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EXECUTIVE SUMMARY

Radioactive waste treatment processes usually involve concentration of radionuclides before waste can be immobilized by storing it in stable solid form. Foaming is observed at various stages of waste processing like sludge chemical processing and melter operations. Hence, the objective of this research was to study the mechanisms that produce foaming during nuclear waste treatment, to identify key parameters which aggravate foaming, and to identify effective ways to eliminate or mitigate foaming.

Experimental and theoretical investigations of the surface phenomenon, suspension rheology, and bubble generation and interactions that lead to the formation of foam during waste processing were pursued under this EMSP project. Advanced experimental techniques including a novel capillary force balance in conjunction with the combined differential and common interferometry were developed to characterize particle-particle interactions at the foam lamella surfaces as well as inside the foam lamella. Laboratory tests were conducted using a non-radioactive simulant slurry containing high levels of noble metals and mercury similar to the High-Level Waste. We concluded that foaminess of the simulant sludge was due to the presence of colloidal particles such as aluminum, iron, and manganese. We have established the two major mechanisms of formation and stabilization of foams containing such colloidal particles: (1) structural and depletion forces; and (2) steric stabilization due to the adsorbed particles at the surfaces of the foam lamella. Based on this mechanistic understanding of foam generation and stability, an improved antifoam agent was developed by us, since commercial antifoam agents were found to be ineffective in the aggressive physical and chemical environment present in the sludge processing. The improved antifoamer was subsequently tested in a pilot plant at the Savannah River Site (SRS) and was found to be effective. Also, in the SRTC experiment, the irradiated antifoamer appeared to be as effective as nonirradiated antifoamers. Therefore, the results of this research have led to the successful development, demonstration and deployment of the new antifoam in the Defense Waste Processing Facility chemical processing.
RESEARCH OBJECTIVES

The Department of Energy’s (DOE) Savannah River Site (SRS) is responsible for the safe storage, processing and immobilization of the High Level (radioactive) Waste (HLW) currently stored in approximately fifty million-gallon underground storage tanks. Foam is present in many areas of the HLW processing including HLW chemical processing, HLW evaporation and HLW cesium decontamination. Foam impacts the production rates of each of these facilities (1). The presence of foam during chemical processing and evaporation steps leads to slower production rates in the high level waste evaporators and in the Defense Waste Processing Facility (DWPF) waste pretreatment, and may lead to higher capital costs or slower production in cesium decontamination. Also, excessive foam causes radioactive contamination of the condensate and equipment.

Much of the Savannah River Site high level radioactive waste is in the form of alkaline suspensions of insoluble, inorganic (“sludge”) particulates. The chemical processing of the sludge to produce melter feed suitable for a glass melter involves the boiling of the sludge. Boiling of the sludge creates an environment often ignored in fundamental studies of foam formation, a three-phase gas/liquid/solid system. Therefore, such three-phase foams, which incorporate finely divided solids (colloidal particles), are quite different from usually encountered foams formed from surfactant solutions. The physical mechanisms of the formation of foam in radioactive waste treatment and waste immobilization processes are poorly understood. Hence, the objective of this research is to study the mechanisms that produce foaming during nuclear waste treatment, to identify key parameters which aggravate foaming, and to identify effective ways to eliminate or mitigate foaming.

METHODS AND RESULTS

Experimental and theoretical investigations of the surface phenomena, suspension rheology, and bubble generation and interactions that lead to the formation of foam during waste processing
were pursued under the EMSP Project No. 60143. During the grant period, the following three objectives were accomplished; namely determination of the effects of solid particles on foaminess, determination of the effects of the thin film rheology on foaminess, and development of advanced antifoamers/defoamers. The results are described below:

I. Effects of Solid Particles on Foaminess

A novel capillary force balance technique (Figure 1A) was developed in conjunction with interferometry to examine the particle-particle interactions at the foam lamella surface as well as the stability of the foam lamella containing fine solids. Figure 1B shows a photomicrograph depicting solid particles forming a network structure at the foam lamella surface of the simulated HLW waste prepared by SRTC. Foaming tests were conducted at IIT using the non-radioactive simulant sludge containing noble metal oxides and hydroxides of aluminum, iron and manganese, and mercury similar to the High Level Waste (Figure 2A). The photomicrograph in Figure 2B, depicts accumulation of particles inside the foam lamella, and shows that some of the solid particles are partially wetted (biphilic). Biphilic particles have hydrophilic (attracted to water) and hydrophobic (repels water) ends, and these adsorb at the surfaces of the foam lamella providing a steric barrier against the coalescence of bubbles, thereby causing foaming (Figure 1C). These results were presented by us at the first annual DOE Environmental Management Science Program Workshop held in Chicago, July 29-30, 1998, and a paper based on this work has been published in the *Journal of Environmental Science and Technology* [“Foaming in Simulated Radioactive Waste” S.K. Bindal, A.D. Nikolov, D.T. Wasan, D.P. Lambert and D.C. Koopman, *J. Enve. Sci. Tech.* 35, 3941-3947 (2001)].
Figure 2B shows that there are at least two kinds of particles in the system, coarse and fine. It could be seen in reflected light that fine (colloidal) particles surround the coarse particles. They are seen as a brown “cloud” in the photomicrograph. A foam lamella is formed during the generation and interaction of bubbles. Hydrophilic colloidal particles get trapped inside the lamella. Subsequently, due to the confined boundaries of the film (lamella), these particles form a layered structure inside the foam lamella. Figure 3 shows a set of well-defined, interference stripes of different colors appearing in the upper part of a vertical film. There are six to seven stratified layers in the film. The same phenomenon of particle layering (i.e., stratification) was observed by us in horizontal films using our novel Capillary Force Balance apparatus. It has been shown by us that the concentration of colloidal particles in the film or lamella is higher than that in the bulk and produces a stabilizing pressure (i.e. structural force). The repulsive structural barrier arising due to the in-layer structure formation at high concentration of hydrophilic colloidal particles leads to the stabilization of the foam lamella, and hence, foaminess.

The results of this study were presented at the American Chemical Society (ACS) national meeting held in Dallas, March 1999, and published in a series of our papers [see under PUBLICATIONS]. Results of this research provided a breakthrough in establishing a link between structural forces in liquid films, and...
structural forces in concentrated macro-dispersions such as foams. Thus, our laboratory has pioneered the discovery of the structural forces arising from particle ordering inside thin films or foam lamella, and this discovery was recognized by the ACS with a national award in colloid and surface chemistry presented to the principal investigator (Wasan) in 2000.

**Figure 2.** Part A: Experimental set-up to study foaminess during the boiling of the sludge; Part B. Photomicrographs depicting particles trapped inside the foam lamella.

**Figure 3.** Interference stripes in a vertical macroscopic liquid film from colloidal suspension; a color stripe represents a different number of particle layers inside the film.
An investigation of the two major mechanisms of stabilization of foams containing solid particles was completed: (i) structural stabilization due to the hydrophilic colloidal particles forming a layered structure inside the foam lamella, and (ii) steric stabilization due to the adsorbed biphilic particles at the gas-liquid surface, and. Figure 4 shows the effects on foaminess of both colloidal (hydrophilic) particles and biphilic particles present in the simulant sludge. The figure shows that foaminess increases with an increase in concentration of each of the two types of particles. However, hydrophilic (colloidal) particles produce a maximum of about 260% of foaminess (the amount of air incorporated into the system), whereas the biphilic particles resulted in significantly higher degree of foaminess, i.e. 950% over the same range of particle concentrations. These results were reported in our annual project report submitted to the DOE on June 30, 2000 and presented at the American Institute of Chemical Engineers annual meeting held in Los Angeles, November 2000. A paper based on these results is under preparation for possible publication in a refereed journal.

Fig. 4. Effect of hydrophilic (colloidal) and biphilic particles on foaminess
The development of reliable measurement techniques for examining particle-particle interactions in the foam film was pursued by a direct theoretical approach using Monte Carlo computer simulations and integral equation methods of statistical mechanics. In our preliminary investigation on the particle structure formation and film/lamella stability, for simplicity, we considered local ordering of hard spheres near a plane surface (i.e. single wall) as well as in a film formed by hard walls. These results show that at high concentrations of colloidal particles, better particle in-layer structure develops which increases the energy barrier inhibiting diffusion of particles from the film to the bulk. Furthermore, there exists a critical film or bubble size below which at least one layer of particles always stays in the film. Our experiments on the particle layering (i.e. stratification) phenomenon showed that this critical film or bubble size is dependent upon both particle size and concentration. These results have been published by us in a series of four papers (see under PUBLICATIONS).

II. Foam Rheology

The foam generation and stability are dynamic processes. The rheological behavior of foams depends on the response of the thin liquid film and the Plateau borders during shear and dilation [2]. Several researchers have determined the static and dynamic interfacial properties of gas-liquid interfaces containing surfactants in solutions as those associated with conventional foaming systems. These studies have greatly contributed to our understanding of the important role these properties play in foam generation and its stability [3]. However, no attempts have been made to measure rheological properties of the foam lamella formed in the presence of fine insoluble solid particles which are pertinent to the study of three-phase foams and to the development of advanced antifoams. Therefore, it is one of the objectives of our work to carry out the basic rheological measurements under various physicochemical conditions.

The foam film rheological and film thickness stability are measured by a new film rheometer developed at IIT [4,5] as shown in Figure 5A. A curved, spherical cap-shaped film is formed at the top of a glass capillary with its meniscus adhering to the capillary tip (Figure 5B). This models the actual foam lamella structure inside the foam (Figure 5C). A sensitive pressure transducer is used to measure the capillary pressure versus time. The output of the pressure transducer is fed into a computer using a data acquisition board. The size of the foam lamella is controlled, i.e., expanded or contracted by a feed syringe. The syringe plunger movement is controlled by a computer. The capillary, the pressure
transducer and the feed syringe are built into a unit that is placed in a temperature controlled water bath. The capillary tip and the foam lamella can be observed by a horizontal microscope and the radius of the foam lamella is measured by the image analyzer. From the capillary pressure data, the film tension can be calculated using the Young-LaPlace equation relating the film tension ($\gamma$) to the film radius ($R$), and the capillary pressure ($P$).

The dynamic experiments are conducted by either expanding or contracting the film area. A typical curve of the dependence of the foam film tension on the logarithm of the relative film area ($A$) expansion is shown in Figure 6. The linearity of the curve indicates that the foam lamella tension is constant and the film elasticity ($E$) is given by the slope of the curve. The foam lamella rheological data are very useful in correlating lamella properties to foaminess and foam stability. This apparatus is used simultaneously to measure foam lamella life-time. The specific goal of this part of our study is to reveal the role of solid particles in colloidal range in foam lamella rheology, and thereby, foam formation and foam stability. We plan to use this method in our continuing study to understand the basic mechanisms controlling both the foaminess and foam stability using the HLW radioactive waste simulants obtained from the Hanford site.

**Fig.5.** Part A: Principle of operation of IIT film rheometer; Part B: Foam lamella containing particles; Part C: Photomicrograph of foam comprising foam lamella.
III. Develop and Test Advanced Antifoam/Defoamer Agents

Based on the mechanistic understanding of foam generation and stability, we developed an improved antifoam agent, since the commercial antifoam agent (Dow Corning 544) was found to be ineffective in the aggressive physical and chemical environment in the Defense Waste Processing Facility (DWPF) sludge chemical processing. The addition of the new antifoamer was found to be more effective in minimizing foam and was more effective over time than Dow Corning 544. The improved antifoam agent was subsequently tested in a pilot plant at SRS. Furthermore, in the SRTC experiments, the irradiated antifoam appeared to be as effective as nonirradiated antifoamers. Therefore, the results of this research have led to the successful development, demonstration and deployment of the new antifoamer in DWPF.

The lessons learned and the techniques developed in this research are being applied to develop advanced antifoaming/defoaming agents for the Hanford River Protection Project Waste (EMSP Project No. 81867) and for the SRS Alternative Salt Disposition at HLW Evaporation Systems (6, 7).
RELEVANCE, IMPACT AND TECHNOLOGY TRANSFER

One of the greatest challenges facing the DOE is the remediation of $1 \times 10^8$ gallons of high-level and low-level waste in 334 underground storage tanks (UST) at its Hanford, Savannah River, Oak Ridge, Idaho, West Valley and Fernald sites [8]. With the exception of Fernald and Oak Ridge, the waste was generated primarily from plutonium production processes. In most cases, the high level (HLW) and low activity (LAW) nuclear wastes will be immobilized into glass or, alternatively, ceramic waste forms prior to permanent disposal [9,10,11]. The baseline processing technology includes pretreatment processes that separate water and non-radioactive components from the radioactive waste by evaporation, filtration, precipitation and ion exchange. The concentrated radioactive liquids and solids are ultimately vitrified in joule heated ceramic melters.

The Department of Energy, like commercial companies, is faced with the challenges of determining the most cost effective technologies for their businesses. Uncontrollable foaming can severely impact the production rate and ultimately the cost effectiveness of a chemicals process (i.e. evaporation of condensate would have to be limited to prevent carryover of radioactive waste particulate entrained in the foam). Consequences of foaming, other than the obvious impact on attainment, are the potential for contamination of the evaporator condensate system and plugging of the process vessel vent system. Further, for example, foam carryover actually rendered the melter feed unacceptable for vitrification due to preferential carryover of aluminum [12,13]. Foaming in the DWPF has led to excessive carryover of silica that ultimately led to the shutdown of an SRS HLW evaporator [14]. Excessive foaming has been also observed in the Savannah River Alternative Salt precipitation and filtration processes [15,16,17]. Past operations of the Hanford HLW 242-A tank farm have resulted in severe foaming and numerous evaporator shutdowns during the evaporation of waste [18]. SRTC found that severe foaming occurred during the continuous bench scale evaporation of a radioactive alkaline waste from Hanford tank 241-AN102 [19].

Research to understand the basic mechanisms controlling both the foaminess and foam stability, and antifoaming action in the three-phase gas/liquid/solids system continues to be a high priority need for the DOE [1,6]. Furthermore, the knowledge and understanding developed by this research directly benefits the commercial chemical industry [20]. Long-term pretreatment and immobilization of high-level and low activity wastes in glass media will require control and mitigation of foaming during operation of the baseline waste treatment processes.
PROJECT PRODUCTIVITY

The project accomplished all of the proposed goals. However, a one year no-cost extension was requested and approved by the DOE. This was needed in order to apply the project results to the needs of the Savannah River Site (SRS). The new antifoamer developed by the IIT researchers was tested by irradiating the antifoamer and also by testing the antifoamer in a 1/240th scale pilot plant built primarily for the testing of foam and antifoam agents at SRS’s Defense Waste Processing Facility (21).

PERSONNEL SUPPORT

The project team supported by this grant included Professors Wasan and Nikolov, two graduate students (S. Bindal and G. Sethumadhavan) in addition to a postdoctoral fellow (Dr. A. Trokhymchuk). The research led to one master’s thesis and one doctoral thesis which were completed during the grant period. These are listed as follows:


PUBLICATIONS

This research has resulted in ten papers published in peer-reviewed international journals in addition to an article in Encyclopedia of Surface and Colloid Science.


INTERACTIONS

This research has been presented in the following conferences:

a. EMSP Annual Conference, Chicago, 1998
b. American Chemical Society meeting, Dallas, 1998
c. American Chemical Society annual meeting, San Francisco, 2000
d. American Institute of Chemical Engineers meeting, March 2000
e. EMSP National Workshop, Atlanta, April 2000
f. American Institute of Chemical Engineers meeting, Los Angeles, November 2000
TRANSITIONS

The antifoam agent developed by the IIT researchers is now being deployed by DWPF. An antifoam manufacturer has been producing this agent and the IIT researchers have been testing it to ensure its quality. SRTC researchers, DWPF engineers and the IIT antifoam developers continue to work together to support this implementation. Also, the IIT researchers have been assisting SRTC through the development of a second antifoam agent to minimize foam in the SRS Small Tank TPB process.

PATENTS

There is no patent application or disclosure made yet.

FUTURE WORK

IIT has received a continuing grant [22] from the EMSP program to further develop a fundamental understanding of the physico-chemical mechanisms that produce foaming in the DOE High Level (HLW) and Low Activity (LAW) radioactive waste separation processes and to develop and test advanced antifoam/defoaming agents. Antifoams developed from this research will be tested using the HLW radioactive wastes obtained from the Hanford and the Savannah River sites (SRS). Consequently, the continuing work will be closely coupled to the need of DOE River Protection Project Waste and the SRS HLW, Alternative Salt Disposition Program and Defense Waste Processing Facility (DWPF). The results of this future study will further enhance DOE and the commercial industry understanding of foam technology in alkaline and acidic three phase (gas/liquid/solid) systems and thereby increase the throughput of planned and existing DOE radioactive waste pretreatment and immobilization processes. This research is a collaboration between IIT and SRTC.
LITERATURE CITED

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19. M. L. Crowder, C. L. Crawford, H. H. Saito and T. B. Calloway, Jr., Bench-Scale Evaporation of Large Hanford Envelope C Sample (Tank 241-AN102), WSRC-TR-2000-00469 (Draft), Westinghouse Savannah River Company, 12/15/00. Antifoam was added every 2 –3 hours at a concentration 1 g/L to prevent foaming.


FEED BACK

University and national lab researchers often come up with unique and innovative solutions that are useless to the customer. The reason for the success of this project can be attributed to the fact that the IIT researchers sought to understand the science and limitations in the customer’s waste processing facility (DWPF) through close working relationship with the customer (Dan Lambert) at the SRS.