SUMMARY/PROJECT REPORT REQUIRED DATA

"Foaming and Antifoaming in Radioactive Waste Pretreatment and Immobilization Processes"

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PROGRESS REPORT

RESEARCH OBJECTIVE

The objective of this research is to develop a fundamental understanding of the physico-chemical mechanisms that cause foaminess in the DOE High Level (HLW) and Low Activity radioactive waste separation processes and to develop and test advanced antifoam/defoaming agents. Antifoams developed for this research will be tested using simulated defense HLW radioactive wastes obtained from the Hanford and Savannah River sites.

RESEARCH PROGRESS AND IMPLICATIONS

Savannah River Technology Center (SRTC) has reported severe foaminess in the bench scale evaporation of the envelope C tank. Excessive foaming in waste evaporates can cause carryover of radionuclides and non-radioactive waste to the condensate system. The antifoams used at Hanford and tested by STRC are believed to degrade and become inactive in high pH solutions. Hanford wastes have been known to foam during evaporation causing excessive down time and processing delays.

During the second year of this three-year project, an experimental study to understand foaminess was

carried out using several Hanford simulants. Foaminess and foam texture during boiling of the simulants at low pressure (110 mm Hg) were monitored using digital photomicrographic techniques. Two simulants (Supernates) of AN-102 and AN-107 and a sludge simulant AZ-101 (5 wt% and 10 wt%) were tested for foaminess during boiling at an evaporation flux of 2 kg/min sq. m. which is twice the flux that was previously used in our experimental studies. Previous experimental studies with DWPF sludge indicate that foaminess will increase exponentially with increases in evaporation flux. Supernate AN-102 showed a maximum in foaminess of 550 vol% at a solid concentration of 55 wt% and supernate pretreated AN-107 showed a maximum in foaminess of 275 vol% at a solid concentration of around 60 wt%. For the sludge simulant AZ-101 (5 wt%), a maximum in foaminess of the order of 70 vol% at a total solid concentration of 40 wt% was observed. The sludge simulant AZ-101 (10 wt%) showed foaminess of the order of 20 vol% at a solid concentration of about 60 wt%.]

Radioactive waste foams are typically stabilized by very insoluble particles attached at the air-liquid interface, which prevent coalescence of bubbles, thus enhancing foaminess. A maximum in foaminess is observed for all simulants. Peak foaminess occurs well after salt (or nuclei) crystals precipitate from the solution, thus indicating a particle stabilized foam mechanism. We have observed the salt crystals generated during boiling on the walls of the fleaker. However, Hanford radioactive waste is seen to foam when boiling is first initiated and no insoluble particles are present in the waste. This indicates the presence of surface active agents that may be causing foaming at the onset of boiling. Thus, the foam stabilization mechanisms in actual Hanford radioactive waste may be due to the surfactant stabilized foams at low sodium concentrations and solids stabilized foams at high sodium concentrations.

The presence of organic components such as paraffin hydrocarbon (NPH) aggravates foaminess. For example, addition of 300 ppm of NPH to the Hanford simulant pretreated AN-107 increased foaminess during boiling to 900 vol% from 275 vol% in the absence of normal paraffin. The plausible reason for this increase in foaminess is that the oil droplet from the hydrocarbon attaches itself to the salt crystals and makes them more amphiphilic, which enhances foaminess.

It is known that during the melter feed evaporation of Hanford pretreated AN-102, melter feed off-gas condensate VLS LAWCI is mixed in 50/50 proportions with it. Foaminess during boiling of this simulant is of interest for the pilot plant and full scale operations of the WTP Treated Feed evaporator. Our laboratory tests for this simulant showed a maximum in foaminess of 550 vol% which occurred at a solid concentration of 55 wt%, while the mixed simulant showed a 200 wt% foaminess at a total solid concentration of 40 wt%.

The antifoaming efficiency of two commercially available antifoamers (DOW 1520 and DOW 02-3183A) using the pretreated Hanford simulant AN-107 at higher evaporation flux was also tested this year. The antifoamer DOW 1520 was found to be ineffective. However, antifoamer DOW 02-3183A reduced the foaminess at low pressure from 275 vol% to 180 vol%. Fundamental research into the mechanisms and advanced antifoam development for radioactive wastes is currently in progress. Selection of the final antifoam agent for the Hanford Waste Treatment Plant evaporators is also currently in progress.

The internal structure of simulated radioactive Hanford and DWPF slurries was mapped in situ using a new laser confocal microscopy technique developed at SRTC. Selected Hanford (AZ102) and SRS (tetraphenylborate) slurries were further analyzed to determine the 3-D structure of the slurry/slurry particle-gas bubble interface. This technique allows the slurry to be micro-photographed and 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 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. Three-dimensional representations of Hanford slurries with various surfactants added to modify the bulk slurry properties (e.g rheology) were photographed using the laser confocal microscope. This technique will be used to study the air entrainment of DOE radioactive waste slurries.

Figure 1 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 1 appear to be flocculated into larger (> 5 micron) size flocs. These flocs are suspended by smaller particles.

Figure 2 shows a three-dimensional representation of the AZ102 slurry with 1000 ppm of CTAB added. The image clearly shows CTAB dispersed the AZ102 particles into fine particles that appear to be smaller than 1 micron. Analysis of Figure 1 and 2 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 2 are dispersed and not flocculated together like the particles shown in Figure 1. The effects of various antifoam agents were also investigated.

Understanding of the internal structure of a slurry and gas bubble interface will allow the DOE user to determine the air entrainment mechanism in actual radioactive waste slurry.

An annual site remediation users meeting was held at the Savannah River Technology Center this year. Future directions and plans for the continuing study as well as the difference between the real waste and simulants were discussed at this meeting.

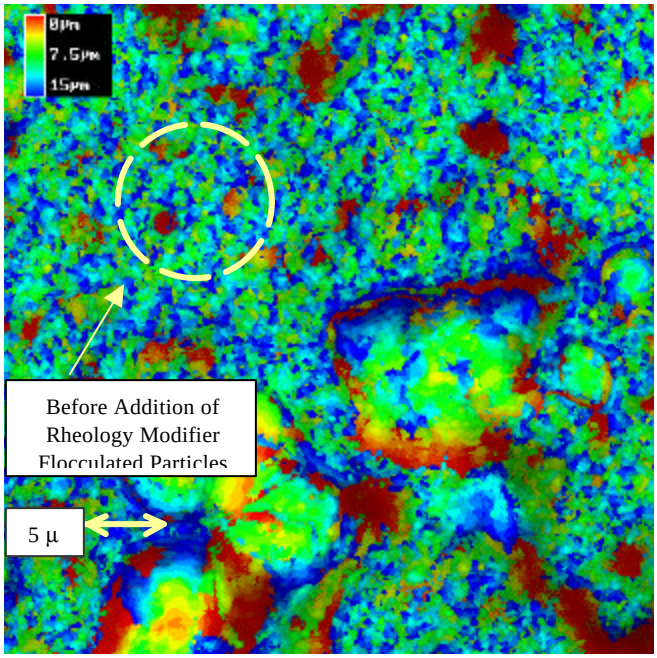

Figure 1 – Three Dimensional Representation of Simulated AZ102 Envelope D slurry - Dashed Circle Shows Examples of Large Flocculated Particles.

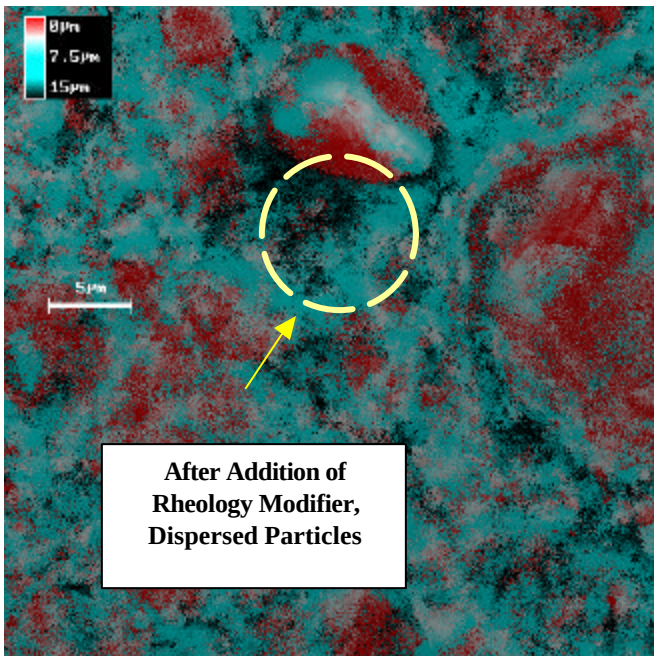

Figure 2 - Three Dimensional Representation of Simulated AZ102 Envelope D Slurry with 1000ppm CTAB – Dashed Circle shows dispersal of AZ102 sludge into fine particle suspension.

PLANNED ACTIVITIES

1. As recommended by SRTC, the effects of the organic complexants on foaminess will be investigated since these components aggravate foaming, especially at higher water evaporation rates.

2. We plan to develop an experimental method to measure the surface pressure at an air-water interface in the presence of fine salt crystals to better gain insight into the fundamental mechanism of foaminess in radioactive wastes.

3. A short list of potential antifoamers will be recommended to the users at Hanford.

4. Develop better understanding of the air-entrainment /foaming in the DOE sludges, and assist in developing effective methods for mitigating this problem.

5. Hold a coordination meeting of all DOE projects related to foaming problems at Savannah River, Hanford and Oak Ridge sites.

6. Prepare a series of papers based on the fundamental results for possible publication in refereed journals.

PUBLICATIONS

1. "New Vistas in Dispersion Science and Engineering", D.T. Wasan, A.D. Nikolov, and D. Henderson, AIChE Journal, 49, pp550-556 (2003).

2. "Computer Modeling of Ionic Micelle Structuring in Liquid Films," A. Trokhymchuk, D. Henderson, A. D. Nikolov, and D.T. Wasan, J. Phys. Chem., 107, pp3927-3937 (2003).

3. "Foaming Mechanisms in Surfactant Free Particle Suspensions" S.K., Bindal, G. Sethumadhavan, A.D. Nikolov, and D.T. Wasan, AIChE J., 48, pp2307-2314 (2002).

4. "Effect of Film Curvature on Drainage of Thin Liquid Films," K. Kumar, A.D. Nikolov, and D.T. Wasan, J. Colloid Interface Sci., 256, pp194-200 (2003).

5. "Rheology Modifiers for Radioactive Waste Slurries," E. D. Kay, T.B. Calloway, D.C. Koopman, R.L. Brigmon, R.E. Eibling. Proceedings of ASME 2003 Fluid Engineering Division Summer Meeting, FEDSM2003-45496, Westinghouse Savannah River Company, Aiken SC, 29808.