

FINAL REPORT

“Foaming and Antifoaming and Gas Entrainment in Radioactive Waste Pretreatment and Immobilization Processes”

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Number of graduate student/post-doctoral students involved: 2

EXECUTIVE SUMMARY

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 construction phase. Both processes utilize slurry-fed joule-heated melters to vitrify the waste slurries. The DWPF has experienced difficulty during operations. The cause of the operational problems has been attributed to foaming, gas entrainment and the rheological properties of the process 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 meter feed processes. Highly viscous material can lead to air entrainment during agitation and difficulties with pump operations. Excessive foaming in waste evaporators can cause carryover of radionuclides and non-radioactive waste to the condensate system.

Experimental and theoretical investigations of the surface phenomena, suspension rheology and bubble generation of interactions that lead to foaming and air entrainment problems in the DOE High Level and Low Activity Radioactive Waste separation and immobilization processes were pursued under this project. The first major task accomplished in the grant proposal involved development of a theoretical model of the phenomenon of foaming in a three-phase gas-liquid-solid slurry system. This work was presented in a recently completed Ph.D. thesis (9).

The second major task involved the investigation of the inter-particle interaction and microstructure formation in a model slurry by the batch sedimentation method. Both experiments and modeling studies were carried out. The results were presented in a recently completed Ph.D. thesis (10).

The third task involved the use of laser confocal microscopy to study the effectiveness of three slurry rheology modifiers. An effective modifier was identified which resulted in lowering the yield stress of the waste simulant. Therefore, the results of this research have led to the basic understanding of the foaming/antifoaming mechanism in waste slurries as well as identification of a rheology modifier, which enhances the processing throughput, and accelerates the DOE mission.

RESEARCH OBJECTIVE

The objectives of this research effort were to develop a fundamental understanding of the physico-chemical mechanisms that produced foaming and air entrainment in the DOE High Level (HLW) and Low Activity (LAW) radioactive waste separation and immobilization processes, and to develop and test advanced antifoam/defoaming/rheology modifier agents. Antifoams/rheology modifiers developed from this research were tested using non-radioactive simulants of the radioactive wastes obtained from Hanford and the Savannah River Site (SRS).

RESEARCH PROGRESS AND IMPLICATIONS

The progress made during the length of this project has been summarized in our first two annual progress reports (Ref. 1, 2). During the third year of this project, both theoretical and experimental investigations were pursued with a model slurry to monitor foaming and antifoaming in particle-laden gas-liquid systems under dynamic conditions such as boiling. Also, sedimentation experiments and theoretical model development studies were completed to probe slurry particle-particle interactions and microstructure which affect rheological properties of the slurry. Scanning confocal microscopy (LSCM) was used to examine the modification of particle-particle interactions of two different waste slurry simulants using rheology modifiers.

The first task accomplished in the final year of the grant period involved development of a theoretical model using the statistical mechanics method of Monte Carlo simulations and integral equations to establish the relationship between the adsorption of fine particles to the gas-liquid interface, clustering in the bulk and the co-existence of the liquid and solid phases in a three-phase gas-liquid-solid slurry system under foaming conditions. This work provided much needed theoretical insight into the foamability of liquid particle suspensions. The modeling results are in good qualitative agreement with the experiments on foaminess with small particles. A technical paper based on these new findings has been submitted for publication in a special volume on particles at interfaces to be published in the *Journal of Physical Chemistry Chemical Physics* (4). The results are also detailed in a recently completed Ph.D. thesis (9).

Under task two the interparticle interactions and microstructure formation in a model slurry system by the batch sedimentation method were investigated. The bulk settling (sedimentation) experiments were performed using a low-charge binary mixture of hydroxylate latex microspheres 500nm in diameter and a non-ionic surfactant micellar solution as a model nanoparticle suspension. The particle concentration profiles and changes in the sedimentation rates were monitored using a non-destructive Kossel diffraction technique. The experimental results showed a reduction in the settling rate when the interparticle distance between microspheres is around

three nanoparticle diameters due to the repulsive structural force arising from the nanoparticle structuring between and around the microspheres; this prevents the larger sized particles from approaching other particles and stabilizes the suspension. When the final separation stage is reached, an acceleration of the settling rate is observed; the depletion attraction destabilizes the bidisperse particle system through the excluded volume effect. The sedimentation separation is more complete in the presence of the nanoparticles (micelles) resulting in a higher packing concentration than that reported for the monodisperse system alone in the last year's annual report (2). In the final settling stage, particle crystallization occurs at the bottom of the settling vessel as evidenced by the iridescent colloidal crystal structure formation. The experiments were carried out for different nanoparticle concentrations and also by varying the ratio of large to small particle size ratios. The structural force dominates when the size of the microspheres is reduced.

The stochastic particle dynamics simulations were carried out to rationalize the experimental observations. The effects of collective particle interactions on the sedimentation velocity and the sediment microstructure formation in the concentrated suspensions were studied using the oscillatory potential of interaction including both the repulsive structural and attractive depletion contributions.

The theoretical predictions were found to be in good quantitative agreement with the experimental data.

Under task three the effectiveness of three dispersants (Dolapix CE64, Dispersant-Ayd W28, and Cyanama P35 as in the last annual report) to modify slurry rheology was examined using rheology measurements and laser confocal microscopy (LSCM) in simulated waste slurries. This work was performed at Savannah River National Laboratory. All of the dispersants lowered the yield stress of the slurries below the baseline samples. The rheology curves were fitted reasonably well to a Bingham Plastic model. The three-dimensional LSCM images of simulants showed that distinct particle aggregates were greatly reduced after the addition of dispersants leading to a lowering of the yield stress of the simulated waste slurries. 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. Microscopic examination of the dispersant and non-dispersed simulated waste treatments demonstrated this activity. For the HLW hydroxide waste simulant, Dolapix CE64, Dispersant-Ayd W28 and Cyanama 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. Dispersant-Ayd W28 was effective at lowering the yield stress of the SB3 SME waste simulant.

Publications Resulting from this Grant

1. “Foaming and Antifoaming and Gas Entrainment in Radioactive Waste Pretreatment and Immobilization Processes,” D.T. Wasan, Alex D. Nikolov, Bond Calloway, Dan Lambert and Michael Stone. Annual Report submitted to DOE September 28, 2005.
2. “Foaming and Antifoaming and Gas Entrainment in Radioactive Waste Pretreatment and Immobilization Processes,” D.T. Wasan, Alex D. Nikolov, Bond Calloway, Dan Lambert and Michael Stone. Annual Report submitted to DOE September 11, 2006.
3. “Foam Formation and Mitigation in a Three-Phase Gas-Liquid-Particulate System,” K. Vijayaraghavan, A. Nikolov, D.T. Wasan, *Advances in Colloid Interface Science* 123-126 p 49-61 (2006).
4. “Foam Formation with Small Particles: Theoretical Modeling,” K. Vijayaraghavan, A.D. Nikolov, D.T. Wasan, and D. Henderson, *Physical Chemistry Chemical Physics*, (Submitted 2007).

5. “Role of Oscillatory Structural Forces in the Sedimentation of a Bidisperse Colloidal Suspension,” S. Vesaratchanon, A.D. Nikolov, and D.T. Wasan, paper to be submitted to *Langmuir*, 2007.
6. “Role of Collective Interactions in the Sedimentation of a Monodisperse Colloidal Suspension,” S. Vesaratchanon, A.D. Nikolov, and D.T. Wasan, paper to be submitted to *Journal of Colloid and Interface Science*, 2007.
7. “Radioactive Waste Foams: Formation and Mitigation,” K. Vijayaraghavan, A. Nikolov, D. Wasan, B. Calloway, M. L. Crowder, M. Stone, and Z.H. Quershi, *J. Environ. Eng.* 132, 7, 716-724 (2006).
8. “Understanding the Effects of Surfactant Addition to Slurry Rheology Using Laser Scanning Confocal Microscopy,” T.L. White, M.E. Stone, T.B. Calloway, R.L. Brigmon, R.E. Eibling, A. Nikolov, and D.T. Wasan, Paper submitted to *J. Radioanal. Nuc. Chem.*, 2007.
9. “Foam Formation and Mitigation in the Presence of Fine Particles.” K. Vijayaraghavan, Doctoral Thesis, May 2007.
10. “Sedimentation of Colloidal Dispersions: Effects of Collective Interactions and Particle Charge,” S. Vesaracthanon, Doctoral Thesis, May 2007.

Personnel Support

The project team supported by this grant included Professors Wasan and Nikolov, and two doctoral students (K. Vijayaraghavan and Jan Vesaratchanon) who completed their doctoral thesis studies. This work was carried out in conjunction with the Savannah River National Laboratory. Bond Calloway, Dan Lambert and Mike Stone are the collaborators.

New Note

The Principal Investigator, Darsh Wasan, received the Alpha Chi Sigma Award in Chemical Engineering Research from the American Institute of Chemical Engineers in 2005. Also, he was elected as a Foreign Fellow of the Indian National Academy of Engineering in 2006.