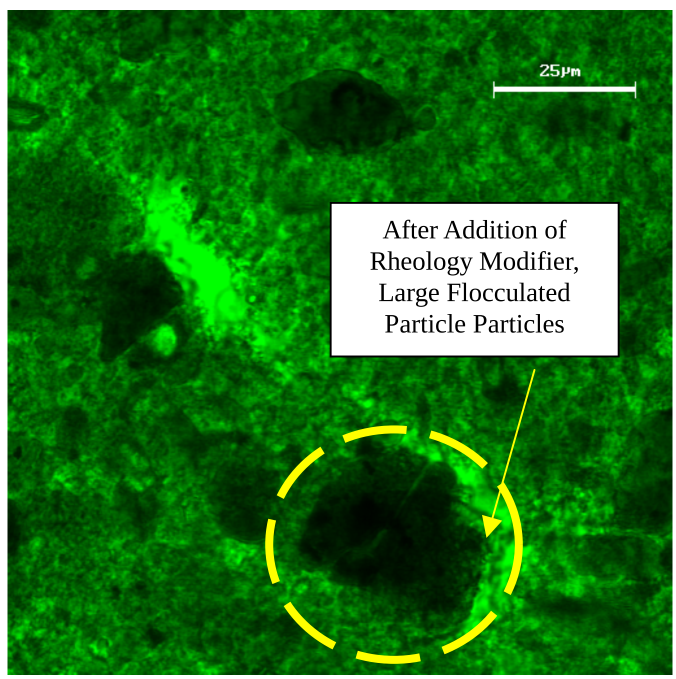


Figure 7 – Yield Stress of Washed Simulated DWPF Slurry – Design Basis of the Sludge delivered to the DWPF Shown in Dashed Box.

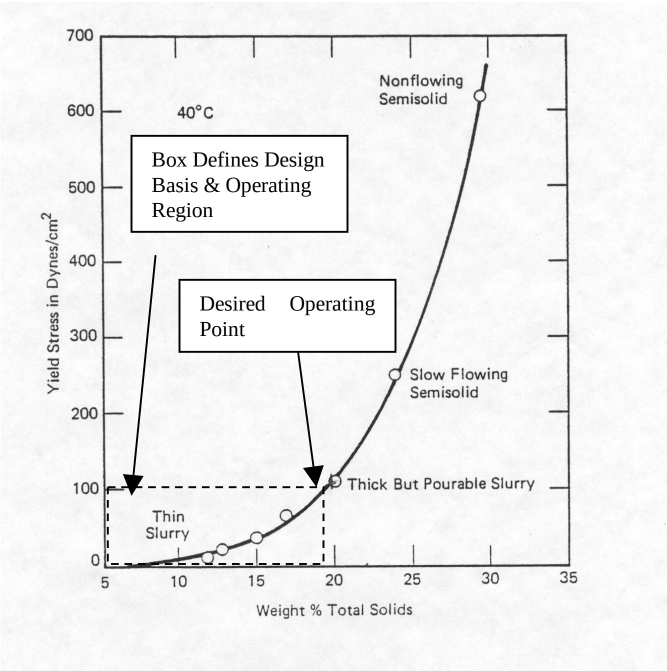
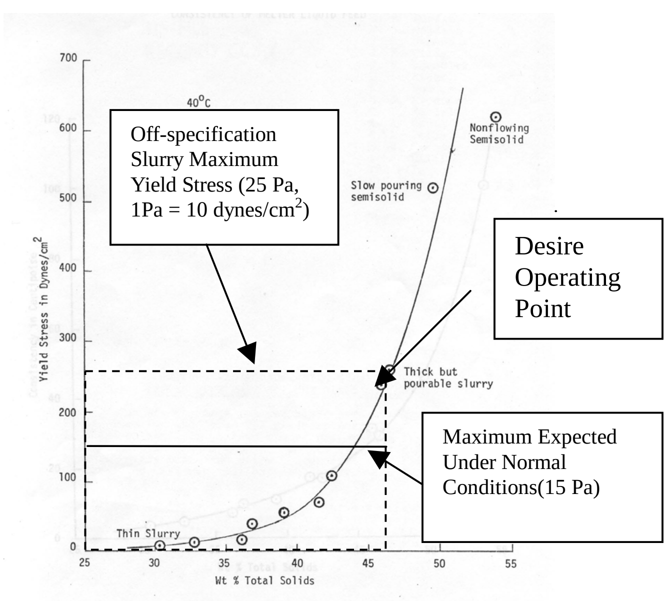


Figure 8 – Yield Stress of Simulated DWPF Melter Feed Slurry – Maximum Design Basis and Operating Region of the Sludge-Frit Slurry delivered to the DWPF Shown in Dashed Box.



Further experimentation should be performed to determine the effectiveness of the following surfactants that were not used in this study: sodium metasilicate, Lomar A-22 and A-23, SDS, Dolapix CE64, and Surfynol. Additionally, components that make-up IIT747, Darvan and D-3005 should be investigated to determine if the individual compounds that are in each of these surfactants have an effect on rheology. Further literature searches may provide additional chemicals to test.

Future work should focus on determining the appropriate surfactant for decreasing the yield stress of the SRS and Hanford simulant slurries under conditions matching those in the actual process, as well as determining the optimal concentration of the wetting agent. Use of confocal microscopy appears to be a promising technology that can be used to understand the behavior of slurries. Confocal microscopy and other techniques such as atomic force microscopy (AFM) can be used to provide a three-dimensional image of the slurry.

Additionally, atomic force microscopy may also be used to determine the mechanical properties of the sample hardness, stiffness, or any other reaction to an applied force. AFM has been recently applied by Balooch to develop an understanding of the visoelastic properties of montmorillonite (clay)[15]. Further understanding of the particle surface chemistry and charge must be understood before final selection of the optimal rheology modifier can be made.

Since the waste composition and physical property relationships (wt. % solids vs. rheology) vary with each new batch of HLW, robust criteria for final rheology modifier selection should be developed in future studies. A target yield stress reduction between 30 – 50% would be desirable starting point for future studies.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy Contract No.DE-AC09-96SR18500. Laboratory assistance was provided by Russ Eibling and Sammie King. We would also like to acknowledge the expertise and advice of Dr. Alex Nikolov and Dr. Darsh T. Wasan, Illinois Institute of Technology for their guidance in the field of surface chemistry and surfactant science. We also acknowledge the South Carolina Universities Research & Education Foundation (SCUREF) for postgraduate research fellowship support. This paper was published as WSRC internal document number WSRC-MS-2003-00136, Rev.0.

NOMENCLATURE

g gravitational constant, m/s^2

L_o final slurry length, m

V slurry sample volume, m^3

W final average slurry width, m

Y slurry thickness, m

Y_{min} final slurry thickness, m (V/L_oW)

ρ slurry density, Kg/m^3

Ω plate inclination angle

τ_o Bingham plastic yield stress, Pa

τ_w wall shear stress, Pa

REFERENCES

1. Bartell, F. E., June 1941, "Wetting Agents", Industrial and Engineering Chemistry, **33**, American Chemical Society, New York pg. 737-740.
2. Braun, D. B. & Rosen, M. R.D.,2000, *Rheology Modifiers Handbook*, William Andrew Publishing, Norwich, New York, pg. 2-67, 194-242.
3. Moreno, R., Córdoba, G., 1997 "Oil-Related Deflocculants for Tape Casting Slips", Journal of the European Ceramic Society, **17**, pp. 351-357.
4. Luckham, P. F. and Ukeje, M. A., 1999, "Effect of Particle Size Distribution on the Rheology of Dispersed Systems", Journal of Colloid and Interface Science, **220**, pp. 347-356.
5. Laarz, B., 2000, "The effect of anionic polyelectrolytes on the properties of aqueous silicon nitride suspensions", Journal of the European Ceramic Society, **20**, pp. 431-440.
6. Stein, H. N., 1995, *The Preparation of Dispersion in Liquids*, Marcel Dekker, Inc., New York, pg. 41-124.
7. Firstenberg, K., Dabney, W. and Jain, V. (1995). "The Role of Deflocculants during Concentration of the Simulated High-Level Radioactive Wastes." *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries, Ceramic Transactions*, **61,** edited by Jain, V. and Palmer, R.: American Ceramic Society, pp. 557-567.
8. M. A. Baich, D. P. Lambert and P. R. Monson, 2000, "Laboratory Scale Antifoam Studies for the STTPB Process", WSRC-TR-2000-00261, Westinghouse Savannah River Company, Aiken, SC.
9. Dinger, D. R. & Funk, J. E., 1993, *Predictive Process Control of Crowded Particulate Suspensions*, Kluwer Academic Publishers, Norwell, Massachusetts, pg. 211-227.
10. Janney, M. A., 2001, "Attaining High Solids in Ceramic Slurries", Webpage: www.ornl.gov/MC-SPG/gelpubs/Mixing.pdf, Oakridge National Laboratory, Oakridge, TN.
11. Yasuda, D. D., Hrma, P., 1991, "The Effect of Slurry Rheology on Melter Cold Cap Formation", Ceramic Transactions—Nuclear Waste Management IV, **23**, pp. 349-359.
12. Tadros, Th. F., Solid/Liquid Dispersions, 1987, Academic Press Inc., Orlando FL, 1987, pp. 10.
13. Carlstrom, E., 1994. "Surface and Colloid Chemistry in Ceramics: An Overview", *Surface and Colloid Chemistry in Advanced Ceramics Processing*, Marcel Dekker, New York, pg. 1-28.
14. Pugh, R. J., 1994, "Dispersion and Stability of Ceramic Powders in Liquids", *Surface and Colloid Chemistry in Advanced Ceramics Processing*, Marcel Dekker, New York, pg. 127-188.
15. Balooch, M, May 2002, "A New Understanding of Soft Materials", Science & Technology Review, Lawrence Livermore National Laboratory, University of California, pg. 11-15.
16. Ortaldo, J. F., September 1982, "Technical Data Summary for the Defense Waste Processing Facility Sludge Plant", DPSTD 80-38-2, E. I DuPont de Nemours & Co. Savannah River Laboratory, Aiken SC 29808.
17. Jones, D. W., November 12, 1979, "Defense Waste Processing Facility Liquid Feed Data for TNX Glass Melter", DPST-79-565, E. I DuPont de Nemours & Co. Savannah River Laboratory, Aiken SC 29808.
18. Eibling, R. E. & Nash, C. A., February 2001, "Hanford Waste Simulants Created to Support the Research and Development on the River Protection Project – Waste Treatment Plant", WSRC-TR-2000-00338, Westinghouse Savannah River Company, Aiken SC 29808.
19. Lorier, T. H., March 30, 2001, "Melt Rate Improvements for DWPF MB3 Frit Preparation", WSRC-TR-2001-00152, Westinghouse Savannah River Company, Aiken SC 29808.

