Experimental Study of SRAT/SME Foaming by Illinois Institute of Technology

by

D. P. Lambert

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

D. T. Wasan

A document prepared for STI SUBCONTRACT DELIVERABLE at , , from - .

DISCLAIMER

WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER

WSRC-TR-97-00378-TL
Revision 0

November 10, 1997

To: M. N. Brosee, 704-S

Attention: W. D. Kerley, 704-25S (4)

Experimental Study of SRAT/SME Foaming by Illinois Institute of Technology (U)

The attached report by Dr. Darsh T. Wasan of the Illinois Institute of Technology (IIT) summarizes the results of experiments performed by IIT in an effort to understand the fundamental science involved in the stable foam formation in the Defense Waste Processing Facility's (DWPF's) Chemical Processing Cell (CPC). The results of this testing will be confirmed in an experimental apparatus designed to be prototypic of DWPF CPC processing.

This study concluded the following:

- The sludge simulant used in the testing (a PUREX simulant which contained high levels of noble metals and mercury) had maximum foaminess at approximately 30 wt % solids. This is slightly higher than the normal solids concentration of 15-25 wt% solids in the Sludge Receipt and Adjustment Tank (SRAT) processing.

- The sludge is more foamy after the addition of Precipitate Hydrolysis Aqueous (PHA) to the sludge simulant. Sludge and PHA are combined in the SRAT during normal DWPF coupled processing.

- The foam produced during sludge processing is very stable because of the biphilic (exhibiting both hydrophilic - attracted to water and hydrophobic - repels water) nature of the sludge solids. The hydrophobic portion of the solids accumulates at the liquid/air interface which leads to steric stabilization.

- The foam is less stable at solids concentrations above 30 wt % solids due to the attractive depletion caused by the close contact of the large colloidal particles.

- IIT recommended the use of a new antifoam solution, IIT 747, to replace the Dow Corning 544 currently used in DWPF. IIT 747 was recommended because it was more effective in minimizing foam and was more effective over time than the Dow Corning 544.

This report fulfills the requirements of "Experimental Study of DWPF SRAT/SME Foaming". per subcontract number AB94263N.

If you have additional questions, please contact L. F. Landon (7-7236) or D. P. Lambert (7-7680).

E. W. Holtzscheiter, Manager
SRTC-Immobilization Technology Section

Authorized Derivative Classifier

C. T. Randall, 704-T

FINAL REPORT ON SUBCONTRACT NO. AB94263N

Experimental Study of SRAT/SME Foaming

By

Professor Darsh T. Wasan
Department of Chemical Engineering
Illinois Institute of Technology
Chicago, IL 60616

October 15, 1997

<u>**Final Report on Subcontract No. AB94263N**</u>
by
Professor Darsh T. Wasan
Department of Chemical Engineering
Illinois Institute of Technology
Chicago, IL 60616

Experimental Study of SRAT/SME Foaming

The EPA has designated vitrification as the best developed available technology

for immobilization of nuclear wastes. The Defense Waste Processing Facility

(DWPF) was designed to process and vitrify high level radioactive waste.

However, excessive foaming (up to 5 feet) was observed during the sludge-slurry

process demonstrations in Savannah River Technical Center (SRTC) pilot

facilities. An antifoamer (Dow Corning 544) in the concentration range of about

100 ppm was used for a temporary reduction of the foaming. However, the

antifoamer must be added every 12-24 hours. The foaming causes serious

problems for the processing of the mixed sludge and during its preparation for

vitrification. The goal of this study was to understand the cause of this foaminess

and to suggest an alternative antifoamer which has a better efficiency than that of

Dow 544. We achieved this goal first by experimentally investigating the effects

of colloidal particle-particle interactions and particle hydrophobicity/hydrophilicity

on both foaming and foam stability. Secondly, both the foaminess and foam

stability were greatly reduced by using a new antifoaming system which was

formulated based on a better mechanistic understanding of the aqueous foam formation in a three-phase system containing colloidal particles.

EXPERIMENTAL

In the present study, a simulated (non-radioactive) acidified sludge was used. The sludge samples were prepared at SRTC using a PUREX sludge simulant, and were shipped to our laboratory at Illinois Institute of Technology (IIT). The pH of the sludge samples measured by us varied from 6 to 6.5. The sludge contained noble metal oxides (e.g. Me_xO_y), and hydroxides [$Me_x(HO)_y$]. HM levels of noble metals (Rh, Ru, Pd, Ag, Se) and mercury were added. The density of the sludge particles as measured by us was 2 g/cm^3. The particle concentration varied from 22 to 35 wt%. The particles had irregular shapes and were polydispersed with a particle size varying from about 0.05 μm to 10 μm. The foaminess of the sludge sample was studied with and without the presence of Precipitate Hydrolysis Aqueous (PHA) product. The PHA was produced using irradiated precipitate. These samples were again prepared at SRTC. The pH of the sample containing PHA was about 4.0.

The experimental set-up is shown in Figure 1. A 200 ml sludge sample was placed in a 1000 ml cylindrical glass container with a diameter of about 9 cm. The boiling temperature of the sludge was 98 ± 1°C. To eliminate over-heating of the sample, some boiling chips were added to the sludge.

3

The role of particle hydrophobicity/hydrophilicity (i.e. biphilicity) in foam formation and foam lamella stability was investigated by using an optical bench shown in Figure 2. A reflected light was used to monitor the slurry particle/air cell interaction. Figure 3 shows a set of microphotographs depicting the accumulation of slurry particles inside the foam cells.

Another optical arrangement (Figure 4) was employed to monitor the trapping of slurry particles inside a single foam lamella (Figure 5). These microscopic observations revealed that the thickness of the foam lamella is of the order of several microns. Two types of particles including coarse and fine colloids were observed trapped in the lamella. In the reflected light, we could see that the coarse particles were surrounded by the fine particles and the foam lamella had an irregular thickness. The fine particles are seen as brown "cloud" in these microphotographs.

RESULTS

A number of different sets of experiments were conducted to investigate the effects of sludge concentration, PHA, heating time, and antifoamer concentration and type on both foam formation and foam stability. Results of these experiments are discussed below.

I.   Effect of Sludge Concentration

These sets of experiments were conducted with the experimental set up shown in Figure 1. The original sludge containing 22 wt% of particles was diluted to 10 wt% using the sludge supernate. During the boiling, water evaporated and the concentration of the particles in the sludge increased. Figure 6 displays results for foaminess as a function of the sludge particle concentration. It is observed that the foaminess is maximum at about 30 to 32 wt% of particle concentration. It is also noted that at low particle concentrations, varying from 10 to 25 wt%, large foam lamellae (several centimeters in diameter) were observed at the top of the foam. Due to the local collapse of large lamellae, the foam height fluctuated with time as indicated by a vertical bar on this graph. When the boiling was stopped, the foam lamellae collapsed. However, some of the large lamellae persisted for several hours.

II.   Effect of PHA

These sets of experiments were performed with 200 ml of sludge with a particle concentration of 22 wt%. This sludge was diluted 220 ml of PHA. After boiling, -the sludge concentration was increased to 40 wt% and the foaminess was monitored. These data for foaminess depicting the effect of PHA are shown in Figure 6 and compared with the data without any PHA. Once again, a maximum was observed with the addition of PHA. However, the position of the maximum

5

in foaminess shifted to a somewhat lower value of 27-28 wt% solids and the foaminess decreased from 350% without PHA to about 300 with PHA. The foam had a somewhat different texture (i.e. it had smaller bubbles, only of millimeter sizes) when the PHA was present. The foam height did not fluctuate much during boiling in this case because of the smaller bubble size. When boiling was stopped by removing the container from the heating plate, the foam collapsed after about a minute.

In summary, although the foam texture and foam stability were quite different when PHA was present, there was a distinct maximum in foaminess just like the case without PHA.

III. Effect of Antifoams

In order to eliminate or mitigate the foaming problem which causes serious technical problems in waste disposal processing in DWPF and other nuclear waste processing units, both Dow Corning 544 antifoamer and the newly formulated IIT antifoamer were tested. The 10 wt% sludge was prepared by diluting the original 22 wt% sludge sample with supernate. The total volume of the diluted sludge was 400 ml. The amount of 100 ppm of each antifoamer was added on top of the diluted sludge as 2.2 ml of 1 wt% water solution. Each antifoamer amount was calculated based on the weight of the sample containing 22 wt% particles with a volume of 200 ml (with a weight of about 220g).

6

Figure 7 shows the foaminess data under the boiling conditions for each of the two antifoamers. The particle concentration in the sludge was increased from 10 wt% to 40 wt% by boiling the water. With the Dow Corning 544 antifoamer, a maximum in foaminess was observed at about 32 to 34 wt%. Here the foam contained 250 wt% of gas incorporated into the sludge sample. It is clear from this figure that Dow Corning 544 is more effective as an antifoamer at particle concentrations less than about 10 wt%. It is to be pointed out that IIT antifoamer reduces the foaminess from a maximum of about 300 % to under 50%, a factor of about 6. The maximum in foaminess for the IIT formulation appears at a particle concentration of about 37 to 38 wt%.

The question of what causes a reduction in efficiency of Dow Corning 544 needs to be answered. Also, the finding that the maximum foaminess shifted to a higher sludge concentration when Dow Corning 544 antifoamer was used suggests that this antifoamer loses its efficiency during the boiling process (i.e., is this decrease in efficiency attributed to an increase in particle concentration or heating time?)

In order to answer these questions, the effect of heating time on antifoamer efficiency was studied keeping the particle concentration at a constant value.

IV. Effect of Heating Time on Antifoamer Efficiency

In order to test the effect of the heating time on the antifoamer efficiency, the boiling vessel was equipped with a condenser as shown in Figure 8. Using this condenser, the antifoaming efficiency could be studied without changing the sludge particle concentration. The particle concentration of 25 wt% in the sludge was chosen for these sets of experiments for a practical reason. In this particle concentration region, the foaminess was observed to be very dependent on the sludge concentration (see Figure 6). One could observe significant differences in the efficiency of the two antifoamers used in this study (see Figure 7).

The effect of heating time on antifoamer efficiency is depicted in Figure 9. It is observed that the antifoaming efficiency of Dow Corning 544 with a concentration of 100 ppm is lost within the first hour of heating. On the other hand, the IIT antifoamer is still effective even after 10 hours of heating.

V. Effect of Antifoamer Concentration

In order to test the efficiency of both Down Corning 544 and IIT's antifoamer, the foaminess of the sludge sample containing PHA was observed using two different levels of antifoamer concentrations, 100 ppm and 200 ppm. Figure 10 presents these data. For both antifoamers, an increase in the antifoamer concentration leads to a decrease in foaminess. However, the IIT antifoamer is much more effective.

The central question then is why two antifoamers with the same chemistry (i.e. similar elemental composition) but having different chemical structures have widely different antifoaming effectiveness. In order to resolve this issue, we need to understand mechanistically how the sludge particles increase foaminess, and why we observed a maximum in foaminess at a particular particle concentration.

DISCUSSION OF RESULTS

First, we need to explain the maximum in foaminess observed during the sludge boiling process when the particle concentration was varied (see Figure 6). In order to explain this phenomenon, we refer to Figure 11 which depicts the particle adsorption mechanism at the surfaces of the foam lamella. Due to the biphilic nature of the colloidal particles in the sludge, these particles are adsorbed at the gas-liquid surface, and during the boiling process the particle concentration increases leading to steric interactions between adsorbed particles. Thus the foam lamellae become more stable and the result is an increase in foaminess. However, as the particle concentration increases, the distance between the larger colloid particles decreases due to the particle-particle interactions, and if the distance between two large particles is less than the diameter of the fine particles, then the fine particles are excluded. This phenomenon is known as the volume exclusion effect (see Figure 12). Consequently, the osmotic pressure inside the narrow gap between the large particles is less than that outside of them, therefore, a net

9

attractive force results in flocculation of the larger particles. This, in effect, is also known as attractive depletion phenomenon. This attractive depletion mechanism results in destabilizing the foaming system. Therefore, the maximum observed in Figure 6 is a direct result of the balance of the two effects, namely the particle adsorption at the gas-liquid surface leading to a steric barrier leading to stabilization, and the attractive depletion effect caused by the particle-particle interaction in a multi-sized particle system leading to destabilization. The net effect of these two opposing mechanisms is a maximum in foaminess and foam stability at a critical particle concentration.

The next question we need to answer is why PHA affect foam texture and foam stability. Our experimental observations show that, in the presence of PHA, foam cells are smaller, more uniform and less stable during boiling. Unfortunately, the information concerning the PHA composition is limited. The pH of the PHA is 4.0, and based on its conductivity, the electrolyte concentration is estimated to be 0.4 to 0.5 mol/l for 1:1 electrolyte concentration. We can assume that by adding PHA to the sludge the electrolyte concentration of the sludge samples will increase during the boiling process, so the particle-particle attraction will be improved, resulting in particle flocculation. It is well known that in the presence of an electrolyte the hydrophobic attractions between the particles become stronger and this leads to flocculation of the biphilic particles. This explanation is consistent with our experimental observations. We observed that

the size of the foam lamellae decreased and the foam became less stable. We also observed that the bubble size, foam height and foam stability decreased when we added $FeCl_3$ or $Fe(NO_3)_3$ to the sludge sample. The ability of Fe^{+3} to coagulate particle suspension is well known. In fact $Fe(OH)_3$ was used in some of the previous studies conducted at WSR facilities. However, to achieve a sufficient reduction in foaminess, a 3 to 4 wt% of Fe^{+3} needs to be added to the slurry. This is a costly proposition.

Finally, in order to improve the efficiency of an antifoamer, we need to understand the mechanism of foam destabilization in the presence of an antifoamer. A typical antifoam such as Dow Corning 544 is a dispersion of silicone oil in an aqueous phase. In our previous study (Refs. 1, 2, 3), we have shown that the efficiency of an antifoamer depends on its ability to destabilize the "pseudo-emulsion" film (i.e. the aqueous film found sandwiched between the gas phase and the oil droplet). If this film is unstable, the emulsified oil droplet spreads on the gas-aqueous surface. Furthermore, during the foam lamella thinning process, oil droplets migrate from the area of the film to the Gibbs-Plateau borders where they accumulate, and when the radius of curvature of these borders increases, the oil droplets inside the border coalesce, thereby destabilizing the foam. Therefore, the emulsified silicone oil droplets play an important role in improving the efficiency of an antifoamer.

Dow Corning 544 is a silicone oil-based antifoamer and it contains Dimethyl, methyl (propylpolyethylene oxide polypropane oxide, acetate); siloxane; Poly (ethylene oxide propylene oxide) monoallyl ether acetate); Dimethyl siloxane, hydroxy-ferminated; Polydimethylsiloxane and polyether polyol acetate. Two of these components (dimethyl siloxane and polydimethyl siloxane) are known to have antifoaming activity. The rest of the other components are probably used to emulsify the antifoamers into oil droplets when Down Corning 544 is dispersed in water. However, it is suspected that colloidal particles in the sludge can cover the silicon oil droplets, thereby contributing to their inefficiency in antifoaming action. IIT's new antifoaming formulation is based on our better understanding of the basic mechanism of antifoaming action (See Fig. 13).

RECOMMENDATIONS

For a better and longer-lasting performance of antifoamer, it is recommended that the IIT antifoamer be used at a 100 ppm concentration and be added in a 1-5 wt% aqueous solution on the top of the sludge before boiling the sludge sample. To avoid overheating during boiling, boiling chips should be added to the sludge suspension.

REFERENCES

1. "Mechanisms for Anti-Foaming Action in Aqueous Systems by Hydrophobic Particles and Insoluble Liquids," K. Koczo, J.K. Koczone and D.T. Wasan, J. Colloid and Interface Sci., 166, No.1, 225 (1994).

2. "Mechanisms of Aqueous Foam Stability and Antifoaming Action With and Without Oil: A Thin Film Approach," D.T. Wasan, K. Koczo and A.D. Nikolov, Foams, Fundamentals and Applications in the Petroleum Industry, Ed. L.L. Schramm, Advances in Chemistry Series 242, Washington, D.C., 47-114 (1994).

3. "Mechanisms of Antifoam Deactivation," G. Rácz, K. Koczo and D.T. Wasan, J. Colloid Interface Sci. 181, 124-135 (1996).

THREE PHASE FOAM

GAS BUBBLES

SLUDGE

BOILING CHIPS

MAGNETIC STIRRER

HOT PLATE

THERMO REGULATOR
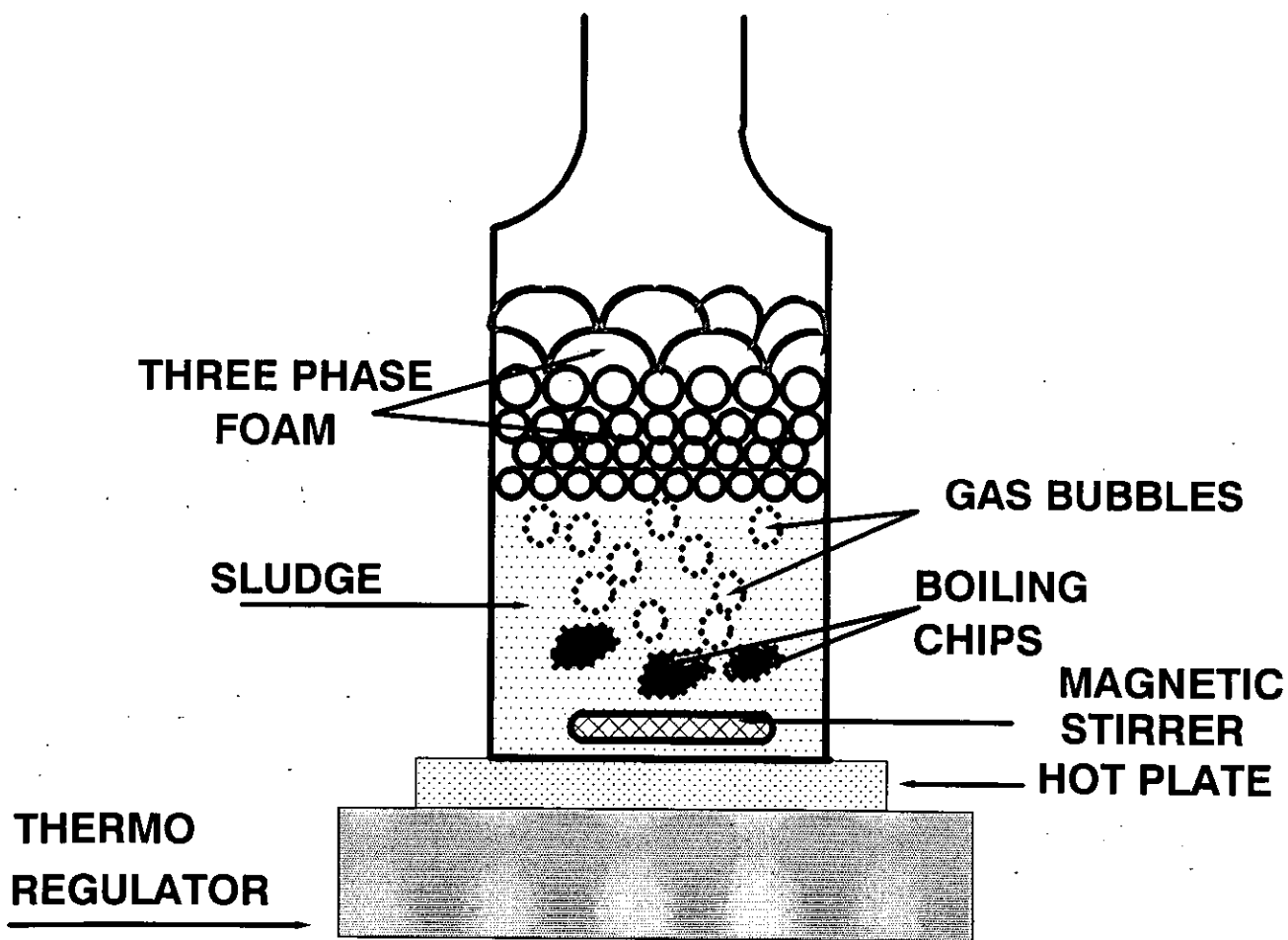
Figure 1

EXPERIMENTAL SET-UP TO STUDY THE FOAMINESS OF SLUDGE DURING BOIL-UP PROCESS.

LIGHT SOURCE

THREE PHASE FOAM

SLUDGE

digital camera

ZOOM
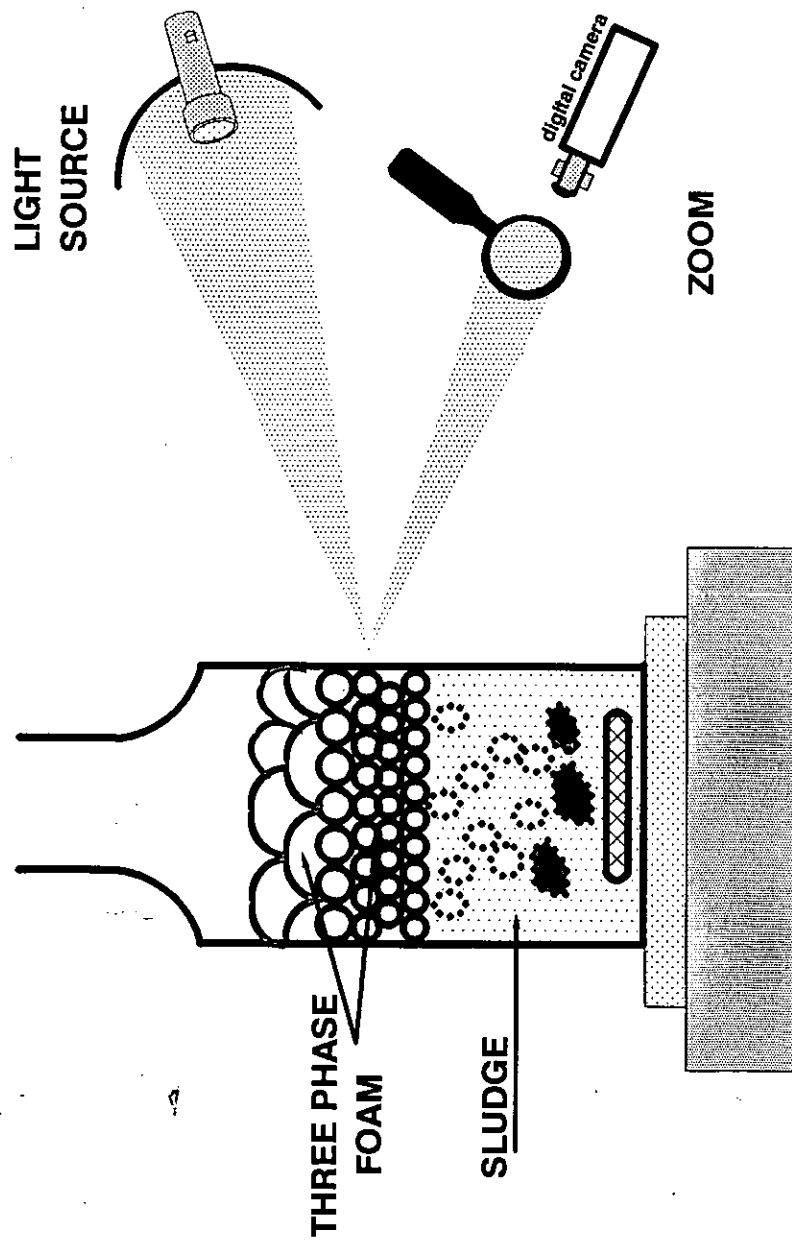
Figure 2

EXPERIMENTAL SET-UP TO STUDY SLUDGE PARTICLES-GAS CELL INTERACTIONS DURING BOIL-UP PROCESS
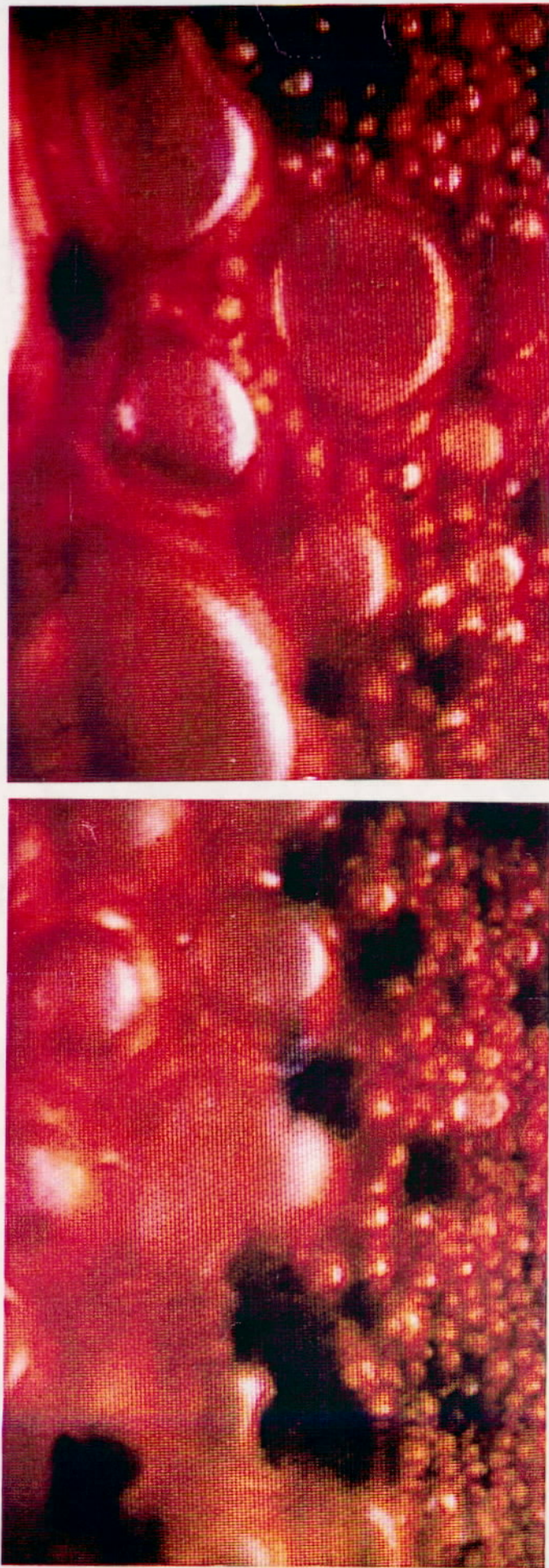
Figure 3

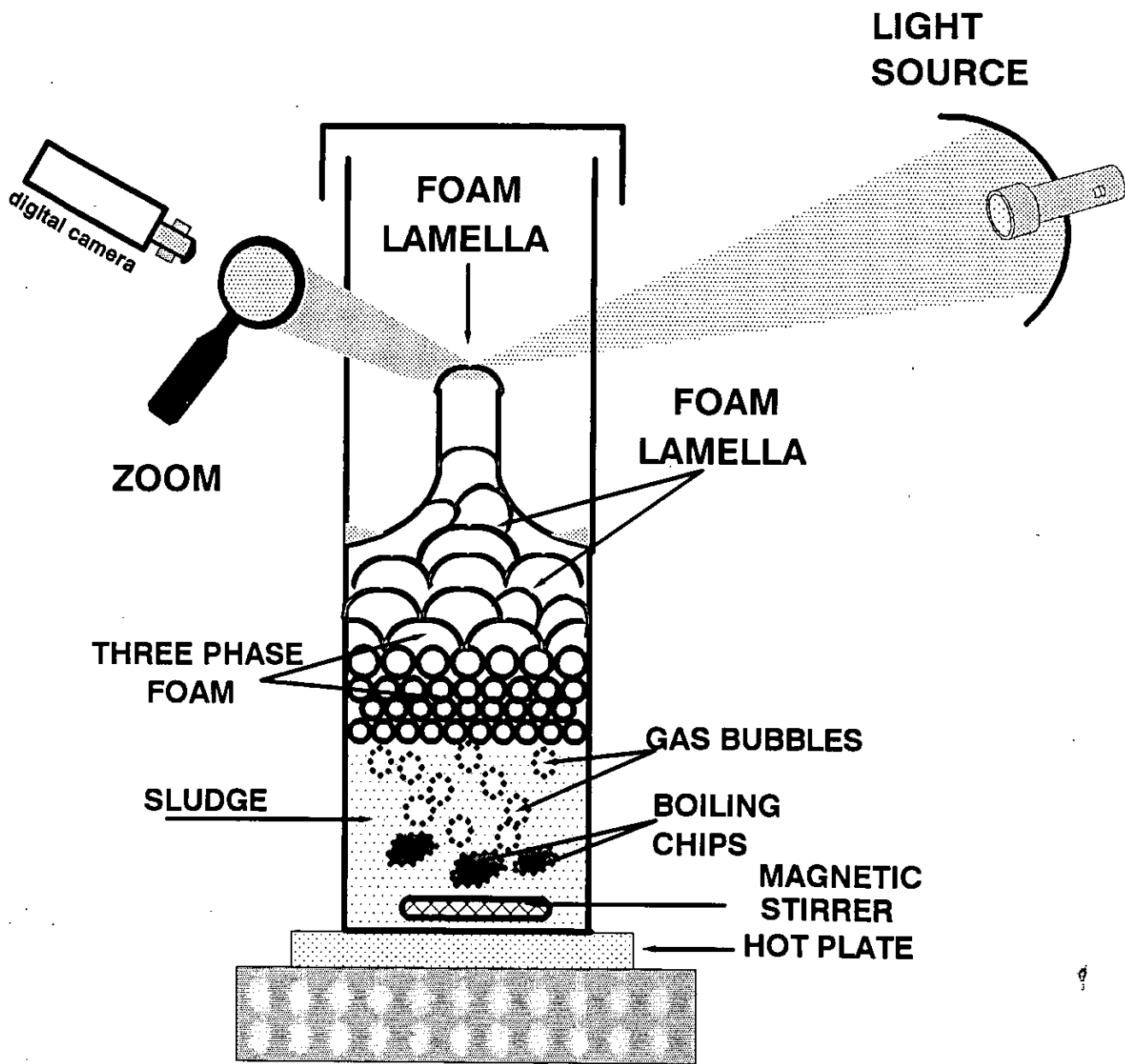MICROPHOTOGRAPHS DEPICT THE SLURRY PARTICLE ACCUMULATION BETWEEN THE GAS BUBBLES

16

Figure 4

EXPERIMENTAL SET-UP TO STUDY THE FOAM LAMELLA PARTICLE STABILIZATION

17

Figure 5

MICROPHOTOGRAPH DEPICTS THE SLURRY PARTICLES TRAPPED INSIDE THE FOAM LAMELLA.

18
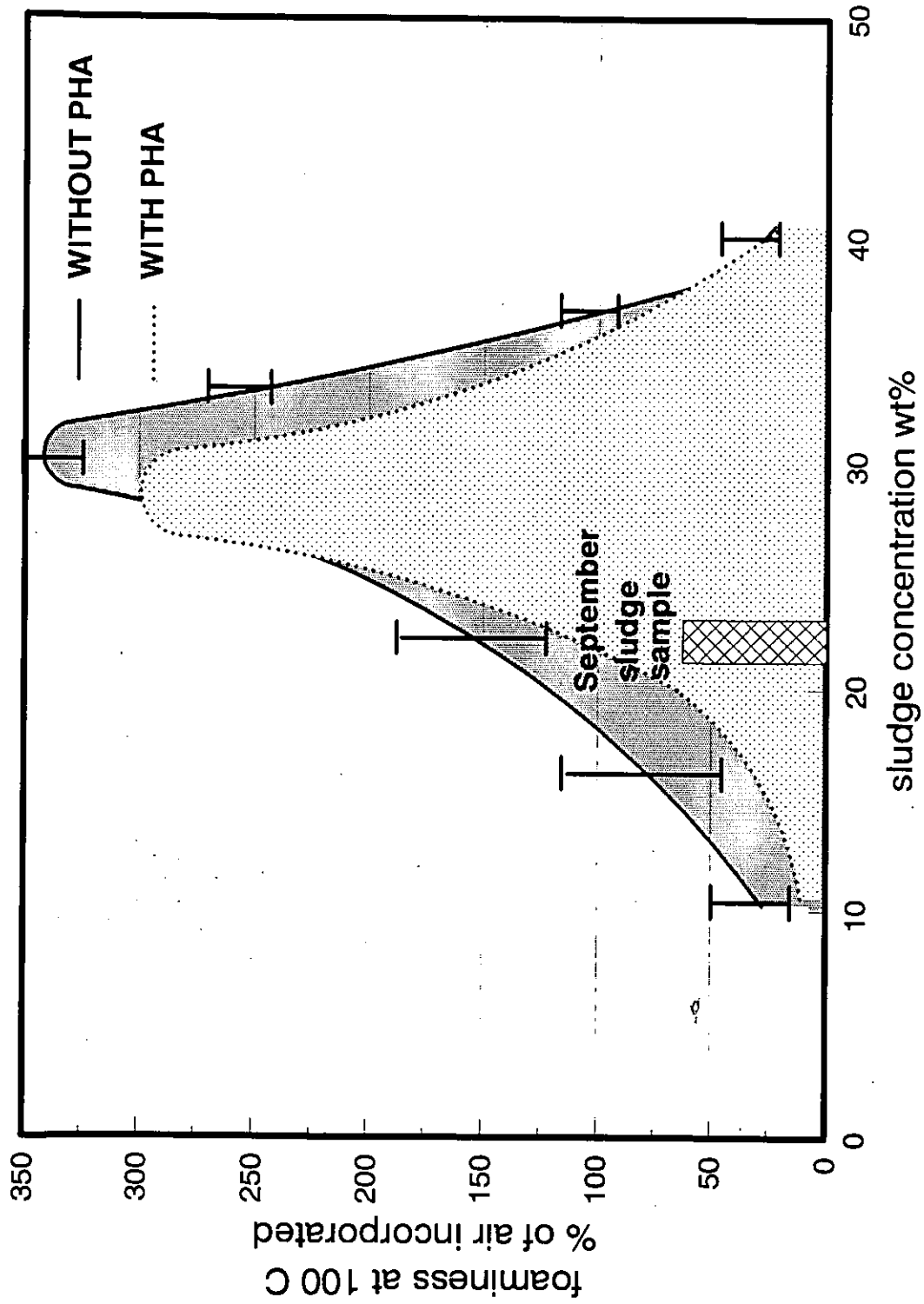
Figure 6

SLUDGE FOAMINESS VERSUS CONCENTRATION AND EFFECT OF PHA ON FOAMINESS
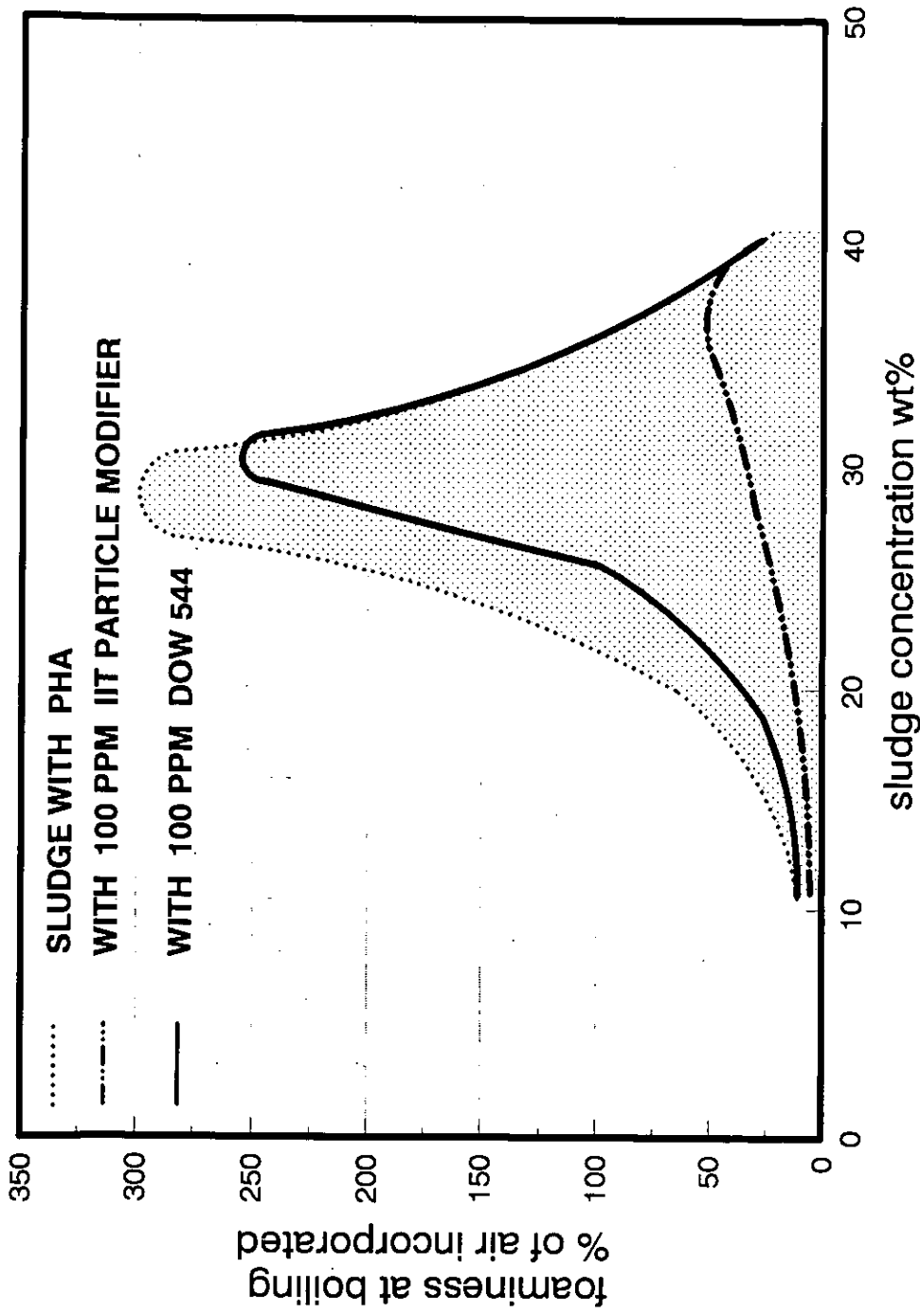
Figure 7

SLUDGE FOAMINESS VERSUS CONCENTRATION AND THE EFFECT OF ANTIFOAMER:
DOW 544 AND IIT PARTICLE MODIFIER.
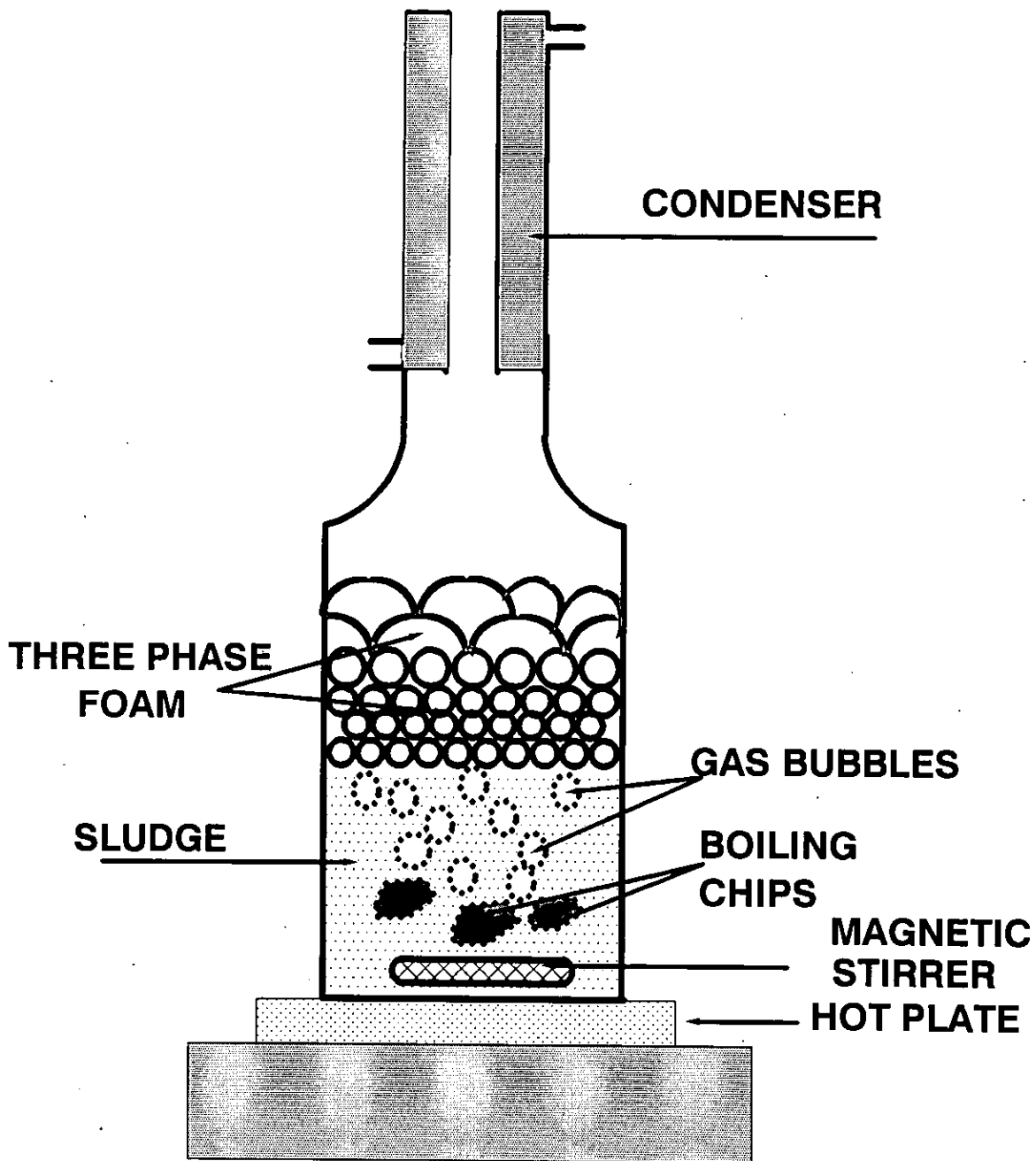
Figure 8

EXPERIMENTAL SET-UP TO STUDY EFFECT OF HEATING TIME ON THE
ANTIFOAMER EFFICIENCY.
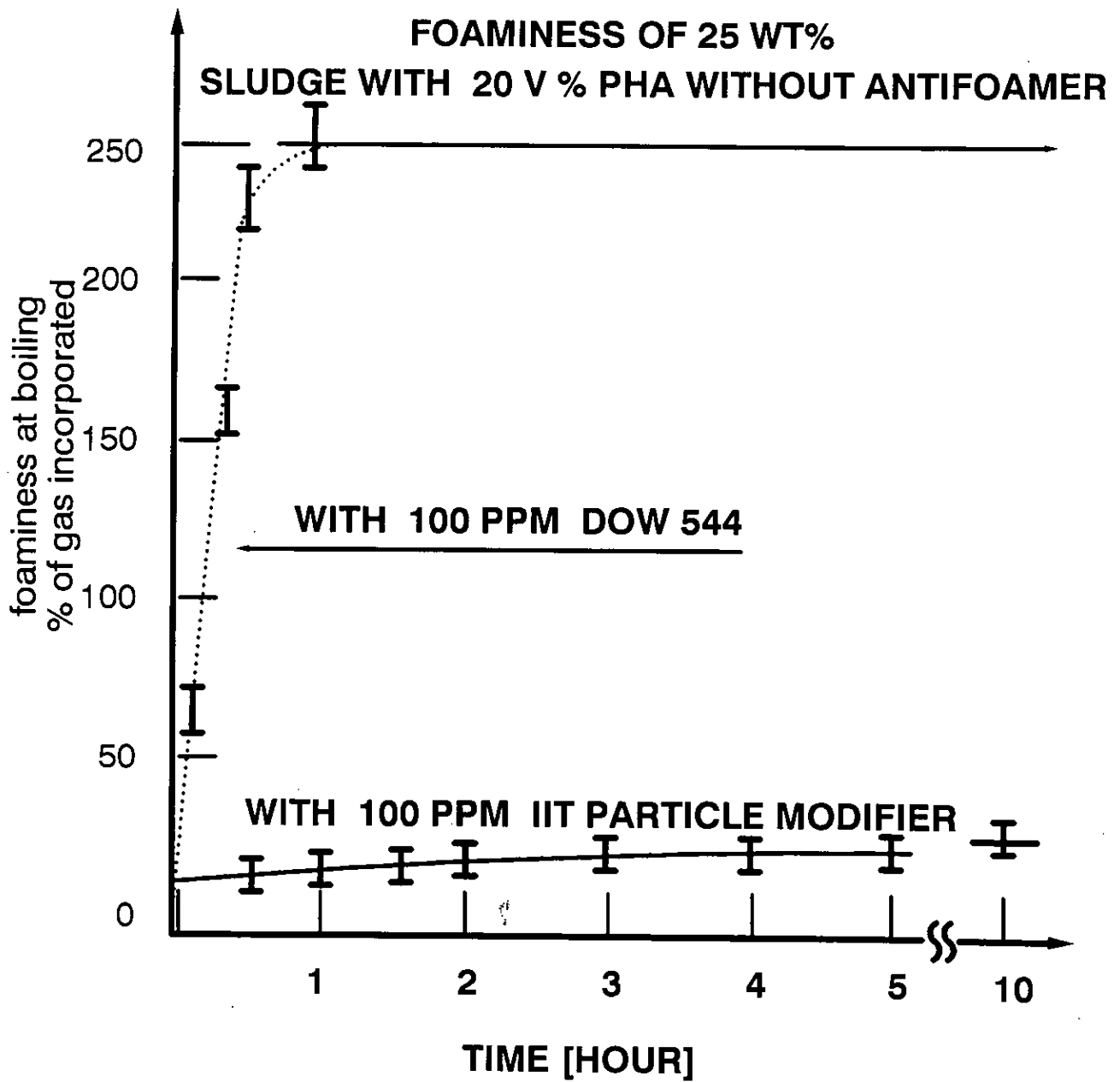
Figure 9

EFFECT OF HEATING TIME ON THE ANTIFOAMER EFFICIENCY
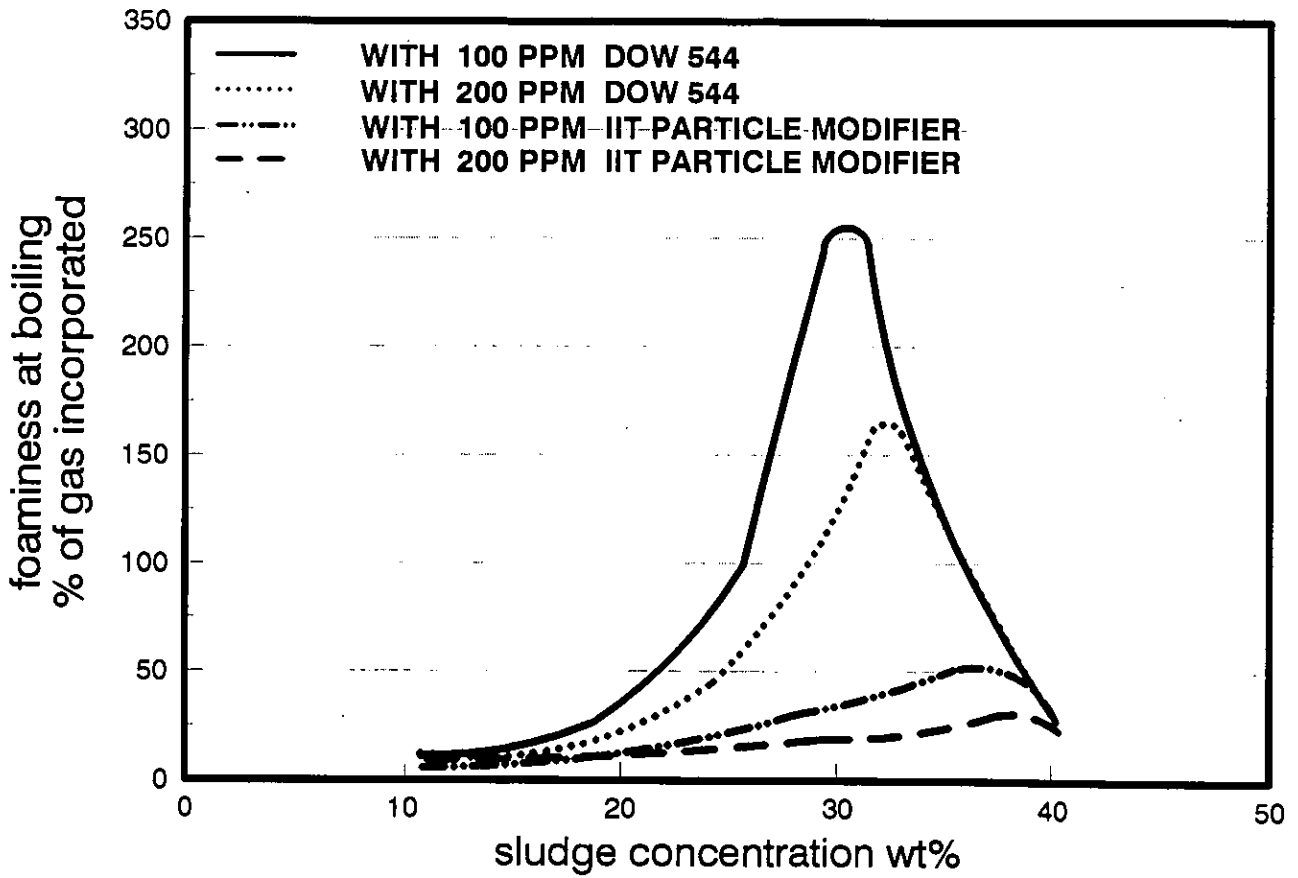
EFFECT OF ANTIFOAMER CONCENTRATION

Figure 10

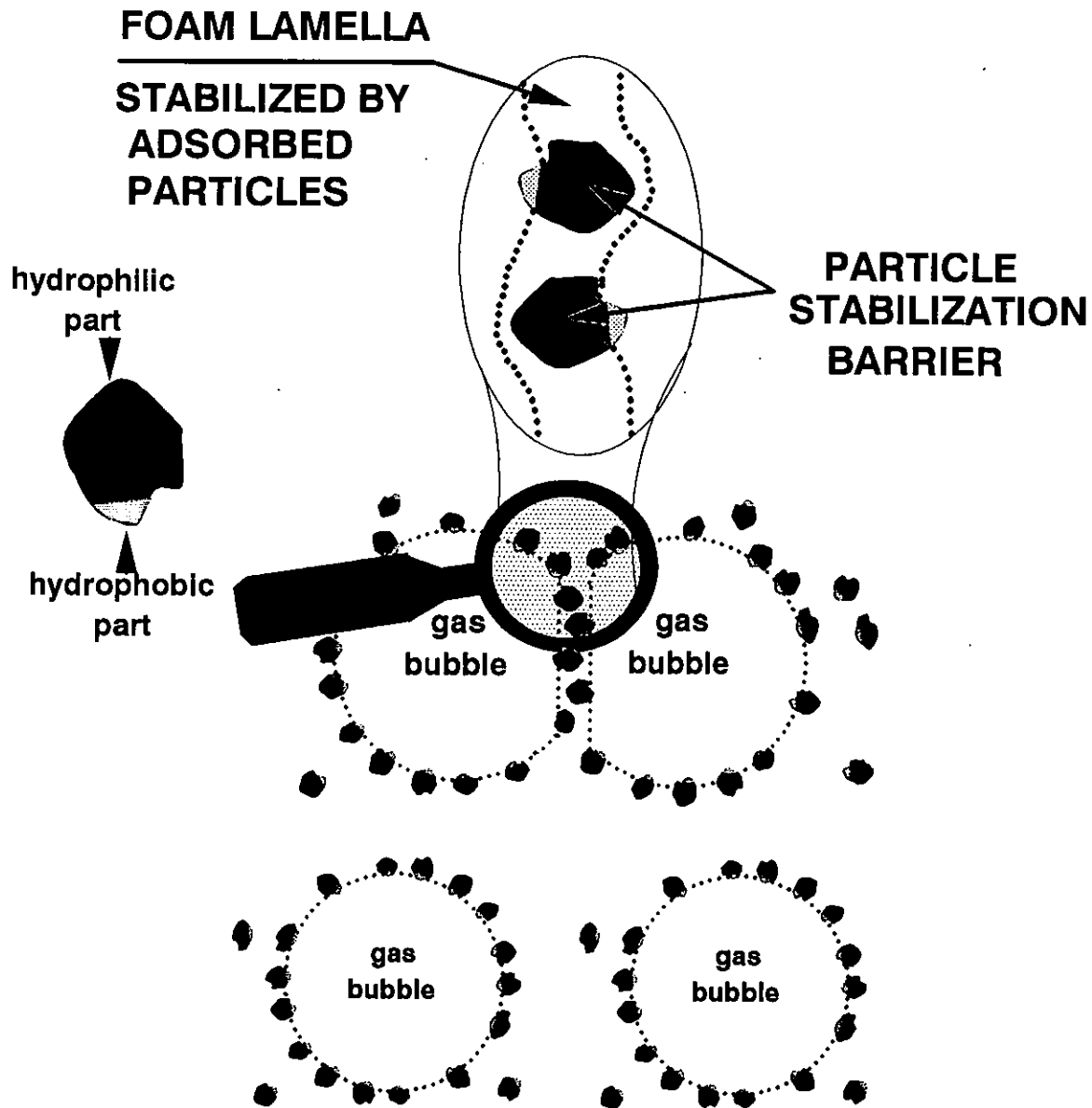SLUDGE FOAMINESS IN THE PRESENCE OF PHA VERSUS CONCENTRATION OF ANTIFOAMER: DOW 544 AND IIT MODIFIER.

23

Figure 11

FOAMINESS AND STABILITY IN THE PRESENCE OF BIPHYLIC POLYDISPERSED PARTICLES. AT LOW CONCENTRATIONS, DUE TO THE PARTICLES' ADSORPTION AT GAS/LIQUID SURFACE, A STABILIZATION BARRIER IS FORMED AND FOAMINESS IS INCREASED.
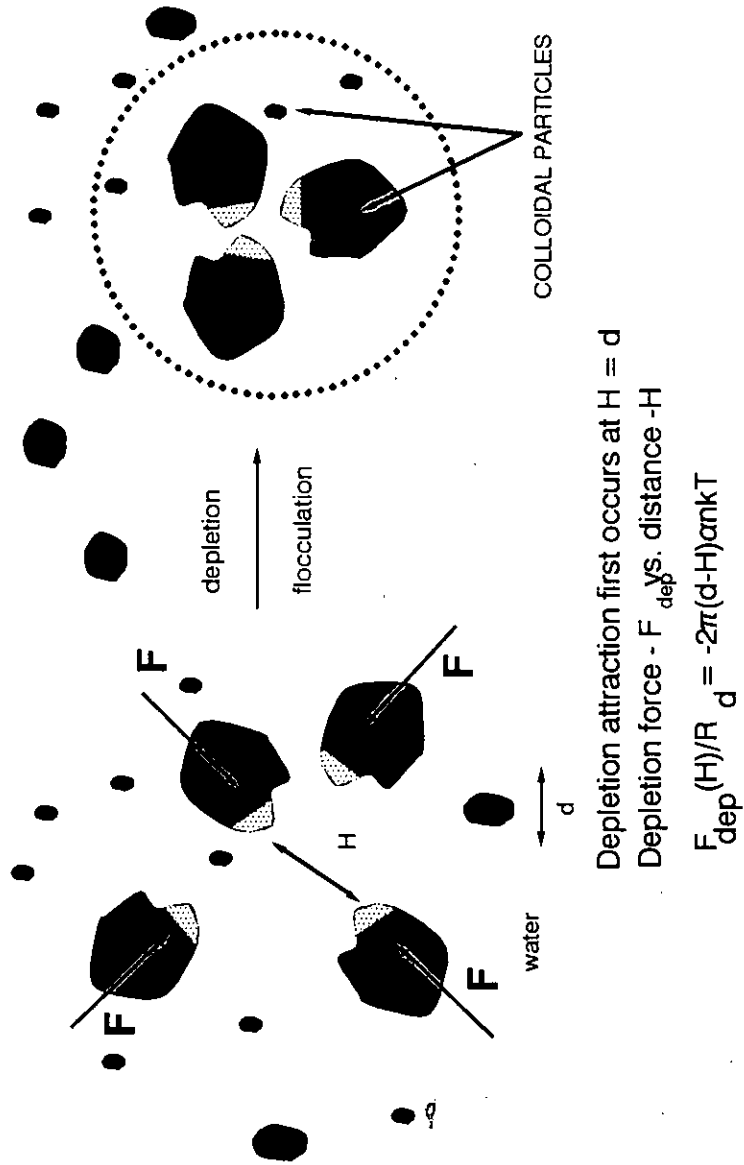
THERMODYNAMIC PRINCIPLES OF SELF-AGGREGATION

COLLOIDAL PARTICLES

depletion

flocculation

water

H

d

Depletion attraction first occurs at H = d

Depletion force - F_{dep} vs. distance -H

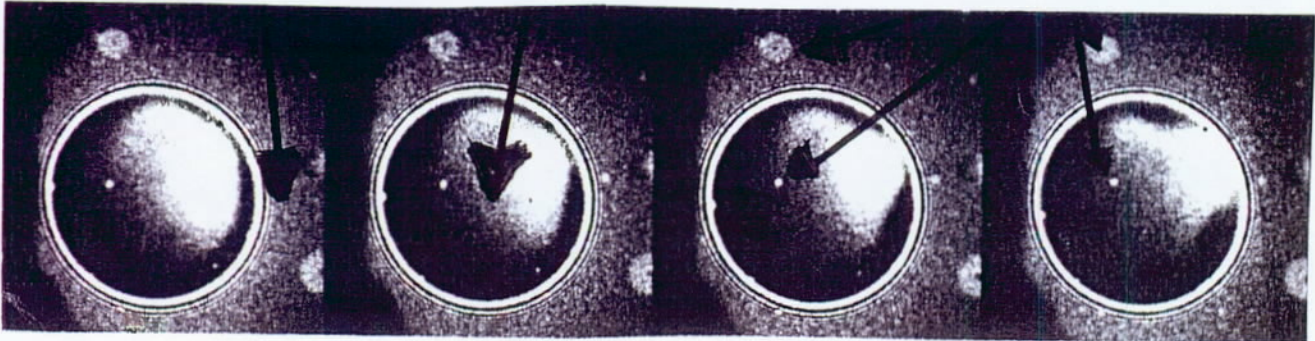$$F_{dep}^{(H)}/R_d = -2\pi(d-H)\alpha nkT$$

Figure 12

AT HIGH CONCENTRATIONS, DUE TO DEPLETION ATTRACTION, PARTICLES BEGIN TO FLOCCULATE AND THE STABILIZATION BARRIER IS DIMINISHED
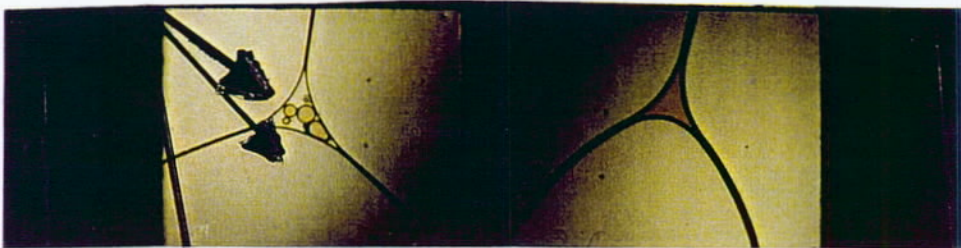
FOAM LAMELLA TOP VIEW

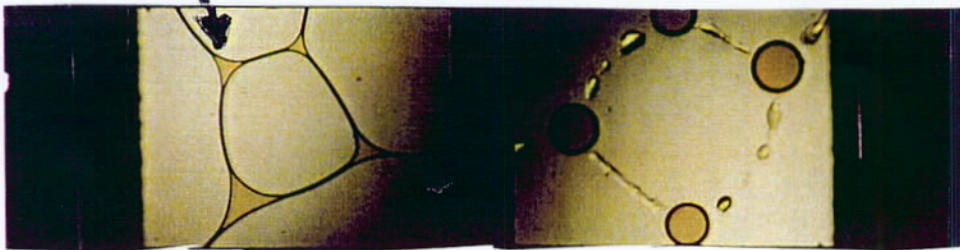GIBBS PLATEAU BORDER   FOAM LAMELLA   OIL DROPLETS

FOAM LAMELLAE SIDE VIEW

CURVATURE RADII

A

B

Figure 13

MECHANISMS OF FOAM LAMELLAE DESTABILIZATION IN THE PRESENCE OF OIL
DROPLETS. A/ MICROPHOTOGRAPHS DEPICT THE OIL DROPLETS' MIGRATION AND
ACCUMULATION TO THE GIBBS-PLATEAU BORDER DURING THE FOAM LAMELLA
THINNING. B/ DURING THE FOAM THINNING THE CURVATURE RADII OF THE GIBBS
PLATEAU BORDER INCREASE AND OIL DROPLETS COALESCE AND FOAM FRAMES
BREAKUP

26